



مرکز سنجش و اعتبار علمی علوم دنیای اسلام



25th  
SAC  
3-5 Sep. 2018

# کتابچه مقالات

# ۲۵ امین

# سمینار شیمی

# تجزیه

## انجمن شیمی ایران

۱۲ تا ۱۴ شهریور ۱۳۹۷

# ایران - تبریز

به همراه بیوگرافی دانش آموختگان  
(دکتری گروه شیمی تجزیه دانشگاه تبریز)



**IN THE NAME OF GOD**

Dear friends and colleagues

It is our great pleasure to welcome you to 25th Iranian Seminar of Analytical Chemistry (25th ISAC). The seminar will be held in Chemistry Department of Tabriz University from Monday September 3<sup>th</sup> to Wednesday September 5<sup>th</sup>, 2018.

The main goal of this seminar is sharing recent achievements and new researches related to Analytical Chemistry. Moreover, the potential application of analytical methods in different fields will be discussed and presented.

The conference covers all aspects of analytical chemistry including electrochemistry, spectroscopy, chromatography and separation techniques, chemometrics, nanochemistry, environmental analytical chemistry, analysis of pharmaceutical and nutritional compounds, and industrial and natural compounds analysis.

This seminar is being organized by Iranian Chemical Society ([www.ics.ir](http://www.ics.ir)) and University of Tabriz in collaboration with Tabriz University of Medical Sciences. Holding this event definitely was not possible without cooperation of researchers, staff and students; therefore, it is important for us to appreciate all of them.

We would like to sincerely appreciate the scientific committee, administration of University of Tabriz, Iranian Chemical Society, Tabriz University of Medical Sciences, organizing committee, the faculty members, staff and students of analytical chemistry of University of Tabriz for their valuable guidance and assistance in organizing this seminar. We wish you a memorable time in our beautiful Tabriz.

Best Regards

A. Naseri

The chairman of seminar

General Schedule of the 25<sup>th</sup> Iranian Seminar of Analytical Chemistry

Day	Time	Program	Place
<b>Sunday</b>	14:30-21:30	Reception beginning	Faculty of Chemistry
	20:30-22:00	Dinner	
<b>Monday</b>	8:30-10:00	Opening ceremony	Vahdat hall
	10:00-10:40	Break time	
	10:40-12:10	Plenary talks	
	12:10-13:50	Prayer, lunch, and workshops	
	13:50-14:20	Poster flash presentation (Session 1)	Faculty of Chemistry
	14:30-16:00	Lectures	
	16:00-17:15	Poster presentation (session 1) and break	
	17:15-17:45	Lectures	
	17:15-20:15	Workshops	
20:15-22:00	Dinner		
<b>Tuesday</b>	8:20-8:50	Poster flash presentation (Session 2)	Faculty of Chemistry
	9:00-10:00	Lectures	
	10:00-11:15	Poster presentation (session 2) and break	
	11:15-12:30	Lectures	
	12:30-13:50	Prayer, lunch, and workshops	
	13:50-14:20	Poster flash presentation (Session 3)	Faculty of Chemistry
	14:30-16:25	Lectures	
	16:25-17:40	Poster presentation (session 3) and break	
	17:00-18:15	Workshops	
	18:30-20:30	Ceremony for 70th Anniversary of the Establishment of University of Tabriz	
	21:00-23:30	El-Goli sightseeing and Dinner in El-Goli mansion	
<b>Wednesday</b>	8:20-8:50	Poster flash presentation (Session 4)	Faculty of Chemistry
	9:00-10:00	Lectures	
	10:00-11:15	Poster presentation (session 4) and break	
	11:15-12:30	Lectures	
	12:30-13:45	Prayer, lunch, and workshops	
	14:15-15:30	Closing ceremony	
	16:00-21:00	Kandovan village tour and Tabriz city sightseeing (with cooperation of Peik Safar agency)	
	20:15-22:00	Dinner	

## مراسم افتتاحیه: ۱۰ - ۸:۳۰

تلاوت قرآن و پخش سرود ملی ایران

خیر مقدم - ریاست محترم دانشگاه تبریز جناب آقای دکتر پورمحمدی

گزارش دبیر همایش جناب آقای دکتر ناصری

سخنرانی رئیس هیئت مدیره انجمن شیمی ایران جناب آقای دکتر شمسی پور

سخنرانی استاد پیشکسوت شیمی تجزیه ایران جناب آقای دکتر گلابی

تجلیل از پژوهشگر برتر شیمی تجزیه ایران

## Opening Ceremony: 8:30 - 10

Quran recitation and playing the Iran national anthem

Welcome speech (President of Tabriz University, Dr. Pour-Mohammadi)

Report of the conference secretary, Dr. Naseri

Speech by chairman of board of directors of the Iranian chemical society, Dr. Shamsipur

Speech by pioneer master of Iran Analytical Chemistry, Dr. Golabi

Celebrating ICS Distinguished Researcher of Iran Analytical Chemistry

**03 Sep 2018, Monday**

	Time	Presenter	University	Title		
<b>Vahdat hall</b>	8:30-10:00	<b>Opening ceremony</b>				
	10:00-10:40	<b>Break time</b>				
	Chair: Mojtaba Shamsipour – Djavanshir Djozan					
	10:40-11:10	Miguel de la Guardia	University of Valencia	Analytical chemistry research based on the use of low cost instrumentation	<b>Plenary Lectures</b>	
	11:10-11:40	ICS Distinguished Researcher; Jahanbakhsh Raouf	University of Mazandaran	DNA based electrochemical biosensors		
	11:40-12:10	Davood Nematollahi	Bu-Ali Sina University	Our research and others in analytical chemistry		
<b>12:10-13:50</b>		<b>Prayer and lunch</b>				
<b>Faculty of Chemistry</b>	12:30-13:45	<b>Workshop</b>				

	Time	Presenter	University	Title	
Allameh Amini Hall (Faculty of Chemistry)	Chair: Mohammad Hossein Pournaghi-Azar – Nahid Pourreza				
	14:30-15:00	Mir Fazlollah Mousavi	Tarbiat Modares University	Electrochemical Energy Storage: Challenges and opportunities	Invited
	15:00-15:30	Habib Razmi	Azarbaijan Shahid Madani University	Graphene based nanocomposites and nanostructures; Analytical applications	
	15:30-15:45	Somayeh Mohammadi	Kermanshah University of Medical Sciences	Highly efficient fluorescence resonance energy transfer sensing of microRNA-155 at attomolar level with high specificity in cancer cells using carbon dots and MnO <sub>2</sub> nanosheets as the energy donor-acceptor platform	Oral
15:45-16:00	Saeedeh Narimani	Urmia University	Rapid, Sensitive and trace analysis of Ceftriaxone using highly fluorescent carbon dots synthesized by hydrothermal method from Chicken meat, and modification of this nanoprobe with silver nanoparticles as a novel highly Sensitive "Turn-On" Fluorescent probe for morphine Sensing		
Faculty of Chemistry	16:00-17:15	Poster presentation (Session 1) and Coffee Break			
	Chair: Zarrin Es'haghi – Maliheh Amirzehni				
Allameh Amini Hall	17:15-17:45	Reza Faridi Majidi	Tehran University of Medical Sciences	Applications of nanostructures in detection and determination of chemical materials and biomarkers	Invited
Faculty of Chemistry	17:15-20:15	Workshops			

	Time	Presenter	University	Title	Type
Allameh Tabatabaie Hall (Faculty of Chemistry)	13:50-14:20	Poster Flash Presentation (Session 1)			Invited
	Chair: Susan Sadeghi - Lida Fotouhi				
	14:30-15:00	Habib Bagheri	Sharif University of Technology	Gradient and superhydrophobic surfaces in microextraction strategies	
	15:00-15:30	Hamed Hamishehkar	Tabriz University of Medical sciences	The role of nanoparticles in drug analysis	
	15:30-15:45	Habibollah Eskandari	University of Mohaghegh Ardabili	Mixed ligand complex formation for solid phase extraction-trace determination of sulfasalazine by using magnetic poly (1-vinylimidazole)	Oral
	15:45-16:00	Rezvan Abdollahzadeh	Shahid Chamran University of Ahvaz	Colorimetric sensing of palladium ions based on in situ generation of palladium nanoparticles as an activator for thionine-hydrazine reaction	
Faculty of Chemistry	16:00-17:15	Poster presentation (Session 1) and Coffee Break			
	Chair: Ali Shayanfar – Amir Abbas Matin				
Allameh Tabatabaie Hall	17:15-17:45	Mahboob Nemati	Tabriz University of Medical sciences	Application of green chemistry extraction methods in analysis of drug residue and contaminants in food	Invited
Faculty of Chemistry	17:15-20:15	Workshops			

Allameh Amini Hall (Faculty of Chemistry)	Time	Presenter	University	Title		
	Chair: Mohammad Hossein Pournaghi-Azar – Nahid Pourreza					
	14:30-15:00	Mir Fazlollah Mousavi	Tarbiat Modares University	Electrochemical Energy Storage: Challenges and opportunities	Invited	
	15:00-15:30	Habib Razmi	Azarbaijan Shahid Madani University	Graphene based nanocomposites and nanostructures; Analytical applications		
	15:30-15:45	Somayeh Mohammadi	Kermanshah University of Medical Sciences	Highly efficient fluorescence resonance energy transfer sensing of microRNA-155 at attomolar level with high specificity in cancer cells using carbon dots and MnO <sub>2</sub> nanosheets as the energy donor-acceptor platform	Oral	
	15:45-16:00	Saeedeh Narimani	Urmia University	Rapid, Sensitive and trace analysis of Ceftriaxone using highly fluorescent carbon dots synthesized by hydrothermal method from Chicken meat, and modification of this nanoprobe with silver nanoparticles as a novel highly Sensitive "Turn-On" Fluorescent probe for morphine Sensing		
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Allameh Tabatabaie Hall (Faculty of Chemistry)	Time	Presenter	University	Title	Type	
	Poster Flash Presentation (Session 1)					
Chair: Susan Sadeghi - Lida Fotouhi						
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Allameh Tabatabaie Hall	17:15-17:45	Mahboob Nemati	Tabriz University of Medical sciences	Application of green chemistry extraction methods in analysis of drug residue and contaminants in food	Invite	
Faculty of Chemistry	17:15-20:15	Workshops				



	Time	Presenter	University	Title	
Allameh Amini Hall	Chair: Mir Fazlollah Mousavi – Afsaneh Mollahosseini				Invited
	9:00-9:30	Yaser Beyad	University of Newcastle	Hybrid Direct Carbon Fuel Cells (HDCFC); from theory and laboratory scale to demonstration plant	
	9:30-10:00	Amir Bagheri Garmarudi	Imam Khomeini International University of Qazvin	A glance on novel applications of infrared spectrometry	
Faculty of Chemistry	10:00-11:15	Poster presentation (Session 2) and Coffee Break			
	Chair: Esmail Tammari - Habibollah Eskandari				
Allameh Amini Hall	11:15-11:45	Nematollah Omidikia	University of Sistan and Baluchestan	Third-Order Advantages: a Step Forward	Invited
	11:45-12:15	Karim Asadpour-Zeynali	University of Tabriz	Quantum Dots in Electrochemiluminescence; Advances and Applications	
	12:15-12:30	Esmail Tammari	Persian Gulf University	Electrochemical kinetics and mechanism study of Raloxifene drug	Or
12:30-14:00	Prayer, lunch and workshop				
Chair: Davood Nematollahi – Morteza Bahram					
Allameh Amini Hall	14:30-15:00	Hamid Abdollahi	Institute for Advanced Studies in Basic Sciences, Zanjan	Information-Accuracy Relation in Chemical Studies	Invited
	15:00-15:30	Masoud Ayatollahi Mehrgardi	University of Isfahan	Early Diagnosis and Efficient Treatment of Cancers by Smart Targeting of the Cancers Cells	
	15:30-15:50	Mandana Amiri	University of Mohaghegh Ardabili	Carbon Nanoparticle Composite based Electrochemical Sensors	
	15:50-16:05	Abdollah Abdollahi Aghdam	University of Tabriz	Emerging New Era Of Analytical Chemistry through Microfluidics	Oral
	16:05-16:20	Somaye Ebrahimi	Bu-Ali Sina University	A Dual-Signalling Electrochemical Recognition of Naproxen Enantiomers Based on Competitive Host-Guest Interaction of a $\beta$ -Cyclodextrin/Graphene modified Electrode	
Faculty of Chemistry	16:20-17:30	Poster presentation (Session 3) and Coffee Break			
	16:30-17:45	Workshop			
	18:30-20:30	Ceremony for 70 <sup>th</sup> Anniversary of the Establishment of University of Tabriz			
El-Goli	21:00-23:00	Dinner in El-Goli mansion			

### 05 Sep 2018, Wednesday

	Time	Presenter	University	Title	
Allameh Tabatabaie Hall	8:20-8:50	<b>Poster Flash Presentation (Session 4)</b>			
	Chair: Hossein Abdolmohammad-Zadeh – Alireza Asghari				
	9:00-9:30	Zarrin Eshaghi	Payame Noor University	New Sorbents for Extraction and Microextraction Techniques	Invited
	9:30-9:50	Tahmineh Baheri	Amin Police University	New Psychoactive Substances Analysis	
	9:50-10:05	Ali Mohebbi	University of Tabriz	Extraction and preconcentration of some organophosphorus pesticides in honey samples using an efficient and green pretreatment method followed by HPLC-UV determination	Oral
Faculty of Chemistry	10:05-11:15	<b>Poster presentation (Session 4) and Coffee Break</b>			
Chair: Farnoush Faridbod – Mandana Amiri					
Allameh Tabatabaie Hall	11:15-11:45	Mohammad Reza Yaftian	University of Zanjan	The potential of Cyphos® IL 101-based polymer inclusion membranes for selective extraction and on-line separation-FIA spectrophotometric determination of vanadium	Invited
	11:45-12:15	Rahman Hallaj	University of Kurdistan	Magnetic based sensors and biosensors	
	12:15-12:35	Azadeh Golshan	University of Newcastle	Multi-Way Data Analysis in Investigating Environmental Variables Regulating Cyanobacteria Species Abundances in a Major Drinking Water Reservoir	
12:30-14:00		<b>Prayer, lunch and workshop</b>			

	Time	Presenter	University	Title	
Allameh Amini Hall	Chair: Biuck Habibi – Karim Asadpour-Zeynali				
	9:00-9:20	Morteza Bahram	Urmia University	Simple methodologies for resolving fluorescence resonance energy transfer (FRET) profiles by matricising the multi-way fluorescence data	Invited
	9:20-9:50	Esmael Alipour	University of Tabriz	Voltammetric DNA biosensors in order to early detection of some dangerous diseases	
	9:50-10:05	Mehri Razavi	Institute for Advanced Studies in Basic Sciences, Zanjan	Investigation of bioconjugation between CdTe@cys quantum-dot and BSA, Trypsin and Cytochrome c proteins applying PARAFAC on fluorescence data	Oral
Faculty of Chemistry	10:05-11:15	<b>Poster presentation (Session 4) and Coffee Break</b>			
Chair: Reza Emamali-Sabzi – Saadat Rastegarzadeh					
Allameh Amini Hall	11:15-11:45	Nader Shokoufi	Chemistry & Chemical Engineering Research Center of Iran	Analytical Instrumentation, Research to Manufacturing	Invited
	11:45-12:05	Mortaza Iranifam	University of Maragheh	Chemiluminescence determination of the antioxidant capacity of honey samples and fruit juices using lab-on-a-chip device	
	12:05-12:20	Zahra Abolghasemi-Fakhri	University of Tabriz	A highly sensitive chemiluminescent probe for detection of glutathione based on gold nanostar@reduced graphene oxide composite	Oral
	12:20-12:35	Afshin Rahimi	University of Guilan	A simple hyphenated method by ultrasound assisted extraction-magnetic solid phase extraction coupled with gas chromatography for determination of caffeine in food	
12:30-13:30		<b>Closing ceremony</b>			
13:30-15:30		<b>Prayer, lunch and workshop</b>			
16:00-21:00		<b>Kandovan Tour</b>			

# Committees

### **Seminar chairmen**

<b>Chairman</b>	<i>Abdolhossein Naseri</i>
<b>Scientific chairman</b>	<i>Mir Reza Majidi</i>
<b>Executive chairman</b>	<i>Saeed Mohammad Sorouraddin</i>

### **Scientific committee**

<b>Seyyed Mahdi Golabi</b>	<i>University of Tabriz</i>
<b>Mohammad Hossein Pournaghi Azar</b>	<i>University of Tabriz</i>
<b>Jamshid Manzouri Lashkar</b>	<i>University of Tabriz</i>
<b>Djavanshir Djozan</b>	<i>University of Tabriz</i>
<b>Mohammad Hossein Sorouraddin</b>	<i>University of Tabriz</i>
<b>Mojtaba Shamsipour</b>	<i>Razi University</i>
<b>Mir Reza Majidi</b>	<i>University of Tabriz</i>
<b>Abdolhossein Naseri</b>	<i>University of Tabriz</i>
<b>Mir Ali Farajzadeh</b>	<i>University of Tabriz</i>
<b>Mohammad Amjadi</b>	<i>University of Tabriz</i>
<b>Esmaeel Alipour</b>	<i>University of Tabriz</i>
<b>Hossein Dastangoo</b>	<i>University of Tabriz</i>
<b>Karim Asadpour Zeynali</b>	<i>University of Tabriz</i>
<b>Saeed Mohammad Sorouraddin</b>	<i>University of Tabriz</i>
<b>Ali Asghar Ensafi</b>	<i>Isfahan University of Technology</i>
<b>Abbas Afkhami</b>	<i>Bu-Ali Sina University</i>
<b>Habib Bagheri</b>	<i>Sharif University of Technology</i>
<b>Nahid PourReza</b>	<i>Shahid Chamran University</i>
<b>Esmaeel Shams Solari</b>	<i>University of Isfahan</i>
<b>Maryam Rajabi</b>	<i>University of Semnan</i>
<b>Farhad Raoufi</b>	<i>Shahid Beheshti University</i>
<b>Abdoraouf Samadi Meybodi</b>	<i>University of Mazandaran</i>

<b>Habib Razmi</b>	<i>Shahid Madani University of Azarbayjan</i>
<b>Abdollah Salimi</b>	<i>University Of Kordestan</i>
<b>Biuck Habibi</b>	<i>Shahid Madani University of Azarbayjan</i>
<b>Alireza Khataee</b>	<i>University of Tabriz</i>
<b>Mohammad Reza Hormozi nejad</b>	<i>Sharif University of Technology</i>
<b>Farzaneh Shemirani</b>	<i>University of Tehran</i>
<b>Morteza Bahram</b>	<i>University of Urmia</i>
<b>Reza Emamali Sabzi</b>	<i>University of Urmia</i>
<b>Jahanbakhsh Raouf</b>	<i>University of Mazandaran</i>
<b>Reza Ojani</b>	<i>University of Mazandaran</i>
<b>Hamid Abdollahi</b>	<i>Institute for Advanced Studies in Basic Sciences</i>
<b>Bahram Hemmati nejad</b>	<i>University of Shiraz</i>
<b>Yadollah Yamini</b>	<i>Persian Gulf University of Boushehr</i>
<b>Davoud Nematollahi</b>	<i>Bu-Ali Sina University of Hamedan</i>
<b>Abbasali Zamani</b>	<i>University of Zanjan</i>
<b>Habib Eskandari</b>	<i>Mohaghegh Ardabili University</i>
<b>Mohammad Reza Yaftian</b>	<i>University of Zanjan</i>
<b>Khalil Farhadi</b>	<i>University of Urmia</i>
<b>Mahmoud Chamsaz</b>	<i>Ferdowsi University of Mashhad</i>
<b>Raouf Ghavami</b>	<i>University of Kordestan</i>
<b>Reza Ansari</b>	<i>University of Gilan</i>
<b>Tayyebeh Madrakian</b>	<i>Bu-Ali Sina University</i>
<b>Mir Fazlollah Mousavi</b>	<i>Tarbiat Modarres University of Tehran</i>
<b>Alireza Asghari</b>	<i>University of Semnan</i>
<b>Hossein Abdolmohammad zadeh</b>	<i>Shahid Madani University of Azarbayjan</i>
<b>Masoud Ayatollahi</b>	<i>University of Isfahan</i>
<b>Mohsen Kompani Zare</b>	<i>Institute for Advanced Studies in Basic Sciences</i>
<b>Mir Mahdi Abolghasemi</b>	<i>University of Maragheh</i>
<b>Ebrahim Ghorbani Kalhor</b>	<i>Islamic Azad University of Tabriz</i>

<b>Jafar Abolhasani</b>	<i>Islamic Azad University of Tabriz</i>
<b>Alimohammad Haji Shabani</b>	<i>University of Yazd</i>
<b>Mir Fazlollah Mousavi Kozeheknonan</b>	<i>Tarbiat Modarres University of Tehran</i>
<b>Farzaneh Shemirani</b>	<i>University of Tehran</i>

### **Executive committee**

<b>Mohammad Reza Pourmohammadi</b>	<i>University President</i>
<b>Asghar Asgari</b>	<i>Deputy of Research and Technology University</i>
<b>Abolghasem Jouyban</b>	<i>Chancellor for Research of Tabriz University of Medical Sciences</i>
<b>Mir Reza Majidi</b>	<i>Dean of the School of Chemistry - Scientific Chairman</i>
<b>Abdolhossein Naseri</b>	<i>Secretary of the Seminar</i>
<b>Saeed Mohammad Sorouraddin</b>	<i>Executive Chairman</i>
<b>Mohammad Amjadi</b>	<i>Head of the Department of Analytical Chemistry</i>
<b>Djavanshir Djozan</b>	<i>Member of Department of Analytical Chemistry</i>
<b>Mir Ali Farajzadeh</b>	<i>Member of Department of Analytical Chemistry</i>
<b>Karim Asadpour Zeynali</b>	<i>Vice Dean for Education and Graduate Studies</i>
<b>Hossein Dastangoo</b>	<i>Member of Department of Analytical Chemistry</i>
<b>Esmael Alipour</b>	<i>Member of Department of Analytical Chemistry</i>
<b>Masoumeh Khatamian</b>	<i>Member of Faculty of Chemistry</i>
<b>Mir Ghasem Hosseini</b>	<i>Member of Faculty of Chemistry</i>
<b>Soheil Aber</b>	<i>Member of Faculty of Chemistry</i>
<b>Reza Najjar</b>	<i>Member of Faculty of Chemistry</i>
<b>Amir Abbas Matin</b>	<i>Head of Chemistry Department At Azarbaijan Shahid Madani University</i>
<b>Mahmoud Zarei</b>	<i>Member of Faculty of Chemistry</i>
<b>MirAbolfazl Naziri</b>	<i>Member of staff of Faculty of Chemistry</i>
<b>Mohammad Sadegh Zolmajd</b>	<i>Member of staff of Faculty of Chemistry</i>
<b>Masoud sheykhzadegan</b>	<i>Member of staff of Faculty of Chemistry</i>

**Babaali Hakimzadeh**

*Member of staff of Faculty of Chemistry*

**Karim Razavi**

*Member of staff of Faculty of Chemistry*

### **Student executive committee**

**Maryam Abbaspour**

**Ali Mohebbi**

**Zahra Abolghasemi fakhri**

**Fariba Mollarasouli**

**Fatemeh Aghaziarati Farahani**

**Rezvan Najafi**

**Parisa Adineh ghahremani**

**Hanieh Nasiri**

**Nasim Aalaie**

**Taher Nasiri**

**Paria Alizadeh**

**Elham Nasirlu**

**Pooneh Alizadeh**

**Hasan Nasrollahpour**

**Sima Alvani**

**Sajjad pourmohammad**

**Somayeh Amali**

**Sanaz Sajedi**

**Mahmoud Ahmadi**

**Rana Salari**

**Saeid Arezoyi**

**Masoumeh sattari**

**Bahare Badrkhani**

**Arash Nourbakhsh**

**Khadijeh Beighdeli**

**Seyyed Morteza Seyyed Alavi**

**Elaheh Behboudi**

**Mir Saeed Seyyed Sajjadi**

**Elnaz Delnavaz**

**Saheleh Sheykhizadeh**

**Ali Fazl-Shokouhi**

**Roghaye Shokri Kalan**

**Sara Fazl-Shokouhi**

**Hessamaddin Sohrabi**

**Ali Ghaffarifard**

**Rana Tajdid**

**Mahdiyeh Ghaffari**

**Ali Zendehtdel**

**Mahdi Ghorbani**

**Afsaneh hemmati**

**Zahra Karimzadeh**

**Roya Kazemian**

**Zahra kouhi**

# حامیان سمینار



شورای اسلامی شهر تبریز



شهرداری تبریز



بنا طیف



مرکز منطقه‌ای اطلاع‌رسانی  
علوم و فناوری



پایگاه استنادی علوم جهان اسلام



نوین ابتکار



شرکت طیف سنج تجزیه



آرین تجهیز آزما



شرکت دانش پیشرفته  
آزمایشگاهی پی پرو



بهسکر



موسسه تحقیقات واکن و سرم سازی رازی



آرمان آفرین آزما



شریف سولار



فادران نانومتاس



صنایع غذایی تکناز



شرکت مهندسی بهشپوه





# REFEREES

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# Plenary Lecture



## ANALYTICAL CHEMISTRY RESEARCH BASED ON THE USE OF LOW COST INSTRUMENTATION

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Nowadays, the analytical needs of our societies increase constantly in fields like health and clinical analysis, food safety and the environmental pollution control. So, there is an increasing demand of suitable analytical methodologies to answer the main questions related to diagnostics and safety. In the aforementioned frame, analysts must try to develop accurate, selective and sensitive methodologies suitable to solve problems in a fast and environmentally friendly way to avoid time delays and environmental deleterious effects of the use of reagents and solvents. The so called Green Analytical Chemistry (1-4) has permitted to put the spot light on the need of sustainable methodologies to improve our analytical tools. It has involved: i) a drastic reduction of the analytical protocol steps, together with ii) the reduction of the power consumption, iii) reduction of reagents and solvents consume and iv) the replacement of toxic products by innocuous, or at least less dangerous ones. All that has been a priority task in the Analytical Chemistry of the XXI century and has permitted to reduce operator and environmental risks together with a reduction of costs of analysis. So, it is time to move from Green Analytical Chemistry to another challenge that I would like to call Democratic Analytical Chemistry.

Democratic Analytical Chemistry means that analytical methods could be applied by using a reasonable cost instrumentation, suitable to be transported to the point of care and also to be managed by every citizen with a basic formation. In such a frame the advantages of the analytical methods could be extended from big hospital with high cost instrumentation to remote places with poor media and, additionally, many citizens around the world could be data producers suitable to alert the police makers about risks for the environment and the health of the people.

In this keynote, I will present some of the research applications made in our laboratory. Studies concern the use of low cost and easy available tools. Extraction of analytes from samples was carried out by using a hard cap espresso machine of the Nespresso type, and direct determination of analytes, without any sample damage, was accomplished by IR methods or image processing, including smartphone images. Additionally, studies on the quality of air and human breath were made using portable gas sensors. In short, our studies evidenced that for the advancement of sciences a mixture of funds and imagination is required, being the last point the most important.

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## تحقیقات ما و دیگران در شیمی تجزیه

داود نعمت الهی

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دانشگاه ها را می توان به سه نسل اول، دوم و سوم تقسیم بندی نمود. دانشگاه نسل اول، دانشگاه های آموزش محور بودند. این دانشگاهها که حدودا تا دهه اول انقلاب فعالیت داشتند وظیفه آموزش دانشجویان و تربیت نیروهای آموزش دیده را بعهده داشتند. دانشگاه نسل دوم، دانشگاه های پژوهش محور هستند. در این دانشگاه ها علاوه بر امر آموزش، به پژوهش نیز پرداخته شده که دستاورد آن علاوه بر تربیت نیروهای متخصص در سطوح فوق لیسانس و دکتری، چاپ مقاله و گسترش مرزهای دانش نیز می باشد. افزایش تعداد مقالات بین المللی ایران و ارتقا جایگاه علمی کشور از دستاورد های این نسل از دانشگاهها می باشند. دانشگاه های نسل سوم یا دانشگاه های کارآفرین، دانشگاه هایی هستند که علاوه بر دو وظیفه دانشگاه های نسل دوم در جهت تجاری سازی علم و کارآفرینی فعالیت می کنند. در این سخنرانی سعی شده است به بررسی فعالیت چندین ساله محققین کشور در زمینه شیمی تجزیه پرداخته شود و مقالات چاپ شده توسط محققان کشور با دیگر محققان در چند دانشگاه معتبر دنیا ونیز برخی از دانشگاههای منطقه پرداخته شود. نقاط قوت و ضعف فعالیتهای علمی داخل کشور در زمینه شیمی تجزیه بررسی شود و توانمندی دانش آموختگان در زمینه تولید علم و همچنین کارآفرینی مورد نقد و بررسی قرار گیرد و در انتها به بررسی امکان و ضرورت ورود پروژه های جاری در شیمی تجزیه کشور به سمت کارآفرینی پرداخته شود.







## DNA based electrochemical biosensors

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Nucleic acid recognition layers can be combined with electrodes to form new and important types of affinity biosensors as DNA based electrochemical biosensors. Genosensors or DNA hybridization biosensors are analytical devices for detection of specific DNA target sequences upon hybridization of the target with complementary probe immobilized on the solid substrate. Electrochemical DNA biosensors rely on the conversion of the DNA base pair recognition events into a useful electrical signal [1]. Recognition of electrochemical DNA hybridization is accomplished via two methods including direct and indirect. In direct DNA hybridization detection that carry out without any label, the signal induces owing to the inherent oxidation of adenine and guanine bases in DNA strands directly [2]. Whereas, in indirect method the oxidation or reduction signal of an electroactive indicator causes detection of hybridization event. Electrochemical indicators for detection of hybridization have usually small molecular weight and different affinities for ssDNA relative to dsDNA. In particular, DNA hybridization biosensors offer considerable promise for obtaining sequence-specific information in a simple, faster and cheaper manner, compared to traditional hybridization assays. Such new strategies hold enormous potential for clinical diagnosis of genetic of infectious diseases, for environmental monitoring or other investigations. The genetic disorders detection is obviously of importance for preventive health care. Numerous of these disorders are created by mutations happened in double stranded DNA (dsDNA) in our body cells, consists of the blueprint of our genetic makeup. The dsDNA is formed, when all the bases of which two complete complementary single strands DNA (ssDNA) bind to each other. If one mismatch happens in the base pairing process, single base-pair mismatch, single nucleotide polymorphism or SNP, is created which can lead to many disorders. In this works, I introduce some compound such as: brilliant cresyl blue, Indigo Carmine, ethyl green, ketamine and tyrosinase as new electroactive labels in electrochemical DNA oligonucleotide sensors based on various working electrodes [3-5], new PNA or DNA biosensor based on p53 tumor suppressor gene corresponding oligonucleotide [6] and proposed genosensor for recognition and determination of thalassemia gene [7], DNA damage detection [8], introduction of some drug as a G-Quadruplex-Binding Ligand [9] and electrochemical DNA-based biosensors for determination of some heavy metal ions [10].

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# **Invited presentation**



## The 25<sup>th</sup> Iranian Seminar of Analytical Chemistry

3-5 September 2018

University of Tabriz



### Information-Accuracy Relation in Chemical Studies

Somaiyeh Khodadai, Mahsa Akbari, Elnaz Tavakoli, Mahdiyeh Ghaffari, Jamile Mohammadjafari, Somaiyeh Valizadeh, Zahra Rasouli, Azam Safarnejad, Saeid Khalili and Hamid Abdollahi\*

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The main aim of most scientists is discovering the nature by measurements and exploiting the basic hidden rules in universe. Chemist has also been involved in solving chemical problems. How much is the solution of a chemical problem accurate? When one don't know anything about the problem then everything is the solution and there is an unbounded range of possible solutions for the problem. Relevant information can improve the accuracy of the solution. Efficient knowledge can reduce the range of accuracy to precision interval of true solution. A solution can be unique but not necessarily true. Incorrect information can produce the unique but not true solution.

There is a range of possible solutions for the results of analyzing any experimental measured data. In the presence of adequate knowledge this range represents the precision of true solution. In most real chemical studies the available information is not enough for reaching to accurate solution. Therefore the results of any chemical studies should be presented as a range of feasible solutions which this range is directly dependent to available relevant information.

The relation between accuracy of the results and the information which has been applied in solving the problems can be visualized in many real examples. In this contribution we have reported several hard and soft modeling chemometrics methods to show the impact of using correct chemical information to obtain more accurate results.





## The 25<sup>th</sup> Iranian Seminar of Analytical Chemistry

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### Application of layered double hydroxides in sample pretreatment and enchantment of luminescence signal

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Layered double hydroxides (LDHs) are a class of synthetic two dimensional nano-structured inorganic materials that have positively charged layers of metal hydroxides, between which are located anions and, in general, some water molecules. The general formula of LDHs can be represented by  $[M_{1-x}^{2+} M_x^{3+} (OH)_2]^{x+} [A_{x/n}^{n-} \cdot mH_2O]^{x-}$ , where  $M^{2+}$  is a divalent cation;  $M^{3+}$  is a trivalent cation;  $A^{n-}$  is an interlayer anion;  $x$  value is equal to the molar ratio  $(M^{3+})/(M^{2+} + M^{3+})$ , and  $m$  is the number of water molecules located in the interlayer region together with anions. The electrostatic interactions and hydrogen bonds between layers and contents of the gallery hold the layers together, forming a three dimensional structure [1,2]. LDHs are of great interest for nano materials science and technology due to their special structural and unique applications. Despite of other applications, LDHs are potentially good adsorbents for a diverse number of anions because of their permanent layer positive charge, high anion-exchange capacity, large surface area, good thermal stability and water resistant structure. Moreover, due to create inorganic-organic host-guest hybrid nanostructures, in recent years the use of LDHs as host materials has become of increasing interest. LDH matrix provides special structure for intercalated fluorophores such as immobilization of fluorophore in a stable environment improving fluorescence efficiency and optical stability of the fluorophore [3, 4]. In this paper, application of layered double hydroxides in solid-phase extraction of several organic and inorganic anions from environmental, biological and food samples along with the role of layered double hydroxides on luminescence signal enchantment have been discussed.

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## The 25<sup>th</sup> Iranian Seminar of Analytical Chemistry

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### Voltammetric DNA biosensors in order to early detection of some dangerous diseases

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Biomarker usually refers to a biological measurable indicator, and sometimes also to a substance whose its presence indicates the presence of a living organism. Biomarkers may be used alone or in combination, to assess an individual's health or disease. Today, a wide range of biomarkers is used. Each biological system (e.g. cardiovascular, metabolic or immune system) has its own biomarkers. The ideal biomarker has certain features that are appropriate to review the terms of certain diseases. In medical field, biomarker can be used in an organism as a detectable substance and means to evaluate the performance of its members. Presence of biomarker in the body may be indicative of a particular disease and this is one of the biomarker applications. Biomarkers are used primarily for the prediction of serious diseases such as diabetes and cardiovascular disease. Each biomarker is used alone or in conjugation to provide an accurate picture of whether a person is healthy or not [1]. Because the concentration of biomarkers is very low, various methods have been used for increasing voltammetric signal, such as Au nano particles, enzymes, carbon nano tubes and quantum dots. In this work, we intend to develop voltammetric DNA biosensor using nano magnetic beads and liposomal or polyerosomal network for measurement of some biomarkers related to some dangerous diseases. Polyerosomes are a group of synthetic vesicles made from block copolymers with amphiphilic properties. Most reported polymersomes contain an aqueous solution in their core and are useful for encapsulating and protecting electroactive indicators. These polymersomes can release electroactive indicators by external stimuli, arriving at the measurement step that significantly increases the voltammetric signal of electroactive indicators.

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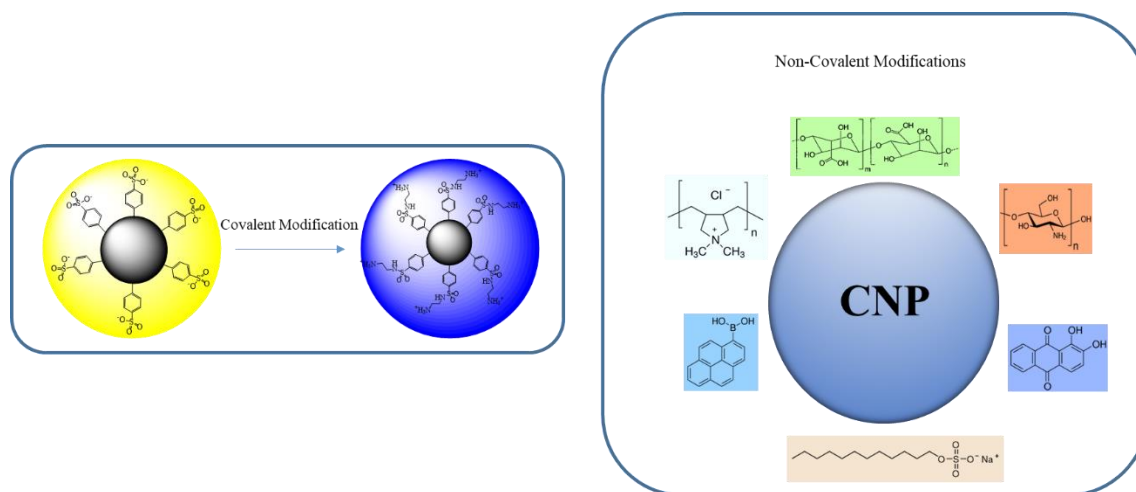
## Carbon Nanoparticle Composites based Electrochemical Sensors

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Carbon materials are broadly applied for modified electrodes in electroanalysis. Recently, the new range of nanocarbons has extended interesting developments in electrochemical sensing. It can be related to the advantages of nanocarbons like significant high surface area, high electrical conductivity, high level of interfacial edge sites and reactive surface sites. Carbon nanoparticles (CNPs) are well known for many years (e.g., as carbon black) and they have been widely used in industry for example as filler and pigments. Nevertheless, these carbon nanoparticles similar to metal nanoparticles are very interesting building blocks in thin film electrode systems and their high level of interfacial edge sites are potentially beneficial in electrochemical processes. Typical particle sizes for commercial blacks are 1 to 50 nm in diameter with a high surface area accessible for chemical functionalization and ideal for effective interaction with redox active species. Functionalization of CNPs and fabrication of CNP composites resulted a great potential to fabricate materials with a range of improved properties such as mechanical, optical, electrical and thermal. The surfaces of CNPs are intrinsically chemically inert and hydrophobic, and they tend to form agglomerates or bundles. Therefore, surface functionalization of CNPs becomes a critical pre-requisite in the fabrication of nanocomposites. Various functionalization methods have been developed including, chemical, mechanochemical, electrochemical, and irradiation reactions in order to activate the carbon surface, which subsequently interact with compounds through covalent bonding or non-covalent interactions. Functionalized CNPs and resulted CNP composites have promise as novel active high surface area electrode materials as nano-building blocks in electroanalysis.



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**Dispersive liquid-liquid microextraction techniques: history, developments and applications**

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In early 2006, a novel form of the liquid-phase microextraction (LPME) technique named dispersive liquid-liquid microextraction (DLLME) was developed [1]. Conventional DLLME has very simple and basic principles based on the ternary component solvent systems. In this simple and fast microextraction technique, an appropriate mixture of a micro-scale volume of water-immiscible extraction solvent (hydrophobic solvent) such as carbon tetrachloride along with a few sub mL of water-miscible disperser solvent (hydrophilic solvent) such as acetone is rapidly injected into an aqueous sample containing analyte(s) by syringe. This action makes the sample solution very cloudy and turbid, which is a result of the dispersion of extraction solvent and formation of small and tiny droplets. After the formation of the cloudy solution, the surface area between the extraction solvent and the aqueous sample becomes very large, so hydrophobic analytes can easily transfer into the extractant phase and the equilibrium state is achieved quickly and therefore the extraction time is very short. This is why DLLME can provide often higher extraction efficiencies in very short time than many other microextraction techniques. In conventional DLLME, phase separation can be accelerated by centrifuging and the extraction solvent settles at the bottom of sample solution. The organic phase can be removed and subjected to final instrumental analysis. DLLME has gained a wide acceptance in the analytical chemistry field due to its advantageous extraction efficiency, low cost and simplicity [2].

Since the introduction of DLLME many modalities of that such as magnetic stirring-assisted-, air-assisted-, ultrasound-assisted-, pressure-assisted-, surfactant-assisted-, vortex-assisted-, displacement-, solvent-demulsification, ionic liquid-, solidification of floating organic drop, and supramolecular-based-DLLME were developed. Also, it is combined with different extraction techniques such as solid-phase extraction (SPE), stir bar sorptive extraction (SBSE), supercritical fluid extraction (SFE), microwave-assisted extraction (MAE) and accelerated solvent extraction (ASE) to improve selectivity and enrichment factors. Up to now, DLLME is used as a sample preparation method for most of the analytical techniques such as gas chromatography (GC), high-performance liquid chromatography (HPLC), inductively coupled plasma-optical emission spectrometry (ICP-OES), electrothermal atomic absorption spectrometry (ET AAS), flame atomic absorption spectrometry (FAAS), UV-VIS spectrophotometry and capillary electrophoresis (CE).

DLLME is applied for extraction and preconcentration of most organic compounds (pesticides, polycyclic aromatic hydrocarbons, polychlorinated biphenyls, flame retardants, explosives, phthalate esters, plasticizers, antioxidants, vitamins, hormones, aflatoxins, mycotoxins, halophenols, polyphenols, amines, antibiotics, drugs and etc.) and inorganic compounds (cadmium, cobalt, nickel, chromium, selenium, lead, zinc, iron, gold, silver, mercury, copper, vanadium, arsenic and etc.) in biological, environmental and food samples [3].

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**Quantum Dots in Electrochemiluminescence; Advances and Applications**

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Quantum Dots (QDs), are known as nanocrystalline semiconductors, that have remarkable fluorescence emission properties. Quantum dots were discovered by the Russian Physicist Alexey I. Ekimov in 1981 and opened a new era in nanoscience and nanotechnology[1-3]. Diameter of QDs typically ranges from 2 to 10 nm and the unique size and properties of quantum dots make them very appealing for a variety of applications and new technologies.

In this paper the advances of quantum dots related to analytical and bioanalytical applications of electrochemiluminescence were presented [4]. Also, in this presentation some examples dealing with the use of quantum dots to improve the analytical and bioanalytical capabilities of electrochemiluminescence were discussed [5].

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### A glance on novel applications of infrared spectrometry

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Infrared spectroscopy with its fast and nondestructive advantages has been qualified for the real-time analysis. Its reliability together with the possibilities for development of portable instruments has provided noticeable progress in its application for several qualitative and quantitative analyzes. Recently, novel instrumental advances such as fiber-optics spectroscopy and operando analysis have opened new doors for on-line monitoring of processes, in-situ evaluation of chemical variations, local determination of chemical structures etc. Nowadays infrared spectrometric investigations are known as informative approaches towards quantitative determination and/or qualitative pattern recognition. However, the noticeable role of chemometric data processing must be also considered for these aims. Chemometric data processing would enable the spectroscopists to deal with the large data set of the spectra in extraction of the most important information and provision of the useful knowledge. A glance on the application of infrared spectrometry in pharmaceutical, petroleum-petrochemical, food and catalyst industries together with introducing its potential for art and cultural heritage evaluations are a part of this wide domain.





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### New Psychoactive Substances Analysis

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New psychoactive substances (NPS) are proliferating at an unprecedented rate, posing a significant risk to public health and a challenge to drug policy. Often, little is known about the adverse health effects and social harms of NPS, which pose a considerable challenge for prevention and treatment. Monitoring, information sharing and risk awareness are needed to counter this new drug problem. NPS have become a global phenomenon with over 110 countries and territories from all regions of the world having reported one or more NPS.

Beyond the routine contributions to solving forensic casework, the discipline of analysis of drugs provides data and information which enriches trend analysis, and contributes to a better understanding of the drug situation and to more effective policy decisions. Such as, the route of synthesis of drug substances, effectiveness of precursor control measures and price–purity analysis, and thus enable a better understanding of the dynamics of drug markets. With regard to the emergence of new substances, forensic data are important in identification to facilitate effective law enforcement and health interventions for the problem. Research on the new substances subsequently plays a pivotal role in raising awareness of and providing the basis for development of methods and tools for identifying NPS.

There are specific challenges in the analysis of NPS. These included difficulties in acquiring NPS reference standards, and in determining which reference materials are required to enable the identification of unknown NPS and the number and diversity of NPS continue to increase, and there are no signs of this slowing down in the immediate future. So research is needed to understand the scope of the problem, and to develop and standard methods of analysis.





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### Gradient and Superhydrophobic Surfaces in Microextraction Strategies

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Gradient and superhydrophobic surfaces are quite fascinating and have been studied in many various fields. The noticeable property of gradient surfaces is the continuous change of chemical or physical properties over the substrate [1]. Until now, various gradient surfaces including the chemical and structural gradients, often with a cumulative nano- to micro-structures and high porosity have been introduced. The special feature of these surfaces is, changing in chemical composition from hydrophilic to hydrophobic which can be extended to the simultaneous and efficient entrapment of various compounds with different polarities. Over the past decades, many publications have been devoted to the fabrication of gradient surfaces, in which the electrochemical methods especially wireless functionalization or bipolar electrochemistry is quite considerable [2]. Bipolar electrochemistry deals with the exposure of an isolated conducting substrate that has no direct connection with a power supply except via an electric field (wireless technique). Briefly, in bipolar electrochemistry, the bipolar electrode acts as an anode and cathode that allows simultaneously oxidation and reduction reactions on the same substrate. A voltage is applied in the bipolar setup between the feeder electrodes that are spaced by a distance in a cell. Therefore, the applied potential  $E_{\text{appl}}$  drop linearly through the electrolytic solution and the interfacial difference of potential between the substrate and the solution become the driving force for the bipolar electrochemical reactions [3]. Recently, a novel gradient fiber coating of organoclay-Cu nanoclusters on a copper wire by bipolar electrochemistry is prepared and implemented in headspace in-tube microextraction of CBs from aqueous samples [4].

The superhydrophobic materials with rough surfaces and low surface energy are also appropriate candidates for to the increased adsorption of non-polar analytes and holding any organic extractive solvent and influential in subsequent extraction enhancement. More recently, superhydrophobic materials have been successfully used as the extractive phase in needle trap microextraction [5,6] and  $\mu$ -solid phase extraction [7].

Considering the characteristics of gradient and superhydrophobic surfaces, their synthesis, modifications and applications as extractive phases and/or probes for holding extractive solvents in various microextraction strategies are discussed.

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**Simple methodologies for resolving fluorescence resonance energy transfer (FRET) profiles by matricising the multi-way fluorescence data**

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Förster resonance energy transfer (FRET) is a mechanism describing energy transfer between two light-sensitive molecules (chromophores) labeled as suitable donor or acceptor. In general, "FRET" refers to situations where the donor and acceptor proteins (or "fluorophores") are of two different types. The efficiency of the distance dependent FRET phenomenon is measured through spectral changes and used to identify interactions between the labeled complexes and hence accurate resolution of the chromophores spectral profiles is of importance. In many biological situations, however, researchers might need to examine the interactions between two or more proteins of the same type or indeed the same protein with itself, for example if the protein folds or forms part of a polymer chain of proteins or for other questions of quantification in biological cells. Obviously, spectral differences will not be the tool used to detect and measure FRET, as both the acceptor and donor proteins emit light with the same wavelengths and this leads to rank-deficiency in the measured data. There are several methods for measuring the FRET efficiency by monitoring changes in the fluorescence emitted by the donor or the acceptor with the aim of revealing the conformational changes in protein hybridizations [1,2].

In this work some simple and reliable methods will be proposed for extracting the true FRET profiles based on the unfolding the obtained three-way FRET data and augmenting in suitable directions. It is already showed by many researches that the augmentation of multi-way rank-deficient data in the direction in which rank-deficiency occurs and analyzing the resulted matrix, could eliminate the problem. Based on this and using the same strategy, Rank Annihilation Factor Analysis [3] and Mean Centering of Ratio Spectra [4] were used for accurate extraction of FRET profiles and consequently determination of FRET efficiency. Rank Annihilation Factor Analysis was used in two modes for eliminating the donor and acceptor pure contributions from data and accurate profile related to component (hybrid component making FRET phenomenon) retained. Similarly Mean Centering of Ratio Spectra was used in two directions on unfolded excitation-emission data matrix obtained for different concentrations of components for eliminating the donor and acceptor pure contributions. Also as the augmented data matrix could be full rank in some situations, Multivariate Curve Resolution [5] can be used for resolving the components FRET profiles. This method has the advantage that the profiles of an unknown component could be extracted or estimated. The efficiency of proposed methods were evaluated by simulating several datasets with different degrees of spectral overlapping and in the presence of noise. The effect of unknown interferent on the obtained responses was also tested.

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**Hybrid Direct Carbon Fuel Cell (HDCFC); from Theory and Laboratory Scale to Demonstration Plant**

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Traditional methods of generating power from coal involve combustion, where chemical energy is converted into electrical energy through a series of energy transformations. Even using state-of-the-art techniques in coal fired power stations, overall efficiencies of less than 40% are generally accepted as best practice. Due to the nature of the combustion process, usually further pre- or post-treatment of the feeding or flue gas is required to generate a clean, sequestration-ready carbon dioxide stream. These treatments are energy intensive and use parasitic energy from the process, reducing efficiency even further.

Direct carbon fuel cell (DCFC) is an innovative technology that has ability to efficiently utilise coal to produce electricity with significantly reduced environmental green-house gas emissions. The DCFC replaces this inefficient pathway through direct electrical energy generation without combustion. Instead, the same reaction employed in a coal-fired power station is broken down into its component electrochemical half reactions using a fuel cell arrangement. Thermodynamically and kinetically its efficiency is much higher than a coal fired power station; i.e., thermodynamic efficiency is 100%, while practical efficiencies are ~80% (compare to efficiency of <40% in a state-of-the-art coal-fired power station). Since carbon dioxide is directly generated as the reaction product, the flue gas has the potential to be pure and sequestration ready carbon dioxide with little to no flue gas treatment required.

Hybrid direct carbon fuel cell (HDCFC), which utilises both solid oxide fuel cell (SOFC) and molten carbonate fuel cell (MCFC) technologies, has significant advantages and shown better performance among other DCFC techniques on the small scale. This presentation will cover research outcomes from our laboratory including theory and technology development towards building a 10 kW DCFC demonstration plant.





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### New Sorbents for Extraction and Microextraction Techniques

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The outlines of this speech is to shine light on recent research and developments in some new classes of sorbents for extraction and microextraction techniques. These results are part of the works carried out by our research team and there has been an attempt to introduce some new applications of nanosorbents in a perspective view. Carbon based nanosorbente such as types of graphene and carbon nanotubes are very stable systems that having considerable chemical inertness due to the strong covalent bonds of the carbon atoms on the nanostructure surface. Molecular Imprinting has proved to be an effective technique in the field of extraction. By a mechanism of molecular recognition, the molecularly imprinted polymers are used as selective tools for the development of various analytical techniques such as solid-phase extraction (SPE) and solid-phase microextraction (SPME). Sol–gel chemistry provides a convenient pathway to create advanced material systems that can be effectively utilized to solve the common solid phase microextraction fiber technology problems. Quantum dots (QD) are very small semiconductor particles that their optical and electronic properties differ from those of larger particles. quantum dots such as CdSe (QDs), graphene QDs and carbon CDs, have attracted much attention due to their unique properties. All of these materials combined with magnetic solid-phase extraction can be used as effective adsorbents for analysis of biological samples. This topic is mainly focused on recent advanced developments in the design, synthesis and application of the nanoadsorbents.





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**Applications of nanostructures in detection and determination of chemical materials and bio-markers**

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Nanostructured materials and systems have been used for tropic and diagnostic proposes in medicine. Among them, diagnostic applications have attracted special interests in recent years especially in biosensors and immunochromatography. Some of these applications have high potential in market and have developed in industrial and large-scales.

This presentation will review briefly two kinds of these applications;

1. Application of electrospun carbon nanofibers as biosensor probes such as aptamers, glucose,...
2. Rapid diagnostic tests based on nanoparticles in immunochromatography which is developed in domestic market for baby check, drug abuse, HIV, HCP, etc.





**Multi-Way Data Analysis in Investigating Environmental Variables Regulating Cyanobacteria Species Abundances in a Major Drinking Water Reservoir**

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The present study provides a detailed understanding of the variation in cyanobacterial communities of Grahamstown Reservoir, a large shallow off-river storage servicing the city of Newcastle on the east coast of Australia. Receiving multiple inflows from two unprotected mixed land-use catchments, it is a model example of a reservoir highly vulnerable to adverse water quality issues, including phytoplankton blooms and their consequent filtration, toxin and taste and odour implications. The spatial and temporal distribution of cyanobacteria were assessed for a period of three years (Jan 2012- Dec 2014) based on samples collected fortnightly from three monitoring stations within the reservoir. Relationships between cyanobacterial abundance and a range of environmental factors was evaluated by application of Multivariate Curve Resolution Alternating Least Squares (MCR-ALS) data analyses.

MCR-ALS analysis indicated that among 22 physico-chemical variables and 14 cyanobacterial species measured, the vertical temperature gradient within the water column and nutrient availability, especially soluble reactive phosphorus (SRP), were the most powerful explanatory factors for the observed temporal and spatial distribution patterns in cyanobacterial species densities. The abundance patterns of the dominant cyanobacterial species, *Aphanocapsa*, *Aphanothece*, *Microcystis* and *Pseudanabaena*, were also strongly linked with rainfall and run-off patterns into the reservoir, while *Dolichospermum* (*Anabaena*) were more closely linked with the seasonal pattern of water temperature.







## Magnetic nanoparticles based Sensors and biosensors

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Magnetic nanoparticles (MNPs) are widely used in the development and fabrication of sensors and biosensors. MNPs be dispersed in the sample and collected the targets then be integrated into the transducer materials by their attraction by an external magnetic field onto the active detection surface of the (bio) sensor. This work describes and discusses our recent applications of MNPs in sensors and biosensors. Core-shell Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> is one of the most used in biosensors, since it contributes to stabilization of MNPs in solution and enhances the binding of ligands at the surface of MNPs. Core-shell Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> is also much used in modifying surfaces of MNPs. The Core-shell Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> modified whit various molecules and biomolecules such Antibodies, DNAzymes and aptamers. Electrochemical based magneto-immunoassay for simultaneous determination of carcinoembryonic antigen (CEA) and alpha-fetoprotein (AFP), electrogenerated chemiluminescence(ECL) for determination of Hepatitis B virus surface antigen and fluorescence based sensors and biosensors are some of the work has been reported.

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### The Role of nanoparticles in Drug Analysis

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Complexity of the biological matrixes e.g. plasma and urine and low doses of the drugs, leads to the growing trends of sample treatment and preconcentration processes in drug analysis which consequently leads to the development of various novel analytical methods. Liquid-liquid extraction (LLE) and solid phase extraction (SPE) are two common sample treatment methods with the limitation of high volumes of toxic organic solvents consumption, being time consuming and frangibility of the cartridges. Magnetic solid phase extraction (MSPE) is a novel sample treatment method with the advantages of magnetic properties that leads to easy separation of the adsorbent from the sample medium in the presence of external magnetic field without any filtration or centrifugation. Moreover, application of nano structure magnetic adsorbents provides high surface-area-to volume that makes maximum extraction efficiency of the analytes from the medium in comparison with other adsorbents. Polymeric magnetic nano adsorbents (PMNAs) are a combination of magnetic cores and polymeric shells. This polymeric shells offer a functional surface for MNPs providing a selective performance for MNPs in drug analysis. The presentation tries to share the experiences of presenter along with new related approaches in the application of MNPs and PMNPs in drug analysis.





**Paper-based Analytical Devices**

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In spite of great achievement in analytical instrumentation, developing inexpensive portable analytical platforms for various applications including disease diagnostics, environmental monitoring, food safety, and water testing at the point-of-care (POC) settings, have attracted a significant interest. Current analytical devices are very complex and expensive, need well-trained operator, consume expensive and harmful chemicals and last but not least have limitation for in-field applications. Lab-on-a-chip analytical devices and micro total analysis systems are relatively new group of analytical tools, capable of analyzing complex within one analytical run.

Paper-based analytical devices (PADs), as a promising and powerful platform, have shown great potential in the development of POC tests. There are a lot interests on using paper as a substrate for development of analytical devices since paper is very cheap, has self-pumping capability because of capillary action, it's surface can be modified easily and is available in different forms and shapes. Microfluidic PADs ( $\mu$ PADs) and colorimetric sensor arrays (or optoelectronic noses) are emerging methods that use paper as substrate.

Since 4 years ago, my research group has directed its research priority toward development of paper-based analytical devices for applications in food, environment and health. In this seminar, I will present the results of the works done or under investigation in my research group regarding paper-based analytical devices. We used paper substrate in development of optoelectronic noses for ultrasensitive determination of volatile organic compounds (VOCs) and used them for authenticate investigation of herbal distillates producing in Shiraz and detection of adulteration in natural vinegars [1,2].

Concerning  $\mu$ PADs, we used simple patterning methods to fabricate hydrophilic microchannels on the paper. These microchannels can automatically flow the liquid samples, mix them and allow chemical reactions to take place at the end. A simple  $\mu$ PADs device was fabricated based on molten paraffin and was then used for colorimetric measurement of acidity constant of indicators [3]. We used electrochemically integrated  $\mu$ PADs for fabrication of an electrochemical concentration cell, which is able to measure highly concentrated ammonia solutions in petrochemical industries. Also,  $\mu$ PADs were used for fabrication of bipolar electrochemical cells based on colorimetric measurements.

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## Playing with Emissions for Naked Eye Detection: Nanoparticle-Based Ratiometric Sensing

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There is a crucial demand to develop a sensitive, fast, low-cost and portable strategy for the on-site detection in environments, medicines and foods, which has always been attracting considerable efforts in the construction of new chemical sensors<sup>1</sup>. With high sensitivity and simplification, fluorescence-based sensors are most widely studied due to a wide range of available fluorescent dyes and luminescent nanostructures including quantum dots (QDs), graphene oxide, and carbon dots (CDs)<sup>2-4</sup>. Instead, fluorescent sensors possess another unparalleled advantage, that is, their visualization capability for the determination of analytes with the naked eye by the aid of a simple ultraviolet (UV) lamp<sup>1</sup>.

In general, a single-colorful fluorescent probe only can display the change of fluorescence brightness by either “turn on” or “turn off” with analytes, greatly limiting their quantitative capability<sup>1</sup>. An accurate/visual quantification mainly depends on the color variations (by the use of two or three fluorescent probes) rather than only brightness, because our eye is more sensitive to colors. However, the use of multicolorful fluorescent probes toward the wide color variations with target dosages remains a fascinating challenge for analytical chemists and still under investigation.

In this presentation, the recent advances in design of color-multiplexing based fluorescent probes for detection and discrimination between different analytes are addressed, with focus on our own work<sup>2-5</sup>.

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**Early Diagnosis and Efficient Treatment of Cancers by Smart Targeting of Cancer Cells**

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Cancer, a complex disease at different aspects, is characterized by irregular and uncontrolled cells growth and proliferation. While significant methods have been developed for the diagnosis and the treatment of cancer during the last few decades, but it remains one of the main causes of death [1]. One of the major challenges of cancer treatment is the early diagnosis for effective treatment and reduction of cancer mortality. Therefore, the development of a sensitive method for diagnosing this disease is very important. Such methods should facilitate the early diagnosis of cancers and increase the patient's survival rate [2].

In this seminar, the recent advances and findings of our research team in the both fields of early diagnosis and efficient treatment of cancers will be presented. To develop the novel strategies for the early diagnosis of cancers as the most vital key in the efficient treatment of cancers, the application of new nanostructures including, carbon dots, graphene nanosheets, metallic nanoclusters and their smart deliveries to cancer cells for developing and prompting the performances of various diagnosis tools including, magnetic resonance imaging (MRI), Fluorescence imaging (FI) and electrochemical Biosensors has been investigated [2-5].

Furthermore, for the efficient treatment of cancers using chemotherapy and radiotherapy, some novel approaches for the smart targeting of cancer cells and hypoxic regions of tumours and smart delivery of anti-cancer drugs and various radiosensitizer including gold nanoparticle and nanoclusters have been investigated [6]

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**Electrochemical Energy Storage: Challenges and opportunities**

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The money that we paid out of pocket for fossil fuels, e.g. gasoline, oil, and natural gas, doesn't reflect the total cost of fossil-based fuels to each of us, as consumption of fossil fuels comes at a cost of serious impact to natural environment and human health. As such, development of efficient energy conversion technologies from renewable sources of energy, such as sun and wind, are highly demanding. However, the intermittent nature of the renewable sources of energy necessitates development of advanced energy storage systems as a grant opportunity. Currently, batteries and supercapacitors are the two widely used energy storage devices, which the former provides a high energy density and the latter offers a high power density and long cycle lives. Technological advancement of energy storage devices lies on the development of single energy storage devices that bring both high energy and power densities along with a long cycle life.

Cost, energy and power performance, safety, calendar and cycle life, and operating temperature range are among the challenges that energy storage devices are face with. Although the requirements for the cost and performance vary with the applications, these two parameters are the most common challenges for all the energy storage devices. Performance of the energy storage devices strongly depends on the electrode active materials. Despite the great successes being made, performance improvement still remains as a challenge. Energy and power performance of the supercapacitors depends on operating potential window of the electrolyte as  $E = \frac{1}{2}CV^2$ . As such, one of the remaining challenges is to develop safe electrolytes with a wide operating potential window. The total weight of an energy storage device is also one of the critical parameters. To cope with this challenge, development of regenerative mechanisms for multiple use of the electrode active materials could be an appealing solution. Self-discharge is another challenge that energy storage devices, especially supercapacitors, are facing. One of the best solutions is to confine redox active species on the solid-state electrode active materials.

In this talk, I will discuss some of my research group's past and present studies on the development of advanced electrode active materials for energy storage devices. With a precise and deliberate selection of the electrode active materials and the electrolyte, along with a deep look into the basic principles of the energy storage phenomenon, we try to provide a viable solution to the bottleneck of energy storage technology. I hope that these strategies along with the activities that others have made would help the energy storage community to take a step forward towards a more sustainable energy future. My research activities can be find via the Google Scholar link provided in Ref. 1 [1].

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### **Application of green chemistry extraction methods in analysis of Drug residue and contaminants in food**

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The development of rapid, sensitive, efficient and automated analytical methods for the determination of drug residues and contaminants in food samples has been attracted more consideration due to food direct effect on human health. In spite of important developments in analytical devices, direct analysis of the compounds in the original matrix is a challenging issue and in many cases preliminary steps for isolation and enrichment of the analytes previous to analysis is vital. Thus many sample preparation methods have been developed. The main objective of sample preparation methods is to purify the sample, increase the concentration of the analytes, and possibly modify the sample to adapt it to the requirements of the test equipment. Three main types of sample preparation methods were developed including single drop microextraction, hollow fiber liquid phase microextraction, and dispersive liquid-liquid microextraction. In all cases the design of methods that minimize or even exclude the use of hazardous substances is a challenging parameter. Hence the need to develop extraction methods that meet the requirements of green chemistry has attracted more attentions. For this purpose, the use of ionic liquids (ILs), deep eutectic solvents (DESs), and lighter than water organic solvents were used in extraction steps.





### Third-Order Advantages: a Step Forward

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Due to the sophisticated analytical instrumentation higher-order data acquisition\resolution appeared at the horizon [1]. In a sequel, several multi-linear algorithms have been proposed to decompose these data tensors [2]. As data acquisitions provide more information for a sample, the required algorithm will be more complex to truly unravel data hidden information [2]. Although, Booksh and Kowalski in a corner-stone paper highlighted the advantages of higher order data sets, but third order advantages left out the famous table in that paper [3]. Oliveri et al. documented that “No additional analytical advantages appear to be known for third-order data processing” [1]. Hence, the main question is that does it really worth to gather higher order data sets?

It is highlighted that third-order decomposition bears all advantages of second order decompositions together with higher sensitivity, selectivity and improved algorithmic resolution of highly collinear third-order data [1].

In this contribution, using direct visualization of the possible solution for a quadrilinear model like four-way PARAFAC, it is emphasized that unique resolution of four-way data arrays in the presence of rank-overlap is possible. To do this, possible solutions of simulated four-way data sets were calculated for the first time in the literature. This can be considered as additional benefit of higher order data resolution, third order advantages. Finally, this finding can be further confirmed using the generalization of the Kruskal’s in-equality to  $N$ -way data arrays relying on theory and simulation are interwoven and mutually supportive [4].

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## Graphene based nanocomposites and nanostructures: Analytical applications

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Metal oxides and carbon nanoparticles are an important group of nanomaterials playing essential role in the development of analytical techniques. A large amount of research is devoted to improve an analytical method from view point of linear response range, limit of detection, sensitivity, selectivity and simplicity. This lecture was aimed to discuss the last scientific achievements in our laboratory in the two subsections:

In the first section, development of cost-effective and simple procedures for immobilization of graphene quantum dots and/or graphene nanosheets to the natural bio-wastes like egg shell calendula (ESC), egg shell membrane, ESM, [22], soluble egg shell proteins (SEP) are described. In some cases the mentioned adsorbents were combined to Fe<sub>3</sub>O<sub>4</sub> magnetic nanoparticles to facilitate extraction procedures. The resulting nanocomposites were used as new adsorbents for removal of textile dyes like Congo red [1], extraction, preconcentration and determination of some organic pollutants such as organophosphate pesticides (OPPs) and polycyclic aromatic hydrocarbons (PAHs) by high performance liquid chromatography, HPLC-UV method. Capability of all proposed methods for analysis of some real samples were thoroughly investigated and compared with other similar methods [2-5].

The second section was devoted to direct electrochemical synthesis of graphene nanosheets as a thin film on the carbon material surface like pencil lead substrates. The resulting probe was referred as graphenized electrode. Various parameters effecting the quality and stability of graphenized carbon substrate were optimized. Graphene coated pencil lead was tested as solid phase microextraction (SPME) fiber for preconcentration and chromatographic analysis of PAHs. When this fiber was coated with polyaniline (PANI) by electro-polymerization procedure, the figures of merits were remarkably improved.

In the third section graphenized pencil lead was used as working electrode and its catalytic properties were surveyed for electroanalysis of amino acids (L-Tyrosine and Tryptophan). This electrode was used for electro-deposition of cobalt oxide nanoparticles (CoO<sub>x</sub>). CoO<sub>x</sub> nanoparticles anchored on the graphene nanosheets showed excellent electrocatalytic activity toward the oxidation of insulin. Linear response range and limit of detection were obtained as 0.46 – 100 nM and 0.11 nM respectively.

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**Ionic liquids: Recent progress in their applications in the extraction and analysis of inorganic and organic materials**

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Ionic liquids (ILs) are mixtures of low melting point organic salts resulting from organic cations, starting with imidazolium cations, and organic or inorganic anions. The cationic component has been varied to other cations such as pyridinium, phosphonium, and thiazolium species. The ionic liquids that have a melting point lower than ambient temperature are defined as room temperature ionic liquids (RTIL) which are labeling as designer solvents. Depending on the structure of the cations and anions, many ILs with different physical properties have been obtained. The designer nature of ILs has driven their exploration and utilization in numerous fields among the physical and chemical sciences such as batteries, dye-sensitized solar cells, fuel cells, electrochemistry, gas separations, polymer chemistry, organic synthesis, biomolecular stabilization and activation, and nanoscience [1]. Deep eutectic solvents (DESs) are a new innovative class of solvents obtained by mixing solid compounds that are not necessarily salts, obtaining a eutectic mixture with a melting point that is much lower than that of the individual components [2].

Due to their unique properties, ionic liquids are regarded as good candidates to replace organic solvents in many industrial processes and have attracted attention as green solvents in extraction in recent years. High viscosity and low vapor pressure of ILs, enable them to form large and stable microdroplets that prohibit them to evaporate during extraction. This can provide superior analyte extraction capabilities as well as improved analytical precision compared to organic solvents. In addition, a wide range of new processes based on ionic liquids has been developed for the selective separation of important components, namely organic compounds, metal species, biomolecules and pollutant gases from waste [3]. To use a solvent for extraction processing of an analyte, the solubility and toxicity are other relevant factors for any chemical to be used in medicine, and other related areas. Fortunately, in recent years, nontoxic ILs have been synthesized by selecting biocompatible organic cations and inorganic anions.

The ability to tune the selectivity of ILs, enables high preconcentration of analytes in various sample preparation and detection techniques. Various task-specific ionic liquids with certain groups have been constructed and are generally used in techniques such as liquid-liquid extraction and solid-phase extraction [4]. On the other hand, IL-modified materials as selective sorbents can be applied as stationary phases with unique selectivities, thermal stabilities, excellent separation efficiency and high peak capacities in gas chromatography, high-performance liquid chromatography and electrophoresis [5]. Magnetic ionic liquids (MILs) have recently generated innovative applications in numerous areas of analytical chemistry. Functionalizing MILs with long aliphatic groups to impart hydrophobic character enables their use in aqueous extraction systems.

In this lecture, recent developments and progress concerning ionic liquids, and their applications in analytical chemistry will be reviewed. It also highlights their emerging use for extraction and separation of analytes. Several examples including some of the current studies in our laboratory will be presented. Potential applications, current challenges and future perspectives will be discussed.

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### Nanofluids in analytical chemistry

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Nanofluids are stable colloidal dispersions of two basic components. A nano-sized particle which can be ceramic nanoparticles, metallic nanoparticles, or carbon nonmaterials and a base fluid such as water, toluene, ethylene glycol and engine oil. Recently, nanofluids have been used in different fields of analytical chemistry because they can improve mass transfer coefficient[1-4].

In recent years, there has been numerous efforts to change the conventional hazardous carriers with environmentally friendly compounds such as ionic liquids (ILs) or deep eutectic solvents in order to make new nanofluids with favorable properties. ILs have unique special properties such as high viscosity, good solubility, good electric conductivity and compatibility with other chemical materials. Due to the specifications listed above, ILs are promising candidates to replace previous dispersant fluids<sup>[5]</sup>. Bucky gels and ferrofluids are types of nanofluids which were used in our laboratory in order to develop dispersive solid phase microextraction method. If we use nanocarbons (such as carbon nanotube (CNTs), graphene (G) and fullerene) as the nano-sized particle and ionic liquid (IL) as the base fluid, the mixture is called 'Bucky gel'. By using Fe<sub>3</sub>O<sub>4</sub> magnetic nanoparticles as the nano-sized particle and the coating in a carrier fluid the resulting material will be ferrofluid. Ferrofluids characteristically have both magnetic and fluid properties and due to their unique physical and chemical properties, they have been finding more and more applications in a variety of fields. For the first time in 2013, application of dispersive-solid phase extraction (D-SPE) based on a ferrofluid has been reported by our group.

In this review, the most recent developments in preparation of new ferrofluids and bucky gels with the aid of different nanoparticles and base fluids are summarized. Furthermore, recent reports on the applications of these nanofluids for developing different microextraction methods for the analysis of various environmental pollutants are reviewed.

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## The 25<sup>th</sup> Iranian Seminar of Analytical Chemistry

3-5 September 2018

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### Analytical Instrumentation, Research to Manufacturing

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Spectrochemical instrumentation is main area for producing & manufacturing of different type of analytical instruments. Analytical instrumentation is the base and important field of Analytical chemistry which has many difficult for research and development in Iran .

In this presentation, we discuss two type of Analytical Instrumentation research that has been reached to manufacturing and prototype. Array Spectrophotometry & Photo thermal Lens Microscopy which was developed to manufacturing & production. Finally, our research papers have been published by the laboratory made instrumens.

Research, innovation and manufacturing of analytical instrument would have prepare high quality research and high tech analytical instruments.

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## The potential of Cyphos<sup>®</sup> IL 101-based polymer inclusion membranes for selective extraction and on-line separation-FIA spectrophotometric determination of vanadium

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Even though supported liquid membrane (SLM)-based separations are alternative to solvent extraction, they suffer from poor stability due to leaching of the organic phase into the adjacent liquid phases. Polymer inclusion membranes (PIMs), a relatively recently developed liquid membranes, are known to be more stable than SLMs because the membrane liquid phase is entangled within the polymer chains. PIMs are composed of an extractant, a base polymer, and, in some cases, a plasticiser. They are typically prepared by casting a solution of all membrane components in a volatile solvent and allowing the solvent to evaporate slowly. PIMs have been applied in extraction and transport processes of a variety of analytes, paper-based sensing, passive samplers and in on-line separation for the selective determination of ions in FIA systems.<sup>[1]</sup>

The gradual depletion of vanadium containing ore reserves and the increased industrial consumption of this metal, have promoted researchs for its recycling from secondary sources, such as spent hydrodesulfurisation catalysts. Beside the economically importance of vanadium recovery, the determination of V(V), as a pollutant, is also essential. Although, spectrophotometric methods are most frequently used for the V(V) determinations, the reagents used in these methods are not generally selective and therefore an appropriate separation step should be introduced to allow reliable determination of V(V).

The first part of this communication is devoted to describe the development and application of a poly(vinylidene-fluoride-*co*-hexafluoropropylene) (PVDF-HFP)-based PIM containing trihexyltetradecylphosphonium chloride (Cyphos<sup>®</sup> IL 101) as extractant, for the selective extraction of V(V) from sulfate solutions. A PIM composition containing Cyphos<sup>®</sup> IL 101, PVDF-HFP and 2-nitrophenyloctyl ether (35:55:10 wt% ratio) was able to efficiently extract V(V) from 0.2 M sulfate solutions, at pH 2.3. It was suggested that the presence of sulfate promoted the formation of VO<sub>2</sub>SO<sub>4</sub><sup>-</sup>, which was extracted via an anion exchange mechanism with Cyphos<sup>®</sup> IL 101. The loaded PIMs could be quantitatively back-extracted with 6 M H<sub>2</sub>SO<sub>4</sub>. The selectivity of the PIM towards V(V) was tested with a mixture of Mo(VI), Al(III), Co(II), Cu(II), Fe(III), Mn(II), and Ni(II). The interference of Mo(VI) was resolved by designing a two-step procedure.<sup>[2]</sup> The optimized PIM was stable for at least five extraction/back-extraction cycles.

The study was followed by introducing a FIA system that incorporates the developed PIM in an extraction cell<sup>[3]</sup> for the on-line selective separation of V(V) which was followed by its spectrophotometric determination using xylenol orange. The developed method was applied to the determination of V(V) in various samples. Univariate sequential optimization of the various parameters controlling the FIA system, was carried out. Under optimal conditions the system was characterized by a linear concentration range of 0.5–8.0 mg/L, detection limit of 0.08 mg/L and sample throughput of 4 h<sup>-1</sup>. The RSD at the 3 mg/L level of V(V) was 2.9% (n=8). The membrane was stable, which was reflected by the standard deviation value for determinations over three consecutive days (24 determinations of 3 mg/L V(V)) of 3.6%. The developed FIA system was applied to the determination of V(V) in water and dietary supplements samples and a good agreement with ICP-OES was observed.

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**In tube solid phase microextraction: A promising technique for extraction ultr-trace amounts of organic and inorganic pollutants from aqueous solutions**

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Sample preparation is important for isolating desired components from complex matrices and greatly influences the reliability and accuracy of their analysis. Solid phase microextraction, which integrates concentration, extraction and sample introduction in to a single step, was first introduced by Pawliszyn and et al. [1]. To further enhance the extraction capacity and improve the stability of the fiber in SPME methods, in-tube solid-phase microextraction (IT-SPME) as a form of capillary microextraction (CME) was developed in 1997 [2]. Since the length and surface area of the coating in IT-SPME method is much higher than that used in fiber SPME, this method can provide greater extracting phase loading, increase sample capacity and improve extraction sensitivity. In addition, IT-SPME offers easy automation of the extraction process by on-line coupling to HPLC. In general, the majority of the commercially available IT-SPMEs are mostly devoted to fused silica capillaries with different polymeric coatings. However, the utility of conventional capillary columns is limited by their low extraction efficiency because of the large breakthrough volume and the small amount of adsorbent phases, low stability, and, in some cases, the long extraction times involved due to the slow diffusion of the analytes from the sample to the capillary coating. Considerable efforts have been focused on developing new adsorbent phases, such as fiber packed, sorbent-packed, and rod-type monolith capillaries, to improve the extraction efficiency, stability, and selectivity [3].

In the present review electrochemically deposition of different coatings like as conducting polymers, layered double hydroxides and various composites on the inner surface of a stainless-steel tube as the unbreakable substrate will be discussed. Coating of surface of metal beads, wires, etc with proper sorbents by electrochemical methods and packing of them into stainless-steel tube will be investigated. Also on line coupling of IT-SPME with HPLC-UV, atomic absorption spectrometry, inductively coupled plasma atomic emission spectrometry will be presented. Applications of IT-SPME and electrochemically controlled in-tube solid phase microextraction (EC-IT-SPME) for extraction and analysis of organic and inorganic species in aqueous matrices will be discussed. Finally IT-SPME's potentials and limitations and its future view will be investigated [4-7].

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# **Oral and Poster presentation**



## Selectivity Evaluation of Methadone Solid Phase Extraction by Molecular Imprinted Polyurethane Foam

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A spectrophotometric method by molecular imprinted polyurethane foam as solid phase extraction was studied for selective extraction of methadone in different complex matrixes [1,2]. It was aimed to prepare a foam structure as a selective adsorbent with high capacity, easy to access, low price, and biodegradable. In the first step the imprinted polyurethane foam synthesized. In order to access to high recovery optimization of pH, elution solvent, solvent volume, time, concentration and temperature was done [3]. Effective parameters for raising selectivity of polyurethane were evaluated and characterized. MIP Characterization by SEM and FTIR spectroscopy confirmed the discussion. Thus the outcome of this study will prepare an applicable MIP as selective adsorbent of methadone from complex matrixes such as biological, pharmaceutical and chemical samples with 32% more selectivity than NIP, due to its active sites in the polymer structure.

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**Highly efficient fluorescence resonance energy transfer sensing of microRNA-155 at attomolar level with high specificity in cancer cells using carbon dots and MnO<sub>2</sub> nanosheets as the energy donor-acceptor platform**

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MicroRNAs (miRNAs) are small non-coding RNAs of 18-25 nucleotides derived either from hairpin or double-stranded RNA precursors [1]. Sensitive, selective and rapid detection of microRNA in cell lines and biological fluids can provide critical information for clinical diagnosis and cancer treatment. Nanomaterial biosensors based on FRET phenomenon have the potential applications in research and clinical practice for DNA hybridization and tumor markers detection [2,3]. Here, fluorescence resonance energy transfer (FRET) sensing platform for sensitive detection of microRNA was developed using C-dots and MnO<sub>2</sub> nanosheets as the energy donor-acceptor pairs. The C-dots with miRNA-155 probe, quenched with MnO<sub>2</sub> nanosheets and restored fluorescence due to the strong affinity between probe and target miRNA-155. The fluorescence intensity possesses a logarithmic correlation to the miRNA-155 concentration in the two ranges from; 0.15 to 1.65 attomolar and from 1.65 to 20 attomolar, respectively, and calculated detection limit was 0.1 attomolar. Furthermore, the presented assay showed high specificity, and was able to discriminate between complementary target miRNA-155 and single-base mismatch miRNA. In addition, this assay revealed good sensitivity and specificity with MCF-7 Breast cancer cells concentrations from 1000 to 45000 cells/mL with correlation coefficient of 0.9937 and detection limit of 600 cells/mL (6 cells in 10  $\mu$ L of injected sample. Furthermore, with analysis of human serum samples which have been spiked with standard micro-RNA concentration the accuracy of the sensing assay-for the measuring of miRNA in human serum samples has been successfully demonstrated with satisfactory results.

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**Salting-out liquid liquid microextraction of determination of mycophenolic acid using terbium-sensitized luminescence method**

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Mycophenolic Acid (MPA) is an immunosuppressant drug used to prevent organ transplant rejection and for the treatment of autoimmune diseases.<sup>[1]</sup> Developing of analysis methods for therapeutic drug monitoring (TDM) is an important issue for measuring of drugs in biological samples.<sup>[2]</sup> Salting-out assisted liquid-liquid extraction is one of the simple methods in bioanalysis which applies the salting-out effect to separate water-miscible organic solvent such as acetonitrile from plasma.<sup>[3]</sup> In addition, terbium-sensitized luminescence methods are one of the simple and sensitive method for the determination of drugs in biological samples.<sup>[4]</sup> This study aimed to develop an analysis method for determination of MPA in biological samples using salting-out liquid liquid microextraction from plasma samples based on the formation of a fluorescent complex with terbium ions.

Under the optimum conditions for the developed analysis method, the method provided a linear range between 0.5 to 5 mg/L with a correlation coefficient ( $R^2$ ) of 0.998 with a limit of detection (LOD) and limit of quantification (LOQ) of 0.1 mg/L and 0.33 mg/L, respectively.

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## Removal of Antibiotics from industrial waste water using Functionalized Magnetic Multi-Walled Carbon nanotubes

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In the recent years, residual antibiotics are considered to be nascent environmental pollutants due to their continuous input and persistence into the aquatic ecosystem even at low concentrations. Therefore, these are necessary to develop efficient methods for the wastewater treatment[2,3]. The present studied describes the efficiency of magnetic multi-walled carbon nanotubes (MMWCNT) for the sorption of the selected antibiotics ( penicillin and enrofloxacin) from wastewater samples. The functionalized MMWCNT were characterized by Fourier transform infrared spectroscopy (FT-IR), scanning electron microscopy (SEM), and transmission electron microscopy (TEM). The obtained antibiotic percentage of sorption was evaluated by quantitative assessment using high-performance liquid chromatography(HPLC) coupled with the Ultraviolet Detector.To optimize the operating conditions, the effects of pH, Time contact, Agitation speed ,adsorbent dosage, and antibiotics initial concentration were investigated by full factorial experimental design method[1].The sorption data were fitted to the Langmuir, Freundlich and Dubinin-Radushkevitch (D-R) equation to establish the sorption isotherm of antibiotics removal by MMWCNT[4]. The best percentages of retention were obtained for penicillin 95%,and enrofloxacin 86.5% .

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**Lab-on-nanopaper: A hand-held microfluidic sensing bioplatfrom based on curcumin nanoparticles embedded in bacterial nanopaper as an albumin assay kit**

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As a recent alternative to paper, bacterial cellulose (BC) nanopaper, as a sheet/film composed of continuous 3D network of nanosized cellulose fibers that are usually produced by specific nonpathogenic bacteria such as *Acetobacterxylinum*, due to having the optical transparency, high chemical, mechanical and thermal stability, low thermal expansion and surface roughness, and also the aforementioned advantageous properties of normal papers, provides an excellent substrate/platform for the development of optical (bio)sensors [1-5].

Herein, we introduce a microfluidic nanopaper-based analytical device ( $\mu$ -NAD) or “lab-on-nanopaper” device for visual sensing of albumin in human blood serums, which relies on embedding of curcumin nanoparticles (NPs) within transparent bacterial cellulose (BC) nanopaper. Because of having the optical transparency and also the advantageous properties of normal papers including high flexibility, porosity, biodegradability and printability, BC nanopaper provides an excellent substrate/platform for the development of optical (bio)sensors. The hydrophilic test zones were created on the fabricated bioplatfrom through creating the hydrophobic walls via laser printing technology. The color changes of curcumin NPs embedded in BC nanopaper (CEBC) due to the inhibitory effect of human serum albumin (HSA) on the curcumin degradation in alkaline solutions, which can be monitored visually (naked eye/Smartphone camera) or spectroscopically using a spectrophotometer, were linearly proportional to the HSA concentration in the range of 10-300  $\mu$ M and 25-400  $\mu$ M, respectively. The developed  $\mu$ -NAD/CEBC as a novel albumin assay kit was successfully utilized to the determination of HSA in human blood serum samples with satisfactory results. Building upon the fascinating features of BC nanopaper as a very promising bioplatfrom in optical (bio)sensing applications we are confident “lab-on-nanopaper” devices/ $\mu$ -NADs, which integrate the advantages of the nanopaper with those of the microfluidics and also meet the ASSURED criteria, could be considered as a new generation of microfluidic based devices that are currently based on paper, glass or plastic substrates/platforms.

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**The Application of response surface methodology for the optimization of parameters and development of a simple spectrofluorimetric method for the determination of atenolol and carvedilol in their pharmaceutical preparations**

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The present work is aimed to study the effect of different parameters on the fluorescence intensity of atenolol (ATE) and carvedilol (CAR) and optimization by response surface methodology (RSM) to provide a simple analytical method for their quantification in pharmaceutical formulations. Various parameters affecting the fluorescence intensity, i.e., sodium dodecyl sulfate (SDS) concentration, pH, volume fraction of solvents were optimized using RSM. Then, the optimized parameters were applied to the validation of a method for fluorimetric determination of  $\beta$ -blockers in their pharmaceutical preparations. It is obtained that, under the optimum conditions for determination of ATE, the method provided a linear range between 65 to 750 ng.mL<sup>-1</sup> with a coefficient of determination (r) of 0.9996. Also, the limit of detection and limit of quantification (LOD and LOQ) were 40 ng.mL<sup>-1</sup> and 130 ng.mL<sup>-1</sup>, respectively. Moreover, it is observed that, the linearity of method for determination of CAR was between 0.25 to 4.0 ng.mL<sup>-1</sup> and LOD and LOQ of method were 0.11 ng.mL<sup>-1</sup> and 0.37 ng.mL<sup>-1</sup>, respectively.





**Solid phase extraction using modified magnetite iron oxide nanoparticles for the extraction and spectrofluorimetric determination of metoprolol in different biological samples**

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A new analytical approach was developed involving magnetic solid-phase extraction (MSPE) and spectrofluorimetric determination of metoprolol in different biological samples. Biological sample was prepared and adjusted to pH 3-4, then metoprolol was quickly extracted using iron oxide magnetic nanoparticles (IOMNPs) modified by the surfactant sodium dodecylsulfate (SDS) and determined applying spectrofluorimetry. Experimental conditions, such as the amount of NPs and SDS, pH value, standing time and desorption solvent type and volume have been adjusted to optimize the extraction process and to obtain analytical characteristics of the method. Linearity was observed in the analyte's concentration range of 5-100 ng mL<sup>-1</sup> with correlation coefficients ( $r^2$ ) of >0.999. The method showed good precision and accuracy, with intra- and inter-assay precisions of less than 6% at all concentrations. Standard addition recovery tests were carried out, and the recoveries ranged from 86% to 107%. The limits of detection was found to be 2.3 to 5.3 ng mL<sup>-1</sup>. The method was applied to the determination of metoprolol in different biological samples.





**Polymeric film decorated with nanomaterials in Nanoporous glassy carbon electrode for sensing of acyclovir**

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In the present study, a new sensor was designed by casting of multi-walled carbon nanotubes (MWCNTs) and TiO<sub>2</sub> nanoparticles (TiO<sub>2</sub> NPs) into the polymeric matrix, which polymerized in the nanoporous glassy carbon electrode. The performance of the electrode was demonstrated by applying it to the analytical determination of acyclovir concentration. The oxidation of acyclovir has a better result on the modified electrode because of the synergistic effect of nanoporous structure glassy carbon electrode and polymeric film and MWCNTs+TiO<sub>2</sub> NPs. Under the optimized conditions the oxidative peak currents increased linearly with the concentration of acyclovir in the range from 0.03 to 1.0 μmol dm<sup>-3</sup> with a detection limit of 0.01 μmol dm<sup>-3</sup>. The measurement of acyclovir concentrations in human fluid and tablet samples demonstrated electrode applicability.

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**A strategy to obtain accurate analytical solutions in second-order multivariate calibration with curve resolution methods**

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A novel procedure is described for processing the second-order data matrices with multivariate curve resolution-alternating least-squares, while the data set is not trilinear and severe profile overlapping occurs in the instrumental data modes. The area of feasible solutions can be reduced to a unique solution by including/applying/considering the area correlation constraint, besides the traditional constraints (i.e. non-negativity, unimodality, species correspondence, etc.). The latter is not implemented only for the calibration set of samples, but also for a number of validation samples with known analyte concentrations which should also contain the interferents to be expected in future specimens. The approach is illustrated with two simulated and one experimental data sets. Borgen plots are employed to adequately visualize the effect of the additional area correlation constraint on the area of feasible MCR solutions.

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**Multi-excitation, hyperspectral autofluorescence imaging for the exploration of a set of images of wheat grains during development**

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Many plant tissues can be observed thanks to the autofluorescence of their cell wall components. Hyperspectral autofluorescence imaging at the macroscopic scale is a fast and efficient way of observing samples with a large field of view and a high resolution. The objective of this work was to evaluate multi-excitation hyperspectral autofluorescence imaging at the macroscopic scale to identify the biological components in wheat grains during their development through their spectral profiles and contribution maps using MCR-ALS under proper constraints. For this purpose two different scenarios were used: 1) analysing the total spectral domain of data sets using MCR-ALS under non negativity constraint in both modes; 2) analysing the reduced spectral domain of data sets using MCR-ALS under non negativity in both modes and trilinearity constraint in spectral mode. Contribution maps and spectral profiles of constituents are complementary information used to identify biological molecules from this kind of data sets.

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**Determination of Anilin blue by dispersive liquid liquid micro extraction**

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In this study a dispersive liquid-liquid micro extraction coupled with vis-us spectrophotometer was used to measure small amounts of aniline blue. In this way the reactive aliquot, aniline blue dye was used as the complexing agent organic and aqueous phases separated after centrifugation and then the amount of aniline blue enriched phase was measured by spectrophotometry. The effective parameters such as type and volume of extraction solvent to efficiency. The sample solution pH, Extraction time and electrolyte type was investigated. The calibration curve in the range of concentrations of 1 to 20 mg per liter ( $\text{mgL}^{-1}$ ) of aniline blue and the detection limit is  $0.7 \text{ ng mL}^{-1}$ . The relative standard deviation for 7 times measure aniline blue. At a concentration of  $50 \text{ ng mL}^{-1}$  equal to 3/33 respectively. This method has been successfully used to measure aniline blue in water samples Karun river, water and wastewater treatment in Ahvaz and Omidyeh were Qazvin industry.

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**Synthesis of graphitic carbon nitride nanosheet and its application for determination of 2-Mercapto benzo thiazole by resonance reighley scattering technique**

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In this study (research), nanosheets of graphite carbon nitride are synthesized by thermal method and optical properties and fluorescence intensity are investigated. In the following, these nanosheets are analyzed with a transmittance electron microscopy (TEM). After that, the fluorescence intensity of synthesized nano plates in the presence of 2-mercaptobenzotiazole is examined and the combination is expected to increase the fluorosic intensity of the nanoplated due to the presence of a sulfur substrate. In the following, various variables affecting the interaction of 2-mercaptobenzotiazole and nanoplates are investigated. So, by finding optimal values, the best fluorescence sensor response range is plotted relative to the amount of 2-mercaptobenzotiazole .

In the end, a system designed to accurately measure the amount of 2-mercaptobenzotiazole in real samples such as tab water and ... is being tested.

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**Synthesis of graphitic carbon nitride nanosheet and its application for determination of Captopril by spectrofluorimetry method**

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In this study, nanoplates of graphite carbon nitride are synthesized by thermal method and optical properties and fluorescence intensity are investigated. In the following, these nanoplates are analyzed by a Scanning Electron Microscopy (SEM). After that, the fluorescence intensity of synthesized nanoplates in the presence of captopril medicine is examined and is expected to reduce the fluorescent intensity of the nanoplates due to the presence of nitrogenous substitute (substrate). In the following, various variables affecting the interaction of medicine and nanoplates are investigated. So, by finding optimal values, the best fluorescence sensor response range is plotted relative to the amount of medicine. At the end, a system designed to accurately determine the levels of captopril in the pharmaceutical and biological samples such as urine.

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## Adsorptive Removal of Sunset Yellow from Aqueous Solutions with Magnetic Iron Oxide Nanoparticles

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Sunset yellow (SY) is an azo dye, which can cause damage to liver function and children's intelligence [1]. On the other hand, magnetic nanoparticle-based adsorbent have attracted much attention as excellent adsorption materials due to their large specific surface area, easy surface functionalization and the fact that magnetic systems can be easily separated and collected by applying an external magnetic field [2]. In this research, the potential of magnetic nanoparticle for removal of sunset yellow dyes from aqueous solutions was investigated. Characterization of the prepared nanoparticles was accomplished by FT-IR, SEM, XRD and VSM techniques. The SEM image of as-prepared MNPs represents plenty of spherical particles, with the average size smaller than 200 nm, that they were used in this study. The recorded VSM showed the magnetization curve was S-like, exhibiting superparamagnetic behavior with no coercivity and hysteresis. Batch adsorption experiments were conducted using synthetic solutions and the effects of initial dye concentration, initial pH of solution, adsorbent dose and contact times were studied. From the results, the removal process reached high percentage within 5 min, and the adsorption efficiency increased with the enhancement of initial dye concentration, adsorbent dosage, but decreased with the enhancement of solution pH. Removal percent of SY reached to 93% by increasing adsorbent dosage and the maximal adsorption capacity of SY occurs in the neutral pH range (5-7). Moreover, the adsorption isotherms could be well-defined with the Langmuir isotherm model instead of the Freundlich isotherm model. The obtained results confirmed that Langmuir isotherm model gives the best fit with the highest  $R^2$  value ( $> 0.98$ ) compared to the other models. The obtained results indicated that synthesized magnetic nanoparticles could be utilized as efficient, magnetically separable dyes from the real sample.

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Comparison of chemical composition of essential oils from Bakhtiari savory (*Satureja bachtiarica* Bunge.) under different extraction methods

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Bakhtiari savory belonging to the Lamiaceae family is an endemic species, which is rich in carvacrol, thymol and other aromatic compounds. The essential oil of the plant could be added in fatty food against radicals similar to synthetic antioxidant, BHT(1).

To determine the best extraction methods on qualitative and antioxidant characteristics of the essential oil, Bakhtiari savory was extracted by eight different methods in two models. Conventional hydrodistillation methods using Clevenger-type apparatus, and steam and water distillation, and innovative techniques, steam distillation, microwave-assisted hydro diffusion with power 400 and 800 watt, microwave-assisted hydro diffusion and steam with power 400 and 800 watt, were used to extract essential oil from the aerial parts of savory and their results were compared(2). For comparison, the essential oils of all samples were analyzed using DPPH and Folin-Ciocalteu agents.

Significant differences occurred among antioxidant activity and total phenol content in different extraction methods (3). High antioxidant activity and total phenol content were observed in microwave-assisted hydro diffusion and steam of 800 watt. This technique was the best extraction methods of the *S. bachtiarica* essential oil.

The microwave-assisted extraction is the best extraction methods with protect high antioxidant activity of the oil. The method is “green technology” in term of excellent quality of essential oil and is a proper tool for the extraction of essential oil from medicinal plants and aromatic herbs.

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**Pre-concentration and determination of nickel in aqueous samples using the liquid-phase microextraction and UV-Visible spectrophotometry**

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In this study, pre-concentrate, extract and determination of Nickel in aqueous samples was accomplished by using classic dispersive liquid-liquid microextraction (DLLME) and air assisted dispersive liquid liquid microextraction (AA-DLLME) combined with UV-Vis spectrophotometry. Independent variables includes: the type and volume of extracting and dispersing solvent, pH, ionic strength solution and the concentration of the complexing agent (DDTP) and the dependent variable was absorption value. Optimization of the variables was carried out according to chemometrics methods in three step. To choose extracting and dispersing solvent a two-way analysis of variance (two-way ANOVA) was initially used. In the second step, screening was achieved by using fractional factorial experimental design (FFD) for other variables. Afterward, optimization was performed via central composite design (CCD) to evaluate remaining variables. The results showed that 113  $\mu\text{L}$  carbon tetrachloride as the extracting solvent, 1.34 mL methanol as a dispersing solvent, pH=3, 0.1% DDTP and without adding any salt were selected as optimum conditions. Finally, validation study was organized according to the ICH guidelines. The results illustrated calibration model was  $Y = 0.0184X + 0.1297$ ,  $R^2=0.9986$ , linearity range was 0.01-100  $\text{mg L}^{-1}$ . LOD and LOQ were 3.4 and 11.6  $\mu\text{g L}^{-1}$ , respectively. Accuracy was evaluated as the repeatability and intermediate precision, which RSDs were  $\leq 8.4\%$  and  $\leq 20\%$ . The accuracy was estimated on tap water, mineral water, river water and industrial wastewater as really samples. The relative error  $\leq 5\%$  was considered in the method specificity study. The proposed method was robustness when some experimental conditions such as centrifugation time ( $\pm 5$  min), wavelength of measurement ( $\pm 2$  nm) and temperature were deliberately changed.





**Co-polymerization of RAFT agents on magnetic nanoparticles for efficient selective removal of Alizarine Reds dyes from water**

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Alizarin Red S is one of the anionic dyes that categorized as an anthraquinone dyes and broadly applied in textile industry. It is known as a carcinogenic substance and also due to its thermal, optical and physicochemical stability it is considered to be highly dangerous and durable pollutants [1]. According to the literature, among numerous chemical and physical processes that have been adopted for dye removal and purification of wastewater, adsorption technique is more favorable, useful and efficient approach due to its easy handling and economic feasibility [1]. Presently, magnetic nanoparticle-based adsorbent are emerged as a promising and popular materials because of their valuable features including large surface area, simplicity of synthesis procedures, easy surface functionalization with organic/inorganic groups, and etc. [2].

The present study was established to analyze the capability of Alizarin Red S dye adsorption onto RAFT surface modified magnetic nanoparticles. The effect of process parameters such as adsorbent dosage, pH, contact time and initial concentration on dye adsorption were studied on the performance of dye removal. The results showed that the removal percent of ARS reached from 72% to 93% by increasing adsorbent dosage. Maximum dye removal was observed at pH 7, therefore; neutral pH was chosen to conduct the following experiments. The isotherms such as Langmuir and Freundlich were examined and the Langmuir isotherm model gives the best fit with the highest  $R^2$  value ( $> 0.99$ ) compared to the other model. The obtained results indicated that the proposed modified magnetic nanoparticles were shown to be a promising adsorbent for the removal of dyes from several aqueous solutions.

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**Application of aspartame modified magnetic dialdehyde starch nano-composite as photocatalyst for the removal of Phenolphthalein from aqueous solution and modeling by response surface methodology**

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Industrial activities generate large volume of wastewater containing hazardous inorganic or organic species [1]. Some of these contaminants due to their natural toxicity, carcinogenic or mutagenic property and also their high bioaccumulation efficiency received special attention even at very low concentrations

The adsorption technique is one of the most effective methods for removal of contaminants, in terms of cost, flexibility, simplicity of design, ease of operation, insensitivity to toxic pollutants and better removal efficiency. Furthermore, it does not result in the formation of harmful substances like most of the other techniques. In order to improve performance of adsorption such as sorption capacity, increased mechanical strength, and resistance to chemicals and enhance the separation rate, the design and exploration of novel adsorbents are still necessary. In the last decade, Fe-containing compounds in the nanometric scale have been used [2]. The advantage of using these materials is the very high surface area available for the catalytic activity.

To ensure a maximum yield, minimum time, energy and materials consumption in reactions, the optimization of the variables involved in the process to select the best conditions is needed. One of the efficient statistical techniques which is used excessively in optimization procedures is Plackett–Burman designs (PBDs) [3]. But the optimum value for each parameter cannot be found. Central composite design (CCD) is frequently used to optimize the significant factors for analytical procedure using k factor experiments.

In this study, the novel magnetic nano-composite has been successfully synthesized by covalently linking dialdehyde starch and amine functionalized Fe<sub>3</sub>O<sub>4</sub> nanoparticle, and modifying with aspartame functional group. Scanning electron microscopy and infrared spectroscopy techniques were used to characterize the composite. The photocatalytic adsorption behaviors of the composite in Phenolphthalein removal, which is widely used as an acidic-basic indicator, from aqueous solution were evaluated by batch equilibrium experiments using response surface methodology and employing a central composite design. The influence of different parameters on the removal of Phenolphthalein was examined. pH, contact time, and sorbent dosage had a significant impact on Phenolphthalein removal. Under the optimized conditions, the maximum sorption capacity for Phenolphthalein was found to be 97.98%. The isotherm models of Freundlich, Langmuir and Dubinin–Radushkevich, were used for the equilibrium data analysis. The kinetic data were analyzed using the pseudo-first-order, and pseudo-second-order models.

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**Electrochemical behavior and analytical application of acyclovir using a  $\beta$ -Cyclodextrin / TiO<sub>2</sub> nanoparticles composite film- carbon paste electrode**

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Acyclovir (ACV) is a synthetic deoxyguanosine analog. ACV is widely used in treatment of herpes simplex, herpes zoster infections, primary genital herpes, herpetic encephalitis, and varicella zoster virus infections in immunosuppressed patients. It is also helpful in inhibiting HSV infections in renal allograft receptors and its anti-hepatitis B virus activity has been demonstrated [1, 2]. ACV may lead to nephrotoxicity (crystallization of ACV within renal tubules, enhancement of serum creatinine, transient), and neurotoxicity [3]. Based on above description the quantitative determination of ACV become very important.

In this work we developed an accurate and sensitive sensor for electrochemical detection of ACV with a high-conductivity  $\beta$ -Cyclodextrin / TiO<sub>2</sub> nanoparticles composite film modified carbon paste electrode ( $\beta$ -CD /TiO<sub>2</sub> NPs-CPE). The surface and electrochemical characterization of the modified electrode was performed by field emission scanning electron microscopy, chronocoulometry, cyclic voltammetry and differential pulse voltammetry. A significant enhancement in the peak current response of ACV was observed accompanied with a negative shift in peak potential at the composite modified electrode compared to the unmodified electrode. The effective surface area (0.55 cm<sup>2</sup>) which is 5 times as much as that of the unmodified CPE, electron transfer coefficient (0.39) and number of electrons involved in the rate determining step (2.03) for ACV were also determined using electrochemical approaches. Under optimal conditions, the prepared  $\beta$ -CD /TiO<sub>2</sub> NPs-CPE film exhibits excellent DPV response towards ACV and the peak current increased linearly with respect to ACV concentration in the linear range between 0.09 to 2.98 and 2.98 to 47.61  $\mu$ M at physiological pH 7.0 with detection limit of 21 nM. Real sample analysis has been successfully carried out in blood serum sample, which revealed good recovery results, 97.2–102.3%. The proposed sensor also displayed good selectivity, repeatability and reproducibility with appreciable long-term stability.

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## Statistical Optimization of Removal of Diazinon from Aqueous System Using Magnetic Bentonite Nanocomposites by Response Surface Methodology

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Diazinon is one of the most generally used pesticides in agriculture. This nonselective organophosphorus insecticide acts as cholinesterase inhibitors in insects and mammals, and bring about a non-reversible phosphorylation of esterases in the organisms' central nervous system [1]. As a result of its widespread application, the residue of this insecticide in environment such as water may be hazardous to human and animal health. Therefore, there is a need to develop a suitable and efficient water treatment method for removal of Diazinon.

Bentonite is a natural clay containing montmorillonite as a major constituent. This material is one of the promising adsorbents for removing diazinon from water samples as a result of their specific surface area, low-cost, availability, high chemical and mechanical stability [2]. Recently, the performance of bentonite has been optimized using different methods. The coating of bentonite with nano-sized material is one of the most widely used methods for its novel application because they possess high surface area and therefore excellent adsorption ability [3].

In this study, Magnetic Bentonite Nanocomposite was synthesized by combining bentonite with Fe<sub>3</sub>O<sub>4</sub> through co-precipitation. Scanning electron microscopy with energy-dispersive X-ray spectrometry and infrared spectroscopy techniques were used to characterize the composite. The adsorption behaviors of the composite in diazinon removal were evaluated by batch equilibrium experiments using response surface methodology and employing a Plackett–Burman (P-B) experimental design. The influence of different parameters such as pH, contact time, agitation rate and sorbent dosage on the removal of diazinon was examined. The significance of independent variables and their interactions were tested by analysis of variance (ANOVA). The optimum contact time, pH, agitation speed and adsorbent dose were found. Under these conditions, the maximum sorption capacity for diazinon was found to be 90.53%. Kinetic and isothermal data fitted well the pseudo-second- order and the Freundlich models, respectively. The method was successfully applied for the removal of diazinon from industrial wastewater and groundwater samples. The results showed that the designed composite is a promising adsorbent for the treatment of diazinon-contaminated waters.

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## The 25<sup>th</sup> Iranian Seminar of Analytical Chemistry

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### Nitrate removal from water by adsorption on Glutaraldehyde crosslinked Chitosan

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In recent years, nitrate concentration increases in drinking water and many studies have explored methods to remove nitrate from drinking water. One of the ways to remove nitrate is to use adsorbent. In this study, Chitosan modified with Glutaraldehyde was used to remove nitrate from water. Chitosan is a good adsorbent because it has amine and hydroxyl groups. In order to investigate the effect of adsorbent efficacy, the role of contact time, adsorbent dose and nitrate concentration were studied. The results showed that by increasing the dose of adsorbent, nitrate removal increases due to the raising functional groups and increasing active sites. Increasing the concentration of nitrate also increases the absorption capacity. Moreover, increasing the contact time rises the probability of interaction as well as occupying active adsorbent sites, and eventually increases the nitrate removal. The results show that Chitosan modified with Glutaraldehyde is an effective adsorbent. If Chitosan is protonated with acetic acid, it will have higher nitrate removal efficiency than the non-protonic Chitosan.





**Synthesis and characterization of Cysteine-functionalized Fe<sub>3</sub>O<sub>4</sub> nanoparticles and its application in removal of heavy metals from waste waters in south pars gas complex**

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Magnetic iron oxide nanoparticles (MNPs) were functionalized with Cysteine, by a cost effective and environmentally friendly procedure, as an alternative route to typical thiol and amine functionalized polymeric coatings. MNPs were synthesized by co-precipitation method and adsorption of Cysteine was investigated as a function of ligand concentration and pH. The as-synthesized products were characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), scanning electronic microscopy (SEM) and FT-IR spectroscopy techniques. The thiol-amine functionalized Fe<sub>3</sub>O<sub>4</sub> nanoadsorbent exhibited high adsorption affinity for aqueous Cd(II), Cu(II), and Pb(II) ions, resulting from complexation of the metal ions by surface thiol and amine groups. Factors influencing the uptake of heavy metal ions such as solution pH, initial metal ion concentration, contact time, and species of metal ions were investigated systematically by batch experiments. The nanoadsorbent was able to remove over 95% of Cd(II), Cu(II), and Pb(II) in 40 mL of solution containing 4 mg/L metal ions at optimized conditions which is larger than some other reports [1,2]. The adsorption rates of Cd(II), Cu(II), and Pb(II) on this nanoadsorbent fit pseudo-second order kinetic models ( $R^2 > 0.99$ ). Furthermore, these nanoadsorbents can be used as highly efficient separable and reusable materials for removal of heavy metal ions from waste waters.

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**Mn(II) Schiff base complex anchored in MCM-41 matrix as a heterogeneous catalyst  
for epoxidation of alkenes**

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Manganese Schiff base complexes have high catalytic activity for epoxidation of alkenes in homogeneous phase but this homogeneous catalyst is not facile separated and recycled. Therefore, more attempts have been made for immobilization of homogeneous catalysts on solid support such as MCM-41[1-2].

In this work anchoring Mn(II)Schiff base complex on MCM-41 matrix by forming urethane linkage between the surface hydroxyl groups of MCM-41 and one of the terminal isocyanate groups of DIC-4(1-4 Diisocyanatobutane) were described, while the other isocyanate ending was attached the hydroxyl groups in the salen ligand [3]. Heterogeneous MCM-41@DIC-Mn (Scheme 1) was synthesized according to literature [3] and their structure are well confirmed by FT-IR, XRD and ICP. A typical epoxidation process with H<sub>2</sub>O<sub>2</sub> (30%) as a green oxidant is processed in a solution of ethanol containing olefin, imidazole as axial base and heterogeneous catalyst. The yields of epoxides were determined by GC.

Furthermore, the effect of various parameters such as reaction time, amount of catalyst, oxidant and imidazole have been investigated. The optimum condition of the reaction shows the maximum conversion (93%) was obtained for cycloocten in optimum condition when Catalyst: Imidazole:olefin molar ratio is 1:100:30. The catalyst reusability confirm that catalyst is stable during oxidation reaction. The stability and reusability of catalyst was studied by separation of catalyst and reuse five times again without a detectable catalyst leaching or a significant loss of its activity (Table 1). Catalyst reusability confirm that catalyst is stable during oxidation reaction.

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## Potentiometric Determination of $\text{HPO}_4^{2-}$ with Chitosan-Zn by Carbon Paste Electrode

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In this article a selectivity potentiometric methodology, using an ion-selective electrode, for determination of  $\text{HPO}_4^{2-}$  anion in aqueous solution was investigated. Chitosan-zinc complexes is used. A room temperature ionic liquid, 3-methyl-imidazolium tetrafluoroborate and paraffin for compare of conductive effect are used. Response time, pH range, electrode selectivity, electrode life have been investigated. Carbon nanotubes (WCNTs) were used in the composition of the carbon paste to improve conductivity and transduction of chemical signal to electrical signal. Also, the effect of different carbon nanotubes (single-wall carbon nanotubes, multi-wall carbon nanotubes and COOH functionalized single-wall carbon nanotubes, COOH functionalized multi-wall carbon nanotubes and  $\text{NH}_2$  functionalized single-wall carbon nanotubes and  $\text{NH}_2$  functionalized multi-wall carbon nanotubes) on the electrode's response has been investigated. The electrode has a short response time ( $\sim 5$  s) and can be used for at least 50 days without any considerable divergence in potentials, and the working pH range was 7.0–8.2. fabricated sensor for determining of  $\text{HPO}_4^{2-}$  demonstrated a maximum Nernstian slope equal to  $29.7 \text{ mVdecade}^{-1}$  along a linear range from  $1 \times 10^{-5}$  to  $1 \times 10^{-2} \text{ mol.L}^{-1}$  and detection limit of  $8.55 \times 10^{-5} \text{ mol.L}^{-1}$ . Finally, the proposed electrode was successfully used as an indicator for potentiometric determination of  $\text{HPO}_4^{2-}$  in Hydroponic farm wastewater samples.

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**Introduction of graphene-periodic mesoporous silica sandwich nanocomposite as a new sorbent for removal of acid blue as model analyte: Process modeling for batch and column study**

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Introducing a new type of sorbents seems to be a great challenge and this issue has become an interesting topic in the field of sample preparation techniques [1]. In this regard, for the first time, a sandwich structure of graphene-periodic mesoporous silica (G-PMS) was synthesized as a novel sorbent [2]. The feasibility of this sorbent for removal of acid blue as model a compound from wastewater samples was investigated through static and column mode studies. The effect of different factors on the dye adsorption in batch experiments, including the amount of sorbent, sorption time, and dye concentration were optimized by response surface methodology (RSM) using Box–Behnken design (BBD). The adsorption isotherm could be well fitted by the Freundlich model with acceptable adsorption capacity of 21 mg g<sup>-1</sup>. Column mode study was also carried out for the removal of acid blue content from the wastewater samples using a fixed bed column. The COMSOL model was applied for experimental data of column study to predict the breakthrough curves. This model has proposed an objective framework to interpret the adsorption system. Also, the obtained results of this model can help to predict the possibility for up scaling and designing of adsorption process at the pilot plant scale level.

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**Mixed ligand complex formation for solid phase extraction-trace determination of sulfasalazine by using magnetic poly (1-vinylimidazole)**

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Pharmaceuticals are produced in huge levels. They may be leaked to the environment from the factories or/and homes, and may produce many problems for humans, living creatures and ecosystems. Therefore, development of efficient monitoring methods to understand the levels of the pollutions is mandatory to control the sources of the leakages.

Sulfasalazine (SZ) is an effective pharmaceutical for rheumatoid arthritis. Also, it controls active ulcerative colitis or crohn's disease. However, it can produce adverse reactions which may lead to disorder of the hemopoietic system and potential carcinogenic effects. SZ has been studied and determined in various samples by high performance liquid chromatography, spectrophotometry and luminescence spectroscopy [1].

In this study, a new magnetic solid phase extraction method has been developed for SZ determination. The surfaces of magnetite nanoparticles (MNPs) were modified by 3-(trimethoxysilyl)propyl methacrylate as a linker. Then, the modified MNPs were used as the magnetic cores to prepare a magnetic (1-vinylimidazole/divinylbenzene) polymer. The magnetic polymer was characterized by scanning electron microscopy, transmission electron microscopy, FT-IR, vibrating sample magnetometry and X-ray diffraction spectroscopy. Due to the electron donating of the nitrogen atoms in imidazole moieties, Ni(II) can be adsorbed by the magnetic nano-polymer. Sulfasalazine contains salicylate moieties capable to be adsorbed by the magnetic polymer through mixed ligand complexation via adsorbed Ni(II) ions. Effects of the affective parameters on the solid phase extraction process such as amount of adsorbent, pH, extraction time and the others were investigated. The eluted sulfasalazine (by an ethanolic solution) was monitored by spectrophotometry at 450 nm. Under optimal conditions, the calibration curve was obtained in the range of 0.04-1.4  $\mu\text{mol L}^{-1}$ . The limit of detection for the sulfasalazine determination method was found as 0.008  $\mu\text{mol L}^{-1}$ . Relative standard deviation and recovery for analysis of an aqueous solution containing 0.1  $\mu\text{mol L}^{-1}$  of sulfasalazine were of 4.1 and 97.0%, respectively. Different river and lake water samples were successfully analyzed by the method.

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**Novel Graphene-Pd/Ag Nanoparticles composite Modified Carbon Paste Electrode as a novel hydrazine sensor**

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In this work, Pd and Ag nanoparticles (Pd/Ag NPs) electrodeposited on an electrochemically reduced graphene oxide (ERGO) modified carbon paste electrode, was prepared for the amperometric determination of hydrazine. It efficiently oxidizes hydrazine at a low over potential of  $-0.1$  V versus SCE. The Pd/Ag/graphene/CPE was used for determination of hydrazine in phosphate buffer solution of pH 7.0. The amperometric current response of the electrode was increased linearly over a hydrazine concentration of  $0.5$ – $200$   $\mu$ M with a limit of detection of  $0.09$   $\mu$ M. The prepared hydrazine sensor exhibited high sensitivity, good selectivity reproducibility and long term stability.

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## An Optoelectronic Tongue for Simultaneous Detection of $\beta$ -Amyloid40 and $\beta$ -Amyloid42

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Alzheimer's disease (AD) is an irreversible, progressive and multifaceted neurodegenerative disorder accompanied by deposition of extracellular amyloid plaques. The main component of amyloid deposits and senile plaques is an aggregated peptide called  $\beta$ -amyloid peptide ( $A\beta$ ) [1]. Although many details of the AD pathology remain unknown, three biomarkers in cerebrospinal fluid (CSF) including  $A\beta_{1-42}$  ( $A\beta_{42}$ ), total tau (t-tau) proteins, and p-tau (phosphorylated tau) protein are established biomarkers for AD. Due to the low level of  $A\beta_{42}$  monomers in plasma, the use of  $A\beta_{42}$  to  $A\beta_{40}$  ( $A\beta_{1-40}$ ) ratio amplifies the difference between AD and normal plasma [2]. Thus, the development of a specific but inexpensive method for simultaneous detection of  $A\beta_{42}$  and  $A\beta_{40}$  (and consequently  $A\beta_{42}$  to  $A\beta_{40}$  ratio) is of great importance.

One strategy to move from specific lock-and-key sensors and approach predetermined aim could be the use of 'nanoparticle (NP)-based optical sensor array' [3]. In a sensor array, instead of focusing on individual signals, the response from all the sensor elements which exhibit various interaction towards different analytes are collected. Plasmonic NPs exhibit unique and tunable photophysical features due to the localized surface plasmon resonance (LSPR). LSPR depends on shape, size and interparticle distance of NPs and the refractive index of the surrounding medium. There have been great studies in terms of utilizing this dependence as the basis for the development of plasmonic sensor elements [3].

In the present study, we developed a 'nanoparticle-based colorimetric sensor array' utilizing label-free gold and silver nanoparticles for visual detection of  $A\beta_{42}$  and  $A\beta_{40}$ . Different aggregation behaviors of nanoparticles through the conjugation of nanoparticles with  $A\beta_{42}$  and  $A\beta_{40}$  and then the coordination of  $A\beta_{42}$  and  $A\beta_{40}$  with Cu(II) led to diverse spectral and color changes. The spectral changes were quantitatively differentiated by supervised pattern recognition method, linear discriminant analysis (LDA). The proposed sensor was able to discriminate among  $A\beta_{42}$ ,  $A\beta_{40}$ , and HSA in different concentrations (50 nmol L<sup>-1</sup> to 500 nmol L<sup>-1</sup>), as well as mixtures of them with an identification accuracy of 100%. Moreover, the sensor array had the capability to identify structurally similar  $A\beta$  peptides in plasma samples.

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Determination Of ultra trace molybdenum in beans Samples

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Molybdenum plays an important role in growth, healthiness and the prevention of tooth decay. Shortage of molybdenum in diet may lead to neurological disorders and even early death [1, 2]. The fertilizers contain molybdenum leads to increased agricultural productions. Therefore, molybdenum is very important in agriculture [3].

A sensitive method to determine the ultra-trace amounts of molybdenum is developed by dispersive liquid-liquid microextraction (DLLME). This method is based on the reaction molybdenum with thiocyanate in acidic media (HCl) and at present of ascorbic acid to form a red complex with the maximum absorption peak at 473 nm. In this method, the chloroform was used as extractant solvent and cetyl trimethyl ammonium bromide was utilized as the disperser agent which also acts as the counter ion of Mo (V) anionic complexes. Under the optimum conditions, the calibration graph was linear over the range of  $2.8 \times 10^{-8}$ – $5.2 \times 10^{-7}$  mol L<sup>-1</sup> (2.0–50.0 ng mL<sup>-1</sup>) of molybdenum with detection limit of  $2.08 \times 10^{-9}$  mol L<sup>-1</sup> (0.2 ng mL<sup>-1</sup>).

For determination of the molybdenum content of beans samplest (Chickpea, Green Lentil, White Beans) adequate amount of wet samples were dried in an oven at 75 °C for 48 h. Determined weight of the well-dried powder of each sample was transferred to a porcelain crucible and laid in ashes at 500 °C for 8 h in a furnace. The residues were digested with nitric acid/hydrogen peroxide until complete dissolution of the sample was obtained [4]. Finally, To 3 balloons 10 mL containing 5 ml of beans, ascorbic acid (0.004 mol L<sup>-1</sup>), hydrochloric acid (0.8 mol L<sup>-1</sup>), and thiocyanat (0.01 mol L<sup>-1</sup>) added, then distilled water to volume It was then passed to a glass-centrifugal tube with a conical end. Then, 200 microliters chloroform containing CTAB (0.03 mol L<sup>-1</sup>) was injected. After that, with speed of 3500 rpm for 5 minutes centrifugation and then transferred to quartz microsel. The absorption was measured using a Uv-visible spectrophotometer apparatus at a constant wavelength of 473 nm.

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**A facile fabrication of electrodeposited metal organic frameworks thin film for headspace solid-phase microextraction of methamphetamine**

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Metal organic frameworks (MOF) have been considered appropriate coating materials for solid phase microextraction (SPME) fibers. This fact can be attributed to their special properties such as large surface area, good thermal stability and uniform structure.<sup>[1,2]</sup> Here, we report fabrication of a thin film of [Cu(btec)<sub>0.5</sub>DMF] (H<sub>4</sub>btec = 1,2,4,5-benzenetetracarboxylate acid) by a one-step in-situ cathodic electrodeposition.<sup>[3]</sup> Electrochemically synthesized MOF was formed on the surface of a stainless steel wire at a constant potential of -1.7 V at the presence of H<sub>4</sub>btec as the organic linker, copper nitrate and sodium nitrate. Surface investigation by scanning electron microscopy (SEM) revealed a highly porous structure. Also, electrosynthesized coating showed excellent thermal and mechanical stability. Parameters affecting the extraction efficiency such as pH, temperature, sample volume, ionic strength and extraction time were optimized to obtain the best recovery. The applicability of the fiber was investigated for analysis of methamphetamine in urine samples. The method provided good linearity over three orders of magnitude with quantification -limit (LOQ) of 0.2 ng mL<sup>-1</sup>, with an analytical recovery between 95% to 102 %. The relative standard deviation for three replicates at the concentration of 50 µg L<sup>-1</sup> was found to be 5.6%.

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**One-pot synthesis of hierarchical mesoporous nano-ZSM-5 zeolite and its catalytic performance in the conversion of methanol to hydrocarbons**

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Conversion of Methanol to hydrocarbons (MTH) using zeolite catalysts is a promising process based on the non-oil based sources [1]. Despite the excellent properties of zeolites as heterogeneous catalysts in the process of MTH, the purely microporous character of zeolites results in difficult to access active sites. These micropores could cause severe diffusion limitations in the zeolite that often result in coking thus affecting catalytic activity [2]. Developing nanocrystal zeolites with hierarchical mesoporous structure is more effective to prolong the catalyst life [3].

In this study, First organic template-free hydrothermal synthesis of ZSM-5 was performed. Then, nano-sized ZSM-5 zeolite with intercrystalline mesopores in an easy one-pot procedure by the use of dodecyltrimethyl ammonium bromide as template in the zeolite synthesis gel was prepared. The textural and acid properties of catalysts were characterized using FTIR, X-ray diffraction, SEM, TEM, TGA, NH<sub>3</sub>-TPD and BET analysis. Characterizations proved smaller crystal size, more specific surface area, lower surface acidity and more uniform dispersion for the surfactant-assisted synthesized sample. The hierarchical nano-zeolite catalyst displayed 228 m<sup>2</sup>g<sup>-1</sup> of BET surface area, in contrast to the 192 m<sup>2</sup>g<sup>-1</sup> of the conventional zeolite. The dehydration of methanol over synthesis catalysts carried out in a fixed-bed reactor at 390 °C and WHSV of 4.5 h<sup>-1</sup> under ambient pressure. The mesoporous nanocatalyst exhibited great improvements in catalytic life time, selectivity to C<sup>5+</sup> hydrocarbons and yield of liquid hydrocarbon products. Also Mesoporous nano-ZSM-5 catalyst converted more methanol than the conventional one and its catalytic lifetime increased about 20% relative to conventional catalyst (>90% for about 58 h). The high activity and stability of the mesoporous nano-ZSM-5 in the MTH process attributed to the reduced diffusion limitations due to the widened pore size distribution, reduced crystal size and lowered surface acidity of mesoporous nano-ZSM-5.

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**Sensitive determination of Gefitinib in human biological samples by differential pulse voltammetry based on carbon paste electrode modified by MMWCNTs/PAN NFs**

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In the present work, the electrochemical oxidation of new generation of anti-cancer drug, Gefitinib, using by differential pulse voltammetry based on carbon paste electrode modified by MMWCNTs/PAN NFs (MMWCNTs/PAN NFs/CPE) has been reported. The result of a study showed that Gefitinib provided well-shaped oxidation peak at positive potential of +1.09 V (vs.  $E_{Ag/AgCl}$ ) in the phosphate buffer solution at pH 2.5. The experimental conditions, i.e. pH, modulation amplitude, a modulation time, a step potential, and a scan rate, were optimized. A simple, rapid, selective and sensitive DPV procedure for the determination of Gefitinib was performed in the concentration range of  $2.24 \times 10^{-9} - 5.59 \times 10^{-5} \text{ mol L}^{-1}$  with the limit of detection (LOD) and the limit of quantification (LOQ) of  $2.9 \times 10^{-10}$  and  $9.6 \times 10^{-10}$ , respectively.

The proposed method with using anodic signal of Gefitinib at MMWCNTs/PAN NFs/CPE shown comparable detection limit as for HPLC method and fluorescent indicator in the determination of this anticancer drug.

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**Sensitive determination of omeprazole in human biological sample by differential pulse voltammetry based on carbon paste electrode modified by MMWCNTs/PAN NFs**

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In the present work, the electrochemical oxidation of new generation of omeprazole drug, using by differential pulse voltammetry based on carbon paste electrode modified by MMWCNTs/PAN NFs (MMWCNTs/PAN NFs/CPE) has been reported. The result of a study showed that omeprazole provided well-shaped oxidation peak at positive potential of +0.89 V (vs.  $E_{Ag/AgCl}$ ) in the phosphate buffer solution at pH 3.0. The experimental conditions, i.e. pH, modulation amplitude, a modulation time, a step potential, and a scan rate, were optimized. A simple, rapid, selective and sensitive DPV procedure for the determination of omeprazole was performed in the concentration range of  $2.89 \times 10^{-9} - 7.2 \times 10^{-5}$  mol L<sup>-1</sup> with the limit of detection (LOD) and the limit of quantification (LOQ) of  $3.9 \times 10^{-10}$  and  $1.3 \times 10^{-9}$ , respectively.

The proposed method with using anodic signal of omeprazole at MMWCNTs/PAN NFs/CPE shown comparable detection limit as for nikel-zinc ferrite graphene glassy carbon electrode and MWCNTs/Gtaphene oxide/Pyrogallol camposite carbon paste electrode in the determination of this omeprazole drug.

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## Catalytic conversion of methanol to aromatics over bimetallic CuO-ZnO/ZSM-5-ZSM-11

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Methanol to hydrocarbon process is becoming increasingly important as methanol can be manufactured from flare gas, biomass, shale gas and coal [1]. In this work, composite co-crystalline zeolites ZSM-5-ZSM-11 synthesized by hydrothermal method [2], Then this nanocomposite catalyst modified with (2 wt %) Zn - (1 wt %) Cu by direct synthesis procedure and characterized by means of techniques such as XRD, SEM, TEM, N<sub>2</sub> adsorption– desorption, XRF, NH<sub>3</sub>-TPD and FT-IR. The results indicate that metal species were successfully incorporated into ZSM-5- ZSM-11 zeolites. The obtained results showed after substitution of the framework Al by metal species crystal size and average diameters decrease while surface area and pore volume increase.

The catalytic performances of prepared nanocrystalline zeolites were investigated by methanol to gasoline (MTG) reaction in a fixed bed stainless-steel reactor to study the synergistic effect of CuO and ZnO. The results indicated that the addition of ZnO promoted the catalytic activity of CuO in methanol aromatization to aromatics [3]. The NH<sub>3</sub>-TPD results imply that the incorporated Cu and Zn species replaced parts of the conventional acid sites and formed some new acid sites in the zeolites. This new acid sites significantly improved the hydrogen transfer and aromatization reaction, increasing the yield of aromatics.

The catalytic results illustrated that the methanol conversion was higher than 90% for about 60 h, meanwhile, the gasoline yield reached up to 44%.

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**The Cu-MOF/RGO modified electrode for determination of metoclopramide**

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A novel electrochemical sensor based on Cu-MOF and reduced graphene oxide (RGO) was fabricated for the determination of metoclopramide (MP)[1-3]. The modification procedure was carried out through casting RGO on the bare glassy carbon electrode (GCE) and followed by the electrodeposition of Cu-MOF on the RGO modified electrode. Cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS) and scanning electron microscopy (SEM) were performed to characterize the electrochemical performance and surface characteristics of the as-prepared sensor. The composite electrode exhibited an excellent electrocatalytic activity with increased electrochemical signals towards the oxidation of MP, owing to the synergistic effect of RGO and Cu-MOF. Under the optimized condition, the linear response range were from 0.1 to 154  $\mu\text{mol L}^{-1}$  for MP. The detection limits for MP were 0.08  $\text{L}^{-1}$ . Moreover, the modified electrode presented the good reproducibility and the excellent anti-interference performance.

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**Silver nanoparticles confined in SBA-15 mesoporous silica**

**Synthesis, characterization and antibacterial properties**

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The growth of silver chloride nanoparticles within the pore channels of functionalized SBA-15 mesoporous was achieved by sequential dipping steps in alternating bath of potassium chloride and silver nitrate under ultrasound irradiation at pH=9 [1-3]. The effects of sequential dipping steps in growth of the AgCl nanoparticles have been studied. The growth and formation of AgCl nanoparticles inside the sulfonated SBA-15 were characterized by X-ray diffraction (XRD), Fourier transformation infrared spectroscopy (FTIR), scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Antibacterial activity of the synthesized materials was investigated against Escherichia coli (E.coli), using the conventional diffusion-disc method. The materials showed high antibacterial activity.

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**Cathodic stripping voltammetric assay of HMX explosive on a carbon nanotube/Ag nanocomposite modified electrode**

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HMX, also called known as cyclotetramethylene-tetranitramine, is a powerful and relatively insensitive nitroamine high explosive. This nitroaromatic explosive, widely used in military and civil applications, can enter the environment through water and soil. Degradation of explosives in the environment is generally slow and initial biotransformation products are often carcinogenic [1]. At present, reverse-phase HPLC have been developed to accurately quantify the concentration of HMX in a variety of matrices in environmental assessments [2]. Also, a range of materials and techniques have found application for cathodic measurements of nitroaromatic and nitramine explosive compounds [1,3], however, limited studies concern the application of voltmmetric methods for the detection and determination of HMX, and in practical, the detection of this explosive on the conventional electrodes, in the aqueous and organic conditions is hard .

In this research, various electrochemical methods was used to study and determine HMX, on a multi-walled carbon nanotubes-Ag nanoparticles (MWCNTs/Ag) modified glassy carbon electrode (GCE). Various kinetic parameters such as transfer electron number, transfer proton number and heterogeneous rate constant and diffusion coefficient constant of HMX were calculated, and various experimental parameters were also optimized. The results demonstrated that the electrochemical response of HMX by adsorption stripping voltammetry on MWCNTs/Ag film can remarkably be enhanced compared to bare carbon nanotubes electrode. Cyclic voltmmatric studies of high concentration of HMX on the GCE doesn't show any reductive signal, but on the MWCNTs modified electrode display a relatively sharp cathodic peak, and by MWCNTs/Ag modified electrode, the reduction potential changes and facilities from -0.7 V (vs. SCE) to -0.3 V, due to specific electrocatalytic properties of the this nanocomposite electrode. Chronoamperometry studies show, a diffusion controlled process with diffusion coefficient of  $2.01 \times 10^{-4} \text{ cm}^2 \text{ s}^{-1}$ , and the number of electrons transferred for electrochemical reduction of HMX are near to 1.72. Under optimized conditions, the reduction peak have a linear dynamic ranges of 10.0-100.0  $\mu\text{M}$  with the practical detection limit of 7.0  $\mu\text{M}$  and a precision of <1.0% (RSD for 5 analysis). This modified electrode was properly used for determination of HMX in soil and ground water samples with satisfactory results.

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## Comparison Between Magnetic Property Of $\text{SrFe}_{12}\text{O}_{19}$ , $\text{SrFe}_{12}\text{O}_{19}@ \text{TiO}_2$ , $\text{SrFe}_{12}\text{O}_{19}@ \text{SiO}_2$ Nano samples

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Fig.1. shows the magnetic hysteresis loops of  $\text{SrFe}_{12}\text{O}_{19}$  nanoparticles and  $\text{SrFe}_{12}\text{O}_{19}@ \text{SiO}_2$  and  $\text{SrFe}_{12}\text{O}_{19}@ \text{TiO}_2$  nanotubes in the range of (-15 to kOe +15). The hysteresis loop of  $\text{SrFe}_{12}\text{O}_{19}@ \text{SiO}_2$  nanotubes is a wasp-waist showing that indicates the presence of two magnetic phases (soft and hard ferromagnetic) in the structure of the  $\text{SrFe}_{12}\text{O}_{19}@ \text{SiO}_2$  nanotubes, which predominates in the lower magnetic fields of the soft ferromagnetic phase [1], and it is dominated by the increase of the ferromagnetic field. Hemophagous waste loop due to the effect of impurity phase on magnetic fields, particle size, size distribution, and field strength [2]. The field of formation of  $\text{SrFe}_{12}\text{O}_{19}$  nanoparticles decreases in the presence of  $\text{TiO}_2$  nanoparticles, which can be due to the presence of non-magnetic ion  $\text{Ti}^{+4}$  substituted with  $\text{Fe}^{+3}$  in octagonal locations in  $\text{SrFe}_{12}\text{O}_{19}$  nanoparticles, which reduces the particle size [3].

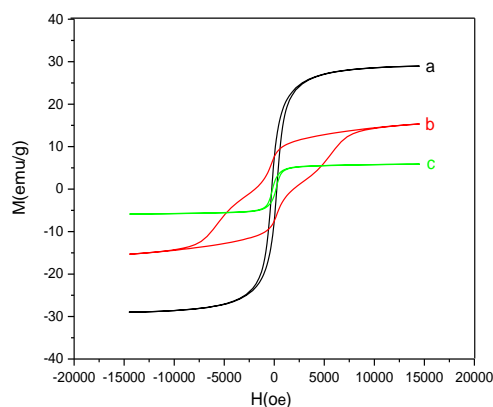


Fig.1. Hysteresis loops of (a)  $\text{SrFe}_{12}\text{O}_{19}$  nanoparticles, (b)  $\text{SrFe}_{12}\text{O}_{19}@ \text{SiO}_2$  nanocomposites and (c)  $\text{SrFe}_{12}\text{O}_{19}@ \text{TiO}_2$  nanocomposites.

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**Interesting Carriage wheels like Structure mixed metal Cu-V Complex at Bulk and Nano-sized, Antimicrobial and Antitumor Activity**

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Anticancer cells and antimicrobial activity of new mixed metal  $(C_7H_9N)_4Cu_2F_2(\mu-F)V(F)_{16}$  Complex at Bulk and Nano-sized have been studied and these new interesting Carriage wheels like structure complex characterized by elemental analysis, IR spectroscopy and its structures studied by single Crystal X-ray crystallography. Nanopowder of this compound synthesized by sonochemical method then characterized by X-Ray Diffraction (XRD), Scanning Electron Microscopy (SEM). The in-vitro anticancer studies reveal that the mixed metal  $Cu(pyr)_4-F-V(F)_{21}$  Complex at bulk and nano-sized had the best anticancer activity against MCF-7 (HBA = Human Breast Adenocarcinoma) cells with  $IC_{50}$  values of 5.89  $\mu M$  and 7.90 Mm. This Complex effects on the antibacterial activity (against Staphylococcus epidermidis (Se) ATCC 14990, Bacillus subtilis (Bs) ATCC 6633, Bacillus cereus (Bc) ATCC 14579, Pseudomonas aeruginosa (Pa) ATCC 9027 and Escherichia coli (Ec) ATCC 25922 strains).

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**Highly dispersed MnO<sub>2</sub> nanoparticles supported on graphene oxide for Removal of Anionic Carmoisine Dye**

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Highly dispersed MnO<sub>2</sub> nanoparticles supported on the graphene oxide have been prepared by a simple method and used as an efficient FA decomposition catalyst for hydrogen generation for carmoisine dye removal from aqueous solution. The morphology, chemical structure of the nanocomposite were characterized by X-ray diffraction (XRD) and Scanning electronic microscope (SEM). Adsorption of carmoisine dye onto Graphene Oxide – MnO<sub>2</sub> was investigated with respect to pH, adsorption time, initial carmoisine dye concentration and temperature. Kinetics data and adsorption isotherm, obtained at the optimum pH 5 for carmoisine, were better fitted by pseudo-second-order kinetic model and by freundlich isotherm [1-4].

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**Removal of Anionic Brilliant Blue Dye from Aqueous Solutions by Graphene Oxide – Cerium Oxide Nanocomposite**

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A novel adsorbent, cerium oxide modified graphene was synthesized for brilliant blue dye removal from aqueous solution. The morphology, chemical structure of the nanocomposite were characterized by X-ray diffraction (XRD) and Scanning electronic microscope (SEM). Adsorption of brilliant blue dye onto Graphene Oxide – Cerium Oxide was investigated with respect to pH, adsorption time, initial brilliant blue dye concentration and temperature. Kinetics data and adsorption isotherm, obtained at the optimum pH 6.3 for brilliant blue, were better fitted by pseudo-second-order kinetic model and by Langmuir isotherm [1-4].

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**Fabrication of GO/Fe<sub>3</sub>O<sub>4</sub>/SDS magnetic nanocomposites as adsorbents  
to remove malachite green from water**

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This work presents the synthesis of magnetic Graphene oxide adsorbents, GO/Fe<sub>3</sub>O<sub>4</sub>/SDS nanocomposites, in which Graphene oxide were grafted to magnetic Fe<sub>3</sub>O<sub>4</sub> particles by a facile hydrothermal method. The morphology, chemical structure and magnetic property of the nanocomposite were characterized by Fourier transform infrared spectrometer (FT-IR), X-ray diffraction (XRD) and Scanning electronic microscope (SEM), respectively. Adsorption of methyl green (MG) onto GO/Fe<sub>3</sub>O<sub>4</sub>/SDS was investigated with respect to pH, adsorption time, initial MG concentration and temperature. kinetics data and adsorption isotherm, obtained at the optimum pH 6.3, were better fitted by pseudo-second-order kinetic model and by Langmuir isotherm, respectively. Moreover, the GO/Fe<sub>3</sub>O<sub>4</sub>/SDS was stable and easily recovered, the adsorption capacity was about 80% of the initial saturation adsorption capacity after being used four times[1-2].

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**AuAg bimetallic nanoparticles decorated graphitic carbon nitride for removal of cationic Methylene blue Dye**

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In this work, a new AuAg bimetallic decorated graphitic carbon nitride (AuAg-C<sub>3</sub>N<sub>4</sub>) have been prepared for removal Methylene blue dye from aqueous solution. The morphology, chemical structure of the nanocomposite were characterized by X-ray diffraction (XRD) and Scanning electronic microscope (SEM). Adsorption of Methylene blue onto AuAg-C<sub>3</sub>N<sub>4</sub> was investigated with respect to pH, adsorption time, initial Methylene blue concentration and temperature. Kinetics data and adsorption isotherm, obtained at the optimum pH 7 for Methylene blue, were better fitted by pseudo-second-order kinetic model and by freundlich isotherm [1-3].

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**Palladium nanoclusters enhanced rhodamine B-K<sub>3</sub>Fe(CN)<sub>6</sub> chemiluminescence system and its application for the sensitive determination of phenobarbital**

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Development of a new sensitive assay for the determination of drugs is of great importance in analytical chemistry. Herein, a reliable chemiluminescence (CL) probe was developed for the sensitive determination of phenobarbital. The method was based on the enhancement effect of palladium nanoclusters (Pd NCs) on the weak CL emission of K<sub>3</sub>Fe(CN)<sub>6</sub>-rhodamine B reaction in alkaline media [1-3]. Pd NCs were prepared by facile procedure and characterized by transmission electron microscopy (TEM), X-ray diffraction (XRD) and Fourier-transform infrared spectroscopy (FT-IR). The oxidation reaction alkaline rhodamine B by K<sub>3</sub>Fe(CN)<sub>6</sub> could generate a very weak CL emission, but in the presence of Pd NCs, a remarkable intensified CL emission was obtained. This effect was ascribed to the catalytic activity of Pd NCs. Besides, it is observed that the addition of phenobarbital in the reaction media caused a remarkable quenching effect on the obtained CL emission. This effect was formed the basis of a sensitive sensor for the detection of phenobarbital. Under the optimized conditions, the proposed CL system exhibited a linear relationship between the CL intensity and phenobarbital concentration in the range of 0.02-300  $\mu\text{g mL}^{-1}$ , with a detection limit ( $3S_b/m$ ) of 5  $\text{ng mL}^{-1}$ . Also, the relative standard deviation (RSD) was found to be 3.4% for repetitive determinations of 50  $\mu\text{g mL}^{-1}$  phenobarbital (n=10).

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**Preparation of pencil modified with Bismuth-Antimony alloys and application of them in determination of Arginine**

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Arginine belongs to amino acids, which has a carboxyl group, an amine group and a side chain attached to a similar carbon atom. Arginine plays an important role in depression and also plays a role in nerve activity and cardioprotection. It is used to treat cancer. The synthesis of arginine occurs in humans from the intestinal and kidney axis [1-5].

In this research, the pencil electrode is activated by the application of potentiostatic or potentiodynamic methods the experimental results showed that pencil electrode generates a broad oxidation peak, while the activated pencil generates shows a sharp peak. In this work, we have tried to advise a precise and low-cost method to detect and measure the amounts of this compound in pharmaceutical samples. The electrochemical oxidation of arginine on the pencil modified with Bismuth-Antimony alloys electrodes using chronoamperometry method at the potential of -0.7 V vs. Ag /Ag Cl reference electrode for 120 seconds in an alloy solution of bismuth and antimony with the same concentration was studied. The metal ratio in alloy was 1:1 and the supporting electrolyte was a 1 molar sulfuric acid solution. The differential pulse voltammetric method was used in the potential range of -0.4 to 0.2 V at a scan rate of 20 mV s<sup>-1</sup>. According to the calibration curve, the linear range was obtained with a differential pulse voltammetric method of 1000 to 9000 μM and a detection limit of 1179 μM for modified electrode. Finally, this electrode was used to measure arginine amino acid in the sample The real spirulina pill was used. A relative standard deviation is obtained 5.3% for the real sample.

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**Fabrication of electrochemical sensor based on the modification of graphite pencil electrode for Pb<sup>2+</sup> and Cd<sup>2+</sup> determination in its real samples**

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Pb<sup>2+</sup> and Cd<sup>2+</sup> are two major toxic and persistent pollutants normally generated from industry and commonly found in soil, drinking water, and aquatic environments [1,2]. So, their determinations using fast, simple, cost effective and sensitive analytical methods are in interest. This work describes the development, fabrication and optimization of a new electrochemical sensor as Metalaxyl /Cu(NP) / PGE modified electrode for simultaneous detection of Cd(II) and Pb(II). This modified electrode has been fabricated by electrodeposition technique using Cyclic voltammetry sweeping procedure on the surface of bare graphite pencil electrode (PGE). The pencil graphite electrodes are found to be more versatile compared to other carbon based electrodes such as glassy carbon electrodes, carbon paste electrodes and diamond electrodes. This is due to the fact that the pencil graphite electrodes possess high reactivity, more sensitivity, low-cost, low background current, ease of surface modification, and easy preparation technique compared to other electrodes [3]. To detect very low levels of Cd(II) and Pb(II), square wave voltammetry technique was used owing to its high sensitivity and linearity [4,5]. Here in, to increase electrode sensitivity, the effect of some variables chemical and instrumental parameters such as pH, supporting electrolyte, and effective instrumental parameters were evaluated on the electrochemical response of the Metalaxyl /Cu(NP) / PGE modified electrode towards Cd(II) and Pb(II). Results showed that the electro-oxidation /reduction peak currents for Cd(II) and Pb(II) were obtained at the pH of 5. Other advantages of these fabricated sensor are high signal to noise ratio, low detection limit, wide dynamic concentration range and high sensitivity and selectivity. Therefore, this sensing platform is capable of simultaneously determination of Cd(II) and Pb(II) in environmental samples without any side interferences.

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**Modification of a carbon ionic liquid electrode by using palladium nanoparticles –capped carbon nitride quantum dots for selective determination of dopamine**

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In this study, we synthesis the Pd nanoparticles (NPs) using graphitic-carbon nitride (g-C<sub>3</sub>N<sub>4</sub>) quantum dots (QDs) and photochemical routes [1], and the use of the material in an voltametric sensor to determination of dopamine (DA). Using of Pd-NPs in modified electrodes can resolve the overlapped voltammetric waves of compounds such as Ascorbic acid (AA) and DA into two well-defined voltammetric peaks [2]. It is necessary to load them on the surface of a supporting substrate, which has high conductivity, large surface area, low cost, etc. Graphitic carbon nitride (gC<sub>3</sub>N<sub>4</sub>) is a graphite-like layered material that is composed of ordered tri-s-triazine subunits connected by planar tertiary amino groups within layers and weak van der Waals forces between layers [3]. gC<sub>3</sub>N<sub>4</sub> quantum dots (CNQDs) with size of <3 nm contain a very high nitrogen content and abundant dangling bonds [3], and they have potential application as crystal seeds for the growth of Pd to form the gC<sub>3</sub>N<sub>4</sub>-Pd heterocomposite. Coupling of ionic liquid and nanomaterials can be improve electrical conductivity bare electrodes for trace analysis of electroactive compounds.

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**Ag nanoparticle/flake-like ZnMOF nanocomposite as a high mimetic nano-enzyme for the sensitive determination of cholesterol**

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Development of a nano-mimics with intrinsic peroxidase-like catalytic activity have been extensively reported [1]. The metal organic frameworks (MOFs) with a porous crystalline structures are inorganic polymers with stable porous structure and a great surface area, providing a superior catalytic activity [2, 3]. Here, Ag nanoparticle/flake-like Zn-based MOF nanocomposite (AgNPs@ZnMOF) with great peroxidase-like activity was applied as an efficient peroxidase-like material for sensitive determination of cholesterol. AgNPs@ZnMOF was simply synthesized by creating AgNPs inside the nanopores of flake-like ZnMOF. The high surface area of MOF remarkably improved the catalytic activity of AgNPs which was assessed by colorimetric technique. The combination of exceptional peroxidase mimetic activity of MOF-based nanocomposites and simple colorimetric detection methods creates a novel attractive investigation field [4]. On the other hand, it's well-known that enzymatic oxidation of cholesterol by cholesterol oxidase lead to the production of H<sub>2</sub>O<sub>2</sub>. We applied the produced H<sub>2</sub>O<sub>2</sub> for subsequent oxidization of 3,3',5,5'-tetramethylbenzidine (TMB) in the presence of AgNPs@ZnMOF as a catalyst. This reaction led to the production of a blue colored product which was recognized by the colorimetric technique. The effect of some important factors (for example pH, buffer, TMB concentration etc.) were optimized to obtain maximum sensitivity. A linear relationship was obtained between the absorption intensity of the produced blue solution and the cholesterol concentration in the range of 0.5-120 μM, with a detection limit of 0.3 μM.

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## High mimetic HKUST-1 MOF for the fluorometric determination of glucose

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Developing a novel peroxidase nano-mimetic is a challenging research topic in bio-sensing field [1], and metal organic frameworks (MOFs) with a great surface area are good candidate for this purpose. They are porous inorganic polymers with crystalline structures which have stable porous structure providing a superior catalytic activity [2, 3]. Herein, HKUST-1 flake-like metal-organic framework (MOF) was introduced as a nano-porous material with improved peroxidase mimetic behavior and used for selective determination of glucose. The catalytic activity of this nano-porous material in chemical reduction of H<sub>2</sub>O<sub>2</sub> was studied using fluorometric technique. First, it was based on the enzymatic oxidation of glucose using glucose oxidase and then, based on the simple measurement of produced H<sub>2</sub>O<sub>2</sub> using terephthalic acid fluorescence system as sensitive detection method. In optimum condition, a linear association was found between the generated fluorescence intensity and glucose concentration in the range of 0.02-600 μM, and the limit of detection (3S/m) was 40 nM. The developed method had superior properties and was successfully applied for the detection of glucose level in human blood.

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## Aggregation-Induced Emission Probe for Specific Quantification of Creatinine

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Creatinine is the metabolic waste molecule and naturally produced by the body from muscle metabolism. Abnormal creatinine levels in body fluids (blood and urine) implies the decrease in kidney functional activity<sup>[1]</sup>. Therefore, CRN serves as a preferred marker for renal dysfunction. The glutathione capped Cu-nanoclusters presented here showed a unique aggregation-induced emission (AIE) feature<sup>[2]</sup>. This novel AIE phenomenon was successfully exploited for selective and sensitive quantification of typical uremic toxin creatinine. When the CuNCs encountered Al<sup>3+</sup> ions, they rapidly formed aggregates which induce significant emission enhancement of CuNCs. The AIE nature of CuNCs was proved via the TEM and enhanced emission in poor solvents. Moreover, the coordination between CRN and Al<sup>3+</sup> ions could lead to the quenching of fluorescence due to the weakening the AIE. Quenched PL intensity showed a linear dependence on the concentrations of CRN in the in the range of 2.5– 34  $\mu\text{gL}^{-1}$  with a detection limit of 0.63  $\mu\text{gL}^{-1}$  and excellent selectivity for CRN. The sensing mechanism of the AIE based fluorescence probe for CRN detection was discussed. Also, the developed probe was applied to determine in CRN human serum and urine samples with satisfactory results.

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**Determination of Platinum in National Iranian Copper Industries Copper Matte sample**

**By Solid Phase Extraction**

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Fire Assay Test Method [1] is used for Platinum Measurement. It has major disadvantages such as high energy consumption, the environmental pollutants, human risks and too much time of Analysis. Today, all these problems are fundamental and important crises. Therefore, Utilization a test method that hasn't these problems is necessary. By Solid phase extraction technique, concentration and separation of small amounts of platinum in Copper Matte samples was presented. In this technique Rubenic Acid [2] as a Ligand and alumina as an adsorbent before determination by flame atomic absorption were used. Critical parameters of this technique such as pH<sub>[3]</sub>, flow rate of sample and elution<sub>[4]</sub>, adsorbent weight and type, concentration and volume of Elution, step by step was achieved<sub>[5]</sub>. Validation process with three method was performed, analysis of standard samples (CRM); Analysis Results Compare with AHK reference laboratory in England and the third method using of spiking technique on samples with Determined value (RM). Statistical evaluations of Validation Process by using of Minitab software were performed. Limit of detection (LOD) based on three times the standard deviation of Blank with five times measurements, 2.20 µg/L was calculated. The linear range of calibration curve in the range of 1 to 100 µg/L with the correlation coefficient 0.9950 was obtained.

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### Fabrication of Bi<sub>2</sub>O<sub>3</sub>-poly para-aminophenol modified glassy carbon electrode

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Bismuth electrode is a suitable replacement for mercury electrode due to low toxicity and similar electrochemical behavior [1]. In this work for the first time a novel and stable electrode, based on Bi<sub>2</sub>O<sub>3</sub>-polymer film coated on glassy carbon was introduced. Fabrication of Bi<sub>2</sub>O<sub>3</sub>-poly *p*-AP (Bi<sub>2</sub>O<sub>3</sub>-Pp-AP/GCE) was carried out in two steps: first a Bi layer was formed on GCE and second, simultaneous oxidation of Bi to Bi<sub>2</sub>O<sub>3</sub> and anodic polymerization of *p*-AP in weak alkaline medium were performed. The prepared electrode was characterized by CV, FT-IR (ATR), H-NMR, SEM, EDS and a suitable mechanism for electropolymerization of *p*-aminophenol is proposed. This electrode is stable over time and can be used repeatedly without renewing the surface of electrode.

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**Determination of anti-platelet drug by differential pulse voltammetry**

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In this work a novel and stable electrode, based on Bi<sub>2</sub>O<sub>3</sub>-polymer film coated on glassy carbon, has been used for electrocatalytic determination of clopidogrel in pharmaceutical preparations by differential pulse voltammetry (DPV). The electrocatalytic effect of Bi<sub>2</sub>O<sub>3</sub> on determination of clopidogrel is discussed and its probable mechanism offered. This compound is an oral thienopyridine derivative which is used to inhibit blood clot formation in coronary artery diseases, peripheral vascular diseases and so on [1,2]. There is a good linear relationship between concentrations of clopidogrel in the range of  $3 \times 10^{-6}$ - $1 \times 10^{-3}$  mol L<sup>-1</sup> and obtained areas of voltammograms. The limit of quantification (LOQ) is calculated to be  $2.5 \times 10^{-6}$  mol L<sup>-1</sup>. The relative standard deviation (RSD) for  $1 \times 10^{-5}$  mol L<sup>-1</sup> of clopidogrel was 2.5 % (n=5). This electrode was successfully applied for measurement of clopidogrel in pharmaceutical preparations directly, which means there is no need to separate the excipients of the tablets for analysis. There is also a good agreement between the results of this method and USP standard method by UV spectrometry.

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**Removal of Anionic Congo Red Dye from Aqueous Solutions by Ionic Liquid–Chitosan-Graphene Oxide composites**

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The objective of the present laboratory-experimental study was to remove congo red from industrial effluents using adsorption by graphene oxid that functionalized with chitosan and ionic liquid (GO/IL/Ch) [1-3]. Various parameters such as pH, different amounts of absorbent, different concentrations of congo red, contact time and temperature were examined. The highest congo red removal was achieved at pH=4. The amount of 0.004 grams of absorbent is optimum for removal of 50 ppm concentration of congo red. Equilibrium data and adsorption kinetics obtained from congo red were observed to obey the Langmuir isotherm and pseudo second-order kinetic models, respectively and also thermodynamic studies show that the adsorption processes are calefactive. The findings indicate that (GO/IL/Ch) is capable of removing congo red from industrial effluents.

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**Determination of Ibuprofen, Aspirin and Venlafaxine by stir bar sorptive extraction coated with Nano absorbent**

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The present work proposes the application of bar adsorptive microextraction coated with Nano absorbent, combined with liquid desorption followed by gas chromatography-mass spectrometry for the determination of trace levels of three typical drugs (Ibuprofen, Aspirin and Venlafaxine) in urine samples[1]. Assays performed on 25 mL of urine samples spiked at the 1 and 10 µg/L level, yielded average recoveries between 90 and 107% for all drugs under study using optimized experimental conditions. The proposed analytical methodology demonstrated suitable detection limits (0.2 µg/L) and good linear dynamic ranges (1–1400 µg/L) with determination coefficients higher than 0.997. By using the standard addition methodology, the present analytical approach was applied on urine samples, where good selectivity and sensitivity were achieved. The proposed method, which operated under the floating sampling technology, proved to be a suitable sorption-based static microextraction alternative for monitoring trace levels of mentioned drugs in urine samples[2]. The methodology showed to be easy to implement, demonstrating good reproducibility and robustness, allowing the possibility to choose the most selective sorbent, or mixed sorbent phases, according to the compounds of interest.

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**The application of chitosan in the measurement of pesticides**

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Today, nanotechnology has been entered as a revolution in all branches of science. Including the sciences, agriculture and environment. Chitin chitosan as a matter of) the second most abundant biological polymer after cellulose in nature (This natural polymer skin from various sources, such as crab, shrimp, cuticle achieved [1]. To control pests, fungi and maintenance products and the rise of new diseases, priority ways that Without the use of chemicals to increase the quality and quantity of the product [2]. Chitosan as an amino poly Natural polysaccharide which has a unique structure and properties of multifunctional, including the specification Biocompatibility, biodegradability, oral agents, anti-fungal and anti-bacterial properties it. With Due to its importance to deal with a wide variety of applications tensions in the planting, harvesting and post for crops has found, and also because of its use in the protection of the environment [3].

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**Phenethylamine functionalized hybrid sol-gel reinforced aluminum foil as a thin film microextraction device for the trace analysis of eight PCBs in edible liquids prior to GC-MS quantitation**

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A novel sol-gel coating on an aluminum foil was produced and applied as a thin film microextraction (TFME) device. Eight selected polychlorinated biphenyls (PCBs) were employed as model compounds to evaluate the extraction performance of the synthesized sol-gel. The analysis was performed using gas chromatography-mass spectrometry [1]. First, pieces of aluminum foil (5 cm × 0.5 cm) was etched in concentrate NaOH and 10% HCl respectively. Then aluminum foil was coated with a thin hybrid sol-gel film of methyltrimethoxysilane-tetraethoxysilane (MTMOS-TEOS). Afterward, Phenethylamine bounded chloropropyltrimethoxysilane used for functionalization of sol-gel reinforced aluminum foil. Its morphology and surface properties were characterized using Fourier transform infrared spectroscopy, scanning electron microscopy and energy dispersive spectroscopy. The performance of new sorbent functionalized with phenethylamine was compared with bare aluminum foil and aluminum foil coated MTMOS-TEOS. Aromatic functional groups in final sorbent leading up to suitable  $\pi$  interactions with PCBs resulting higher extraction efficiency [2]. The parameters affecting the efficiency of TFME such as extraction solvent type and volume, extraction and desorption time, temperature, stirring rate and salt effect were investigated and optimized. Under the optimal conditions, the limit of detection ( $S/N = 3$ ) was 1 ng L<sup>-1</sup> and the linearity was in the range of 10 to 1000 ng L<sup>-1</sup>. The method precision expressed as relative standard deviations (RSD) was 7.0-11 % (intra-day), and of 9.0-12.4% (inter-day) respectively. Finally, our method was successfully applied for trace determination of PCBs in orange juice, cola drink, milk, beer, and honey with acceptable performance.

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**Fast and sensitive analysis of nitro-phenanthrenes in water and soil samples using copper loaded polyaniline@magnetic halloysite nanotube composite coupled with gas chromatography–mass spectrometry**

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In this study, we developed ultrasonication assisted magnetic dispersive solid-phase microextraction (MDSPME) setup for extraction of two types of nitro-PAHs compound include 9-nitrophenanthrene (9-NPhe) and 3 nitrophenanthrene (3-NPhe) in environmental samples prior to GC–MS determination. Nitro-PAHs are derivatives of PAHs and mainly generated by incomplete combustion and pyrolysis of fossil fuels such as diesel and gasoline. These compounds can be 200% higher than the mutagenicity caused by their parent PAHs [1]. However, until the pre-concentration of ultra-trace is not carried out, favorable detection sensitivity might not be achieved. For this reason, new type of modified nanocomposite has made based halloysite nanotubes (HNT). HNT is a type of natural material, have attracted great interest because of their large surface area and high chemical and thermal stability [2]. The hybrid nanocomposite was obtained by fabricating magnetic HNT by polyaniline (PANI) and afterwards with copper. Its morphology and surface properties were characterized using of Fourier transform infrared spectroscopy, field-emission scanning electron microscopy, energy dispersive spectroscopy and vibrating sample magnetometry. The performance of new sorbent was compared with magnetic HNT and magnetic HNT@PANI. Hydrophilic containing functional groups in HNT leading up to a suitable dispersion in aqueous matrixes, while PANI moiety contributes to the hydrophobic and  $\pi$  interactions with nitrophenanthrenes. The presence of copper on the polymeric structure is responsible for  $\pi$  electron-metal interactions and higher sorption capacity. Parameters affecting the extraction efficiencies such as desorption solvent type and volume, extraction and desorption time, sorbent amount, organic modifier content, salt concentration and matrix effect were investigated in detail. Under the optimal conditions, the limit of detection ( $S/N = 3$ ) was  $0.25 \text{ ng L}^{-1}$  and the linearity was in the range of  $0.01$  to  $100 \text{ } \mu\text{g L}^{-1}$ . The method precision expressed as relative standard deviations (RSD) was 4.6-6.1 % (intra-day), and of 7.2-9.6% (inter-day) respectively. Finally, the presented method was successfully applied to the fast determination of analytes in water and soil samples.

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**Enhanced thermal lens effect using surface plasmon resonance of gold nanoparticle for detection of fluorescence molecules**

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A photo thermal lens microscope (PTLM) is a recent promising development of thermal lens spectrometry (TLS) toward miniaturization. A TLM not only has the similar advantage of high sensitivity as the conventional TLS, but also has its unique characteristics such as high temporal (ms) and spatial resolutions ( $\sim\mu\text{m}$ ), which enable it for high-sample-throughput and small-volume detection of a variety of compounds with low sample/reagent consumption when it is coupled to lab-on chip chemistry, such as in microfluidic chips or miniaturized microliter plates [1].

In the TLM, when the analyte molecules in the confocal region absorb the excitation beam, they emit heat via radiationless processes. The temperature at the confocal region increases, and usually the refractive index (RI) decreases because of the heat. The laser intensity profile is nearly a Gaussian distribution, and the heat source distribution is in proportion to it. The RI distribution becomes a nearly Gaussian distribution and acts as a concave lens.

Resonant energy transfer (RET) systems consisting of organic dye molecules and noble metal nanoparticles have recently gained considerable interest in biophotonics [2]. If the donor molecule is placed in the vicinity of a metal surface instead of an organic acceptor, not only resonant energy transfer takes place but also the radiative lifetime of the donor molecule changes [4].

In this work, a combined photo thermal lens microscopy (PTLM) system was assembled for highly sensitive determination of dye molecule vicinity of gold nanoparticle as acceptor. We used Triazene component as donor molecules in the vicinity of AuGNs. Triazene component has a fluorescence emission peak at 510 nm when excited at 405 nm. We show Gold nanoparticles in focal point make the overlap of the molecule's emission with the nanoparticle's absorption spectrum that cause temperature at the focal point increases and enhance thermal lens signal of triazene. The detection volume is equal to the focal volume of the excitation beam; the focal volume was calculated to be 1.18 fL. The results show the possibility of direct determination of 7 to 100 triazene molecules in the vicinity of 2.5 AuGNs in the focal volume of the excitation beam.

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**Preparation of a new magnetic nano adsorbent modified with poly ionic liquide for the extraction and preconcentration of fluoride from different samples followed by indirect detection using flame atomic absorption spectrometry**

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Fluoride is usually present in different natural water samples at low concentrations. In drinking water, fluoride concentration of about 1 mg/L reduces dental caries and has not harmful effects on health. But, at the levels more than this amount, fluorosis may occur [1]. Maximum acceptable fluoride concentration in drinking water is 1.5 mg/L according to World Health Organization (WHO) [2]. The most common methods to determine fluoride concentration is using ion selective electrodes, ion chromatography, Zr SPADNS and other dyes [3].

In this research we have proposed a solid phase extraction method for extraction and enrichment of fluoride from different samples. A new type of poly ionic liquid coated magnetic nanoparticles (MNPs@PIL) was designed and prepared via free radical polymerization. Designing the nano adsorbent and selecting the ionic liquid was so that, to be able to adsorb fluoride anion. The as synthesized MNPs were characterized using Fourier transform infrared spectroscopy (FT-IR), X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), thermo gravimetric analysis (TGA) and elemental analysis (EA). Then, it was successfully used as adsorbent in magnetic solid phase extraction (MSPE) method for the extraction of fluoride from different samples. The effect of several experimental variables (including pH of sample solution, amount of the adsorbent, extraction and desorption time) were studied and the optimum values were determined. The adsorbed ions were eluted from the adsorbent and little volume of high concentration of Ca<sup>2+</sup> solution was added to convert fluoride to CaF<sub>2</sub> sediment. After filtration, residue of ca<sup>2+</sup> was determined using flame atomic absorption spectrometry and so fluoride concentration in sample was determined. Under the optimum experimental conditions, detection limit (S/N=3) of the proposed method for fluoride was obtained as 0.1424µg/mL and a preconcentration factor of 225 was achieved. The proposed method was applied for determination of fluoride in different real samples successfully.

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## Modified pencil graphite electrode as a novel electrochemical sensor for the determination of paroxetine

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Paroxetine (PRX) is a selective serotonin reuptake inhibitor, with antidepressant and anxiolytic activity [1]. To date various analytical methods have been developed for the determination of paroxetine such as chromatography [2], spectroscopy [3] and electrochemistry [4]. Among these, chromatographic methods are most commonly used, while non-chromatographic direct methods are rare. Compared to other determination techniques, electroanalysis has the advantages of simplicity, high sensitivity and in most cases, selectivity.

In this work, An electrochemical sensor was developed for determination of paroxetine using a physical pretreated and electrochemical modified pencil graphite electrode (PGE). Pretreatment of the electrode was done by placing the PGE in a stirring sulfuric acid solution for an hour at 80°C. Modification of the pretreated pencil graphite electrode (PPGE) was then performed by the reduced graphene oxide-phosphotungstic acid (RGO-PTA) with potentiostatic procedure at -1.2 V for 5 min in 0.1 M phosphate buffer solution of pH=7. Surface morphology of the modified PGE was analyzed with SEM, FT-IR and electrochemical impedance spectroscopy (EIS) techniques while the electrochemical studies were done. The kinetic parameter charge transfer coefficient,  $\alpha$ , was determined for oxidation of PRX at modified PPGE. In optimum experimental conditions, differential pulse voltammetry (DPV) was used for determination of PRX, which exhibits a linear calibration graph of  $I_p$  versus PRX concentration in the range of  $15-3.3 \times 10^4$  nM with a correlation coefficient of 0.999. The calculated detection limit was obtained equal to 8 nM. Modified PPGE was successfully used for determination of PRX in paroxetine tablets and biological samples such as human serum and urine samples.

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**Fast derivatization of aliphatic aldehydes followed by gas chromatographic analysis**  
**Application: for human exhaled breath analysis**

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Aliphatic aldehydes which have unpleasant pungent odors are usually present at trace amount in various complex material such as food, air and water pollution samples, car exhaust, cigarette smoke, physiological fluid and exhaled breath (EB) [1]. These compounds in EB are divided into two groups, namely exogenous volatiles and endogenously produced compounds. Exogenous volatiles include those inhaled from the environment, the oral ingestion of food, and smoking cigarettes. Endogenously produced volatiles include materials newly made from cells in the body and those made by intestinal bacteria. Aliphatic aldehydes present in very low concentrations from malignant cells of human organs, e.g. lung diseases [2]. Breath analysis is a promising non-invasive approach that allows the identification of the various respiratory conditions such as breath cancer.

Exhaled C<sub>1</sub>-C<sub>10</sub> aldehydes have been detected in all healthy volunteers, smokers and lung cancer patients. Exhaled pentanal, hexanal, octanal and nonanal concentrations were significantly higher in lung cancer patients than in smokers and healthy controls. Lung cancer patients could be therefore screened by means of exhaled pentanal, hexanal, octanal and nonanal concentrations [1].

C<sub>1</sub>-C<sub>10</sub> aldehydes analysis in EB present certain difficulties because of their high volatility and polarity. Therefore, derivatization and enrichment procedures are usually required for GC analysis [3]. The proposed method is based on co-liquefaction of the analytes existing in human EB followed by air assisted dispersive microextraction (AADME) with small volume of extraction solvent.

In this work 1000mL of smoker exhaled breath sample was taken in the specially fabricated extraction device. 1.4mL of methanol was added. The extraction device was exposed to ultrasonic bath for the evaporation of solvent and then co-liquefaction at -18°C with any VOCs present in exhaled breath. 0.4 mL of 3-Methyl-2-benzothiazolinone hydrazone hydrochloride hydrate (MBTH) solution, 0.4mL of phosphate buffer (pH=5.5) and 0.2mL H<sub>2</sub>O was added into collected methanolic solution. The extraction of derivatized aldehydes was performed using AADME with 0.1mL hexane for 5 min. 2 μL of extract was analysed. Under optimal conditions, the method displayed good linearity for the studied aldehydes within a range of 0.1-10 ng.mL<sup>-1</sup>, with correlation coefficients > 0.9975. The limits of detection (LODs) and the limits of quantitation (LOQs) were ranged from 0.04 to 0.11ng.mL<sup>-1</sup> and 0.1 to 0.3ng.mL<sup>-1</sup>, respectively. The relative standard deviations were less than 8.8%. Moreover, enrichment factors (EFs) were in the ranges of 8100 to 9100-fold. The overall time for sampling and extraction is 40 minutes.

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**Synthesis, characterization of ion imprinted polymeric nanoparticles for selective extraction and purification of <sup>65</sup>Cu**

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Copper is an important element which is widely used in electrical power, metallurgy and as a target for production of radio pharmacy. <sup>65</sup>Cu stable isotope is used to produce <sup>65</sup>Zn in a cyclotron for medical applications [1-3]. This work presents synthesizing of a copper ion imprinted polymeric nanoparticles based on the inclusion of 4-vinylbenzoic acid (4-VB) as a ligand into the polymer matrix to complex with copper ions. The prepared complex was then copolymerized with ethylene glycoldimethacrylate, methyl methacrylate and 2, 2-azobis-isobutyronitrile in 2-methoxyethanol via a precipitation polymerization method. Moreover, non-imprinted polymeric (NIP) particles were similarly prepared without Cu (II) ion. The characterization of polymers was carried out by Uv-vis, FT-IR, SEM, EDX, TGA-DSC, BET, ICP-AES. The effect of several parameters such as solution's pH, sorption and desorption time, type, concentration and volume of eluent on the extraction of the polymers were investigated and optimized by one variable at the time. Optimized parameters were, pH 6; mass sorbent 0.1 g; sorption time, 30 min; desorption time 10 min; aqueous phase volume, 10 mL. Moreover, it is found that 20 mL of EDTA (1 M) provided the most effective elution of Cu (II) ion from IIP sorbent. The maximum sorbent capacity of the IIPs was 6.23 mg g<sup>-1</sup>. The detection and determination limits of the method were evaluated to be 12.00 and 42.70 ng mL<sup>-1</sup> respectively. The precision of the method (%RSD, n=5) was % 0.054. The <sup>65</sup>Cu recovery yield was % 98.58.

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**Evaluation of chemical compositions, antimicrobial and antimalarial activities of essential oil of the aerial parts of *Artemisia fragrans* wild**

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This study aimed to determine chemical compositions and biological activities of *Artemisia fragrans* wild (family Asteraceae) growing in East-Azərbayjan province of Iran. 100g of dried aerial parts of *A. fragrans* wild were powdered and submitted to Clevenger apparatus for hydro-distillation. Subsequently, the essential oil (EO) analyzed by Gas chromatography- Mass spectroscopy. Thirty nine components were identified in the oil. Furthermore, anti-microbial and antimalarial activities of the EO was screened by disc diffusion and cell free  $\beta$ -hematin formation assay methods, respectively. The major constituents of the EO showed antimicrobial and antimalarial activities.

The genus *Artemisia* (Family Compositae) belongs to the group of aromatic and medicinal plants comprising about 300 species found in the northern hemisphere. There are approximately 34 native *Artemisia* species in Iran. This large genus has been the object of numerous chemical studies. *Artemisia* genus has been reported to contain number of coumarins, flavonoids and terpenes. In continuation of our studies on the chemical compositions of the essential oil, we decided to investigate the essential oil, anti-malarial and anti-microbial activity of *Artemisia fragrans* Willd.[1]

Aerial parts of *A. fragrans* were collected from Mughan in East Azarbaijan province, Iran. A Voucher specimen for this collection has been deposited at the Herbarium of Faculty of Pharmacy, Tabriz University of Medical Sciences, Tabriz, Iran. 100g of dried aerial parts of *A. fragrans* powdered and submitted to Clevenger apparatus for hydro-distillation. Then the essential oil (EO) analyzed by Gas chromatography-Mass spectroscopy (GC-MS). Moreover, anti-microbial activity of the EO against two gram positive strains (*Staphylococcus aureus* and *Staphylococcus epidermidis*), one gram negative strains (*Escherichia coli*) and a fungi (*Candida albicans*) was screened by disc diffusion method. Furthermore, antimalarial activity of the samples were tested using cell free  $\beta$ -hematin formation assay methods.[2]

The hydro-distillation of the aerial parts of *A. fragrans* Willd yielded light yellowish oil. Thirty nine components were identified in the oil. The major constituents of the EO were 3-Thujanone (47.43%), Eucalyptol (18.04%) and Alpha-thujone showed antimicrobial activity against *Staphylococcus epidermidis* and *Escherichia coli* with Diameter inhibition zone of 17 and 22 millimeter, respectively. Also, antimalarial activity of the mentioned oil was remarkable (IC<sub>50</sub> value of 0.42±0.15 mg/ml) compared to the standard antimalarial compound, chloroquine (IC<sub>50</sub> = 0.014 ± 0.003 mg/mL)

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**Development of carbon paste sensor for low level and selective determination of sitagliptin phosphate in pharmaceutical and biological samples**

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Sitagliptin phosphate (STA), [(R)-4-oxo-4-[3-(trifluoromethyl)-5,6-dihydro[1,2,4] triazolo [4,3-a]pyrazin-7(8H)-yl]-1-(2,4,5-trifluorophenyl)butan-2-amine] phosphate, is an orally active and selective inhibitor of dipeptidyl peptidase-IV that is used for treatment of type II diabetes. DPP-4 inhibitors represent a new therapeutic approach to the treatment of type 2 diabetes that functions to stimulate glucose dependent insulin release and reduce glucagons levels [1]. Several analytical methods have been reported for the determination of STA such as spectrophotometry [2], spectofluorimetry [3,4] and potentiometry by liquid membrane electrode [1]. However, no potentiometric carbon paste electrode (CPE) for this drug has been reported so far. The most advantages of CPEs are ease of preparation, modification and regeneration and low cost. Thus, the introduction of a carbon paste sensor for fast, simple, selective and sensitive determination of STA is very valuable.

In this study a new CPE based on incorporation of the ion-association complex of the sitagliptin phosphate-phosphotungstate were studied. The electrode exhibited Nernstian slope of 59.2 mV/decade to sitagliptin over a wide concentration range from  $1.7 \times 10^{-8}$  -  $2.2 \times 10^{-5}$  M with low detection limit of  $9.0 \times 10^{-9}$  M. The potentiometric response of the electrode was studied in buffered solution. The proposed sensor manifested advantages of fast response, long life time and most importantly, good selectivities for sitagliptin relative to a wide variety of common foreign inorganic cations and biological species. The influence of temperature on the potential response of the sensor was tested at different temperature and the temperature coefficient of the sensor was calculated. The sensor was successfully applied as an indicator electrode in potentiometric determination of sitagliptin in sitagliptin tablet and blood serum samples.

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**Combination of salt-induced homogeneous liquid-liquid and solidified organic droplets  
dispersive liquid-liquid microextraction for extraction of some tricyclic antidepressants in  
urine samples prior to their determination by HPLC-UV**

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Nowadays, millions of people all over the world are affected with a common mental disorder named depression. This disorder causes the patients to experience serious problems such as depressed mood, feelings of guilt, disturbed sleep, and loss of interest or pleasure. The effective treatment of this disorder was proposed in the 1950s with the development of antidepressants which can elevate a patient's mood. The antidepressants commonly have been classified in two main groups: the monoamine oxidase inhibitors and tricyclic antidepressants (TCAs) [1]. TCAs are one of the oldest classes of antidepressants and impeded the reuptake of serotonin and norepinephrine in the central nervous system [2]. Due to the narrow therapeutic range of TCAs, the development of sensitive and rapid analytical method for the determination of TCAs concentration in biological fluids in order to achieve the best therapeutic concentration with at least overdose and adverse problems is of great importance [3]. In this work, an efficient and green sample pretreatment method by combining salt induced-homogenous liquid-liquid extraction, dispersive solid phase extraction, and dispersive liquid-liquid microextraction based on the solidification of floating organic droplet has been developed for the extraction and preconcentration of some tricyclic antidepressant drugs (nortriptyline, amitriptyline, desipramine, clomipramine, and imipramine) in urine samples prior to their determination by high performance liquid chromatography-ultraviolet detection. In the suggested method, initially the analytes are extracted from urine samples into acetonitrile (ACN) separated by adding a salt. Then the obtained ACN phase is treated with a mixture of appropriate sorbents (50 mg PSA, 50 mg C<sub>18</sub>, and 25 mg GCB) to remove interferences. Afterward, the purified ACN is mixed with menthol as an extraction solvent and rapidly injected into alkaline HPLC-grade water as a preconcentration step. Next, after centrifuging the solution is placed in an ice bath and menthol is solidified and collected on the top of the solution. The solidified organic drop is then removed and dissolved in 10  $\mu$ L ACN and injected into the separation system for quantitative analysis. Under the optimum experimental conditions, the enrichment factors and extraction recoveries of the selected drugs ranged from 345-420 and 69-84%, respectively. The limits of detection and quantification were obtained at the ranges of 0.22-0.31, and 0.71-1.1  $\mu$ g L<sup>-1</sup>, respectively. The relative standard deviations of the proposed method for the selected analytes were  $\leq$  6% for intra- (n=6) and inter-day (n=4) precisions at a concentration of 10  $\mu$ g L<sup>-1</sup> of each analyte. Finally, the proposed method was used in the determination of the selected drugs in various urine samples.

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**Determination of zinc (II) ion using carbon paste electrode modified with Zn-ion imprinted polymeric nanoparticles**

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Zinc is an essential element for human, plant and animals. It is necessary for many biological functions and plays a crucial role in enzymes in the human body, fertility, growth, taste, smell, skin, hair and immune system [1-3], so monitoring of this element in water, soil and food samples is very important. This study describes the development of an electrochemical sensor based on the use of zinc (II) ion imprinted polymeric nanoparticles (IIP-NPs) and its application for determination of the Zn-68 stable isotope. Ion imprinted polymeric particles synthesized by precipitation polymerization method and used as identification element in the construction of the sensor. Also for comparison, the non-imprinted polymer (NIP) particles prepared in a similar manner but in absence of Zn<sup>2+</sup> ion. The SEM images of obtained polymers showed that the IIP particles have dimensions in nano-scale. The electrochemical performance of the sensor investigated by cyclic voltammetry. The results depicted that the IIP-CP electrode has much higher adsorption ability to Zn<sup>2+</sup> ion than the NIP-CP electrode. The effect of some parameters affecting the sensor response, such as electrode composition, adsorption and desorption conditions studied and then calibration curve was drawn. Under the optimal conditions, the linear dynamic range and limit of detection were 0.05 to 0.5 nM and 4.3 %, respectively. The sensor was successfully used to determination of the Zn-68 stable isotope.

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**Process optimization and stability investigation of spearmint nanoemulsion formation by low energy method using mixture experimental design**

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Essential oils (EOs) are water-insoluble compounds, which are unstable in the presence of oxygen, light and temperature [1, 2]. Entrapment methods are used to overcome the essential oils problems [3]. A number of different processing methods, such as high- or low-energy methods was used for fabrication of nanoemulsions [4]. In the current work, we applied an isothermal low-energy method (spontaneous emulsification) for producing transparent spearmint nanoemulsions suitable for utilization in beverages and foods.

The purpose of this study was to produce and optimize nanoemulsion of spearmint. This spontaneous emulsification was formed by titration of an organic phase (containing spearmint oil (2%),  $1 \leq$  eumulgin  $\leq 2$ ,  $1 \leq$  Tween 20  $\leq 3$  and  $1 \leq$  Tween 80  $\leq 3$ ) into an aqueous phase ( $5 \leq$  PG  $\leq 20$ ,  $5 \leq$  PEG 400  $\leq 20$  and  $50 \leq$  water  $\leq 85$ ) with continuous stirring. Mixture experimental design [5] was applied to elevate the main and interactive impact of independent variables on the turbidity of spearmint nanoemulsion, as a response. The model was validated by correlation of determination ( $R^2$ , adjusted  $R^2$  and predicted  $R^2$ ), and ANOVA was used to verify the adequacy of the regression model in terms of a lack of fit (LOF). ANOVA results are based on the confidence level of  $\alpha=0.05$ , and influence of each variable should be obtained according to its probability value (P-value). Therefore, the terms with P-value  $\geq 0.05$  assume significance. The high coefficients of correlations ( $R^2$ : 0.9877, adjusted  $R^2$ : 0.9704 and predicted  $R^2$ : 0.9145), low coefficient of variation and standard deviation show the goodness of the model. The mathematical model showed that the optimum formulation for preparation of nanoemulsion spearmint 2.00% has the desirable criteria with 2.00% of eumulgin, 3.00% of Tween 20, 2.94% of Tween 80, 19.53% of PEG 400, 19.53% of PG and 51.00% of water. Under optimum formulation, droplet size and zeta potential of the nanoemulsion were 81.28 nm and -0.480 mV, respectively. The droplet size of optimized nanoemulsion remained stable after 4 weeks of storage. These results have important implications for the design and utilization of nanoemulsions as delivery systems in the food and pharmaceutical industries.

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**Investigation of the media pH effects on the amount of protein secretion of *Burkholderia mallei* by UV-VIS spectroscopy**

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Glanders occurs primarily in equines, but other species, including humans, may become incidental hosts [1]. The causal agent of glanders is the bacterium *Burkholderia mallei*, a small, Gram negative, non-motile, encapsulated, facultative intracellular rod [2,3]. The disease presents in three main forms: pulmonary, nasal and cutaneous [4]. The malination test is used to identify the disease. Because of the low concentration of these mallein-derived proteins, optimization of existing methods was carried out. One of the factors affecting the secretion of these proteins is pH bacterial culture. Media were prepared, adjusted to the desired pH with HCl or NaOH and sterilized in the autoclave. Before using, the pH of the broth was determined electrometrically. *Burkholderia mallei* after 72 days incubation in 37° C the broth culture with difference pH as: 6.4, 6.8, 7, 7.2 was steamed at 100 for 1 hour, sterility-tested, centrifuged at 10000g and the supernatant filtered and stored aseptically at 4 C. this filtrate served as crude mallein and was further processed for separation of malleo-proteins. After incubation, by observing the growth of the bacteria and activating the bacteria in order to obtain the most suitable culture conditions, the Lurie method was used to protein assay by using the UV spectrometer. The Lowry protein assay is a biochemical assay for determining the total level of protein in a solution. The total protein concentration is exhibited by a color change of the sample solution in proportion to protein concentration, which can then be measured using colorimetric techniques. The method combines the reactions of copper ions with the peptide bonds under alkaline conditions with the oxidation of aromatic protein residues. The Lowry method is based on the reaction of Cu<sup>+</sup>, produced by the oxidation of peptide bonds, with Folin-Ciocalteu reagent (a mixture of phosphotungstic acid and phosphomolybdic acid in the Folin-Ciocalteu reaction). Experiments have shown that cysteine is also reactive to the reagent. Therefore, cysteine residues in protein probably also contribute to the absorbance seen in the Lowry assay [4]. The result of this reaction is an intense blue molecule known as heteropolymolybdenum Blue [5]. The concentration of the reduced Folin reagent (heteropolymolybdenum Blue) is measured by absorbance at 660 nm [6]. As a result, the total concentration of protein in the sample can be deduced from the concentration of tryptophan and tyrosine residues that reduce the Folin-Ciocalteu reagent. With regard to read absorption, It was found that the highest growth was observed in pH 7 and This pH has the highest protein content. So the sample with the pH 7 is suitable for the production of PPD Mallein.

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**Application of a new modified carbon paste electrode for low level potentiometric determination of cetirizine**

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Cetirizine hydrochloride (CT) with name, ( $\pm$ ) - [2- [4- [(4-chlorophenyl)phenylmethyl] -1 piperazinyl] ethoxy]acetic acid, dihydrochloride is an antihistamine is used for relieve allergy symptoms such as watery eyes, runny nose, itching eyes/nose, sneezing, hives and seasonal allergic rhinitis [1,2]. Few methods have been used for quantitative determination of cetirizine including fluorimetry [3], high-performance liquid chromatography [4] and voltammetry [5]. Carbon paste is an ideal electrode substrates due to its chemical inertness, low cost, fast response time, ease of fabrication in different configuration and renewability. These attractive features of carbon paste electrodes have been reasons for the considerable attention at the production of carbon based electroanalytical sensors. Since no potentiometric carbon paste sensor has been reported for the determination of cetirizine, the introduction of a modified carbon paste electrode for easy, fast, selective and sensitive quantification of this drug in different media is very important.

This work describes the possibility of using a derivative cetirizine-phosphotungstat as ionophore in the preparation of cetirizine potentiometric carbon paste sensor. The constructed sensor show a linear response with Nernstian slope of 59.5 mV in the concentration range of  $7.4 \times 10^{-9}$ - $5.6 \times 10^{-5}$  M with a low detection limit of  $5.0 \times 10^{-9}$ . The sensor was fully optimized in terms of composition, usable pH range, life and response time. The sensor show excellent selectivity for CT respect to cations and biological species. Temperature dependence of the sensor potential response was examined and the thermal coefficient of the sensor was calculated. The sensor was successfully used for the determination of cetirizine in real samples such as cetirizine tablet and blood serum samples.

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**Synthesis, structural, Magnetic and Photocatalytic properties of Ni -doped Bismuth Ferrite Nanoparticles for pollutant dye**

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Double oxide of bismuth ferrite with BiFeO<sub>3</sub> formulation in the structure of perovskite and in the rhombus arrangement is crystallized. This compound is important due to its structural characteristics, multiproduct properties and photocatalytic properties. It should be. Hence, extensive studies have been carried out in various fields. In this thesis, BiFeO<sub>3</sub> nanoparticles and enriched bismuth ferrite with nickel have been synthesized using the sol-gel method, and the effect of substitution of nickel on its physical properties has been studied. X-ray diffraction spectroscopy was used to identify these materials, and the results indicate that these compounds are formed in rhombus structure. The size of the nanoparticles synthesized by the transmitted electron microscope (FESEM) and the Scherrer equation were determined. The photocatalytic properties of these compounds have been investigated for using Spectrometry (UV-Vis).

The results indicate that the dual nickel-vanadate substitution induces a change in the photocatalytic property of bismuth ferrite. The effect of operating parameters such as radiation time, color concentration, and photocatalytic quantity were studied to obtain favorable conditions.

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**Synthesis, structural, Magnetic and Photocatalytic properties of Sm -doped Bismuth Ferrite Nanoparticles for pollutant dye**

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Double oxide of bismuth ferrite with  $\text{BiFeO}_3$  formulation in the structure of proscate and in the rhombus arrangement is crystallized. This compound is important due to its structural characteristics, multiproduct properties and photocatalytic properties. It should be. Hence, extensive studies have been carried out in various fields. In this thesis,  $\text{BiFeO}_3$  nanoparticles and enriched bismuth ferrite with samarium have been synthesized using the sol-gel method, and the effect of substitution of samarium on its physical properties has been studied. X-ray diffraction spectroscopy was used to identify these materials, and the results indicate that these compounds are formed in rhombus structure. The size of the nanoparticles synthesized by the transmitted electron microscope (FESEM) and the Scherrer equation were determined. An IR spectrometry was used to verify the synthesis of  $\text{Bi} (0.98) \text{Sm} (0.02) \text{FeO}_3$ . The photocatalytic properties of these compounds have been investigated for Using Spectrometry (UV-Vis).

The results indicate that the dual samarium-vanicol substitution induces a change in the photocatalytic property of bismuth ferrite. The effect of operating parameters such as radiation time, color concentration, and photocatalytic quantity were studied to obtain favorable conditions.

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**Preparation of titanium electrodes containing titanium dioxide nanotubes and their photoelectrochemical ability in the degradation of some phenolic compounds**

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Photoelectrochemical oxidation featuring strong oxidation performance, low-volume application, and environmental compatibility has been an effective method for degradation of refractory organic pollutants. To further increase the effect and application potential of the photoelectrochemical oxidation method, it is essential to develop the electrode with high photoelectrochemical activity and strong stability[1].

In this study, Ti/TiO<sub>2</sub> photoelectrode was prepared with anodic oxidation of Ti foil electrode and then the photoelectrocatalytic (PEC) degradation of 2-nitrophenol (2-NP) was performed via this electrode, comparing with direct photolysis, electrochemical and photocatalytic degradation by ultraviolet light. 2-NP concentration monitoring was carried out with differential pulse voltammetry. Results showed that PEC degradation has highest effect on concentration decreasing of 2-NP at solution. Finally, effects of solution pH and applied potential on degradation efficiency were investigated.

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**Electrochemical determination of ascorbic acid in orange juice using a pencil electrode modified with chromium (III) hexacyanoferrate**

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Ascorbic acid (AA) is a water-soluble vitamin essential in the human nutrition, an antioxidant, a scavenger of free radicals in biological systems and a cofactor of several enzymes. For the precise detection of AA concentration in biological samples there is important the option of the determination method [1-3]. In electrochemistry the working electrodes may be modified to improve the analytical signal, the detection range, the sensitivity, and the selectivity of this technique. Thus, the present work sought to use a pencil electrode modified with Cr (III) hexacyanoferrate (CrHCF) to determination of AA. The influence of parameters on the voltammetric electrode response, supporting electrolyte, scan rate, precursor reagent, in drugs containing AA have been evaluated. A CrHCF-modified pencil electrode was used to determination of Ascorbic acid tablets by Differential pulse voltammetry (DPV) technique. The influence of several parameters on the voltammetric electrode response was studied. The linear range found was of 0.3 mM to 2.00 mM of AA, with  $r = 0.999$  and relative deviation of 0.01, RSD is 4.76%. The limits of detection and quantification were 0.073 and 0.246 mM, respectively. The electrochemical behavior of film of CrHCF was studied in different electrolytes. The experimental results showed that (phosphate/KCl 0.1 M) electrolyte, pH= 3 is a good supporting electrolyte.

The study of the scan rates on the voltammetric response of the CrHCF-modified electrode shows an increase in the anodic peak current with the scan rate in low scan rates, suggesting that there is an adsorption process on the electrode surface. In high scan rates the anodic peak current proportion with root of scan rates, this shows a diffusional process. The prepared electrode was applied to determination of AA in real samples such as vitamin C tablets. This was done by standard addition method. The experimental curve showed that the Real sample (orange juice) has 0.21 mM concentration of AA. Real Sample

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## The antibacterial activity of Ag nanoparticles in MCM-41 and Fe<sub>3</sub>O<sub>4</sub> porous materials

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Noble metal nanoparticles due to their excellent physicochemical properties have been used in biological application. Directly using silver nanoparticles in drinking water or other liquids might bring some potential risk and because of that using a template is necessary. Both Ag@porous Fe<sub>3</sub>O<sub>4</sub> and Ag@MCM-41 were synthesized by hydrothermal method and characterized by XRD, SEM, TEM and BET. XRD patterns results indicated that Ag nanoparticles (NPs) incorporated in MCM-41 and Fe<sub>3</sub>O<sub>4</sub> samples. TEM images of Ag core @ Fe<sub>3</sub>O<sub>4</sub> shell showed that Ag NPs with diameter size 135 nm was rounded with Fe<sub>3</sub>O<sub>4</sub> shell with diameter size 44 nm. Ag NPs incorporated in MCM-41 with average crystal size 12 nm. However both Ag@porous Fe<sub>3</sub>O<sub>4</sub> and Ag@MCM-41 showed great antibacterial activity for Gram-positive and Gram-negative bacteria but there was some differences in amount of loading of silver ions.

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**Modification of magnetic graphene oxide nanohybrid surface with  $\beta$ -Cyclodextrin: Synthesis, characterization, and application as doxorubicin carrier**

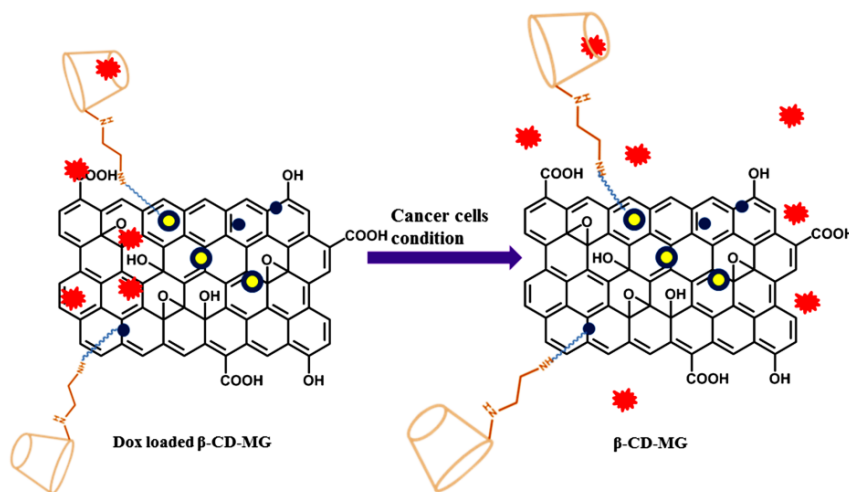
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Although chemotherapy is a common technique for the treating cancer, it has some drawbacks. Side effects of chemotherapy agents for normal cells, insufficient dosages for cancer cells killing and nonspecific drug delivery are some examples of these disadvantages [1]. Recently, drug carriers based on nanomaterial have attracted much attention in the biomedical applications due to the efficient loading, controlled release and targeted delivery of drugs [2-4]. Between the nanoparticles, magnetic graphene oxide (MG) nanohybrid could be a suitable system for drug delivery since it has both superparamagnetic properties and high surface area. In this work, magnetite nanoparticles precipitated on the graphene oxide surface using inverse coprecipitation method. In the next step, obtained MG modified with 3-chloropropyltriethoxysilane and MGSi-Cl was achieved. Finally, as a result of aminated  $\beta$ -cyclodextrin reaction with MGSi-Cl, MG surface was modified ( $\beta$ -CD-MG). Prepared nanocomposite was characterized using Fourier transform infrared spectroscopy (FT-IR), powder X-ray diffraction (XRD) and thermogravimetric analysis (TGA). The Doxorubicin (Dox) loading efficiency for the nanocomposite was obtained  $\sim 37.4\%$ . Dox release results showed that the  $\beta$ -CD-MG has a better performance in the cancer cells conditions compare to normal cells conditions.



**Scheme 1.** Releases of DOX from  $\beta$ -CD-MG nanocomposite.

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**The new lactate dehydrogenase nanosensor for electrochemical determination of pyruvate**

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Pyruvate is an important intermediate in several metabolic pathways. So, it could be indicator for intensity of circulatory disorder [1]. In this work, in order to pyruvate determination new lactate dehydrogenase (LDH) nanosensor was fabricated by using graphene oxide (GO)/AuNP/Poly vinyl alcohol (PVA) composite. Pyruvate concentration was determined by decreasing in NADH signal according to enzymatic reaction. Due to a high surface to volume ratio and electrical conductivity of GO/AuNPs/PVA, the electrochemical signal was increased. The step by step electrode modification was confirmed by cyclic voltammetry and electrochemical impedance spectroscopy successfully. This nanobiosensor was employed for pyruvate detection by differential pulse voltammetry and under optimum condition (pH= 7, 0.1 M PBS, 10 mM NADH), the detection limit of 8.69 nM with two linear range and RSD of 4.3 and 3.6% for reproducibility and repeatability was obtained. The selectivity of this method was investigated by adding ascorbic acid, citric acid and glucose in absence and presence of pyruvate and indicated they did not have significant effect on pyruvate determination. The apparent Michaelis-Menten constant ( $K_m^{app}$ ) was determined 1.5 mM amperometrically. The stability of this LDH nanosensor was investigated and it showed a good stability after 15 days. LDH nanosensor was successfully applied for real sample (serume and onion) analysis and the recoveries were an interval of 93 – 104.

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## Facil preparation of stimuli-responsive graphene oxide/polymer brush nanocomposites as drug delivery agent

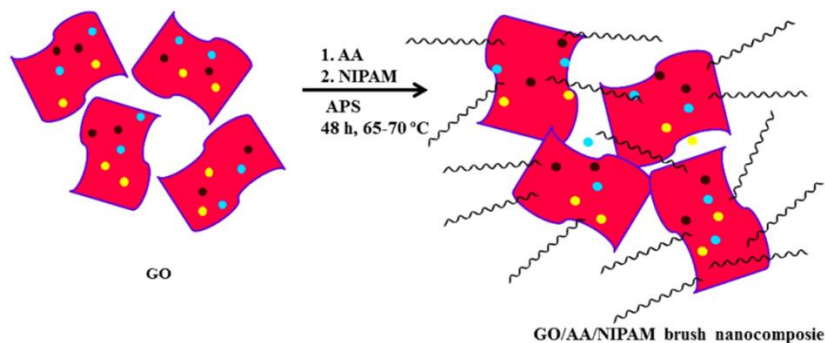
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Graphene oxide (GO) as a nanosheet with the high surface area has a two-dimensional structure which carbon atoms bonding together in the honeycomb lattice and oxygen-containing functional groups are attached to it [1,2]. Due to its unique physicochemical properties, in the recent years, GO-based nanocomposites attracted a lot of attention in the nanomedicine such as drug delivery, antibacterial system designing and etc [3,4]. For improving graphene dispersity, numerous researchers have focused on the modification of GO with compounds that are appropriate for the medical application. In this work, Go surface was modified with acrylic acid (AA) and N-isopropylacrylamide (NIPAM) via facil and eco-friendly radical polymerization. Polymerization of AA and NIPAM on the GO surface results stimuli-responsive graphene oxide/polymer brush nanocomposite. Nanocomposite was characterized with Fourier transform infrared spectroscopy (FT-IR), X-ray diffraction (XRD) and Scanning electron microscopy (SEM). Amount of grafted polymers was calculated from the thermogravimetric (TGA) curves. Prepared nanocomposite showed the good performance in doxorubicin load and releases.



**Scheme 1.** Preparation schematic for GO/AA/NIPAM brush nanocomposite

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**Synthesis, characterization and analytical application of nano structured Sm(III)-ion imprinted polymer for purification of <sup>152</sup>Sm**

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Samarium as a rare element has been interested in last decades due to their wide applications in different fields such as nuclear industry (as neutron absorber), chemistry (as a chemical reagent in organic synthesis and as a target for production of radiopharmacy [1-3]). This work presents the synthesis of samarium nano-structured ion imprinted polymer as the sorbent for separation and chemical purification of <sup>152</sup>Sm enriched stable isotope. The samarium-152 is used as a target in producing of <sup>153</sup>Sm (as a radiopharmacy). The unleached Sm<sup>3+</sup>-IIP nanoparticles prepared by the copolymerization of Sm<sup>3+</sup> - acrylic acid- 4-vinyl pyridine ternary complex with methyl methacrylate as functional monomer and ethylene glycol dimethacrylate as a crosslinker in presence of 2, 2-azobisisobutyronitrile as an initiator, then Sm<sup>3+</sup> ions were leached to obtain Sm<sup>3+</sup>-IIP nanoparticles. Moreover, non-imprinted polymer (NIP) particles were similarly prepared without Sm<sup>3+</sup> ions. The effect of several parameters such as solution's pH, sorption and desorption time, type, concentration and volume of eluent on the extraction of the polymers were investigated and optimized by one variable at the time. Optimized parameters were, pH 4; mass sorbent 0.1 g; sorption time, 120 min; desorption time 120 min; aqueous phase volume, 10 mL. Moreover, it is found that 30 mL of HCl (3 M) provided the most effective elution of Sm<sup>3+</sup> ion from IIP imprinted beads. The maximum sorbent capacity of the IIPs is 14.91 mg g<sup>-1</sup>. The detection and determination limits of the method were evaluated to be 0.27 and 2.7 ng mL<sup>-1</sup> respectively. The Precision of the method (%RSD, n=6) was % 0.47. The samarium-152 recovery yield was % 99.67.

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**MnCo<sub>2</sub>S<sub>4</sub> nanosheet arrays supported on Ni foam as a high-performance electrode for supercapacitors**

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In recent years, supercapacitors have been extensively developed as a unique class of energy storage devices due to their high power density, fast charge-discharge rate and long-term stability [1-3]. In this respect, ternary transition metal sulfides are promising as new electrode materials due to their higher energy storage capacity [4]. In this study, sulphospinel MnCo<sub>2</sub>S<sub>4</sub> nanosheet arrays were in situ grown on Ni foam substrate through a facile two-step hydrothermal method. In a typical synthesis, a 60 mL mixed solution of 16 mM MnSO<sub>4</sub>·H<sub>2</sub>O, 33 mM Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O and 100 mM hexamethylenetetramine was added to a Teflon-lined stainless steel autoclave with a cleaned Ni foam and heated at 90 °C for 10 h to obtain Mn-Co precursor on Ni foam. After that, the substrate with loaded products was dried at 60 °C for further characterization. Then, in order to obtain MnCo<sub>2</sub>S<sub>4</sub>, a 75 mL solution of 25 mM Na<sub>2</sub>S was added to a Teflon-lined stainless steel autoclave with Ni foam supported Mn-Co precursor and maintained at 120 °C for 8 h. After the solution was subsequently cooled naturally, the as-synthesized electrode was washed with deionized water and dried at 60 °C for 5 h. XRD, SEM and TEM images confirmed the preparation of MnCo<sub>2</sub>S<sub>4</sub> nanosheet arrays. The electrochemical experiments of obtained electrode were carried out in a three-electrode cell in 2 M KOH electrolyte, with Ag/AgCl, platinum plat and the Ni foam as the reference, counter and working electrodes, respectively. The resultant MnCo<sub>2</sub>S<sub>4</sub> electrode delivered high areal capacitance of 5.43 F cm<sup>-2</sup> at a current density of 1 mA cm<sup>-2</sup>. Additionally, with a 20-fold increase in current density from 1 to 20 mA cm<sup>-2</sup>, 61.87% of the initial capacitance was retained in the MnCo<sub>2</sub>S<sub>4</sub> electrode, indicating its high rate capability which is significant in practical supercapacitor applications. Owing to the unique structural features, the as obtained MnCo<sub>2</sub>S<sub>4</sub> nanosheet is considered as an effective electrode for the next generation energy storage device.

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**Extraction of celecoxib from human plasma by surfactant assisted dispersive liquid-liquid microextraction and its determination by HPLC**

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Surfactant-assisted dispersive liquid-liquid microextraction followed by high-performance liquid chromatography with uv detection is a green microextraction that has been developed for the preconcentration and trace detection of celecoxib in human plasma. In this method, the extraction is carried out by forming the ion pair between analytes and surfactant in the sample solution and transferring it to a low density solvent. A conventional cationic surfactant called cetyltrimethyl ammonium bromide (CTAB) was used as a disperser agent in the proposed approach. 0.5 mL of CTAB ( $0.09 \text{ mmol L}^{-1}$ ) (disperser solvent) containing 40.0  $\mu\text{L}$  of 1-undecanol (extraction solvent) was injected rapidly into the 9.0 mL of diluted plasma. A cloudy solution was formed in the test tube. After formation of cloudy solution, the mixture was centrifuged and 20  $\mu\text{L}$  of collected phase was injected into HPLC for subsequent analysis [1]. The use of surfactant (Emulsifier) and low density solvent (extraction solvent), which have a low toxicity, is one of the benefits of this method, which will provide the best recovery in the shortest possible time and making it an environmentally friendly method. The predominant parameters affecting extraction efficiency such as the type and volume of extraction solvent, the type and concentration of surfactant, sample pH and the concentration of salt added to the sample were investigated and optimized [2]. Under the optimum conditions (extraction solvent and its volume, 1-undecanol, 40  $\mu\text{L}$ ; surfactant and its concentration, 0.5 mL of ultra-pure water containing  $0.09 \text{ mmol L}^{-1}$  cetyltrimethyl ammonium bromide; sample pH = 10 and salt content of 4% NaCl w/v), the extraction recovery was 96%. The proposed method was successfully applied for preconcentration of the drug in plasma sample with the enrichment factor of 340 and the method showed good linearity range of  $1\text{-}500 \mu\text{g L}^{-1}$  ( $R^2 > 0.9981$ ). The validated method showed a satisfactory performance and can be served as a simple and sensitive method for drug monitoring in the plasma samples.

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**Investigation of the effect of synthesis parameters including reaction temperature and initial concentration of Cu precursor on the size and size distribution of zero-valent Cu nanoparticles by UV–Vis spectroscopic analysis**

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One of the important features of Cu nanoparticles is their localized surface plasmon resonance peaks in the visible light region that are used for their optical characterization [1]. The synthesis temperature of nanoparticles and initial concentration of precursor are the most important parameters that affect the size and size distribution of metal nanoparticles. At the optimum temperature and initial concentration of precursor, the purity of the product is increased and oxidation of nanoparticles is reduced [2].

In this study, Copper nanoparticles were synthesized by a convenient and rapid chemical reduction method in ambient condition using  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  as a precursor, hydrazine hydrate as reducing agent and deionized water as solvent. For the investigation and optimization of the effect of initial concentration of Cu precursor and reaction temperature on the size and size distribution of Cu nanoparticles, several experiments were performed. All parameters were fixed during the experiments except the initial concentration of  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  and reaction temperature. The UV–Vis spectra of prepared Cu nanoparticles were used to investigate the effect of initial concentration of Cu precursor and reaction temperature on the size and size distribution of obtained Cu nanoparticles. According to the results, smallest copper nanoparticles with a narrow size distribution were obtained in the optimum concentrations of  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  as  $41 \text{ mmol l}^{-1}$  and the optimum reaction temperature was determined to be  $120 \text{ }^\circ\text{C}$ .

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**Magnetic dispersive solid phase microextraction for the separation and quantification of brilliant green in various water samples**

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This work reports preparation and application of reduced graphene oxide-cobalt oxide (rGO-Co<sub>3</sub>O<sub>4</sub>) nanocomposite [1,2] as selective and regenerable magnetite sorbent for the preconcentration and determination of brilliant green (BG) by UV-Vis spectrophotometry. The properties of the graphene/Co<sub>3</sub>O<sub>4</sub> nanocomposite were characterized by UV-visible spectrophotometry, Fourier-transform infrared (FT-IR) spectroscopy, X-ray diffraction (XRD), and field emission scanning electron microscopy (FE-SEM). Magnetic dispersive solid phase microextraction (MD-SPME) [3], as a green, simple and sensitive method has been proposed for separation and preconcentration of trace quantities of BG. The ferromagnetic properties of the synthesized nanocomposite allowed effective separation and recyclability of the material by simple application of an external magnet. The experimental parameters affecting the MD-SPME efficiency for the target analyte including sample pH, brilliant green concentration, adsorbent dose and shaking time were investigated and optimized by central composite design coupled with desirability function approach [4]. Under the optimized conditions, the enrichment factor was 33. The detection limit and relative standard deviation (RSD) were 2.8 ng mL<sup>-1</sup> and 1.3% (n=5) respectively. Finally, the applicability of the proposed method was successfully evaluated by determination of trace amounts of BG in various water samples.

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### Adsorption of basic dyes on MCM-41@pyridine

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Several classes of dyes are stable molecules that are resistant to degradation by light, chemical, biological and other exposures and are considered as possible carcinogens or mutagens to humans [1]. Therefore, it is necessary to reduce dye concentration in the wastewater before it is released into the marine environment. The removal of dyes from wastewater is considered to be an important application of adsorption process using suitable adsorbent. Highly functional porous materials with high surface areas are generally used for such applications because they show excellent removal efficiency [2-4]. Therefore, in this study, we synthesized MCM-41 and then used of [3-(2-amino ethyl amino) propyl-tri-methoxysilane modified MCM-41 with NH<sub>2</sub> groups. Then MCM-41-NH<sub>2</sub> used to immobilization 3-pyridinecarbaldehyde by a multistep-anchoring method, is donated MCM-41@pyridine. The synthesized compounds were characterized by XRD, FT-IR, DR-UV-Vis and BET. The adsorption of two basic dyes (Rhodamine B (RB) and Yellow 13(YD)) onto MCM-41 was studied to examine the potential of MCM-41@pyridin for the removal of dyes from water solution. The adsorption capacity of MCM-41@pyridin for the two dyes followed a decreasing order of RB~YD. It was experimentally concluded that MCM-41@pyridin might be a good adsorbent for the removal of basic dyes from water solution.

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**Determination of Single Stranded DNA using gold nanoparticle as a label by Photo Thermal Lens Microscopy in Microfluidic Chip**

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DNA analysis is one area that is highly suited to the microfluidic technique due to limited biological sample size and a demand for high speed and throughput [1,2]. In this regard, Photo thermal lens microscopy (PTLM) is a powerful optical detection technique that can be used in microfluidic techniques [3,4]. In the present study, detection of single-stranded deoxy ribonucleic acid (ssDNA) in microfluidic chip using nonspecific adsorption of DNAs to gold nanoparticles, is considered.

The ssDNA is sufficiently flexible to partially uncoil its bases, they can be exposed to the gold nanoparticles. Under these conditions, the negative charge on the backbone is sufficiently distant so that attractive van der Waals forces between the bases and the gold nanoparticles are sufficient to cause ssDNA to stick to the gold nanoparticles and effectively prevent nanoparticles from salt-induced aggregation [5]. There is a relationship between ssDNA concentration and the effect of salt-induced aggregation of AuNPs on the PTLM signal. Thus, this relationship can be used for ssDNA detection in the channel of microfluidic chip.

Herein, we developed Microchip-PTLM method for ssDNA detection in microfluidic chip. The used PTLM setup, microchip were designed, constructed and optimised in our lab. In order to evaluate performance of the present method, two types of ssDNAs are considered. Under optimum conditions, PTLM intensity of AuNPs increased with ssDNA concentration linearly. The linear responses for ssDNA I and II in a concentration range from 20 to 350  $\times 10^{-9}$  mol L<sup>-1</sup> are obtained with a detection limit of 14  $\times 10^{-9}$  mol L<sup>-1</sup> for ssDNA I and 9  $\times 10^{-9}$  mol L<sup>-1</sup> for ssDNA II. The relative standard deviations (n=8) for both ssDNAs are about 3.6%.

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**Effects of salt, and silica nanoparticles on rheological behavior of polyacrylamide solutions used in chemical enhanced oil recovery**

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In recent years, much attention has been focused on the use of polymer flooding as one of the enhanced oil recovery (EOR) methods [1]. The occurrence of high shear rates in reservoir and near well bore through polymer flooding cause shear degradation of polymers and therefore a decrease in polymer viscosity. Rheological behavior of polymer solution in different conditions of oil reservoir is one of the key factors to develop the use of polymer solutions. Recently, nanoparticles have attracted much attention due to their unique properties. Rheological studies showed that the viscosity of PAM increases by adding SiO<sub>2</sub> NP. The interactions SiO<sub>2</sub>-PAM was evaluated through FT-IR spectroscopy. The role of nanoparticles in modification of the polymer performance in the presence of NaCl salt was investigated. The effect of concentrations on the viscosity of solution was investigated by adding silica nanoparticles to polyacrylamide at different NaCl salt concentrations. The results of viscosity measurements showed that increasing SiO<sub>2</sub> nanoparticles concentration increases the viscosity of polyacrylamide solution and the influences of NaCl salt on the effective viscosity of PAM and PAM/SiO<sub>2</sub> hybrids were examined at 25 °C, The viscosity was found to significantly increase at low salt concentrations, reaching a peak value, and then start to decline.[2,3]

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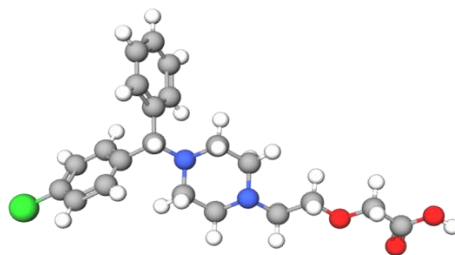


## Characterization and antioxidant activity of the inclusion complexes of different types of cyclic oligosaccharides and cetirizine dihydrochloride in aqueous solution by Spectroscopy

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Cyclodextrins (CDs) are cyclic oligosaccharides consisting of six (alpha-cyclodextrin), seven (beta-cyclodextrin), and eight (gamma-cyclodextrin) glucopyranose units linked by  $\alpha$ -(1,4) bonds. These compounds contain a hydrophobic internal cavity which provides a microenvironment for appropriate sized molecules and a hydrophilic outer surface which makes them water soluble. As a result, CDs are able to form inclusion complexes with a wide variety of drug substances by including a whole drug molecule, or some part of it into their cavity [1]. In this work study on host-guest inclusion complex formation of  $\alpha$ ,  $\beta$  and  $\gamma$ -cyclodextrine with Cetirizine was performed experimentally. Complexation properties of cetirizine dihydrochloride (cetirizine) with cyclodextrines (CDs) were investigated by ultra violet (UV) and fourier transform infrared (FTIR) spectroscopies at temperature room. The UV absorption maximum of cetirizine and its complex with CDs appears at 230 nm in pH~7 [2]. The use of the continuous variation method (Job's plot), applied on UV data [2], demonstrated 1:1 complex stoichiometry for all cetirizine/ $\alpha$ -CD, cetirizine/ $\beta$ -CD and cetirizine/ $\gamma$ -CD. The stability constant was calculated by using a modified Benesi-Hildebrand equation at 25°C [3]. Antioxidant activity studies by the scavenging of stable radical 2,2'-diphenyl-1-picrylhydrazyl (DPPH•)[2] revealed that Cetirizine in complex forming with cyclodextrins was the most reactive than its free form into antioxidant activity. We have chosen simple, highly sensitive and selective methods for the characterization of inclusion complexes such as fourier transform-infrared (FTIR) spectrometry, proton nuclear magnetic resonance (<sup>1</sup>HNMR) spectrometry and ultraviolet-visible (UV-Vis) spectrometry.



*Cetirizine*

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## Study of Adsorption of Copper Ions on Functionalized MCM-41 by Experimental methods and Molecular Dynamic Simulations

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Copper is an essential element at the trace level (i.e. catalytic action in heme synthesis) [1], but the intake of large quantities can be toxic. So the techniques, such as ion exchange, precipitation, adsorption, membrane processes, electro-dialysis, have been employed for removing heavy metals from wastewater [2]. Adsorption is an effective and economic method for removing heavy metals from wastewater. The mesoporous molecular sieves with MCM-41 type structures were applied for the adsorption of metal ions from aqueous solutions [3]. In this work, a functionalized MCM-41 with amine and furfuran groups have been prepared and used for removing  $\text{Cu}^{2+}$  from aqueous solutions. The MCM-41 mesoporous was synthesized and the surface of MCM-41 was functionalized with  $\text{NH}_2$  by 3-aminopropyl-trimethoxysilane and 3-(2-aminoethylamino) propyl-trimethoxysilane. Afterwards, the Furfuran functional group was stabilized on MCM-41- $\text{NH}_2$ . The synthesized structures were characterized by FT-IR, BET, UV-Visible and XRD spectroscopy methods. We have used this functionalized MCM-41 to elimination of copper ions from water. In order to determine the concentration of acquired ions from the filtrated solution, the flame atomic absorption spectrometry (FAAS) was utilized. The effect of some variables like adsorbent quantity, time of reaction, pH and temperature was investigated. The results show that, the adsorption capacity of  $\text{Cu}^{2+}$  on the modified MCM-41 with Furfuran is 3.8 mgCu/g. The Adsorption properties of metal ions on MCM-41 [4] and on modified MCM-41 by different organic groups (chloropropyl, phenyl, benzyl, mercaptopropyl, cyanopropyl, butyl groups) were calculated based on grand canonical Monte Carlo (GCMC) simulation [5]. We have study the adsorption properties of functionalized MCM-41 structure by molecular dynamics (MD) simulation. The spectral properties and adsorption isotherms of  $\text{Cu}^{2+}$  adsorbed in functionalized MCM-41 were calculated based on grand canonical Monte Carlo (GCMC) simulation. Equilibrium modeling of the adsorption showed that the adsorption of  $\text{Cu}^{2+}$  ions was fitted to a Freundlich isotherm. The qualitatively consistent results of molecular dynamics simulations with experiments suggest the possibility of applying computer simulation for preliminarily selection of adsorbent functional groups for removal of  $\text{Cu}^{2+}$ .

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**Development of simple and efficient microextraction method for extraction of some pesticides in fruit juice samples prior to their determination by GC-FID**

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Pesticides are defined as any substance or mixture of substances that destroy or reduce the severity of pests. Over the past decades, different kinds of pesticides have been widely used to increase agricultural productivity [1]. However analysis of pesticide residues in food samples is necessary due to their toxicity for human. Different analytical methods have been used for this purpose. In most cases performing a sample preparation step is needed before performing the analytical methods. Liquid-liquid extraction (LLE) [2] and solid phase extraction (SPE) [3] are two commonly used methods for sample preparation of pesticides in different samples. In the present study, a simple, green, and rapid sample preparation method namely vortex-assisted liquid-liquid microextraction based on solidification of floating organic droplet has been developed for the extraction and preconcentration of diazinon, ametryn, chlorpyrifos, penconazole, oxadiazon, diniconazole, and fenazaquin in fruit juice samples prior to their analysis with gas chromatography-flame ionization detection. In this method, menthol as a green extraction solvent is added into sample solution and then vortexed. The obtained cloudy solution is centrifuged and the dispersed fine droplets of the extraction solvent are collected on the top of the aqueous phase as a single drop. Some important parameters such as ionic strength, vortexing time, pH, etc were investigated and optimized. Under the optimum experimental conditions, limits of detection and quantification were obtained in the ranges of 0.50–1.3 and 1.7–4.3  $\mu\text{g L}^{-1}$ , respectively. The obtained values for enrichment factors and extraction recoveries were in the ranges of 263–421 and 53–84%, respectively. Repeatability of the method expressed as relative standard deviation was  $\leq 7\%$  for intra- (n=6) and inter-day precisions at a concentration of 50  $\mu\text{g L}^{-1}$  of each pesticide.

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## The 25<sup>th</sup> Iranian Seminar of Analytical Chemistry

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### Electrochemical behaviour of *N,N'*-diphenylbenzidine: synthesis of 4,4'-(5,10-diphenyl-5,10-dihydrophenazine-2,7-diyl)bis(*N*-phenylaniline)

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Organic electrochemical synthesis provides a powerful strategy for the synthesis of organic compounds in both laboratory and industry scale. Electrochemical synthesis of main organic compounds has been extensively employed as a synthetic method in a variety of chemical transformations due to its unique properties such as direct and short-cut synthetic route, eco-friendly nature, high current efficiency values, high selectivity and sustainability of the reactions. Selective synthesis of compounds has been a challenging goal for synthetic chemists [1-3]. Our interest in the design and electrochemical synthesis of new compounds prompted us to synthesize new molecules under mild and ambient conditions [4]. The electrochemical dimerization of *N,N'*-diphenylbenzidine (DPB) has been studied. The data indicate that electrochemically generated (*N4,N4'*-diphenyl-[1,1'-bi(cyclohexylidene)]-2,2',5,5'-tetraene-4,4'-diimine) (DPBox) can serve as a Michael acceptor in the reaction with starting molecular (DPB) forms and converts to the corresponding dimer. The mechanism of anodic dimerization of DPB has been successfully performed under constant current condition in good yield and purity in an undivided cell. Controlled-potential coulometry was performed in an aqueous buffer solution (pH= 1.0, c = 0.1 M), containing DPB (1.0 mmol) at  $E_{app} < E_{pA}$  versus Ag/AgCl, to obtain more data on electrochemical oxidation of DPB. The number of the electrons transferred (n) for the anodic oxidation of one molecule of DPB obtained 2 electrons. The results indicate dimerization was happened by ECE mechanism and the obtained spectral data represents synthesis of the corresponding dimer.

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**Development of counter current salting-out homogenous liquid–liquid extraction for  
determination of some pesticides in fruit juice samples**

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Pesticides such as insecticides, herbicides, and fungicides are widely used during cultivation and post-harvest storages of crops. It is intended that their use to prevent the destruction of crops by controlling agricultural pests or unwanted plants and thereby improve food production [1, 2]. In this study, a new extraction method based on counter current salting-out homogenous liquid–liquid extraction followed by dispersive liquid–liquid microextraction–solidification of floating organic droplet has been developed for the extraction and preconcentration of some widely used pesticides in fruit juice samples prior to their analysis by gas chromatography–flame ionization detection. In this method, initially sodium sulfate as a phase separation agent is filled into a column and a mixture of water (or fruit juice) and acetonitrile is passed through the column. By passing the mixture sodium sulfate is dissolved and the fine droplets of acetonitrile are formed due to salting-out effect. The produced droplets go up through the remained mixture and collect as a separate layer. Then, the collected organic phase (acetonitrile) is removed and mixed with menthol (extraction solvent at  $\mu\text{L}$ -level). In the second step, for further enrichment of the analytes the above solution is injected into de-ionized water placed in a test tube with conical bottom in order to dissolve acetonitrile into water and to achieve a sedimented phase at  $\mu\text{L}$ -level volume containing the enriched analytes. Under the optimal extraction conditions, the extraction recoveries and enrichment factors ranged from 82 to 93% and 3266–3728, respectively. Repeatability of the proposed method, expressed as relative standard deviations, ranged from 2–6% for intra- and inter-day precisions at a concentration of  $30 \mu\text{g L}^{-1}$  of each pesticide. Limits of detection were obtained between 0.20 and  $0.60 \mu\text{g L}^{-1}$ .

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**Hollow fiber liquid phase microextraction followed by high performance liquid chromatography for determination of some anti-dementia drugs in human plasma, urine and wastewater samples**

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Three-phase hollow fiber microextraction technique combined with high performance liquid chromatography-ultra violet (HPLC-UV) was applied for the extraction and determination of anti-dementia drugs rivastigmine and donepezil. In hollow fiber liquid phase microextraction (HF-LPME), the organic solvent is injected into the lumen of the porous hollow fiber, and the fiber acts as an interface between the sample solution and the extracting phase. Since very little amounts of the solvent are used, exposure of the operator to toxic organic solvents is minimized.[1] An important advantage of three-phase LPME is an excellent clean-up that enables the extraction of drugs and metabolites from biological matrixes and pollutants from the environmental samples with simultaneous clean-up of the extracts.[2] The target drugs were extracted from 10.0mL of aqueous solution with pH 12.0 (source phase) into an organic extracting solvent impregnated in the pores of a hollow fiber and finally back extracted into 40 $\mu$ L of acidic solution with pH 1 (receiving phase) located inside the lumen of the hollow fiber. The extraction was performed due to pH gradient between the inside and outside of the hollow fiber membrane. Different factors affecting the HF-LPME efficiency were studied and optimized. Under the optimum conditions (n-tetradecan) as membrane impregnation solvent, pHs of the source phase and receiving phase equal to 12.0 and 1, respectively, extraction time of 30 min, stirring speed of 1100rpm and 5% (w/v) NaCl for adjusting the ionic strength. Under the optimized conditions, enrichment factors up to 250 were achieved and the relative standard deviation (R.S.D.%) of the method was in the range of 4.6–9.3%. The calibration curves were obtained in the range of 4–1000 ng mL<sup>-1</sup> with reasonable linearity ( $R^2 > 0.994$ ) and the limits of detection (LODs) ranged between 0.5 and 0.6 ng mL<sup>-1</sup> (based on  $S/N = 3$ ). Finally, the applicability of the proposed method was evaluated by extraction and determination of the drugs in urine, plasma and wastewater samples. The results indicated that hollow fiber microextraction method has excellent clean-up and high-preconcentration factor and can be served as a simple and sensitive method for monitoring of anti-dementia drugs in the biological samples.

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## Filter-based emulsification liquid-phase microextraction for efficient determination of amphetamine and methamphetamine in biological and environmental matrices

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In this paper, an efficient method, named filter-based emulsification liquid-phase microextraction, is applied for the rapid and selective determination of amphetamine and methamphetamine in complex matrices. At therapeutic doses, the psychostimulant amphetamine (Amph) is the most efficacious treatment for attention-deficit hyperactivity disorder (ADHD). At larger doses, Amph is rewarding, abused, and addictive [1,2]. Methamphetamine (Meth), which is one of the most harmful and addictive drugs, is widely abused worldwide [3]. The popularity of this drug worldwide seems to be due to its easy production, low cost and powerful psychostimulant properties [4]. The developed method consists of two steps. In the first step, an organic extraction solvent is dispersed into an aqueous sample solution (20 mL, pH 12). As a result, a cloudy mixture is formed, and the analytes and the extractable interfering species are rapidly extracted into the organic solvent. The mixture is passed through a hydrophilic polytetrafluoroethylene syringe filter, and the organic phase is retained behind the hydrophilic membrane. In the second step, the filter is detached from the syringe, attached to another syringe containing an aqueous solution (pH 2.0, 150  $\mu$ L). By the in-syringe dispersion of the organic phase into the aqueous phase, the analytes are ionized and selectively back-extracted into the aqueous phase. In addition to the preconcentration of the analytes in the aqueous phase, which can cause the elimination of the problem of injection of the organic solvent into the final instrument analyzer as well, the method provides a high sample clean-up since acidic compounds, large molecules, and neutral components are not extracted into the acceptor phase. The effective parameters involved are optimized to achieve the best extraction efficiency. Under the optimized experimental conditions, the proposed method provided a good linearity in the range of 5-600 ng mL<sup>-1</sup>, good extraction repeatabilities (RSDs below 8.6%, n = 5), a low limit of detection (1.5-2.0 ng mL<sup>-1</sup>), and enrichment factors of 41-48.

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## Synthesis of Chitosan-based hydrogels and investigation of its capability for loading and releasing of electroactive Methylene Blue (MB) indicator

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Hydrogels are three dimensional insoluble networks in the water that have cross-links and swell in contact with water. Nowadays, hydrogels are used in various fields due to their variety of structures. These compounds have tendency to absorb water due to the presence of hydrophilic groups such as  $-SO_3H$ ,  $-CONH_2$ , and  $-CONH$ . Gels can be hydrated in a variety of proportions, which in some cases it reach more than 90 percent by weight of polymer, it can be due to the nature of the aqueous medium and the polymer structure [1]. Medications or electrophobic species are trapped in the pores in the structure of the hydrogels and released from their structure based on a mechanism that depends on the spreading coefficient of the drug or the electroactive species [2].

Hydrogel-based drug delivery systems are divided into two major groups: 1. Systems with time control. 2. Release systems due to the presence of a stimulus. Environmentally sensitive hydrogels, known as smart systems, are divided into three sub-branches: 1. Release system with physical stimulation such as temperature, electrical current, light and pressure. 2. Release system with chemical stimulation such as pH, the composition of solvents, ions, and special interactions that lead to identify the molecules. 3. Release systems with other stimuli [3].

Chitosan-based hydrogels were synthesized and utilized in this study. Then, the amount of hydrogel absorption of water in distilled water and solutions with different pHs, as well as the release of electroactive substance methylene blue (MB) was investigated by these hydrogels at pH 1-12. For this purpose, the hydrogel nanocomposite was synthesized by glutaraldehyde and Methylene Bis Acrylamide in acidic environments (hydrogels have been synthesized separately). Their structure and features were confirmed by XRD, SEM, FTIR devices. Their swelling rate in distilled water was measured and in solutions with different pH (1 to 12), which the highest swelling rate was observed at pH = 1. Electroactive methylene blue was loaded inside the hydrogel nanocomposites and the methylene blue amount released from the hydrogels was measured by electrochemical method and using Autolab instrument.

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**Modification of Natural Clinoptilolite Zeolite with Iron Oxide Magnetic Nanoparticles and Sodium Sulfide Salt for Removal of Heavy Metal Cations such as Lead, Cadmium, and Manganese**

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In this study, the efficiency of natural clinoptilolite zeolite modified with iron oxide magnetic nanoparticles and sodium sulfide salt in the removal of three heavy metals including lead (Pb), cadmium (Cd), and manganese (Mn) was investigated. All of the measurements were carried out by atomic absorption spectrometry. The modified zeolite was characterized by FTIR, SEM, and XRD techniques. The effects of various parameters on adsorption process such as initial concentration of metal ion, contact time, adsorbent dosage, and pH have been studied. According to the obtained results, the removal efficiencies in the optimized conditions for Pb, Cd, and Mn were 98%, 92%, and 75%, respectively. The adsorption studies confirmed the potential recyclability of the modified zeolite. The results of the current study have indicated that the modified clinoptilolite zeolite can be used as an efficient and inexpensive adsorbent for the removal of heavy metals in aquatic environments.

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## Square Wave Voltammetric Determination of Methamphetamine using Glassy Carbon

### Electrode Modified with Nanoceria Decorated Reduced Graphene Oxide

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Methamphetamine (METH), a potent central nervous system stimulant, is the second most widely abused drug in the world [1]. Based on its chemical structure, it can be an electroactive species. However, its oxidation on the electrode surfaces is not facile. In this work, considering the structure of the METH, cerium oxide (called nanoceria; CeO<sub>2</sub> NPs) decorated on reduced graphene oxide (rGO) [2,3] was used as electrode modifier to study the redox behavior of METH. A suitable amount of CeO<sub>2</sub> on rGO showed a synergistic electrocatalytic effect for optimizing the METH signal. On the modified electrode surface, enhancing of the oxidation peak of METH in cyclic voltammogram compare to bare electrode was observed at 0.6 V potential, in phosphate buffer 0.01 M, pH 10, and scan rate of 0.07 V/s, Square wave voltammetry (SWV) technique was then used as determination method. Different experimental parameters were optimized to achieve the maximum response. Under the optimized experimental conditions, the lowest linear dynamic range and limit of detection for the proposed electrode were obtained 16 μM to 33 μM and 4 μM, respectively. Analysis of METH in real sample showed no significant interference from the matrixes.

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## Synthesis of PS-PAA based polymersome and investigation of its capability for loading and releasing of electroactive Methylene Blue (MB) indicator

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Polymersomes are a type of synthetic vesicles composed of amphiphilic block copolymers (a molecule that has both a hydrophilic region and a hydrophobic region), which is used due to the characteristics of the adjustable membrane and the ability to encapsulate a wide range of drugs and molecules due to their colloidal stability [1]. Polymersomes can be synthesized in different sizes (from 50 nm to 10  $\mu$ m), which these sizes vary depending on the chemical composition, length of the polymer groups, the preparation method and the reaction conditions [2].

Polymersomes with different species of copolymers have also been designed and produced as pharmaceuticals, which have the physicochemical stability, the loading mechanism and simultaneous release of hydrophobic and hydrophilic drugs and adjustable permeability. Polymersomes with respect to their synthesis conditions can exhibit different behaviors relative to external stimuli, such as temperature, pH, chemical stimulus, which various behaviors can be made in form of deformation, change of surface properties, dissolution, etc. There are various methods to synthesize polymersomes, such as atom transfer radical polymerization (ATRP) and radical polymerization controlled by reversible addition-fragmentation chain transfer (RAFT) process [3].

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**Tandem dispersive liquid-liquid microextraction followed by high performance liquid chromatography for simple determination of thebaine and ketamine in biological fluids**

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A simple and efficient method named tandem dispersive liquid-liquid microextraction is applied for the determination of thebaine and ketamine in biological fluids. Thebaine is an ideal starting material that can be transformed into several opiates [1]. Ketamine induces loss of consciousness, amnesia, immobility, pain relief and sedation while the cardiopulmonary functions and the protective airway reflexes remain unchanged [2]. This method, which is based upon two consecutive dispersive microextractions, is totally accomplished in 7 minutes, and by performing a fast back-extraction step, it provides a high sample clean-up [3]. The back extraction step is performed in less than 2 min, and very simple tools were required for this purpose. In addition to the increase in the sample clean-up, the analytes were extracted into the aqueous solution. Thus this step could cause eliminating the problem of injection of the organic solvent into the final instrument analyzer as well. On the other hand, unlike most methods coupled with DLLME for improving the sample clean-up, back-extraction of the analytes was a green step in the proposed method [4]. In order to achieve the best extraction efficiency, optimization of the variables affecting the method is carried out. Under the optimized experimental conditions, the relative standard deviations for the method was in the range of 8.9–9.7%. The calibration curves were obtained in the range of 3–1000  $\mu\text{g L}^{-1}$  with a reasonable linearity ( $R^2 > 0.995$ ), and the limits of detection ranged between 1.0 and 1.5  $\mu\text{g L}^{-1}$  (based on  $S/N = 3$ ). Finally, the applicability of the proposed method was evaluated by the extraction and determination of the drugs under study in the human plasma samples.

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## Adsorptive Stripping Voltammetric Determination of Venlafexine at a Carbon

### Nanocomposite Ionic Liquid Electrode

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A carbon nanocomposite electrode has been designed by incorporation of multiwalled carbon nanotubes (MWCNT) into ionic liquid 1-octylpyridinium hexa fluorophosphate (OPFP) that can be well used as an electrode for electrocatalytic oxidation of venlafaxine (VEN). This drug is an antidepressant which inhibits reuptake of serotonin, norepinephrine. However, an overdose of VEN results in the most common symptoms such as depression, serotonin toxicity, seizure, or cardiac conduction abnormalities. Hence, their determination is of great significance.<sup>1</sup>

One of the dominant techniques for detecting trace levels of VEN is chromatography.<sup>2</sup> However, this method has disadvantages of being expensive, effortful, and time-consuming sample pre-treatment. Electrochemical techniques are good candidates for the analysis of VEN because of their simplicity, low-cost, rapidity and sensitivity. Moreover, concerning the electrochemical measurements of VEN, only a few reports are available.<sup>3, 4</sup> To the best of our knowledge, the electrochemical behavior of VEN was not studied at carbon paste electrodes.

In the present study, Adsorptive stripping voltammetry was applied as a sensitive analytical method for the determination of VEN in pharmaceutical formulations as well as blood serum. The effects of amount of multi-walled carbon nanotube used for the modification of the carbon ionic liquid electrode (CILE), pH of the solution, accumulation potential, accumulation time and scan rate on the response of modified electrode for the oxidation of VEN were investigated.

The oxidation peak potential of VEN appeared at 640 mV at the MWCNT modified carbon ionic liquid electrode (MWCNT/CILE) in the 0.1 M phosphate buffer solution (PBS), pH 9.0 containing 1mM of VEN, that is about 150 mV lower than the peak potential at traditional carbon paste electrodes. Under the optimum conditions, the anodic peak current was linear to VEN concentration in the ranges of 10.0 to 500.0  $\mu$ M. Low detection limit of 0.47  $\mu$ M was found. The proposed electrode has the features of being sensitive, reproducible, easily renewable and cost effective. Determination of VEN in pharmaceutical formulations and blood sample were performed with MWCNT/CILE.

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## Fabrication of Cysteic acid/ gold nanoparticle Composite Film- Modified Glassy Carbon electrode for the Simultaneous Voltammetric Detection of Acetaminophen and Tramadol

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In this study a voltammetric sensor by electrochemical deposition of gold nanoparticles (AuNPs) and L-Cysteine on glassy carbon electrode is fabricated. Simply, after formation of a compact and uniform cysteic acid layer film by electrochemical oxidation of L-cysteine, AuNPs is immobilized on its polymeric structure. As well as, the fabricated sensor show great sensitivity and selectivity for simultaneous determination of Acetaminophen (ACOP) and Tramadol (TRA) with square wave voltammetry (SWV) method in a wide linear range, with detection limits of 0.03 and 0.17  $\mu\text{M}$  respectively. As an electrode modifiers, amino acids play an important roles in fabricating the electrode surface for immobilizing nanoparticles and increasing sensitivity. For instance l-cysteine due to the presence of sulfhydryl, can be electrochemically converted to cysteic acid (CA), an electroactive, stable, biocompatible, conductive polymer, that strongly adsorbed at surface of electrode [1,2]. In addition gold nanoparticles (AuNPs) in which have some advantages like conductivity, electro-catalytic activity, chemical stability, and large surface area have been extensively used [3-5]. In this work square wave voltammetry (SWV) and cyclic voltammetry (CV) were performed with  $\mu$ -Autolab type III, potentiostat/galvanostat instrument and driven by the NOVA 1.11 software. The modified GCE was utilized as the working electrode, a platinum wire as the counter electrode, and satAg/AgCl (3M KCl) as reference. All the chemicals were analytical grade and were used directly without purification. Moreover l-cysteine and hydrogen tetra-chloro-aurate ( $\text{HAuCl}_4$ ) were from Merck. The anodic peak current of ACOP is decreased from pH 2.0 to 5.0 then increased to pH 7.0 and re-decreased. In the case of TRA in the pH range of 2.0 to 4.0 no evident peak is observed. After that, in pH 5.0 the TRA peak appears and it reached to maximum at pH 7.0 then, it decreased. Thus, the electrochemical measurements were carried out in PBS (0.1 M, pH 7.0). In light of efficient and comparable results, the cysteic acid/AuNPs composite film was applied for the determination of ACOP and TRA in spiked serum samples using the standard addition method.

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**Pre-concentration of Celecoxib drug in breast milk using Air-assisted dispersive liquid – liquid microextraction and its determination by HPLC**

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Breast milk is the optimal food for babies, but the sucking infant may be exposed to drugs during maternal pharmacotherapy. It is important to know the extent of drug transfer into human breast milk in order to assess the likely 'dose' ingested by the infant and therefore quantify risk [1]. so we need a simple and efficient extraction method. Air assisted dispersive liquid-liquid microextraction is a sensitive, rapid and efficient method for the extraction of celecoxib as well as its determination in breast milk. In this method (AALLME), which is a new version of dispersive liquid-liquid microextraction (DLLME) no dispersive solvent is required and dispersion of extraction solvent lighter than water, is carried out by air bubbles[2]. Fine organic droplets were formed by sucking and injecting of the mixture of aqueous sample solution and extraction solvent with a conventional 2 mL glass syringe for several times in the handmade centrifuge tube with narrow neck which was specially designed for ease of withdrawing supernatant phase [3]. The influence of different parameters affecting including the type and volume of the extraction solvent, sample pH, ionic strength and number of extraction cycles were evaluated and optimized. Under the optimum conditions (type and volume of the extraction solvent, 1-undecanol, 50 $\mu$ L; sample pH =7; salt content of 6% NaCl w/v and number of extraction cycles = 4 ), extraction recovery of 91% with relative standard deviation less than 10% were obtained for 3 replicated measurements which are satisfactorily consistent with predicted results and limit of quantification (LOQ) of 1  $\mu$ g L<sup>-1</sup> were obtained. The proposed method was successfully applied for preconcentration of the celecoxib drug in breast milk.

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**Investigation of bioconjugation between CdTe@cys quantum-dot and BSA, Trypsin and Cytochrome c proteins applying PARAFAC on fluorescence data**

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Quantum dots (QDs) have gained a lot of attention in the past decade. The quantum confinement of their electronic states makes them quite attractive, showing some unique optical properties such as high quantum yield, symmetrical emission spectra, broad-band excitation, photostability, and readily tunable spectra<sup>1</sup>, compared to conventional dyes. QDs and their molecular conjugates are becoming increasingly important for a wide range of applications in biotechnology, and medicine<sup>2</sup>.

The water soluble cysteine functionalized CdTe@cys quantum dots were synthesized. The three-way data array was recorded by measuring excitation emission matrix (EEM)<sup>3</sup>, during the covalent interaction between CdTe@cys QDs and BSA, Trypsin and Cytochrome c proteins using different cross-linkers such as: Formaldehyde, glutaraldehyde (G) and 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide hydrochloride (EDC)/Nhydroxysuccinimide (NHS).

Multiway analysis was performed to analyze the resulting data. The PARAFAC model<sup>4</sup>, is useful for the identification of pure components spectra and leads to estimation of concentration and pure spectral profiles of components in the considered bioconjugation system<sup>3</sup>. PARAFAC showed two, three and three components when using formaldehyde, EDC/NHS and G cross linkers in this bioconjugate systems. Third component was present for this bioconjugation systems when using EDC/NHS and G cross linkers, with a distinctly different location and emission intensity compared to CdTe@cys and proteins. Although new very strong fluorescent peaks<sup>5</sup>, appeared after addition of G cross linker, for CdTe@cys and three proteins. This was further proof that the QDs and three proteins were covalent conjugated successfully. The new peak obtained from bioconjugated component can be used for improving sensitivity and limit of detection analysis of proteins.

Therefore, we using spectroscopic data and multiway analysis, as a simple method, low cost, fast and efficiency for determination correct number of component in CdTe@cys with BSA, Trypsin and Cytochrome c, and improve detection proteins. This work ability to extend to similar systems by different QDs and proteins. The improvement in the latter could lead to an increase in applications of the QDs such as in fluorescence imaging and other biological applications such as pathogen and toxin detection<sup>6</sup>.

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**Application of self organizing maps and GA-MLR  
for the estimation of stability constant of 18-crown-6 ether  
derivatives with Cerium cation**

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A quantitative structure–property relationship (QSPR) study of a binding constant of 18-crown-6 ether derivatives with cerium cation was performed. Constitutional, derivatives with cerium cation was perform. Constitutional, Topological and WHIM, as well as GETAWAY, 3D-MoRSE, and Aromaticity Indices descriptors generated from Dragon, were selected to describe the molecules. Self organizing map (SOM) was used to split the original data set into calibration and test set. Genetic algorithm-multiple linear regression technique was used to establish QSPR model for calibration set. Finally, the best six-dimensional model, developed on a calibration set of molecules and the external validation was performed on test set of molecules. The stability and predictability of QSPR model determined with the leave one out cross validated variance and the external-validated variance. This QSPR approach can contribute to a better understanding of structural factors of the crown ethers with metal cations and be useful in predicting the binding constant of other organic compounds with metal ions.



## Green synthesis of NiO nanoparticles using Aloe Vera extract

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In recent years, there is an emerging interest to synthesize nanoparticles of Ni due to their superior properties and application in various fields like sensors, memory storage devices, photocatalytic and catalysis [1-2]. In recent years, nanoparticles are synthesized using plant extract. Plant extracts not only acts as a fuel, but also as capping agents and renders a coordination action capturing the metal ion in the amylose helix in well defined sites. Present research work focused on to synthesis of NiO nanoparticles from leave extract of Aloe Vera plant using Green synthesis method. To synthesis the NiO nanoparticles, dissolve 1.0 M of NiCl<sub>2</sub>.6H<sub>2</sub>O in 100 ml of distilled water. Added leaves extract dropwise under constant stirring upto achieve pH of solution became 7. The mixture was subjected to stirring for 8 hours continuously. In this process nano particles were formed, afterwards separate this nanoparticles using what man filterpaper and washed the materials with water repeatedly to remove the by-products. The nanoparticles were dried at 110°C for overnight and calcined at 700°C for 5 hours. The obtained NiO nanoparticles have been characterized by DRS, XRD, FTIR and SEM. The appearance of a sharp band at 460 cm<sup>-1</sup> in the FTIR spectrum confirms the synthesis of NiO (Fig.1). The XRD results showed that the product is pure and has good crystallinity with cubic structure (Fig.2). The particle size calculated from XRD was in the range 37-44 nm. SEM image reveals the uniformity of the average particles size and shape of the obtained NiO nanoparticles (Fig.3). DRS spectrum reveals a characteristic absorption peak of NiO at wavelength of 359 nm, which can be assigned to the intrinsic band-gap absorption of NiO due to the electron transitions from the valence band to the conduction band.

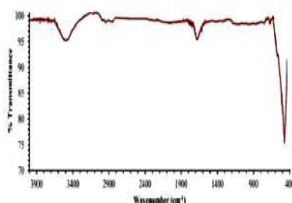


Fig.1 FTIR spectrum of NiO

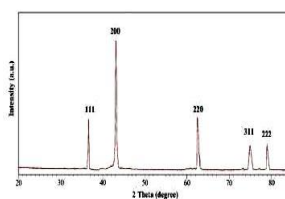


Fig.2 XRD pattern of NiO

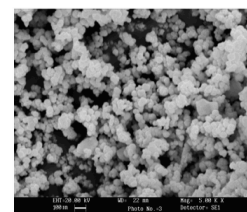


Fig.3 SEM image of NiO

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## Improving human embryos selection in vitro fertilization (IVF) by ATR-FTIR spectroscopy and chemometric approach

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Potential Embryo quality is crucial to the outcome of in vitro fertilization (IVF); however, the ability to precisely distinguish the embryos with higher reproductive potential from others is poor. Morphologic evaluation used to play an important role in assessing embryo quality, but it is somewhat subjective. The culture media is the immediate environment of the embryos in vitro, and a change of the substances in the culture medium is possibly related to the embryo quality. FT-IR spectroscopy analysis were used to report metabolomic parameters, established on the basis of observed biomarker targets. FT-IR may also be used as a quantitative method for determining concentrations of components within a sample.

FT-IR spectra contain information on functional group vibrations resulting in the absorbance of infrared light at specific wave numbers ( $1/\lambda$ ). The majority of these regions can be identified to be vibrational modes from water (O–H stretch centred at  $3400\text{ cm}^{-1}$ ), fatty acids (CH<sub>x</sub> stretches at  $2956\text{--}2850\text{ cm}^{-1}$ ), proteins (amide I, C = O at  $1652\text{--}1648\text{ cm}^{-1}$ ; amide II, N–H, C–N at  $1550\text{--}1548\text{ cm}^{-1}$ ), polysaccharide (ring and C–O vibrations at  $1085\text{--}1052\text{ cm}^{-1}$ ), and there is also a mixed region from  $1460\text{--}1110\text{ cm}^{-1}$  which contains information from fatty acids, polysaccharide, nucleic acids and proteins.[1-3]

In this prospective embryo quality was determined by analyzing culture media after fertilization by attenuated total reflection Fourier-transform infrared (ATR-FTIR) spectroscopy with classification technique. Classification model was built using Partial Least Square-Discriminant Analysis (PLS-DA) and the performance model was evaluated in terms of sensitivity, specificity, accuracy, efficiency and Matthews's correlation coefficient. The PLS-DA models give sensitivity, specificity, accuracy and efficiency values in the ranges of 80–100%, showing good performance of the classification models.

Results showed that the Fourier transform infrared spectroscopy with PLS-DA can be used as an analytical tool to analyze human embryo culture media in IVF treatment.

This procedure is also rapid, reliable, and reducing the influence of the embryologist experience on results.

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**Design of photoelectrochemical sensor based on mixed metal oxide modified TiO<sub>2</sub>-NTs for determination of galantamine in real samples**

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Photoelectrochemical (PEC) sensors are a kind of electrochemical methods which includes a light source and a suitable photoactive modified electrode. The light source excites a photoactive modified electrode to generate a photocurrent signal. Various active species, such as organic small molecules, metal complexes graphene nanocomposites and semiconducting nanoparticles have been investigated for PEC study [1]. Among them, nanoscale TiO<sub>2</sub> has been widely considered one of the most promising photocatalytic materials due to its low cost, nontoxic, photostable properties and strong photooxidation ability [2]. Ti-nanotubes (NTs) were grown on titanium foils by electrochemical anodization in water-ethylene glycol solution containing ammonium fluoride. The anodization was conducted in the constant 25 V for 2 h. Then the as-prepared Ti-NTs electrode was calcinated at 450 °C for 150 min [3]. Cobalt-copper alloy was electrodeposited on the TiO<sub>2</sub> NTs using electrochemical coating method for 30 s under an applied potential of -1.0 V [4]. The photoelectrocatalytic oxidation behaviour of galantamine (Gal) was studied in the present work using the Co<sub>3</sub>O<sub>4</sub>-CuO modified TiO<sub>2</sub>-NTs electrode. The results showed remarkable enhanced UV light photoelectrochemical response of the Co<sub>3</sub>O<sub>4</sub>-CuO modified TiO<sub>2</sub>-NTs in comparison with TiO<sub>2</sub>-NTs and Co<sub>3</sub>O<sub>4</sub>/TiO<sub>2</sub>-NTs. The photocurrent of Gal oxidation (under the UV irradiation) was assessed using the hydrodynamic photoamperometric method in buffer solution. The optimum conditions for Gal determination were studied and citrate buffer solution (pH=4.2) and E=2.0 V (vs. Ag/AgCl reference electrode) were selected as an optimum supporting electrolyte and applied bias potential. It was found that the photocurrent of Gal was linearly dependent on the concentration of Gal in the range of 10 nM to 10 μM, and the detection limit of Gal determination was found to be 7.60 nM.

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### A sensitive electrochemical sensor based on PEI@magnetic multi-walled carbon nanotubes for the determination of ciprofloxacin in biological sample

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A simple and expedite electrochemical methodology was developed for the determination of ciprofloxacin, based on a glassy carbon (GC) electrode modified by a composite of magnetic multi-walled carbon nanotubes (MMWCNTS) with Polyethyleneimine (PEI) [1,2]. The combined use of PEI and MMWCNTS in the electrochemical sensor leads to a significant signal improvement. The PEI/MMWCNT modified GC electrode exhibited efficient electrocatalytic behavior in the oxidation of ciprofloxacin with relatively high sensitivity, stability and lifetime [3]. The characterization of the nanocomposite was carried out by scanning electron microscopy, X-ray diffraction and Fourier transform infrared spectroscopy. The performance of the GC electrode modified with PEI@MMWCNTS was investigated using cyclic voltammetry and differential pulse voltammetry to detect ciprofloxacin selectively. Also, we established the electrochemical behavior and the oxidation mechanism of ciprofloxacin by using CV as technique. Furthermore, kinetic studies were done with the aim of calculate the number of transferred electrons in the entire process and to know if it is controlled by adsorption or diffusion. Under optimized conditions, a linear calibration curve was obtained for ciprofloxacin in the concentration range 0.04 – 70  $\mu\text{M}$  with a detection limit of 0.001  $\mu\text{M}$ . Furthermore, the method was applied for the determination ciprofloxacin in biological fluids such as human serum samples with acceptable recoveries and minimal matrix effect. A comparison of figures of merit between the developed method and other previously developed methods showed that a powerful alternative method for the determination of ciprofloxacin in biological samples has been developed.

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## Preparation and examination of potential of polymer inclusion membranes containing crown ethers towards Cr(VI)

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Recently membrane based processes have attracted attention as a valuable technology for many industries. Polymer inclusion membranes (PIMs) are a type of liquid membranes has developed because of their chemical and mechanical stability that even higher than supported liquid membranes (SLMs).<sup>[1]</sup> Thus, PIMs can be reused for several times without significant decreasing in their application.<sup>[2]</sup> PIMs are thin and flexible films that are formed by casting an organic solution containing an extractant, a base polymer and, if necessary, a plasticizer.<sup>[3]</sup>

In this communication, the removal of Cr(VI) as a highly toxic chemical species with PIMs containing macrocyclic crown ethers dicyclohexano-18-crown-6 (DC-18C6) and dibenzo-18-crown-6 (DB18C6) is reported. A variety (46 PIMs) of poly(vinylidene-fluoride-co-hexafluoropropylene) (PVDF-HFP)-, cellulose triacetate (CTA)- and poly(vinyl chloride) (PVC)-based PIMs containing DC-18C6 and DB-18C6, as ligand, and various plasticizers/modifiers including 2-nitrophenyloctyl ether (NPOE), tributyl phosphate (TBP), dibutyl phosphate (DBP) and tris(2-ethylhexyl)phosphate (TEHP) were prepared. The PIMs were prepared by dissolving different proportions of the polymer, ligand and modifier in THF or CH<sub>2</sub>Cl<sub>2</sub>. The prepared solution was poured into a petri dish and allowing the solvent to evaporate. Among the fabricated PIMs, the appearance and mechanical stability of one of them including 45 wt% PVC, 20 wt% DC-18C6 and 35 wt% NPOE was suitable for using in the extraction experiments of Cr(VI) from sulfate solutions (pH 1.2) and hydrochloric acid solutions (1.2 M). The extraction experiments were performed by immersing of a 3.5 cm diameter round disk PIMs with average mass 0.087±0.006 g into 50 mL of aqueous solutions containing Cr(VI) (2×10<sup>-4</sup> M). The analyses of the Cr(VI) concentration remained in the aqueous phase were done spectrophotometrically using 1,5-diphenylcarbazide or by FAAS.

In the extraction experiments from the sulfate medium the effect of parameters including pH, extraction time and sulfate ion concentration were evaluated. The maximum extraction of the analyte was found under conditions: pH 1, extraction time 20 h, sulfate concentration 0.6 M. The effect of the type of electrolyte used was also assessed by comparison the extraction percentage of Cr(VI) by the PIMs from the aqueous solutions formed by potassium sulfate (0.6 M, pH 1), sulfuric acid (0.6 M), KCl (1.2 M) and HCl (1.2 M). The extraction percentage was highest in hydrochloric acid solutions. This arouse us to examine the effect of the acid concentration, in the range 0.6-3 M, on the extraction process. The optimal value was 1.2 M. The back-extraction experiments of the loaded PIMs were studied with 50 mL nitric acid, perchloric acid, sodium nitrate, sodium sulfite, sodium thiosulfate, ammonium acetate and sodium hydroxide. The highest value of back-extracted Cr(VI) was achieved by 0.1 M NaOH. The experimental capacity of PIM was evaluated under optimum conditions as a function of initial Cr(VI) concentration. The capacity of the PIMs was found to be 3.6 mg chromium/g PIM. It is found that the presence Pb<sup>2+</sup>, Ni<sup>2+</sup>, Cd<sup>2+</sup>, Zn<sup>2+</sup> and NO<sub>3</sub><sup>-</sup> with concentrations up to 10 times higher than the chromium ions concentration did not an interference effect on the Cr(VI) extraction.

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**Red emitting carbon dots – gold nanostar fluorescence resonance energy transfer based fluorescent probe for turn-on sensing of melamine**

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Fluorescent carbon dots (CDs), as a class of newly discovered carbon nanomaterial, have received increasing attention as substitutes for organic fluorophores and conventional semiconductor quantum dots (QDs) [1, 2]. However, emission wavelengths of most reported CDs which are mainly located in the blue-light region hinders their application in the bioimaging and biosensing fields due to the commonly blue auto-fluorescence of biological matrix [3]. In this work a novel probe was prepared for determination of melamine. The sensing approach is based on fluorescence resonance energy transfer (FRET) between red emitting carbon dots (R-CDs) and gold nanostars (AuNSs), which act as energy donor and acceptor, respectively. Amino-functionalized CDs could be readily adsorbed onto the surface of AuNSs through Au–N interactions, leading to the aggregation of AuNSs and the quenching the fluorescence of CDs due to fluorescence resonance energy transfer. Upon addition of melamine, melamine molecules can interact with AuNSs via covalent binding of the amino group (NH<sub>2</sub>–) of melamine to the surface of AuNSs, which prevents the interaction of R-CDs and AuNSs, thus reduces the FRET effect, resulting in the increase of the fluorescence intensity. We optimized some important factors including incubation time, AuNSs concentration and media pH, which would affect the efficiency of the FRET system. Under the optimized experimental conditions, melamine could be detected based on fluorescence intensity of C-dots. We could get a linear relationship between 30 nM and 1000 nM and the detection limit was 9 nM. The proposed method was applied to the determination of melamine in raw and pasteurized milk samples with satisfactory results.

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## Designing and Fabrication of a Microfluidic Device Using a 3D Printer and It's Application in Bipolar Electrochemical Systems for the Detection of Single Nucleotide Polymorphism by Luminol Coated Platinum Nanoparticles

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A SNP is a single nucleotide variation at a specific location in the genome that is by definition found in more than 1% of the population<sup>[1]</sup>. The development of simple, inexpensive, hand-held, user-friendly biosensor for High throughput and multiplexed genotyping of various single nucleotide polymorphisms (SNPs) in a single run experiment by a non-specialist user is the main challenge in the analysis of DNA<sup>[2]</sup>. In the present manuscript, a novel wireless electrochemiluminescence (ECL) DNA sensor is introduced for genotyping of different SNPs on the basis of ECL of luminol/hydrogen peroxide system on a bipolar electrode (BPE) platform that is integrated with microfluidic channels constructed with three-dimensional printers.

In a bipolar electrochemistry (BE), a driving potential is applied through an electrolyte solution containing conducting object (bipolar electrode; BPE) using two deriving electrodes connected to a power supply. This driving potential causes a potential drop in the solution and therefore induces a potential difference along the length of the BPE. If this potential difference is sufficient, the faradaic reactions simultaneously occur at the ends of BPE<sup>[3]</sup>. Recently because of simplicity, low-cost, ease of operation and device fabrication, BE has been applied in a number of interesting analytical studies. Especially this method does not require a direct electrical connection between BPE and the external power supply (wireless), as a result, using BE allows employing large number of BPE arrays. As well as, integration of BPE and ECL (BPE-ECL) have drawn much more attention in bioanalysis. The wireless nature of the BPE and no need for the light source in ECL, not only simplifies detection system for BPE-ECL, but also, improves detection limit and sensitivity, due to no scattered light in the sample and no excitation source fluctuations. The luminol along with hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) as its coreactant is a well-known system to produce strong ECL at positive potentials, under a variety of experimental conditions. Recently, the catalytic properties and high loading amount of luminol functionalized nanoparticles for ECL emission, instead of the solution of luminol, have attracted many interest of the researchers. Then we use luminol-functionalized platinum nanoparticles<sup>[4]</sup>. the integration of BPE systems by microfluidic devices increases the sensitivity of the methods, as well as reducing the consumption of materials and energy.

microfluidics is the science and technology of systems that process or manipulate small (10<sup>-9</sup> to 10<sup>-18</sup>litres) amounts of fluids, using channels with dimensions of tens to hundreds of micrometers. The first applications of microfluidic technologies have been in analysis, for which they offer a number of useful capabilities: the ability to use very small quantities of samples and reagents, and to carry out separations and detections with high resolution and sensitivity; low cost; short times for analysis; and small footprints for the analytical devices<sup>[5]</sup>.

After modification of anodic poles of the BPEs with the DNA probe and its hybridization with the targets, genotyping of various SNPs is carried out by exposing them to different monobase modified luminol-platinum nanoparticles (M-L-PtNPs). Upon the hybridization of M-L-PtNPs to mismatch sites, the ECL of luminol is followed using a photomultiplier tube (PMT). In this method, the ECL of luminol molecules was observed for mismatch sites but in the presence of a complementary strand, no ECL signal is observed. Similarly, for the different concentrations of the DNA strand, the observed light has a trend.

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**RuO<sub>2</sub> nanowires on electrospun CeO<sub>2</sub>-Au nanofibers/functionalized carbon nanotubes/graphite oxide nanocomposite modified screen-printed carbon electrode for simultaneous determination of ascorbic acid, dopamine and serotonin**

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Neurotransmitters, such as dopamine (3,4-dihydroxyphenylethylamine, DA) and serotonin (5-hydroxytryptamine, 5-HT) are chemicals in the brain that transmit signals from the neurons to the target cells. Simultaneous measurement of DA and 5-HT is particularly important since these molecules coexist typically and their relative levels have implications in many diseases and response to drug treatments [1]. Ascorbic acid (AA) is a common interference that coexists with DA and 5-HT in the brain at concentrations 100–1000 times higher than that of DA [2].

In this work, for the first time, a novel hybrid architecture of CeO<sub>2</sub>-Au nanofibers (CeO<sub>2</sub>-AuNFs) and single-crystalline RuO<sub>2</sub> nanowires (RuO<sub>2</sub>NWs) have been synthesized by a combination of electrospinning and thermal annealing process. The CeO<sub>2</sub>-Au hybrid nanofibers were fabricated by the electrospinning technique and then annealed in air [3]. The amorphous Ru(OH)<sub>3</sub> precursors at relatively low temperature were efficiently converted into highly single-crystalline RuO<sub>2</sub>NWs on electrospun CeO<sub>2</sub>-AuNFs. The electrospun CeO<sub>2</sub>-AuNFs, RuO<sub>2</sub>NWs–CeO<sub>2</sub>-AuNFs and other nanostructure were characterized by different methods such as field emission scanning electron microscopy (FESEM), transmission electron microscope (TEM), energy dispersive X-ray analysis (EDS) and fourier transform infrared spectroscopy (FT-IR). Novel RuO<sub>2</sub>NWs–CeO<sub>2</sub>-AuNFs hybrid architecture in combination with graphite oxide (GO) and functionalized multiwalled carbon nanotubes (f-MWCNTs) further employed to modify screen printed carbon electrode (SPCE) in order to develop a sensitive electrochemical method with suitable properties for the simultaneous determination of ascorbic acid (AA), dopamine (DA) and serotonin (5-HT). The dependence of the oxidation peak currents on the pH of the solution, amount of modifier, scan rate and concentration of the analytes was studied to optimize the experimental conditions.

Under the optimum operating conditions, linear calibration curves were obtained in the range of 0.5–100, 0.01–120 and 0.01–150 μM with a detection limit of 160, 2.8 and 2.4 nM for AA, DA and 5-HT, respectively. The proposed electrochemical sensor provided a good performance for the simultaneous determination of AA, DA and 5-HT by not only significantly improved their current responses, but also decreased the overpotentials as well as resolved the overlapping of the oxidation peak potentials. This sensor was successfully applied for the determination of AA, DA and 5-HT in biological fluids and pharmaceutical samples.

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**Flexible and wire shaped supercapacitor material based on nanoflakes  
Co(OH)<sub>2</sub>@nanosheets Ni(OH)<sub>2</sub>/3D nickel fibers**

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Flexible and lightweight wire-shaped supercapacitors have recently attracted increasing interest, due to their versatility in the device design and application potentials in portable or wearable electronics. Herein, we demonstrate a wire-shaped supercapacitor by virtue of material fabrication strategy. In this article, three-dimensional (3D) porous nickel structure was fabricated via an electrochemical deposition process. The construction of the foam structure was achieved by means of a hydrogen bubble dynamic template, prepared from Ni electrodeposition at high current densities [1]. Subsequently, a Ni(OH)<sub>2</sub>@Co(OH)<sub>2</sub> hierarchical core/shell nanostructure was grown on the 3D nickel wire using two step electrochemical process with fine control over the structure/morphology [2,3], which displays a largely improved specific capacitance, high rate capability and long cycling lifespan. When investigated as binder-free electrodes for supercapacitors, such unique Ni(OH)<sub>2</sub>@Co(OH)<sub>2</sub> electrode exhibits ultrahigh specific capacitances, which are several times larger than the pristine Ni electrode. Because of reduced charge transfer resistance of the Ni wire, electron transfer capability is enhanced and the electrochemical performance is improved. These results suggest that the fabricated device has excellent potential as a power source for flexible, portable and wearable application as well as self-powered systems. Results showed that the proposed supercapacitor had a higher specific capacity of about 888 F g<sup>-1</sup> at current density of 1.0 A g<sup>-1</sup> and exhibited energy density of 27.24 Wh kg<sup>-1</sup> and power density of up to 234.99 W kg<sup>-1</sup>.

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## Diphenhydramine Hydrochloride Injectable, Stability and Impurities

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Diphenhydramine Hydrochloride having chemical name 2-(diphenylmethoxy)-N,N-dimethyl ethylamine hydrochloride. It is white, crystalline powder, is freely soluble in water and alcohol. The molecular formula is  $C_{17}H_{21}NO.HCl$  and molecular weight is 291.82. Diphenhydramine Hydrochloride in the parenteral form is a sterile, pyrogen-free solution. Each ml contains a concentration of 50 mg of Diphenhydramine Hydrochloride and water for injection, for intermuscular and intravenous use. The solution for parenteral use has been adjusted to a pH between 4 and 6.5 with either sodium hydroxide or hydrochloric acid. Diphenhydramine Hydrochloride is an antihistamine drug, clear and colorless solution available as 50 mg/ml in 1 ml ampules. Diphenhydramine Hydrochloride contains NLT 98.0% and NMT 102.0% of Diphenhydramine Hydrochloride calculated on the dried basis [1]. For identification 3 methods are used [1]:

1-Infrared Absorption 2-HPLC: the retention time of the major peak of sample solution corresponds to that of the standard solution, as obtained in the Assay. 3-Identification Test-General Chloride [1]

For calculating Assay, gradient HPLC method with a buffer of monobasic potassium phosphate, that adjusted with phosphoric acid to a pH of 3.0 and diluent (Acetonitrile and Buffer (35:65)) with a L7 column is used [1], Tailing factor NMT 1.8. There are seven known impurities for Diphenhydramine Hydrochloride [2,3,4]. These impurities decrease Assay during the stability time. Impurities measured by HPLC method [1]. In order to more stability manufacturing conditions must be controlled. For calculating impurities, HPLC method with a buffer of monobasic potassium phosphate, that adjusted with phosphoric acid to a pH of 3.0 and mobile phase (Acetonitrile and Buffer (35:65)) with a L7 column is used [1].

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## Development on Generalized Rank Annihilation Problem by Implementing Duality

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The analytical chemist is frequently confronted with the problem of analyzing complex mixtures in the presence of any component in the sample that is not included in the calibration model. In these cases, it is desirable to be able to obtain quantitative information for a particular component without concern for the rest of the components in the sample. The property of quantitation of an analyte in the presence of unknown constituents is called second-order advantage<sup>1</sup>.

Additionally, in recent studies it has been shown that, when the solution is unique or information is available for obtaining the unique solution, the duality concept<sup>2-3</sup> is a useful approach to extract information in Self Modeling Curve Resolution<sup>4,5</sup>.

In this work, a new duality based algorithm to achieve “second order advantage” and determination of standard component in the presence of unknown components is developed. For this purpose, duality relation as a powerful mathematical approach is used to define the interference(s) subspace. Afterwards, the concentration ratio of the standard component in the test sample to its amount in standard,  $\lambda$ , has been calculated in a systematic way. With the help of provided estimations of  $\lambda$ , the standard component is quantified more precisely with error intervals.

Moreover, the geometrical visualizations beside algebraic formulas are used to show the quantitative analysis of this study. By illustrating the procedure in graphical plots, it has been tried to explain the details of the proposed method in an understandable way.

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Potentiometric Determination of  $\text{HPO}_4^{2-}$  with Chitosan-glutaraldehyde by Carbon Paste Electrode

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In this article a selectivity potentiometric methodology, using an ion-selective electrode, for determination of  $\text{HPO}_4^{2-}$  anion in aqueous solution was investigated. Chitosan- glutaraldehyde complexes is used. A room temperature ionic liquid, 3-methyl-imidazolium tetrafluoroborate and paraffin for compare of conductive effect are used. Response time, pH range, electrode selectivity, electrode life have been investigated. Carbon nanotubes (WCNTs) were used in the composition of the carbon paste to improve conductivity and transduction of chemical signal to electrical signal. Also, the effect of different carbon nanotubes (single-wall carbon nanotubes, multi-wall carbon nanotubes and COOH functionalized single-wall carbon nanotubes, COOH functionalized multi-wall carbon nanotubes and  $\text{NH}_2$  functionalized single-wall carbon nanotubes and  $\text{NH}_2$  functionalized multi-wall carbon nanotubes) on the electrode's response has been investigated. The electrode has a short response time ( $\sim 5$  s) and can be used for at least 60 days without any considerable divergence in potentials, and the working pH range was 6.5–8.5. fabricated sensor for determining of  $\text{HPO}_4^{2-}$  demonstrated a maximum Nernstian slope equal to  $30.06 \text{ mVdecade}^{-1}$  along a linear range from  $1 \times 10^{-5}$  to  $1 \times 10^{-2} \text{ mol.L}^{-1}$  and detection limit of  $8.55 \times 10^{-5} \text{ mol.L}^{-1}$ . Finally, the proposed electrode was successfully used as an indicator for potentiometric determination of  $\text{HPO}_4^{2-}$  in Hydroponic farm wastewater samples.

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**Simultaneous Electroanalysis of Tricyclic Anti-depressant drugs (TCAs) using Nanocomposite Electrode based on Copper Molybdate Nanoplates in Mesoporous Carbon**

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This paper describes a novel, simple, reliable and sensitive electroanalytical procedure proposal for the determination of both effective antipsychotic drugs with low redox activity and poor hydrophilicity imipramine (IMP) and carbamazepine (CBZ) in human plasma sample.<sup>[1]</sup>

In this work, we demonstrated the synthesis and applications of nanocomposite electrode based on CuMoO<sub>4</sub> nanoplates-Mesoporous Carbon (CuMoO<sub>4</sub>/Meso) for electrochemical determination of TCAs. CuMoO<sub>4</sub> nanoplates was synthesized through sedimentary method.<sup>[2]</sup> The characterization of the synthesized CuMoO<sub>4</sub> nanoplates was accomplished by utilizing FT-IR, FESEM, XRD, EDX and Zeta-potential technique, also the characterization of modified electrodes accomplished by FESEM, EDX and EIS. Modification of the working electrode showed an excellent electrocatalytic oxidation activity toward TCAs at less positive potential with increased current intensity. Differential pulse voltammetry technique was used to carry out electrochemical determinations. The influence of parameters like scan rate, pH (aqueous acid, neutral, and alkaline conditions), amount of the modifiers and concentration on the peak current of the drug were studied.

The results showed a well-defined oxidation peak of IMP and CBZ with potential of 0.83 V (instead of 0.88) and 1.09 V (instead of 1.15) vs. Ag/AgCl/3M Cl<sup>-</sup>, in 0.1 M acetate buffer solution (pH 5.0) as supporting electrolyte, respectively. The obtained negatively charged modified electrode showed fast and sensitive current response to IMP over a wide dynamic linear range of 0.10-100.0 μM ( $r^2 = 0.9933$ ) and 0.5 μM-100.0 μM for CBZ ( $r^2 = 0.9953$ ), with detection limit of 0.030 μM for IMP and 0.089 μM for CBZ (S/N=3) revealing the high-sensitivity properties, respectively. Reproducibility, long life-time (durability) and multiple reusability of the electrode besides its detection limits and wide dynamic linear ranges, are the main advantages of the proposed sensor in comparison with previously reported ones.<sup>[3-5]</sup> Finally, the proposed method was successfully applied for the determination of IMP and CBZ in biological species.

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**A colorimetric method for discrimination of amino acids based on the kinetics of gold nanoparticle aggregation**

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Gold nanoparticles (AuNPs) exhibit a unique phenomenon known as Surface Plasmon Resonance, which is responsible for their intense red color. This color changes to blue upon aggregation of AuNPs. The color changes associated with the aggregation of AuNPs has led to the development of colorimetric based assays for a variety of target species [1,2]. Recently, the conjugation of AuNPs with biomolecules such as aminoacids and proteins has attracted considerable attention [3]. Some of the amino acids at low pH are capable of binding to the surface of AuNPs by various affinities and inducing nanoparticle aggregation with different kinetics. As a result of the induced aggregation, the UV–Vis spectra of colloidal AuNPs change with time. So, the differential interactions of amino acids with AuNPs give a distinct pattern for each of them as a fingerprint, which is employed for classification and identification.

In this work, the kinetic absorption spectra related to the AuNPs aggregation in the presence of selected amino acids i.e. histidine (His), cysteine (Cys), lysine (Lys) methionine (Met) and arginine (Arg) has been recorded as a function of time for 45 min at different concentrations. The collected spectra were then analyzed with unsupervised pattern recognition techniques, including hierarchical cluster analysis (HCA) and principal component analysis (PCA). The proposed method could successfully discriminate the five amino acids and the identification accuracy was found to be 97%. Moreover, the method has the capability of discrimination of amino acids mixtures.

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## Electrochemical kinetics and mechanism study of Raloxifene drug

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Electrochemical methods are widely applied to the study of the electroactive compounds. Voltammetric techniques are frequently and routinely used today to obtain information about homogeneous reactions coupled with electron transfer [1]. In this work the electrochemical oxidation of raloxifene was studied in the absence and presence of 2-mercaptopyrimidin in aqueous-ethanol solution on the surface of a glassy carbon electrode by cyclic voltammetry. The results indicate electrode reaction process is a quasi-reversible kinetics and the exchange of two electrons and two protons are involved in the process [2]. Investigation of voltammogram at different concentrations of raloxifene shows that raloxifene is oxidized at the surface of the electrode and its oxidized form partially participated in a side reaction such as dimerization. Investigation of raloxifene cyclic voltammograms in the presence of 2-mercaptopyrimidine shows that at high concentration of 2-mercaptopyrimidine and at low scan rates, a catalytic reaction is performed. As a result of the relative stability of oxidized form of raloxifene, it doesn't contribute in an addition reaction with nucleophiles such as diethyl amine. However raloxifene perform an addition reaction with 2-mercaptopyrimidine at high concentrations of it. During the electrode oxidation raloxifene lose two electrons and the raloxifene-oxide has positive charge [3]. Due to the structure of the raloxifene-oxide, the positive charge is distributed throughout the molecule and has a resonant structure. This resonance structure causes the oxidative stability of raloxifene and its reluctance to react with these compounds.

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**Air-Assisted Surfactant-Enhanced-Emulsification Liquid-Liquid Microextraction with Solidification of Floating Organic Droplet Coupled with HPLC for the Determination of Clozapine in Biological Samples**

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This Study presents a simple, rapid, sensitive, low cost, and environmentally friendly microextraction method coupled with High Performance Liquid Chromatography-Ultraviolet detection, to preconcentration, determination and analysis of Clozapine in biological samples. Clozapine, dibenzodiazepine derivative, is an effective drug in treatment of schizophrenia. However, harmful side effects of this drug in high concentrations makes it necessary to determine its concentration in biological samples including plasma and urine. To this aim, in this study a green microextraction method based on DLLME is developed, called air-assisted surfactant-enhanced-emulsification liquid-liquid with solidification of floating organic droplet (ASLLME-SFO). In this method, the extraction is carried out by forming the ion-pairs between analyte and surfactant in the sample solution and transferring them to the extraction solvent. Also, in order to decrease the toxicity and harmful effects of disperser and high-density solvents on operators and environment, surfactant as emulsifier is replaced with disperser solvent, and low-density solvent is replaced with chlorine solvent. Moreover, using a glass syringe to disperse extraction solvent as fine droplets into aqueous solution, makes it possible to reduce the probability of sample degradation, cost, and complexity of this method in comparison to ultrasonic or vortex methods. In addition to the above mentioned advantages, the most significant feature of this approach is higher extraction efficiency in a shorter time compared to DLLME method. In this study, the effective parameters on extraction efficiency such as type and volume of extraction solvents, type and concentration of surfactants, type and amount of salt, pH, numbers of aspirating/dispersing cycles and centrifuge time are investigated and optimized. According to the test results, the proposed method is shown good analytical characteristics, including low LOD, LOQ, repeatability and reproducibility values, high preconcentration factor and satisfactory recovery.

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**Polyacrylonitrile nanofibers/ Ni<sub>0.5</sub>Zn<sub>0.5</sub>Fe<sub>2</sub>O<sub>4</sub> nanocomposite as a modifier in carbon paste electrode for selective and sensitive determination of sunitinib in biological samples**

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Due to the importance of drugs determination in pharmaceuticals for quality control in pharmacopeia, many routine analytical methods such as HPLC have been developed. But, these methods suffer from some disadvantages such as time-consuming, expensive, and need to labor operators. Among various analytical methods, electroanalytical methods are rapid, inexpensive and easy to operation [1, 2].

In the present work, a novel modifier, polyacrylonitrile nanofibers/Ni<sub>0.5</sub>Zn<sub>0.5</sub>Fe<sub>2</sub>O<sub>4</sub>, for carbon paste electrode has been synthesized using a simple electrospinning method. The synthesized nanocomposite was fully characterized using methods such as Fourier transform infrared spectroscopy, scanning electron microscopy, cyclic voltammetry, and electrochemical impedance spectroscopy. Preliminary experiments showed that the nanocomposite had an electro-catalytic effect on the electro-oxidation of sunitinib and a significant improvement in the drug anodic current was obtained at +0.665 V (vs. Ag/AgCl). Various chemical parameters and instrumental parameters which could potentially affect the electrochemical signal were optimized. Under the optimum conditions, the analytical figures of merit were extracted and the method was fully validated. A relatively wide dynamic linear range of 0.018-18.77  $\mu$ M with a detection limit of 0.9 nM was obtained. Furthermore, the method was applied for the determination sunitinib in biological fluids such as human serum samples with acceptable recoveries and minimal matrix effect. A comparison of figures of merit between the developed method and other previously developed methods showed that a powerful alternative method for the determination of sunitinib in biological samples has been developed.

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## Extraction of azathioprine drug from plasma samples by modified magnetic iron oxide nanoparticles and its determination by HPLC

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In recent years modified iron oxide magnetic nanoparticles (MNPs) were used as new sorbents in analytical chemistry. They can interact with different analytes by  $\pi$ - $\pi$ , dipole-dipole, Van der Waals, hydrogen bonding and ion-dipole interactions and thus MNPs is suitable for extraction of analytes with a wide range of polarity [1]. In the present work, application of MNPs, has been investigated for development of a ultrasound-assisted dispersive magnetic solid phase extraction (UADM-SPE) coupled with high performance liquid chromatography (HPLC) was developed for preconcentration and determination of azathioprine in plasma samples. In UADM-SPE the sorbent is dispersed under sonication in the sample solution, providing a high surface contact with the analyte. Then, due to its magnetic properties, the sorbent is easily isolated from the solution using a magnet. Subsequently, a suitable solvent is used for analytes' desorption and the sample is then subjected to instrumental analysis [2]. The method provides important advantages such as fast, simple, inexpensive and environmentally friendly condition procedure [3]. MNPs

were prepared through the co-precipitation method. Then, the synthesized nanoparticles were characterized by Fourier transform infrared spectroscopy (FT-IR), scanning electron microscopy (SEM) and X-ray diffraction (XRD) [4]. The variables affected the extraction efficiency of Azathioprine (i.e. amount of MNPs, pH, sample volume, temperature and sonication time) were screened by fractional factorial design to find significant variables and optimized by response surface methodology using the central composite design (CCD). Finally, under optimal conditions the method was applied for analysis of the Azathioprine in plasma samples and good results were obtained.

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**Carbon paste electrode modified with polyacrylonitrile nanofibers/ Ni<sub>0.5</sub>Zn<sub>0.5</sub>Fe<sub>2</sub>O<sub>4</sub> nanocomposite as a voltammetric sensor for the determination of noscapine drug in biological samples**

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Measuring drugs in biological matrixes is one of the most important issues in the pharmaceutical industry. Drugs determination in the biological and human sample has many commonly used approaches such as chromatography methods. But, these approaches are often expensive, complex, time-consuming, and difficult to handle. Not surprisingly, electrochemical approaches are inexpensive and easy to operation [1, 2].

Herein, a method has been developed for the direct voltammetric determination of noscapine in biological samples utilizing polyacrylonitrile nanofibers/Ni<sub>0.5</sub>Zn<sub>0.5</sub>Fe<sub>2</sub>O<sub>4</sub> nanocomposite as a novel modifier in carbon paste electrode (CPE). The modifier was synthesized according to a simple electrospinning method and was fully characterized using methods such as Fourier transform infrared spectroscopy, scanning electron microscopy, cyclic voltammetry, and electrochemical impedance spectroscopy. Preliminary experiments showed that the nanocomposite had an electro-catalytic effect on the electro-oxidation of noscapine and a significant improvement in the drug anodic current was obtained at +0.633 V (vs. Ag/AgCl). Therefore, the nanocomposite was utilized to modify CPE electrodes for differential pulse voltammetric determination of the investigated drug. The experimental conditions and instrumental parameters such as pH, modulation amplitude, modulation time, step potential, and scan rate were optimized. Under the optimum conditions, the calibration curve was linear in the concentration range of 2-400  $\mu$ M with a detection limit of 0.8  $\mu$ M. The spiked/recovery experiments showed that the developed method could be successfully applied to the determination of noscapine in biological fluids with good recoveries and minor matrix effects.

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**Extraction of crocin from saffron using nanomagnetic molecularly imprinted polymer**

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Saffron is the dried stigmas of *Crocus sativus* and the most expensive spice used in industry, with many different uses as drug. The saffron and its coloured carotenoids (crocin) have memory improving properties anti Alzheimer, antidepressant, antioxidant, antitumor and anti-cancer effects. Due to these reasons, introducing and establishing a simple and effective method for extraction of crocins from its natural sources would be necessary and useful [1,2]. In the current study, a new strategy for the extraction of crocin from saffron has been employed by using nanomagnetic molecularly imprinted polymer (MMIP) as sorbent. MMIPs due to the super paramagnetic properties, good chemical and physical stability and simple synthesis methodology. They have the characteristics of the magnetic adsorbents property, high adsorption capacity to template molecule, re-usability, selectivity and high efficiency. These materials have been widely used in the different fields such as chemical, biological and medical science [3,4]. The MMIPs were synthesized as follows: firstly, magnetic Fe<sub>3</sub>O<sub>4</sub> nanoparticles (NPs) were prepared by the co-precipitation of Fe<sup>2+</sup> and Fe<sup>3+</sup> ions in an ammonia solution. The Fe<sub>3</sub>O<sub>4</sub> nanoparticles modify with SiO<sub>2</sub> by TEOS shell (Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>) was prepared and then surface of magnetic nanoparticles was functionalized with 3-(trimethoxysilyl) propyl methacrylate (MPS). After the well-defined MMIPs for crocin were further fabricated on the surface of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>@MPS using gentiobiose as template molecule, methacrylic acid (MAA) as functional monomer, 2,2-azobisisobutyronitrile (AIBN) as Initiator and ethylene glycol dimethacrylate (EGDMA) as cross-linking agent. The prepared nanomagnetic molecularly imprinted polymer were characterized and confirmed by FT-IR, XRD, TGA, SEM and VSM. For achieving optimal pre-concentration and reducing nonspecific interactions, various parameters affecting the extraction efficiency such as sorbent amount, eluting solvent, sample concentration and contact time have been investigated and established. The resulting MMIP showed high adsorption capacity, proper selectivity and fast kinetic binding for the template molecule. The results of re-binding experiments indicated that the MMIPs had fast adsorption kinetics and could reach binding equilibrium during 45 min and the adsorption capacity of the MMIPs was 9.76 mg/g. This is higher than that of the corresponding non imprinted polymer (MNIP).

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**Investigating Soft Known-Value Constraints in Multivariate Curve Resolution Studies**

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In multivariate curve resolution studies (MCR), applying partial or incomplete knowledge of reference values as known-value constraints can considerably reduce the extent of rotational ambiguity. MCR under known-value constraints can be applied for both quantification and identification analysis [1]. In the presence of noise and non-ideal behavior of chemical species, MCR may not find a set of solutions that completely obey the constraints and, sometimes, the estimated solutions show severe lack of fit. In practice, limitations in the reference methods or procedures cause deviation in measured known values. In these situations, applying known values may result in considerable quantification errors in MCR results and also can challenge identification analysis.

This contribution investigates the effect of applying known-value constraint on the results of MCR methods. For this purpose, a new Matlab code is written that provides the possibility of calculating the range of feasible MCR solutions under soft known-value constraints. Several simulated examples and an experimental data set were analysed using this code by providing sufficient information that theory suggests for obtaining a unique solution. The obtained ranges of feasible solutions were compared to the results of multivariate curve resolution alternating least squares (MCR-ALS) [2], and partial least squares (PLS) [3]. In the case of simulated data, an experimental design was used to evaluate the effect of two factors: (1) the amount of experimental noise, (2) and the amount of deviation of known values from true ones on the extent of rotational ambiguity.

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**Electrochemical assembly of poly (diphenylamine)/phosphomolybdic acid/PGE for methanol oxidation**

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In direct methanol fuel cell (DMFC), methanol is used as a fuel because it can be completely electrooxidized to the final product due to its simple molecular structure. Thus, a great deal of interest exists in the development of materials with a capability for electrocatalytic oxidation of methanol [1,2]. In this work, a layer-by-layer (LbL) film assembly was constructed that comprises alternative layers of poly (diphenylamine) (PDPA) and phosphomolybdic acid (PMA) [3]. First, a layer of oxidized PDPA (referred to as PDPA (+)) was deposited by electropolymerization in constant potential 1.2 V. The constructed electrode was characterized using field emission scanning electron microscopy (FESEM), electrochemical impedance spectroscopy (EIS) and cyclic voltammetry methods. The cyclic voltammetry of (PDPA/PGE) and (PMA/PDPA/PGE) was recorded in 0.5 M H<sub>2</sub>SO<sub>4</sub> solution containing 1.0 M CH<sub>3</sub>OH. The effects of various parameters such as the cycle numbers, deposition potential and time in the polymer formation stage and concentration of PMA and also its adsorption time were investigated on the electrode response. This study showed that the modified electrode has good electrocatalytic activity and ability to its application in the DMFC anodes.

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**Electrosynthesis of a new weak catex from *p*-nitrobenzoic acid and its application in separation and preconcentration of some organic compounds before measuring by HPLC**

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In this work a new weak catex was prepared by electropolymerization of *p*-nitrobenzoic acid under controlled potential of working electrode on Pb cathode. The electrochemical cells were separated by a thin layer of agar and electropolymerization was carried out at pH=8. After 8 hours a pale yellow polymer was precipitated and it was collected and after purification by soxhlet and water as solvent, it was characterized by CV, FT-IR, DSC and NMR. The electrode-product was slightly soluble in water, MeOH and soluble in DMSO. The prepared polymer was coated on a suitable solid support and was used for separation of some aniline derivatives from aquatic samples before measuring by HPLC. The results of experiments show that the prepared polymer (catex) has a high tendency towards organic compounds containing nitrogen atom. In some cases the percentage of extraction is about 95 to 98 percent [1-5].

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**Design of photoelectrochemical sensor based on graphitic carbon nitride (g-C<sub>3</sub>N<sub>4</sub>) coated titanium dioxide nanotube arrays for sensitive determination of glutathione**

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The photoelectrochemical (PEC) process is an electrochemical process based on the light signal. During PEC process for molecule, ion or semiconductor materials, the electron is excited when absorbing photons, which results in charge transfer and energy transfer from light to electrical [1]. PEC detection based on photon-to-electricity conversion has attracted considerable interest due to its high sensitivity as well as simple and cheap instrumentation [2]. In this work, we report the fabrication of titanium dioxide nanotube array coated by graphitic carbon nitride (g-C<sub>3</sub>N<sub>4</sub>/TiO<sub>2</sub>-NTs) and poly thiophene (PTh) as a novel PEC sensor. This sensor was prepared by anodizing of the Ti foil in the constant potential of 25 V for 2 h. Then the as-prepared TiO<sub>2</sub>-NTs/Ti was calcinated at 450 °C for 150 min. Herein, in situ growth of g-C<sub>3</sub>N<sub>4</sub> on the surface of TiO<sub>2</sub>-NTs was achieved via the vapor-pyrolysis of melamine [3]. The content of g-C<sub>3</sub>N<sub>4</sub> in the composite was adjusted by varying the addition quantities of melamine (0 to 8 g) in the calcination process. The photocurrent density generated by the fabricated PTh/g-C<sub>3</sub>N<sub>4</sub>/TiO<sub>2</sub>-NTs/Ti electrode is higher than the photo-response of the pristine TiO<sub>2</sub>-NTs/Ti. The photocurrent of PTh/g-C<sub>3</sub>N<sub>4</sub>/TiO<sub>2</sub>-NTs/Ti was drastically improved upon the addition of glutathione (GSH), which was attributed to the life improvement of the electron-hole pairs. Based on the enhanced photocurrent signal, a PEC methodology for ultrasensitive determination of GSH has been developed. Finally, the effects of solution pH and applied potential on photoelectrochemical response were studied and results showed that optimum supporting electrolyte is phosphate-citrate buffer solution (pH=5.0) and optimum potential is 2.0 V vs. Ag/AgCl reference electrode. It was found that the photocurrent of GSH was linearly dependent on the concentration of analyte in the range of 5 to 700 nM and the detection limit of GSH determination was found to be 1.0 nM.

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## Spectrophotometric Methods for Simultaneous Determination of Catechol and Resorcinol in their Binary Mixtures

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Catechol (1, 2-dihydroxybenzene, CT) and resorcinol (1,3-dihydroxybenzene, RS) are isomers of dihydroxybenzene, which usually coexist in biological and environmental samples [1]. They are produced during biological degradation processes, and are commonly found in a wide variety of industries such as the cosmetic, plastic, dye, and pharmaceutical ones [2]. These environmental pollutants are toxic to the humans, and are difficult to degrade in ecological environments [2]. Therefore, the development of reliable and readily accessible procedures for the simultaneous determination of their concentration is an interesting and demanding subject in environmental analysis [3].

Two novel spectrophotometric methods were successfully developed and validated for the determination of catechol and resorcinol in their binary mixtures. Those methods are well established methods namely ratio difference (RD) [4] and constant center (CC) [5] methods. Accuracy, precision and linearity ranges of the proposed methods were determined and the specificity was assessed by analyzing synthetic mixtures of both Materials.

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## A Combination of Molecular Docking, and Molecular Dynamics Simulation Studies of S-Trityl-L-Cysteine Analogues as Kinesin Eg5 Inhibitors.

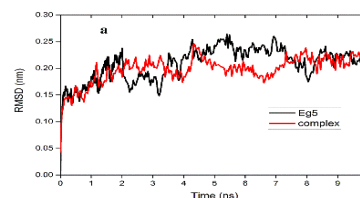
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kinesin Eg5, a member of the kinesin-5 superfamily, is responsible for the formation and maintenance of bipolar spindle in the early stage of mitosis. Since Eg5 plays a crucial role in cell division, inhibition of this protein causes mitotic arrest, which can lead to cell death. Therefore it is an interesting drug target for the design of potent inhibitors. In the past few years, a large number of chemicals were synthesized and evaluated as Eg5 inhibitors [1, 2]. In the recent years, Kosielski and coworkers introduced S-trityl-L-cysteine (STLC) as a potent Eg5 inhibitor [3]. Due to its high efficiency, new analogues of STLC with improved activity against Eg5 were synthesized by Wang and coworkers [4]. In order to know the interaction between these new STLC analogues as inhibitors and Eg5 an investigation of molecular docking and MD simulation were carried out in this work, in which two inhibitors (Mol 1, and Mol 2) were selected. Molecular docking was carried out by using the AutoDock 4.2 program. Preparation of protein (PDB ID code: 2WOG) and ligand was done using the AutoDock Tools. we performed MD simulations on Eg5 and optimal docked structures of Eg5 with 2-(((3-ethylphenyl)diphenylmethyl)thio)ethan-1-amine (Mol 2) as the most potent inhibitor. MD simulations were performed with the NAMD 2.9 program using the CHARMM 22 force field. The results obtained from docking show the binding pocket of Eg5 is mainly contributed by residues Thr112, Ile136, Pro137, Leu132, Ala133, Asp130, Gly117, Arg221, Arg119, Leu214, Glu116, Ala218, Trp127, Glu118 and Tyr211, which are similar to residue in the active site of 2WOG. Obviously, it is observed that the hydrophobic interaction plays significant role in the binding of inhibitors to Eg5 because of the presence of phenyl groups. In addition, docking result showed the presence of strong hydrogen bond between inhibitors and protein residues. Besides, in order to further investigate the binding mode and the conformation change of Eg5-inhibitor complexes in the presence of solvent MD simulation of Eg5 and Eg5-Mol 2 complex with lowest docked energy were successfully run for 10 ns scale. The RMSD value of protein backbone with simulation time was assessed in order to explore the dynamic stability of the complex. According to Fig. 1 the RMSD of Eg5 and Eg5-Mol 2 complex reach equilibration and oscillates around in average value after 2 ns simulation time. This indicates that the trajectory of the MD simulation is stable after 2 ns, so, it is reasonable to investigate binding pocket based on the snapshot extracted from 2 to 10 ns.

Fig. 1 The root mean square deviations (RMSD) for Eg5 (black) and Eg5-Mol 2 complex (red) in the MD simulation system.



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**Extraction and preconcentration of some organophosphorus pesticides in honey samples using an efficient and green pretreatment method followed by HPLC–UV determination**

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Pesticides are chemical compounds that are intended to control weeds, insects, herbs and pests [1]. In spite of many advantages of using pesticides in the agricultural activities like increase production volume and improve the appearance of grown foods, they can show a serious risk to human health because of either direct exposure or residues in food and drinking water [2, 3]. Organophosphorus pesticides (OPPs) are placed among the mostly used pesticides worldwide. They can reach the food chain and cause a potential threat to the consumers. OPPs can be toxic when they are absorbed by human organisms and may be life threatening because of acetyl–cholinesterase deactivation [4]. So, it is very important to develop convenient analytical methods for the survey of OPP residues in various samples. In this work, an efficient and green sample pretreatment method based on the combination of dispersive solid phase extraction and temperature–induced homogenous liquid–liquid microextraction has been developed for the extraction and preconcentration of some organophosphorus pesticides (parathion–methyl, triazophos, parathion, diazinon, and phoxim) in honey samples before their determination by high performance liquid chromatography–ultraviolet detection. In the proposed method, firstly, the analytes are adsorbed onto a sorbent (C<sub>18</sub>) dispersed into an aqueous sample by vortexing. Then cyclohexyl amine is used to desorb the analytes from the sorbent. In the next step, the obtained supernatant is mixed with water thermostated at 0 °C to obtain a homogenous solution. This solution is transferred into a heated water bath. During this process solubility of cyclohexyl amine in water is decreased and its produced fine droplets are dispersed in whole of the solution. The produced droplets go up through the solution and collected on top of the solution. Finally, an aliquot of the extractant is taken and injected into the separation system for analysis. Under the optimum conditions, limits of detection and quantification were in the ranges of 0.90–1.75 and 3.0–5.8 ng g<sup>-1</sup>, respectively. Enrichment factors and extraction recoveries were in the ranges of 148–183 and 59–73%, respectively. The relative standard deviations of the proposed method were ≤ 5% for intra– (n=6) and inter–day (n=4) precisions at a concentration of 25 ng g<sup>-1</sup> of each analyte. Finally, the proposed method was successfully applied to the analysis of the selected pesticides in 21 honey samples supplied from local vendors of different origins of West and East Azerbaijan provinces–Iran.

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**Study of binding interaction of Capecitabine with human serum albumin using spectroscopic and molecular dynamics simulation approach.**

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5-Fluorouracil (5-FU) has known a key anticancer drug that played an important role in the treatment of breast and gastrointestinal cancers, in either monotherapy or combination therapy with various cytotoxic drugs [1]. Capecitabine (CAP) is an orally administered prodrug of 5-FU, which make it a convenience option for self-administration. It is readily passes intact through the intestinal mucosa and is ultimately converted to 5-FU especially in tumor cells. This selectivity is achieved by the enzyme thymidine phosphorylase (TP), as a final conversion of capecitabine to 5-FU, that is more active in tumor cells compared with normal tissues [3]. Nowadays, binding of a drug to the plasma proteins play an important role in pharmacokinetics and pharmacodynamics. HSA as the most abundant protein in human blood plasma has the ability to bind reversibly a wide variety of drugs with higher affinity compared to other transport proteins. Drug-HSA interaction improves the drug solubility, decreases its toxicity and protects the drug's elimination from the human body [4]. This work reports a detailed study on the interactions between CAP and HAS by employing, molecular dynamics (MD) simulation, fluorescence, and absorption methods. MD simulation was performed on the CAP-HSA complex to investigate the stability of docked conformation and to study the binding interactions in detail. MD simulation was done with the NAMD 2.9 program using the CHARMM 22 force field. The capecitabine structure was parameterized to generate topology and parameter by using the swissparam server. Before the production run, the system was energy minimized and equilibrated using 1000 steps of steepest descent algorithm and subsequently 1000 steps of conjugate gradient algorithm. The system was subjected to MD simulation for 15 ns. The RMSD value of protein backbone with simulation time was assessed in order to explore the dynamic stability of the complex. The RMSD of CAP and CAP-HSA complex reach equilibration and oscillates around in average value after 2 ns simulation time. The average RMSD value of HSA and HAS-CAP complex from a 2-15 ns trajectory are  $3.107 \pm 0.05$  nm and  $2.773 \pm 0.03$  nm respectively. Moreover, the quenching mechanism associated with the CAP-HSA interaction was determined by performing fluorescence measurements at different temperatures. As shown in Table 1 the value of K<sub>sv</sub> for CAP-HSA decrease with increasing temperature, suggesting that CAP quenches the intensity of HSA through a static process. The thermodynamic parameters  $\Delta H^\circ$ ,  $\Delta G^\circ$ , and  $\Delta S^\circ$  were calculated, in which the negative  $\Delta G^\circ$  suggested that the binding of cytarabine to HSA was spontaneous, moreover the negative  $\Delta S^\circ$  and negative  $\Delta H^\circ$  revealed that van der Waals force and hydrogen bonds were the major forces to stabilize the protein-cytarabine (1:1) complex.

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**Effect of a protrombin activator isolated from Iranian *Echis carinatus* venom on hemostasis**

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*Echis carinatus* venom is a complex mixture of toxins. This venom contains metalloproteinases which convert prothrombin to meizothrombin. The prothrombin activator leads to the formation of small blood clots inside the blood vessels throughout the body. To understand the effect mechanism of Iranian *Echis carinatus* venom, in this study we investigated the effect of EV on human plasma proteins (prothrombin and fibrinogen) and on blood coagulation. The aim was the purification and characterization of procoagulant factor from the Iranian *Echis Carinatus* venom and the evaluation of the procoagulant activity on human plasma.

Crude venom from the Iranian snake species *E. carinatus* was selected. The prothrombin activator was purified from the crude venom of *Echis carinatus* by combination of the procedures by gel filtration and ion-exchange chromatography. The sample was applied into a Superdex G-75 column and fractions were collected at 4°C and their absorbances were recorded at 280 nm. Than sample was loaded into ion exchange column (DEAE-Sepharose) and equilibrated with 50 mM Tris-HCl buffer, pH 8.2 and eluted with a liner gradient of NaCl concentration from 0.0 to 0.5 mM. The peaks were monitored at 280 nm.

The Iranian *E. carinatus* venom was able to coagulate human plasma very rapidly. The coagulation time was reduced from 13.4 seconds (SD= ±0.59) to 8.6 seconds (SD= ±0.64) when human plasma was treated with crude venom (concentraion of venom was 1 mg/ml).

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Preparation, spectroscopy study of the inclusion complex of Neurontin drug  
with  $\beta$ -cyclodextrin

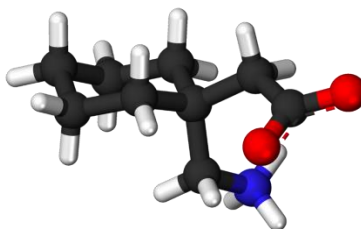
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Neurontin is an anticonvulsant and analgesic drug that stirs more and more the interest of the researchers. Neurontin is an adjuvant anticonvulsant drug for the treatment of refractory partial seizures. Subsequently, it was shown to be effective in treating a variety of chronic pain conditions. The cyclodextrin inclusion complex was well done in enhancing drug solubility, stability and bioavailability [1,2]. The inclusion complex of Neurontin with  $\beta$ -cyclodextrin was prepared and characterized by ultraviolet spectroscopy (UV-Vis), fourier transform infrared spectroscopy (FTIR) and <sup>1</sup>HNMR. The stoichiometry was established using Job's method and mole ratio method. The stoichiometry ratio was also determined to be 1:1 for the inclusion complex of  $\beta$ -CD with drug. The stability constant was calculated by using a modified Benesi-Hildebrand equation at 25 °C. The apparent formation constant obtained was 810 L/mol. Phase solubility equilibrium plot was obtained for  $\beta$ -CD complex. According to the method reported by Higuchi and Connors, the diagram was classified as a typical A<sub>L</sub>-type, where the stoichiometry of the inclusion complex was determined to be 1:1 in consistent with the result from spectroscopy study. The antioxidant activity of drug and its inclusion complex were determined by the scavenging of stable radical DPPH. Kinetic studies of DPPH with GBP and  $\beta$ -CD complex were done. The experimental results confirmed the forming of neurontin complex with  $\beta$ -CD also indicated that the drug/ $\beta$ -CD inclusion complex was the most reactive than its free form into antioxidant activity[3].



Neurontin drug

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**A highly improved sensor for selective detection of dopamine in human plasma samples using a luminol–KMnO<sub>4</sub> chemiluminescence system in the presence of nano-structured layered double hydroxides**

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In recent years, there has been a great deal of interests in the development of chemiluminescence (CL)-based sensors due to their wide linear dynamic range, relative simple and inexpensive instrumentation, no interference from background scattering light and versatility for the determination of a wide variety of species [1]. Enhancement of CL intensity via the choice of the appropriate solvent, catalyst, or surfactant is of great importance to improve the sensitivity of CL detection systems. Recent reports show that nanomaterials can act as catalysts to amplify the emission of CL systems. Due to their unique physicochemical properties, many CL systems based on different kinds of nanomaterials have been developed [2]. Layered double hydroxides (LDHs) are an important class of host-guest layered nanomaterials consisting of positively charged metal hydroxide sheets with charge-balancing intercalated anions and water molecules. LDHs exhibit a well-defined layered structure with relatively large surface area, high porosity, high layer charge density and interlayer anion mobility [3]. In the present study, we reported on a simple, sensitive and selective chemosensor for determination of dopamine in human plasma samples. It is based on the inhibitory effect of dopamine on the chemiluminescence signal of KMnO<sub>4</sub>–luminol system, which could be improved by at least 10-folds in the presence of LDHs. The possible mechanism to explain this finding was studied. The structure and morphology of the synthesized LDHs were characterized by x-ray diffraction, Fourier transform infrared spectroscopy, transmission electron microscopy and scanning electron microscopy. Several parameters affecting the analytical signal such as concentration of luminol, KMnO<sub>4</sub>, NaOH and LDH were optimized. This simple CL approach showed a limit of detection of 8.5 ng L<sup>-1</sup> and exhibited a linear response in the concentration range from 0.025 to 20 µg L<sup>-1</sup>. In addition, the method exhibited high specificity toward dopamine over other species, metal ions or anions. The method was successfully applied to determine dopamine in several human plasma samples.

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**Dual wavelength thermal lens spectroscopy as a detection system in microchip for determination of mercury after rotative liquid-liquid microextraction**

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It is first time that a dual wavelength (DW) laser was used as a source in thermal lens spectroscopy (TLS). In that way, one wavelength acts as excitation beam and the other acts as probe beam. The biggest advantage of this system is having high sensitivity of dual-beam method [1] and it has the simplicity of single beam method at the same time. We perform DWTLs as a detection system in a glass microchip [2] for determination the trace amount of mercury in environmental samples after rotative liquid-liquid microextraction (RLLME) [3]. Dithizone was used as a chelating agent that extract mercury in organic phase [4]. In this step extraction solvent, pH, dithizone concentration, solvent value, extraction time and salt concentration was optimized. This method was used for determination of mercury in many samples such as tap water, well water, seawater and industrial waste water that a high percentage of recovery achieved.

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## Voltammetric determination of total phenol with potato tissue on a paper based analysis device

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Among of all the pollutants, phenols have the notoriety because of their strong stability, great harmfulness and poor biodegradability [1]. Therefore, determination of phenols by efficient, fast and low cost methods have been developing [2]. In the recent years, the miniaturization of analytical systems has become an interesting research section [3]. In this research, the paper based electrochemical nanobiosensor as simple and fast device was developed by immobilization of the nanoparticles and potato tissue at fiber matrices of the paper disc. For determination of total phenol in aqueous media in this direction, the propylamine functionalized silica nanoparticles was dropped on the paper disc. After being dried at room temperature, the potato tissue in phosphate buffer solution as the source of the polyphenol oxidase was immobilized at fiber matrices of the paper disc via physical adsorption. After drying, this paper disc was placed on the top of the graphite screen printed electrode and was connected to potentiostat/ galvanostat electrochemical device. Electrochemical characterization of this biosensor was studied by cyclic voltammetry and electrochemical impedance spectroscopy methods. After optimization of effective parameters such as pH and potato tissue percentage, phenol measurements were done by differential pulse voltammetry method. This biosensor showed a linear response for phenol in the wide concentration ranges of 0.10-160  $\mu\text{M}$  with a detection limit about 0.07  $\mu\text{M}$  (3) and limit of quantification about 0.23  $\mu\text{M}$ . The selectivity against some interferences and real sample analysis were studied and showed good applicability for this paper based device. This method has some advantages such as simplicity, demanding a little sample for analysis and do not require specialized users.

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**Application of metal-organic frame work (MOF) as a very efficient sorbent for the separation and determination trace amount of anthracene in various real samples**

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In this work, a novel metal-organic frame work (MOF) as a very efficient sorbent in dispersive solid phase microextraction method is synthesized and applied for the separation/preconcentration of anthracene (An) and its determination by fluorescence spectroscopy [1-3]. The properties of the synthesized MOF were characterized by Fourier-transform infrared (FT-IR) spectroscopy and X-ray diffraction (XRD). To examine the most important parameters including amount of MOF, extraction time, concentration of the analyte and pH of the solution and their interactions in the microextraction optimization procedure, a four-factor central composite design (CCD) combined with response surface modeling (RSM) was implemented [4]. Under optimum conditions, the enrichment factor (EF), relative standard deviation (RSD) and limit of detection (LOD) of the method were found to be 40, 2.1%, and 0.57 ng mL<sup>-1</sup>, respectively. Finally, the proposed method was successfully applied for the selective determination of trace amounts of An in fruit and water samples.

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## The third-order nonlinear optical properties of Gold Nanoparticles-Methylene Blue conjugation

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Third-order nonlinear properties of a thiazine dye (methylene blue (MB)) and a plasmonic nanoparticle (gold nanoparticles (GNPs)) have been studied by Z-scan method with a 50 mW diode pumped solid state laser (DPSSL) operating at 532 nm. The nonlinear parameters (nonlinear refractive (NLR) index ( $n_2$ ) and nonlinear absorption (NLA) coefficient ( $\beta$ )) are determined. The mechanism of the observed NLA and nonlinear refraction is attributed respectively to reverse saturable absorption (RSA) and thermal nonlinear effects. The magnitude of the measured NLR index ( $n_2$ ) and NLA coefficient ( $\beta$ ) are founded to be the order of  $10^{-8}$  cm<sup>2</sup>/W and  $10^{-4}$  cm/W respectively. The effect of MB and GNPs on each other has been studied. Z-scan experiments for GNPs-MB conjugation shows noticeable increase in nonlinear parameters.

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**Peak extraction and noise reduction of IMS signal based on wavelet transform algorithm**

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Signal processing is an integral technique in the analysis of ion mobility spectrometer's (IMS) data. IMS data are especially appropriate for wavelet transform because of the uniform Gaussian peak shapes of spectra. These peaks need to be distinguished from higher frequency signals such as noise signals. Today, wavelet transform is one of the most common compression and denoising methods applied to IMS data [1]. This transform is a mathematical transformation for graded decomposing signals [2]. Wavelets admit complex data to be decomposed into elementary forms at different positions and scales and finally reconstructed with high accuracy. Signal transmission is based on transmission of a series of numbers. The series representation of a function is important in all types of signal transmission. The wavelet representation of a function is a new technique that is the improved version of Fourier transform. In this paper, we present an improved algorithm that combines the continuous wavelet transform (CWT) and discrete wavelet transform (DWT) to find out the advantages of wavelet transform compared to Fourier transform. The raw data used in this study has been acquired from a home-made ion mobility spectrometer which designed and constructed in Institute of Material and Energy. The results revealed that the proposed method has a good performance to find peaks and reduce the noise.

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**Cathodic electropolymerization of 4-nitroaniline and preparation a new weak anex for application in analysis of some compounds**

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In this work ,4-nitro aniline was electropolymerized on Pb cathode under constant current condition (10mA).The electrochemical cells were separated by a thin layer of agar and catholyte was sodium acetate.After 10 hours a black product was precipitated. It was collected and after purification by soxhlet it was characterized by CV ,FT-IR and DSC .A suitable mechanism for electrode reaction was proposed.The electrode-product was soluble in DMSO. The obtained result showed that the electrode product contains NH<sub>2</sub> and polymerization was carried out through NO<sub>2</sub> group. The prepared polymer was coated on a suitable solid support and was used for separation of some compounds like soluble flavenoides from various samples before measuring by HPLC .The synthesized polymer showed high tendency towards phenolic compounds. Consequently a high preconcentration factor and high percentage of extraction were achieved [1-3].

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**Design and construction of Portable Columnless Gas Chromatography- Ion Mobility Spectrometry (PCGC-IMS) for identification of contraband materials**

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A mass spectrometer at normal pressure was the dream of the analytical people for a long time. It became realistic in the 1990s. Modern analytical IMS is an atmospheric pressure ionization method for detection of vapors. The primary ionization event is usually affected by a  $^{63}\text{Ni}$  (beta radiation) ion source. A series of ion-molecule reactions ensue involving primary, background, and analyte vapors, and an equilibrium mixture of ions is established. The ions are electrically injected into a drift region and move under the influence of an electric field through a reverse flow of buffer gas (air or nitrogen) until collision occurs with a Faraday cup detector. Charged ionic species move primarily according to their mass and shape (size) and are characterized by their drift time (typically several milliseconds) or ion mobility [1]. When detecting narcotics, it is necessary to vaporize compounds with a wide range of molecular weights. In order to do this, the desorber has to be set to a high temperature. A benefit of operating the desorber in this way is the evaporation of all chemicals in a very short time and, in turn, accommodation of the quick analysis requirement during field use. A drawback to this high temperature operation is the reduction of the detectability of each chemical and sometimes causes interference problems [2]. There are two ways to eliminate or to reduce this phenomenon of decreased detectability. One is to pre-separate mixed chemicals using a gas chromatography (GC) column placed before the IMS reaction region. GC-IMS instruments have been reported successful in the separation of chemical mixtures [3]. Although these approaches have demonstrated their potential in solving the separation problem, the total analysis time was more than a couple of minutes. This is unacceptable to users when performing daily routine analyses of samples obtained for illicit drug detection. Another way is to evaporate chemicals based on their vapor pressure by applying a temperature ramping process to the sample. In this way, overcrowding in the reaction region with chemicals is avoided. Columnless GC-IMS is a valuable alternative technique for the isolation of volatile compounds from non-volatile solid, semi- solid and, occasionally, liquid matrices. This paper addresses, the design and construction of a home-made novel portable columnless gas chromatography - ion mobility spectrometry (IMS) system for rapid screening of narcotics for the first time in institute of Materials and Energy of Isfahan. Desorber of this instrument works by controllably releasing analytes from a solid sample by thermally desorbing and releasing a selected subset of compounds through rapidly raising the temperature to a pre-determined value that has been chosen to desorb particular chemical compounds of interest, but not others. By providing a sufficiently long delay period in-between heating, and by selecting the optimum temperatures, then different chemical species can be controllably released in well-defined batches at different times to an IMS.

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**Platinum nanoflowers on zein nanoparticles-wrapped multiwall carbon nanotubes as a new composite to modify glassy carbon electrode for living tumor cells monitoring**

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During the past two years, due to progress in nanotechnology, a great concern has arisen for monitoring of living tumor cells using hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) as a reliable biomarker by employing different electrode devices with various nanocomposite modifiers [1]. In this study, an efficient free-enzyme biosensor was constructed using electrochemically deposition of platinum nanoflower (PtNF) [2] on a glassy carbon electrode (GCE) modified with multiwall carbon nanotubes/zein bio-nanocomposite which was characterized by X-ray diffraction, field emission electron microscopy as well as transmission electron microscopy. The electrochemical studies and measurements were carried out by using cyclic voltammetry, amperometry and linear sweep voltammetry. Under an amperometric sensing, the sensor provided attractive electrocatalytic performances for sensitive and selective enzyme-free detection of H<sub>2</sub>O<sub>2</sub> within a linear concentration range of 1.0 nM to 215.0 μM H<sub>2</sub>O<sub>2</sub> with a detection limit of 15.0 nM H<sub>2</sub>O<sub>2</sub> in 0.1 M phosphate buffer at pH 7.2. Furthermore, the biosensor was successfully checked for being utilized in living tumor cells monitoring through nanomolar level probing of H<sub>2</sub>O<sub>2</sub> as released from both human dermal fibroblasts (HDF) and human hepatocellular carcinoma cells (HepG2; liver cancer cell).

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**Lanthanum-incorporated MCM-41 composite as peroxidase mimetics for glucose detection**

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In this study, lanthanum-containing mesoporous MCM-41 (La-MCM-41) were synthesized and were used for colorimetric detection of glucose. The synthesized composite were characterized by X-ray diffraction (XRD), Fourier-transform infrared spectroscopy (FT-IR) and scanning electron microscopy (SEM) (Fig.1). The prepared La-MCM-41 provided high intrinsic peroxidase-like activity in the presence of peroxidase 3,3',5,5'-tetramethylbenzidine (TMB) and H<sub>2</sub>O<sub>2</sub> for accurate determination of glucose. This process produced a blue colour in aqueous solution that directly relates to H<sub>2</sub>O<sub>2</sub> concentration[1]. The effect of different parameters such as the content of incorporated lanthanum, pH and temperature on the peroxidase-like activity was studied. The colorimetric detection of H<sub>2</sub>O<sub>2</sub> was led to a linear dynamic range from 50 to 1000 μM ( $r^2 = 0.9988$ ) for glucose in aqueous solution(Fig.2). These results are comparable (close to) or better than some previous reports.

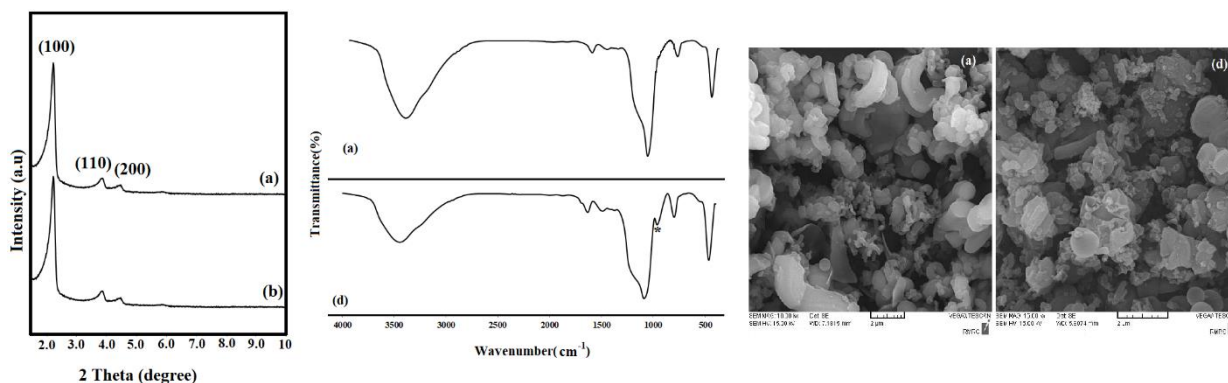


Fig1. XRD Patterns, FT-IR spectra and Scanning electron micrographs of (a) MCM-41, (b) La-MCM-41.

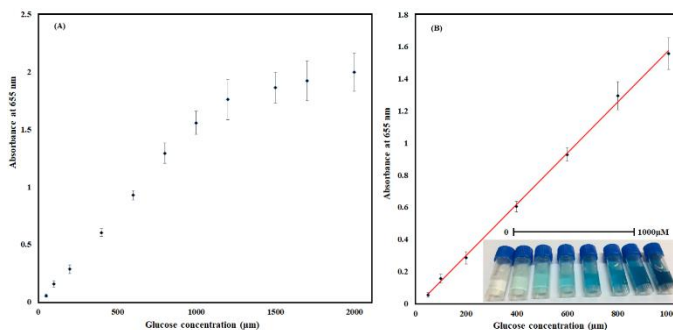


Fig.2 Absorbance vs. glucose concentration in presence of GOx and La-MCM-41

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**Application of magnetic molecularly imprinted polymer for extraction and determination of antihypertensive drugs from biological samples**

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Hypertension is a progressive cardiovascular syndrome with a variety of causes, including cardiovascular risk factors that can lead to changes in heart and blood vessel function and structure. Therefore, hypertension, as a chronic disease, has negative effects on human health and is the main cause of cardiovascular-disease related deaths, further increases disability-adjusted life year and death [1]. Valsartan (VAL) is a promising angiotensin II receptor blocker which is rapidly absorbed from GI tract after oral administration but suffers from the drawbacks of poor oral bioavailability of about 23% primarily due to its lack of solubility in the acid milieu of the GI tract [2]. For some of antihypertensive drugs a low level of concentration, normally in ng/mL occurs in human plasma after oral administration, posing problems for their detection and/or monitoring. A sensitive method should thus be established to detect these drugs in bodies of human beings.

In this work, a rapid and simple method for the extraction and preconcentration of VAL in biological samples using magnetic molecularly imprinted polymer (MMIP) was developed. The superparamagnetic Fe<sub>3</sub>O<sub>4</sub> particles prepared by the coprecipitation method were coated successively by SiO<sub>2</sub>, vinyl end groups and molecularly imprinted polymer (MIP) shells to afford a pomegranate-like core/shell superparamagnetic particle (Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>@MIP). Finally, the Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>@MIP particles were successfully applied to simultaneously enrich and separate VAL. The separation of VAL was reached in less than 5 min using a C<sub>18</sub> column and an isocratic binary mobile phase (acetate buffer- pH 4: water (50:50, v/v)) with flow rate of 1.0 mL min<sup>-1</sup>. Influence variables such as Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>@MIP amount, volume of desorption solvent, pH and extraction time were screened. The significant variables were optimized by using a Box–Behnken design. At optimum conditions values of variables set as 12 mg sorbent, 1 mL methanol, pH = 3 and 18 min extraction time.

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**Analysis of effective parameters of Columnless gas chromatography ion mobility spectrometry by response surface methodology for improving instrument capability**

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The Chemometrics is a science of using mathematics and statistics to help chemists in designing optimal experimental procedures and providing maximum relevant chemical information[1]. The focus of this article is on the modeling and optimization of Column less gas chromatography ion mobility spectrometry (CLGC-IMS) parameters for the detection of narcotics. Column less gas chromatography ion mobility spectrometry is a sensitive, portable, robust, short response and low priced sensor that has a variety of potential applications. CLGC-IMS has the potential to yield low cost suitable sensors for narcotics detection and identification [2]. However, the low sensitivity of (CLGC-IMS) and the presence of memory effect make it difficult for the detection and identification of interested chemicals. Response surface methodology (RSM) is a kind of mathematical and statistical technique for designing experiments, building models, evaluating the relative significance of several independent variables, and determining the optimum conditions for desirable responses [3]. The effects of the duty cycle of the pulse width modulation, carrier gas flow and drift tube temperature were investigated by Central composite design (CCD).The results showed that the quadratic model is fitted well the experimental results in this work.

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**A novel strategy based on surfactant-assisted solvent stir bar microextraction for trace analysis of nitrite in environmental water samples**

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Nitrite is a common surface and groundwater contaminant that causes acute and chronic toxic effects in humans and animals. Thus, monitoring the concentration of nitrite in water sample sources is one of the major analytical tasks of water quality control management. Several methods including, electrochemical technique, fluorometric method, and paper microfluidic device have been reported for the determination of the nitrite ion in different matrices [1, 2]. Recently, a novel form of hollow fiber liquid phase microextraction (HF-LPME) namely solvent bar microextraction (SBME) has been introduced. SBME provides higher pre-concentration factor and the enhanced mass transfer of analyte from donor solution into the extraction solvent in comparison with HF-LPME due to the random and free movement of the fiber [3, 4]. A new design introduced for the preconcentration of nitrite in environmental water samples using surfactant-assisted two phase solvent stir-bar microextraction (SSBME), followed by microcell UV-Vis spectrophotometry. The method relies on the reaction of nitrite with iodide excess in acidic donor phase to form triiodide, and then its extraction into organic acceptor phase using tetrabutylammonium bromide (TBAB) as a cationic surfactant. The main parameters in detail that affect the triiodide formation and the extraction efficiency (SSBME procedure) investigated and optimized. Under the optimized conditions (extraction time 8min., stirring rate 300 rpm., donor phase 50 mL, acceptor phase 10  $\mu$ L, organic solvent 1- Octanol) the proposed method provided good linearity in the range of 16 to 1000 ng mL<sup>-1</sup>, satisfactory repeatability (RSDs < 6 %) with preconcentration factor of 250 fold. Finally, the developed method successfully applied to the determination of nitrite in environmental water samples. The proposed method has some advantages in comparison with the other methods for nitrite determination including, simplicity of operation, generation of little or no waste, low cost of the extraction device, no memory effect due to the single-used and disposable nature of hollow fiber, low solvent consumption and environmental benignity with wide application prospects in trace analysis.

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Application of dispersive liquid-liquid microextraction in the determination of remained Diazinon and by-products in a combined Fenton-anaerobic biological treatment process

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In this work dispersive liquid-liquid microextraction followed by gas chromatography equipped with flame ionization detector (DLLME-GC-FID) was used to determine Diazinon concentration before and after coupled Fenton-anaerobic biological treatment. Also, dispersive liquid-liquid microextraction coupled with gas chromatography-mass spectrometry (DLLME-GC-MS) was used for the detection of Diazinon's by-products after the Fenton and biological oxidation steps. In this extraction method, a mixture of 70  $\mu$ l chloroform (extraction solvent) and 1.0 ml methanol (disperser solvent) was rapidly injected into the 5.0 ml water sample by syringe [1]. Thereby, a cloudy solution was formed. In fact, the cloudy state was created because of the formation of fine droplets of chloroform, which were dispersed in the sample solution. In this step, the Diazinon in water sample was extracted into the fine droplets of chloroform [2]. After centrifuging (5 min at 6000 rpm), the fine droplets of chloroform were precipitated in the bottom of the conical test tube ( $50 \pm 10$   $\mu$ l). The precipitated phase (1.0  $\mu$ l) was injected into the GC column. The GC-Mass analysis was utilized to characterize the intermediates such as Cyanthoate, Sulfotep, and Diazoxan which are produced during the Fenton step. It was indicated that Fenton process is not capable to mineralize Diazinon, completely and toxic intermediate compounds such as Diazoxan was produced. So, using the integrated processes including biological and chemical oxidation for complete degradation of these intermediates is necessary. Different experiments were done to reach the optimum condition for the integrated treatment. According to the obtained results, treatment by Fenton process which was done by using 1 ppm  $\text{Fe}_2\text{SO}_4 \cdot 7\text{H}_2\text{O}$  and 5 ppm  $\text{H}_2\text{O}_2$  within 30 minutes followed by biological treatment within 96 hour led to 89.4% removal of Diazinon. Diazinon concentration was determined at each step by using GC-FID analysis.

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## Voltammetric determination of 2,4-dichlorophenoxyacetic acid using poly L-methionine-AuNPs /PGE

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2,4-dichlorophenoxyacetic acid (2,4-D) and its derivatives are from phenoxy or phenoxyacetic acid herbicide family which belong to one of the largest herbicides group. 2,4-D is a white crystalline solid with chemical formula  $C_8H_6Cl_2O_3$ . These type of herbicides family are popular among the farmers because of their low cost, effectiveness even in low doses and good water solubility [1]. Ingestion, skin contact and inhalation are three main of human exposure to 2,4-D herbicides [2]. Due to their broad range of application and excessive usage, they have becoming a serious problem as they can cause pollution to the environment. 2,4-D causes an array of adverse effects to the nervous system: disruption of the activity of nervous system chemicals and behavioral changes. The researchers also postulated a possible association between exposure to 2,4-D and cancer in humans. For the given reasons, measuring this compound is very important in environmental samples. Some reported methods for measuring this herbicide include gas chromatography [3] and high performance liquid chromatography [4]. In this project, an electrochemical method is used to measure this herbicide. To prepare the modified electrode, the pencil graphite electrode (PGE) first are placed in a solution containing carbon nanotubes and chitosan for a specified period, and then it was dried in room temperature. The pencil electrode is then subjected to a voltammetric cell containing a specified amount of methionine and Au(III) solution and then a composite from poly methionine and gold nanoparticle were placed on the electrode surface using cyclic voltammetry. After electrode preparation and its drying, the oxidation current of 2,4-D was measured at different concentrations in optimum pH 5.0. In order to achieve the best voltammetric response for the sample, electrode components and other effective parameters were optimized and then 2,4-D was determined using differential puls voltametric method. The linear dynamic range was obtained as 10-100  $\mu$ m.

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## Determination and Quantitation of Methadone in Syrup by Ion Mobility Spectrometry

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Methadone hydrochloride is used for the treatment of severe pain and for the treatment of dependence on opioid drugs. pharmacological dosage regimens is a prerequisite to the success of most treatments [1]. Methadone syrup contains the various ingredients. Concentration of Methadone hydrochloride in syrup should be 5mg/mL. Furthermore, variable dose of it hasn't effect on patients treatment. Therefore, methadone dosage should be individually determined and quantitated [2]. In this work, First, the extraction steps optimized and then methadone concentration determined with gas chromatography- mass spectroscopy (GC-MS) and Ion mobility spectrometry (IMS) methods and then, the results were compared together. In this study, IMS was developed to quantitate methadone hydrochloride in syrup. The aim of this work has been the development of ion mobility spectrometry (IMS) technique which designed and constructed in Institute of Materials and Energy, preceded by a extraction step optimized for the analysis of methadone hydrochloride. Several samples of the syrup were extracted and analyzed with these two methods. Test results of IMS and GC-MS were compared with statistical and chemometrics methods. Results revealed that the performance of IMS and GC-MS in identification and quantification of methadone in syrup are almost the same.

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**Synthesis of g-C<sub>3</sub>N<sub>4</sub>-PDA as a new adsorbent for efficient micro extraction of Pb(II) and Cu(II) metal ions: OPTIMIZATION BY MULTIVARIATE ANALYSIS**

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Due to the growth of industry, environmental pollution by heavy metal ions have increased [1]. Copper and lead are two common types of heavy metals that even at low concentrations threaten human health [2]. Therefore, the determination of these metals in the environment is very important. There are various methods for separation of these metal ions. The SPE method due to simplicity, high speed, low amounts reagent and also more environmentally friendly, has been very much considered[3]. But, in this method, a completely uniform dispersion of the solid phase in the sample solution is very important. In the present work a new method named "effervescent-assisted dispersive micro solid-phase extraction" (EA-D $\mu$ -SPE) was used. In this method due to used the solid effervescent agents in sample solution, the interactions between co-polymer with analyte was increased that lead to the dispersion of the adsorbent occurs in a short times. As the result, the extraction efficiency was increased. In this work, a graphitic carbon nitride modified with polydopamine (g-C<sub>3</sub>N<sub>4</sub>-PDA) was successfully synthesized, and used for extraction of the Pb(II) and Cu(II) ions by using effervescence-assisted dispersive micro-solid phase method. The structure of the g-C<sub>3</sub>N<sub>4</sub>-PDA co-polymer was corroborated by FT-IR, XRD, FE-SEM analysis. Then, the extraction ions were quantified by micro sampling-flame atomic absorption spectrometry ( $\mu$ S-FAAS). The limits of detection (LODs) was obtained 0.16 and 0.06  $\mu$ g L<sup>-1</sup> for Pb(II) and Cu(II), respectively. Also, the relative standard deviations (%RSDs, for n = 3) was obtained 1.14 and 1.2% for Pb(II) and Cu(II), respectively. In addition to, the adsorbent was reused for 8 times with negligible changes in the extraction recoveries (more than 99%). In order to achieve optimal conditions, the central composite design (CCD) method was used as a statistical method. This method was also applied successfully for the simultaneous detection of the Pb(II) and Cu(II) ions in the real samples of water and sunflower oil.

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**Gas Chromatographic Fingerprint Analysis of Secondary Metabolites of *Salvia Reuterana* Combined with Antioxidant Activity Modelling Using Multivariate Chemometric Methods**

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Chromatographic fingerprinting is widely used for classification and authentication of several samples such as plant extracts. Gas Chromatography (GC) is a common instrument for fingerprinting of natural samples. On the other hand, plants are noticeably used as important sources of antioxidant compounds. Due to the various biological activities such as antioxidant activity, *Salvia Reuterana* has been used in Iranian traditional medicine among the 58 *Salvia* types [1]. In addition, due to the complexity of natural sample matrices and lack of selectivity in analytical instruments, multivariate chemometric methods have been largely used to extract maximum useful information from chromatographic fingerprints [2]. In the present work, a chemometrics-based strategy is proposed for GC fingerprints analysis of *Salvia* and modeling their antioxidant activity. On this matter, ultrasonic-assisted extraction-dispersive liquid-liquid microextraction (UAE-DLLME) was used for extraction of chemical components of twenty eight *salvia* samples from eight populations. The optimum extraction conditions were obtained using factorial based response surface methodology (RSM). The optimum extraction parameters were 60 mg of powdered aerial parts of dried *Salvia* sample, 2.5 mL of methanol as first extraction solvent, 45 min first sonication time, 40°C extraction temperature, 30  $\mu$ L of tetrachloroethylene as preconcentration solvent, 2 min second sonication time and NaCl 7% (w/v) [3]. The GC profiles were arranged in a data matrix and this data matrix was mean-centered, baseline corrected and aligned using correlation optimized warping (COW) method before cluster analysis. The data matrix was then analyzed using principal component analysis (PCA), hierarchical cluster analysis (HCA) and *k*-nearest neighbors (*k*NN) clustering methods to explore similarities and dissimilarities among different *Salvia* samples according to their secondary metabolites. Evaluation of the PCA score plot (explaining 85.8% of variance accounted for three PCs) showed that *Salvia* samples belong to six clusters. In order to specify borderlines between classes, the degree of class separation (DCS) was calculated. These results were then confirmed by HCA and *k*NN and six clear-cut clusters were determined using HCA and *k*NN dendrograms. For antioxidant activity measurement, 30  $\mu$ L of the extracted *Salvia* sample and 20  $\mu$ L methanol (99.9%), were added to 5 mL of 1,1-diphenyl-2-picryl-hydrazyl (DPPH) (50  $\mu$ M). After 30 minutes at room temperature, absorbance was measured at 517 nm [4]. The values of inhibitory concentration (IC<sub>50</sub>) were then arranged in a data vector. The profiles of preprocessed chromatograms were auto-scaled and modeled by partial least squares-regression (PLS-R) to correlate *Salvia* clusters to their antioxidant activity. The optimum number of LVs (respectively explaining 74.32% and 97.5% of variance accounted for six LVs for **X**- and **y**-blocks) in PLS model was determined using error rate (ER) values obtained by leave-one-out cross-validation. The classification figures of merit including calibration regression coefficient and RMSECV were respectively 0.9779 and 0.01674. The PLS score plot represented 6 different classes that confirmed the clusterig results obtained by PCA score plot, HCA and *k*NN. Finally, variables were decreased using variable importance in projection (VIP) method and the most important components which affect the antioxidant activity were detected. It is concluded that the poroposed strategy in this work can be used for classification of chromatographic fingerprints of natural samples and modelling of their antioxidant activity according to their class separation.

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## Loading cobalt phthalocyanine onto graphene: preparation of an active photocatalyst

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A conventional method for the preparation of graphene oxide (GO) was used. This method describes as Hummers' method ( $\text{KMnO}_4$ ,  $\text{NaNO}_3$ ,  $\text{H}_2\text{SO}_4$ ) which is most common method used for preparing graphene oxide. Nitrogen-doped graphene (NG) sheets were also prepared by thermal annealing graphite oxide using melamine as source of nitrogen. Reduced graphene oxide (RG) was also synthesized by hydrazine hydrate. The products were characterized by XRD, UV-Vis, EDX, SEM, Elemental Maps Analysis and FTIR. It was shown that parts of the cobalt phthalocyanine (CoPc) immobilized onto (GO), (NG) and (RG) layers. The photocatalytic activity of the CoPc/GO, CoPc/NG and CoPc/RG were evaluated. The degradation efficiency of the produced photocatalysis dichlorophenol DCF were tested under visible light irradiation. CoPc/NG showed the best efficiency and nearly complete degradation of DCP occurs with 135 min.

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**Chemically modified a magnetic graphene oxide nanoparticles based micro solid phase extraction for effective pre-concentration of highly toxic metal ions from food stuff sample**

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With the rapid development of industrialization, heavy metal contamination has become an important environmental problem, that leading to serious health problems for human beings[1]. There are various methods for separation of the metal ions. The SPE method has been very much considered among of the available methods. On the other hand, the nature of the adsorbent in SPE effectiveness is so important. So far, various carbon-based nanoadsorbents including graphene oxide (GO), carbon nanotubes (CNT), and activated carbon (AC) have been provided, and their use on a variety of environmental pollutants have been investigated. Graphene oxide (GO) has attracted more attention in recent years. GO contains various effective functional groups such as hydroxyl, carboxyl and epoxy to combine with heavy metals to efficiently adsorb heavy metals[2]. However, time-consuming separation of GO is as a problem (due to the use of centrifuge step). In order to improve performance of GO-based adsorbents, usually, the GO surfaces were modified. In the current research, for the first time a magnetic graphene oxide (GO-Fe<sub>3</sub>O<sub>4</sub>-DA) modified with dopamine (DA) was successfully synthesized. Fe<sub>3</sub>O<sub>4</sub> nanoparticles were selected for two purposes: i) easy separation of adsorbent from soluble target analyte ii) graphene oxide connection to the surface of Fe<sub>3</sub>O<sub>4</sub> nanoparticles as a functional group for increasing the metal ion adsorption[3]. The structure of the synthesized nano-adsorbent was confirmed by XRD, SEM, FT-IR and VSM analysis. In this work a new method based on SPE was used to enhance the interactions in the shortest possible time. This technique named “effervescent-assisted dispersive micro solid-phase extraction (EA-D $\mu$ -SPE). in this method was used the dispersant reagents in the sample solution, that lead to increased interactions of adsorbent with analyte and decreased of extraction time. Eventually, the extraction ions were quantified by micro sampling-flame atomic absorption spectrometry (  $\mu$ S-FAAS). The limits of detection (LODs) was obtained 0.5, 0.03 and 0.7  $\mu$ gL<sup>-1</sup> for Pb(II), Cu(II) and Ni(II), respectively. Also, the relative standard deviations (%RSDs, for n = 3) was obtained 1.09%,1.25% and 1.03% for Pb(II), Cu(II) and Ni(II), respectively. This method was also applied successfully for the simultaneous detection of the Pb(II), Cu(II) and Ni(II) ions in the real samples of water and sausages (herbal and meaty).

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**Extraction and determination of monocyclic aromatic hydrocarbons (BTEX) in urban air with solid phase nano-extraction**

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The BTEX are volatile monoaromatic hydrocarbons that comprise one of the most ubiquitous and hazardous groups of ambient air pollutants of concern [1] The objective of this research was to develop a simple, low-budget, and accurate method by solid phase nano-extraction (SPNE) for quantification of BTEX in ambient air based on SPNE -GC-FID.

The electrospinning technique was successfully used to create nano-fiber of the polydimethylsiloxane/polyacrylonitrile as a synthesis SPNE coating. Standard 20 mL head-space vials were used for field air sampling and calibration. SPNE experimental conditions, such as extraction time, extraction temperature, desorption time, desorption temperature, were optimized using one-at-time. The optimum conditions were extraction time 40 min, extraction temperature 25°C desorption time 5 min and desorption temperature 250 °C. Under these conditions, calibration curve in the two range for benzene and toluene 20-1000  $\mu\text{g}/\text{m}^3$  and ethylbenzene and xylene 5-1000  $\mu\text{g}/\text{m}^3$  were linear with  $R^2= 0.998, 0.997, 0.998$  and  $0.998$ , respectively. The repeatability at two concentration levels (50 and 400  $\mu\text{g}/\text{m}^3$ ) was calculated. Relative standard deviations were 10-12%, 9.1-10.7% and 9.3-11.9% for inter-day, intra-day and fiber-to-fiber, respectively. The limit of detection and limit of quantification were found 0.3-2.8 and 1-9.6  $\mu\text{g}/\text{m}^3$ . The relative recoveries were obtained from 91-105%. Air samples were collected from the bus station and analyzed by the mentioned method. The mean concentration of ethylbenzene and xylene in the air samples were 6 and 8  $\mu\text{g}/\text{m}^3$ , respectively.

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## Design and construction of portable ion trap-ion mobility spectrometer for monitoring of organic particles

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A nonlinear novel ion source ion trap interface for an ion mobility spectrometer has been developed for sliding generation, accumulation and focusing of ions produced by Ni<sup>63</sup> ionization. The interface improves sensitivity efficiencies compared conventional IMS by factors of 50-90. With these improvements, it is possible to increase in detection limits of analytes. We demonstrate the approach for several narcotics and an assessment of the detection limits is given. Additionally, we demonstrate the utility of the approach in the field of narcotics detection. Based on this approach a portable ion trap ion mobility spectrometer (IMS) was designed and fabricated in Institute of Materials and Energy[1]. This design consists of Fast Sampling and Injecting (FSI) system coupled with ion trap IMS. FSI design provides fast and easily applied method for real time injection of real sample accompanied by particles with no additional sample preparation. Required analysis cycle time for each run is less than 15 sec. The high sample load and sharp injection decrease the peak widths, and improve detection limits[2]. In addition for coupling of ion trap to IMS detector and other considerations in hardware design, miniaturization of IMS cell was done to increase sensitivity and selectivity and decrease warm up time. Data analysis was enhanced with adapted short time Fourier transform algorithm[3]. This homemade customized instrument is an alternative to other time consuming technologies for monitoring of organic particles in real samples without sample preparation.

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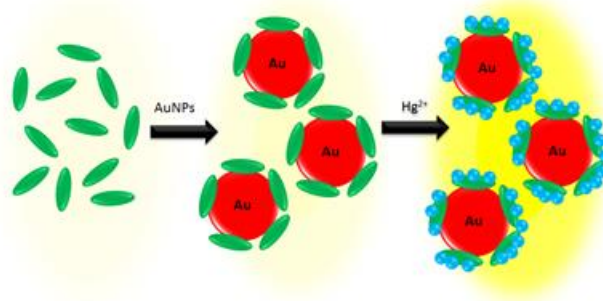


## Turn-on Fluorescence Detection of Mercury(II) Ion using a Triazole thiol indole Derivative and Gold Nanoparticles

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Development of simple, rapid and cost-effective methods for detection of mercury ions in environmental samples has a great importance due to the serious health risk of  $\text{Hg}^{2+}$  ions poses to human [1]. A new and sensitive fluorescent nanosensor was proposed for  $\text{Hg}^{2+}$  detection based on covalent bonding of S-H group [2, 3]. The design of the nanosensor was carried out using a new synthetic organic ligand which was a derivative of Triazole thiol indole. The ligand was assembled on the chemically prepared gold nanoparticles (Au NPs) to enhance the sensitivity and repeatability of the response [4]. The proposed nanosensor showed a fluorescence emission at 477 nm by exciting at 360 nm. Upon the addition of  $\text{Hg}^{2+}$  ions, the fluorescence intensity of the probe increased linearly in the range from  $1 \times 10^{-7}$  to  $5 \times 10^{-6}$  mol  $\text{L}^{-1}$  with detection limit of  $4.8 \times 10^{-8}$  mol  $\text{L}^{-1}$ . The strategy offered excellent selectivity toward  $\text{Hg}^{2+}$  in comparison with other metal ions. Meanwhile, this sensor was applied to determine  $\text{Hg}^{2+}$  ions in some water samples with satisfactory recoveries (94.3-103.7%).



Schematic representation of the proposed fluorimetric sensor for determination of  $\text{Hg}^{2+}$  ion concentration

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**Development of electromembrane extraction method by reusable membranes**

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Membrane technology is the most promising process for contaminations separation operation if the hydrophilicity, fouling and reusability properties could be improved. Superhydrophobicity property of the membrane surface diminishes interaction between the contaminations and membrane surface. This causes a reduction in the fouling tendency and self-cleaning characteristic. There are many methods to produce superhydrophobic properties such as layer-by-layer assembly, anodic oxidation grafting fluoroalkylsilane (FAS) on the membrane surface and electrospinning [1]. Electromembrane extraction (EME) has gained a lot of popularity among the researchers because of their aforementioned unique potentials such as high selectivity and high pre-concentrations [2].

In this study, we are focusing on fabricating a flat polymeric membrane that can be used in EME setup. Therefore, for the first time, reusable polyacrylonitrile (PAN)/polydimethylsiloxane (PDMS)/TiO<sub>2</sub> nanofibrous flat membranes were fabricated by electrospinning process. The prepared membranes were characterized by FT-IR, AFM, EDAX, SEM and contact angle analysis. After that, their performance in electromembrane extraction of some ionizable phthalates, as model molecules were investigated. The affecting parameters on EME method were optimized by CCD experimental design. The optimum conditions were 200 V, 20 min, 1100 rpm, 10 ml and 1 ml for voltage, time, agitation rate, volumes donor and acceptor phases, respectively. Under these conditions, calibration curves in the range of 1-200 and 100-4000 ng/ml for diethylhexyl phthalate (DEHP) and dibutyl phthalate (DBP) are linear with R<sup>2</sup>>0.990. The repeatability at two concentration levels (20 and 100 ng/ml) for DEHP and two concentration levels (15 and 2000 ng/ml) for DBP and at concentration of 200 ng/ml for the membrane-to-membrane were calculated. Relative standard deviation were less than 7, 9 and 12% for inter-day, intra-day and membrane-to-membrane, respectively. The limits of detection were found (0.08 and 7.4 ng/ml) and limits of quantification were (0.25 and 21.06) for DEHP and DBP, respectively. Three kinds of waters were used as real samples and the recoveries of those compounds in spiked water samples at a concentration of 20-2000 ng./ml were obtained from 86-107%. On the optimum conditions the reusability study was performed too. The obtained results showed that the prepared membranes can be used at least 10 cycles without any loss in performance, as their RSD% was less than 6%

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**A systematic approach to study functionalization of MCM-41**

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The pore size of mesoporous silica is large enough to accommodate a variety of species to convert them to affective sensors. The high density of silanol groups on the pore wall is beneficial to the introduction of functional groups with a high coverage. Actually, various kinds of surface modifications have been conducted in providing new functions for the surfaces [1]. Among various functional groups, the introduction of the amino groups onto the mesoporous materials have great interests for preparation of sensors, catalysts and adsorbents. In this study functionalization of mesoporous MCM-41 was done using 3-aminopropyltrimethoxysilane (APTS) *via* post-synthesis method. We tried to find optimal conditions for functionalization by variation of the solvent, temperature and time [2]. Studying the adsorption behavior of methyl orange (MO) onto the functionalized MCM-41 as an anionic dye was also performed [3]. Characterization of the modified MCM-41 was studied by BET, FTIR, XRD and UV-vis. The results obtained by now show that n-hexane as solvent, temperature of 65 °C and a period of 6 h are adequate to provide high concentration of functional groups onto MCM-41. The high amount of ATPES concentration onto mesoporous MCM-41 increases the amount of methyl orange dye adsorption.

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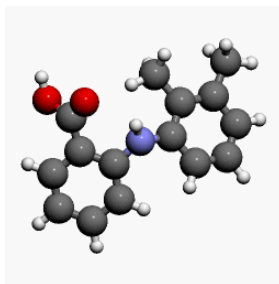


**Spectroscopy study of synthesis and stability of inclusion complexes of 2-(2,3-dimethylphenyl)aminobenzoic acid with beta cyclodextrin in aqueous solution**

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2-(2,3-dimethylphenyl)aminobenzoic acid belongs to a family of nonsteroidal anti-inflammatory drugs (NSAIDs) [1]. The main objective of this study was to synthesize the host-guest inclusion complexes of 2-(2,3-dimethylphenyl) aminobenzoic acid with beta-cyclodextrin and study of stability and solubility of drug/ $\beta$ CD by UV-Vis FT-IR and <sup>1</sup>HNMR spectroscopy. The UV absorption maximum of drug appears at 335nm. Cyclodextrins (CDs) are cyclic oligosaccharides of  $\alpha$ -(1,4) linked D-glucose units in a ring formation containing a relative hydrophobic central cavity and hydrophilic outer surface. The synthesis involved a series of protection and deprotection reaction. The experimental results revealed that the inclusion process is a spontaneous process [1]. The enhancement of drug solubility in the presence of  $\beta$ -CD was detected. The stability constants were calculated by data to Benesi-Hildebrand equation [3]. Solubility studies demonstrated the formation of the drug/ $\beta$ CD inclusion complex with 1:1 stoichiometry. antiactivity of 2,2-diphenyl-1-picrylhydrazyl (DPPH $\cdot$ ) with drug and cyclodextrins complexes were done. The experimental results that the inclusion complexes of drug- $\beta$ CD was the most reactive than its free form into antioxidant activity [2]. All these techniques revealed that 2-(2,3-dimethylphenyl)aminobenzoic acid form inclusion complexes with  $\beta$ -CD in aqueous solution.

**2-(2,3-dimethylphenyl)aminobenzoic acid****References**

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## Application of $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-NH}_2$ for extraction of diclofenac from environmental waters and its determination with HPLC

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Diclofenac (DFC) is a non-steroidal antiinflammatory pain reliever drug. It is often used for the treatment of rheumatoid arthritis, ankylosing spondylitis, osteoarthritis, and sports injuries. The determination of the low level of DFC in pharmaceutical and biological samples is very important for medical and pharmaceutical practical aspects where it is used for the treatment of various diseases. The determination of the low level of DFC in pharmaceutical and biological samples is very important for medical and pharmaceutical practical aspects where it is used for the treatment of various diseases [1]. Several methods have been reported for the determination of diclofenac in pharmaceutical preparations or biological fluids, such as high-performance liquid chromatography (HPLC), spectrophotometry, high-performance thin layer chromatography, capillary zone electrophoresis and electrochemical detections [2]. In this work a simple, rapid and novel method for the extraction and preconcentration of DFC in water samples using amino-functionalized  $\text{Fe}_3\text{O}_4@\text{SiO}_2$  core-shell magnetic nanomaterial was developed. The properties of particles were characterized by Transmission electron microscopy transmission Scanning electron microscopy and X-Ray Diffraction. The  $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-NH}_2$  particles were successfully applied to simultaneously enrich and separate DFC. The separation was reached in less than 5 min using a  $\text{C}_{18}$  column and an isocratic binary mobile phase (acetonitrile: water (70:30, v/v)) with flow rate of 1.0 mL min<sup>-1</sup>. Influence variables such as pH,  $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-NH}_2$ , volume of desorption solvent and extraction time were screened. The significant variables were optimized by using a central composite design (CCD). At optimum conditions values of variables set as pH = 4, 12 mg sorbent, 0.5 mL methanol, and 10 min extraction time.

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**Activity enhancement of platinum electrocatalyst supported on functionalized carbon nanotubes by amide groups**

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Insufficient catalytic activity and durability are key barriers to the commercial deployment of low temperature polymer electrolyte membrane (PEM). On the other hand, oxygen reduction reaction (ORR) is one of the key processes of energy systems. The ORR sluggish kinetics requires a substantial amount of Pt, which has limited the scaling-up of technologies [1]. Recent observations suggest that carbon-based catalyst support materials can be doped with nitrogen to create strong, beneficial catalyst-support interactions which substantially enhance catalyst activity and stability. Pt-loading onto multi wall carbon nanotubes (MWCNTs) which has a large specific surface area and good conductivity has been reported as a successful approach for reducing the cost of catalysts [2,3]. In this study, Pt nanoparticles were placed on amide modified-MWCNTs (Pt/MWCNTs-A) and used as electrocatalyst for reduction of oxygen. Pt/MWCNT-A nanocomposite was characterized by scanning electron microscopy, Fourier-transform infrared spectroscopy and energy dispersive X-ray spectroscopy.

After impregnation of catalyst ink on the gas diffusion layer, the electrodes were dried at 80°C for 8 h to form gas diffusion electrode (GDE). Catalyst coated membrane electrode (CCME) was prepared with hot pressing a Nafion 117 membrane and GDE having an active area of 0.785 cm<sup>2</sup> with Pt/MWCNT catalysts of 0.5 mg cm<sup>-2</sup> loading at the cathode side. The CCME is placed inside a homemade half-cell which is used as an ex situ method in fuel cell studies. The CCME electrochemical studies including polarization curves, EIS measurements, cyclic voltammetry and chronoamperometry were used to study electrochemical properties of obtained electrocatalyst.

It was found that Pt/MWCNT-A was catalytically more active than Pt nanoparticles decorated on MWCNT. On the other hand, the Pt/MWCNT-A catalyst has satisfactory stability and improve catalytic activity in continues cycling makes it more attractive for fuel cell applications.

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## Protein-Based Electrochemical Nanobiosensor

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Ferritin is a globular protein complex consisting of 24 protein subunits to form cage architecture of 12 nm diameter with an interior cavity of 8 nm diameter in which a hydrated ferric oxide/phosphate is mineralized. Mammalian ferritins consist of H- and L-chains (heavy and light chains, respectively). The H-subunit encodes the ferroxidase site, which oxidizes the iron (II) ion and produces the iron (III) hydroxide cores. In the assembled form, ferritin L chains are known to have a greater negative charge on their interior, with clusters of glutamates and aspartates that make up the nucleation site. Ferritin has been used as a biological template for nanomaterial synthesis. In addition to Fe, ferritin can also encapsulate other electroactive materials such as CdS, Co, Co:Pt, Ni, Pd, Mn, and Pt, making ferritin suitable for electrochemical biosensor fabrication [1-2]. In this study, manganese nanoparticles (MnNPs) were created within horse spleen apoferritin (HsAFr) cavity nanotemplates. Then, these MnNP-HsAFr were incorporated into the surface of a carbon electrode using a two-step process. CS polymer film containing MCWNTs was deposited on the electrode surface by drop coating. Then, MnNPs-HsAFr was immobilized onto MWCNTs entrapped into CS matrices by covalent glutaraldehyde (GA) cross-linking. GA has had great success because it is commercially available and inexpensive in addition to its high reactivity. It reacts rapidly with amine groups at around neutral pH and is more efficient than other aldehydes in generating thermally and chemically stable cross-links. [3]. CS contains large numbers of  $-NH_2$  and  $-OH$ , and it has been used as a modifying reagent to construct modified electrode due to its excellent biocompatibility, nontoxicity, cost effectiveness, and high mechanical strength. CS has been selected as an orientation directing matrix due to possessing large quantities of amino and hydroxyl groups on its units, which have a strong binding ability to biomolecules. However, it is a nonconducting biomaterial, therefore compounds with good conductivity such as CNTs need to be combined with CS to achieve a high-performance biosensor [4]. Generally speaking, two immobilization methods were postulated.

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**Determination of cadmium in water samples by stir bar sorptive–dispersive microextraction and flame atomic absorption spectrometry.**

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Stir bar sorptive–dispersive microextraction (SBSD $\mu$ E), has been applied as a novel, fast and simple method, for the preconcentration and determination of trace amounts of Cd (II) ions in water samples. SBSD $\mu$ E is a new microextraction technique that combines the principles of stir bar sorptive extraction (SBSE) and dispersive micro solid phase extraction (D $\mu$ SPE). In this method magnetic sorbent, that magnetically is coated on a neodymium stir bar, dispersed in the sample solution at high stirring rate as D $\mu$ SPE method and re-attracted to magnetic bar when stirring is stopped alike SBSE. Then stir bar is eluted by an appropriate solvent, which is used for analysis. This approach is benefited from the advantages of SBSE and D $\mu$ SPE, including high extraction recovery, no need to an external stirring device that avoids potential analytes losses, easy to apply, lower extraction time because of dispersion of sorbent in sample solution and more variety sorbents by using different coated magnetic composites [1].

In this work, Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>@ZnO core–shell microspheres that have been used as magnetic sorbent were prepared by a simple three-step method. The synthesized composite was characterized by Fourier transform infrared spectroscopy (FTIR), field emission scanning electron microscopy (FESEM) and X-ray diffraction (XRD) analysis that illustrated Fe<sub>3</sub>O<sub>4</sub> microspheres coated with two distinct nanolayers, silica and ZnO [2]. After elution of stir bar by proper solvent, cadmium ions were determined in eluent by flame atomic absorption spectrometry (FAAS). The effective factors on extraction of Cd (II) were investigated and optimized. For optimization of adsorption conditions (pH, stirring rate, salt effect and extraction time), response surface methodology (RSM) was used as a strong statistical technique. Elution condition (type of eluent, eluent concentration, eluent volume and elution time) were optimized with one variable at a time optimization method. Under the optimal conditions, linear range of SBSD $\mu$ E method was 1-150 ng mL<sup>-1</sup>, the relative standard deviations ( RSD% ) at 80ng mL<sup>-1</sup> concentration level was 3.7% (n=5), the limit of detection was 0.37ng mL<sup>-1</sup>. The proposed microextraction analytical method was successfully used for determination of ultra trace amounts of cadmium in water samples (tap water, river and well).

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Effects of the Ni-based MOFs structure as a case study on the extraction process

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Metal organic frameworks (MOFs) are an attractive class of porous materials, which have exciting features such as high surface area, great potential for post synthetic modification and good thermal stability. Here as a case study, effects of the shape and size of the pores in the nanostructured MOFs on the adsorption and extraction of analytes were investigated. For this purpose, two MOFs based on Ni<sub>2</sub>(1,4-benzene dicarboxylic acid)<sub>2</sub> triethylenediamine were synthesized adapting two different methods. Although in both methodologies identical constituents were employed, discriminated crystallographic and morphological structures were produced. The method based on the solvothermal methodology (MOF1) led to the cubic pores, and the one at room temperature (MOF2), gave trigonal and hexagonal pores<sup>[1]</sup>. The main aim in this study was to investigate whether the MOF cages have any possible influence on the extraction efficiency of some molecules in which their sizes are compatible with the size of the cages. The synthesized nanoscale MOFs were characterized by PXRD, BET, TGA, FESEM and FT-IR. Extraction experiments were performed in a headspace needle trap extraction setup using chlorobenzenes (CBs) and benzene homologs including benzene, toluene, ethylbenzene and xylene (BTEX). After performing the extraction, the entrapped analytes were thermally desorbed and transferred into gas chromatography-mass spectrometry (GC-MS)<sup>[2]</sup>. To evaluate the effects of pore size on the extraction and adsorption selectivity, CBs and BTEX were selected as analytes and their extraction were examined by the two synthesized MOFs. Results show different patterns for extraction of benzene, toluene and monochlorobenzene, which could be related to the size of trigonal pores in MOF2. These pores apparently, can trap these three molecules based on size similarity between them and trigonal cages. The performance of MOF2 toward CBs and BTEX was favorable. Influencing parameters affecting the extraction process were optimized<sup>[3]</sup>. Eventually, the developed method was validated by GC-MS. At the optimum conditions, the relative standard deviation (%RSD) values for a double distilled water fortified with the selected CBs at 100 ng L<sup>-1</sup> were 5-12% (n = 6) while the limits of detection results were between 2-10 ng L<sup>-1</sup>. The linear dynamic range was ranged from 6 to 1000 ng L<sup>-1</sup> (R<sup>2</sup> > 0.988). Finally the developed method was applied to the analysis of some rivers and tap water samples and the relative recovery values were in the range of 85-96%.

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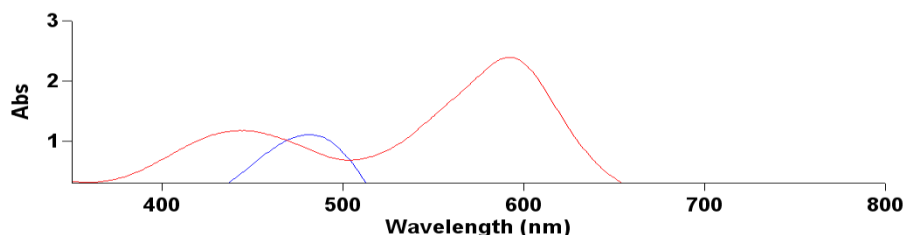
**Development of Spectrophotometric method for detection of trace of lead in aqueous ethanol system without using a preconcentration step.**

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Lead is in focus of analytical chemists for a very long time due to its toxicity and its widespread use as a material in a variety of application including water piping, soldering, the printing industry, ballast, shielding, bullets, batteries, additive in gasoline pigment, and many others[1]. Naturally, The preconcentration steps slow the analytical process, which is a drawback when a large number of samples are to be analyzed. UV-Visible spectrophotometry employ less expensive instrumentation and is more suitable for automation of analytical procedures.[2]

A modification of the dithizone Spectrophotometric method for determination of lead has been developed in this work by working in an aqueous ethanol system(80% ethanol by volume) and extraction and any Preconcentration step is avoided. The complex formation of lead in aqueous ethanol system with dithizone was completed rapidly at room temperature. The average molar absorption coefficient was found to be  $1.16 \times 10^7$  L mol<sup>-1</sup> cm<sup>-1</sup>. Two linear calibration graphs were obtained for 0.1-1 mg/L and 1-10 mg/L of pb(II). The interference from over 20 cations, anions has been studied at 3 mg/L of pb(II). The maximum absorbance were observed in the pH 11 and in  $\lambda_{max}$  500nm. The standard deviation and %RSD of the method for ten determination of 3 mg/L of pb(II) is 0.00988 and 1.2%. This cost-effective sensing system allows for rapid and facile determination of pb(II) ions in aqueous sample.



**Figure 1. Spectrophotometric absorbtion curves in 80% ethanol. Lead dithizone(blue), Dithizone(Red)**

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**Monitoring reaction of biodiesel production with Near-IR spectroscopy and chemometrics methods**

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The purpose of this study, was using Near infrared spectroscopy for on-line monitoring of the biodiesel production in the presence of homogeneous base catalyst by spectroscopic – chemometrics method. [1,2]The homogeneous NaOH base catalyst used to investigate the chemical reaction of the biodiesel production , Near IR spectroscopy was employed to obtain data from reaction solution at different time and spectral data were processed by software techniques to monitoring the reaction. MCR-ALS method was used as a Process analytical technology (PAT) tool to extract analytical information from reaction of biodiesel production and information about of certain pure component spectra and pure component concentration profiles which were created during the process of production was investigated. [3]

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**Glassy carbon electrode modified with a layer of single-walled carbon nanotube and polypyrrole doped with new coccine: Application to the sensitive electrochemical determination of Salbutamol**

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Carbon nanotubes (CNTs), discovered by Iijima in 1991 [1], have attracted the attention of scientists in many research fields such as chemistry, physics and material science, due to their extraordinary structural, mechanical, chemical and electronic properties. CNTs display high electrical conductivity, high surface area, good mechanical strength, high elasticity and tensile strength and excellent thermal and chemical stability [2]. Conducting polymers (CPs) are conjugated polymers, which have similar electronic properties (magnetic, conductivity and optical) to metals, while retaining properties of conventional organic polymers [3].

A promising electrochemical sensor was developed based on a layer by layer process by electropolymerization of pyrrole in the presence of new coccine (NC) as dopant anion on the surface of the single-walled carbon nanotubes (SWCNTs) pre-coated glassy carbon electrode (GCE). The modified electrode was used as a sensitive electrochemical sensor for voltammetric determination of salbutamol (SAL). The electrochemical behavior of SAL was investigated on the surface of the modified electrode using linear sweep voltammetry (LSV). The results showed a remarkable increase (~60 times) in the anodic peak current of SAL in comparison to the bare GCE for 5  $\mu\text{M}$  SAL. The effect of experimental variables such as, drop size of the casted SWCNTs suspension, pH of the supporting electrolyte, accumulation conditions and the number of cycles in the electro-polymerization process on the electrode response was investigated. Under the optimum conditions, the modified electrode showed a wide linear dynamic range of 0.04-0.1  $\mu\text{mol L}^{-1}$  and 0.1-1  $\mu\text{mol L}^{-1}$  with a detection limit of 1.3  $\text{nmol L}^{-1}$  for the voltammetric determination of SAL. The prepared electrode showed high sensitivity, stability and good reproducibility in response to SAL. This sensor was successfully applied for the accurate determination of trace amounts of SAL in pharmaceutical and clinical preparations.

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## A new procedure for ultratrace determination of lead in a single phase water-ethanol system by fluorescence measurements

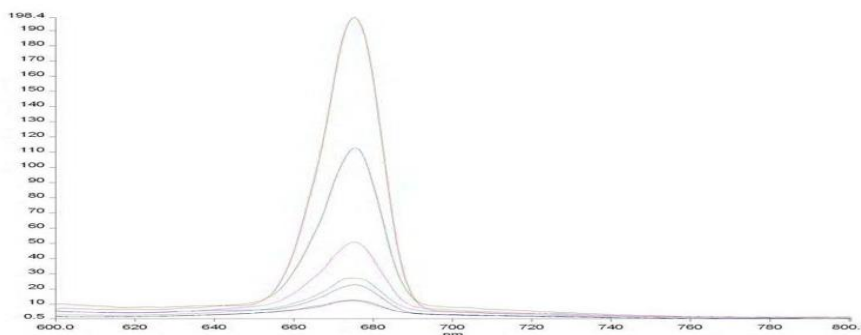
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Lead is cumulative poison[1] that enters the body from lead water pipes, and lead based paints. Lead pollution is a serious danger to the environment and human health[2-3]. Lead intake causes many fatal diseases including disfunction of renal, blood and neurological systems. Lead (II) easily deposits in blood, kidney, reproductive system, nervous system and brain and cause lead poisoning[4]. Even low levels of lead in children cause brain and neurodevelopmental diseases[5]. Hence the determination of trace amounts of lead is important for environmental monitoring and this demands sensitive and accurate determination of lead.

In this work a new procedure was found for determination of lead(II) in aqueous ethanol system. The proposed method is based on the complex formation between of lead(II) and dithizone. The parameters such as pH, concentration of dithizone, and solvent ratio was optimized at pH 6, concentration of dithizone  $1.16 \times 10^{-5} M$ , and solvent ratio (50 % ethanol by volume). The fluorescence intensity (excitation/emission maxima 450/670) of Pb-Dtz complex was proportional to the concentration of  $Pb^{2+}$  ions in the range of 2.63nm-0.26 $\mu m$  with linear correlation coefficient ( $R^2 = 0.993$ ) and LOD(S/N=3) of 0.5ppb and %RSD = 3. Fig 1. Fluorescence intensity graph in the different concentration of  $Pb^{2+}$



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**Investigation of Disulphiram compounds on metallic ions**

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New optode membranes for the sensitive and selective determination of Zinc(II) ion based on a change in the absorption of a polymer film is proposed. The interaction between sulfide bis (2-propoxycarbonyl), with various cations containing :  $\text{Cu}^{2+}$ ,  $\text{Hg}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Ag}^+$ ,  $\text{Fe}^{3+}$  and  $\text{Mn}^{2+}$  in Acetonitrile as a solvent was studied by spectrophotometry method and the results have exhibited interaction between SBPT and different Cations. The membranes composed of plasticized poly vinyl chloride (PVC) , plasticizers , additive and SBPT as a ionophore were prepared. The influence of some parameters such as time , nature of plasticizers and membrane composition on the response of sensors were investigated and membranes with optimum composition were selected. The optodes of 5, 6 and 7 respectively have a dynamic range  $4.36 \times 10^{-11} \text{M}$  to  $4.42 \times 10^{-4} \text{M}$  ,  $4.3 \times 10^{-10} \text{M}$  to  $4.01 \times 10^{-3} \text{M}$  and  $1.9 \times 10^{-9} \text{M}$  to  $2 \times 10^{-4} \text{M}$ . optical sensors based on SBPT respectively, exhibited detection limit  $4.36 \times 10^{-11} \text{M}$ ,  $4.3 \times 10^{-10} \text{M}$  and  $1.9 \times 10^{-9} \text{M}$ . The sensors have a response time 6 minutes.

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**Chemical hard modeling as a new approach for designing optimum chemical sensor arrays based on indicator displacement assay**

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The superior features of cross-reactive colorimetric sensor arrays have made them very attractive in the past two decades. In the sensor array system, a group of responses provided by semi-selective sensor elements, produce a distinct pattern (signature of each analyte) for the identification and discrimination of several analytes<sup>[1]</sup>. Colorimetric sensor arrays have been widely explored as a method of detection and discrimination for a range of analytes (i.e. metal ions, amino acids, pesticides)<sup>[2]</sup>. Indicator displacement assays (IDAs) with simple metal ions or complexes as receptors are typically not very selective, but they are well suited for building colorimetric sensor arrays. In indicator displacement assays (IDAs) a suitable indicator must be able to reversibly bind to the receptor, also the analyte must be able to bind to the receptor<sup>[3]</sup>. In the presence of analyte, the binding equilibrium between indicator and receptor would be altered because of competitive binding, which would cause changing optical properties of indicator, which are sensitive to the analyte total concentration. Recently, it has been noticed the sensitivity and selectivity of an IDA can be modulated by simply altering ratios and concentrations of a receptor–indicator couple<sup>[4]</sup>.

In this study, the IDA system has been applied as sensor elements, due to knowing the chemical model of this system, it is possible to design optimum sensor array in order to qualitative and quantitative determination of mixtures of analytes. In our research a couple consisting of pyrocatechol violet (PV) and Cu<sup>2+</sup> (indicator and receptor respectively) in different concentrations produce the sensor array. Using complexation constants for equilibrium reactions between indicator and receptor, and [equilibrium](#) constant for displacement of analytes with indicator, the optimum concentrations of receptor and indicator have been computed by chemical hard modeling, and then the results of hard modeling optimization have been practically used for simultaneous determination of two different amino acids in different samples. Linear and nonlinear calibrations have been used for the prediction of amino acids concentration in different mixtures.

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**Optimization of ZSM-48 zeolite desilication parameters for catalytic conversion of methanol to hydrocarbon using experimental design and response surface methodology**

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The MTH is considered one of the widely used technologies for production liquid hydrocarbon from biomass, natural gas, and coal [1]. The most important limitation in microporous zeolites is the diffusion limitation which is the consequence of blocking the micropores [2]. The existence of mesopores in zeolites promotes the reactants access to active sites [3]. The medium pore zeolites have been widely used for conversion of methanol to aromatics due to suitability of medium size pores for the ring formation in aromatic production.

The present work reports ZSM-48 catalyst design for the methanol to liquid hydrocarbon conversion. Mesoporous ZSM-48 zeolite was prepared through desilication at optimized conditions by employing central composite design (CCD) under response surface methodology (RSM). The temperature of desilication ranges between 40 and 80 °C and NaOH concentration was varied between 0.1 and 0.3 M. The software gave thirteen (13) runs experiment within the conditions. Optimal results showed that to achieve a high BET surface area and medium pore diameter, the temperature of treatment and concentration of NaOH should be at 60 °C and 0.15 M respectively. The reliability of the model used was successfully validated by additional tests. Analysis of variance (ANOVA) study suggested the equation to be significant for the desilication with major impact of sodium hydroxide concentration on the desilication than temperature. Statistical results showed a  $R^2$  of 0.95 and 0.98 for temperature and NaOH concentrations, respectively. The influence of the post-synthesis desilication on the pore characteristics, crystallinity, morphology and acidity of the catalyst obtained under the optimal conditions was examined using  $N_2$ -adsorption, XRD, SEM and  $NH_3$ -TPD. Optimised catalyst presented a BET surface area of  $260 \text{ m}^2 \text{ g}^{-1}$  and mean pore diameter of 5 nm. The prepared catalyst was used to methanol to hydrocarbon conversion in a fixed-bed stainless-steel reactor at 390 °C and weight hourly space velocity of  $2.5 \text{ h}^{-1}$ . Over modified ZSM-48 zeolite,  $C_4$  and aromatic production was promoted. The yield of liquid hydrocarbon over this catalyst was increased about 35% and catalytic life time increased about 8% relative to microporous ZSM-48.

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## Influence of Mo (VI) on modified graphene in excellence of low cost composite activity over the noble metal for hydrogen evolution reaction in acidic media

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Sustainable hydrogen production from water splitting is one of the most attractive methods for energy storage and conversion. Hydrogen evolution reaction is the production of hydrogen through the cathodic process in water electrolyzers. Pt exhibits excellent electrocatalytic activity in HER, but the scarcity and high prices of the noble metals prohibit their widespread applications [1]. The excellent electrocatalytic performance along with high abundance in earth and low-cost alternative to the precious metals has made Mo gradually become a rising star in clean energy fields. The several reports molybdenum (VI) complexes were used for H<sub>2</sub> production [2]. In this perspective, for first time the complex of Mo (VI) supported functionalized graphene ([Mo-f-rGO]) has been investigated as a catalyst for H<sub>2</sub> production. To provide the Mo ligands, GO was covalently modified with groups contained nitrogen and oxygen atoms. The performance of [Mo-f-rGO] catalysts can be improved by accompanying some noble metals. In contrast to Pt and Au, Pd is relatively cheaper than Pt and Au. In this paper were showed [Pd/Mo-f-G] catalysts to be significantly more active than either Pd or Mo alone for H<sub>2</sub> production in acidic media. In Figure 1(a-b), FTIR spectra and SEM image of the (Pd/Mo-f-rGO) are illustrated.

The synthesized samples with the various amounts of Pd and Mo complexes were evaluated as the HER electrocatalysts in 0.5 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub> solution. Several electrochemical techniques such as cyclic voltammetry (CV), linear sweep voltammetry (LSV) and electrochemical impedance spectroscopy (EIS) were employed to determine the optimized composition for HER. Results showed that the addition of Mo complex to the Pd- functionalized graphene, makes the possibility of decrease the Pd amount in composite, with no activity drop. The composite with 5 wt% of Mo complex + 5 wt% of Pd, showed the onset overpotential ( $\eta_{\text{onset}}$ ) of -83 mV, equal to the composite with 10 wt% of Pd. The obtained results and same activity of 5 wt% Mo complex + 5 wt% Pd compared to 10 wt% Pd guarantees the new synthesized structure application in acidic HER with the lowering of noble metal amount and decrease of electrocatalyst price.

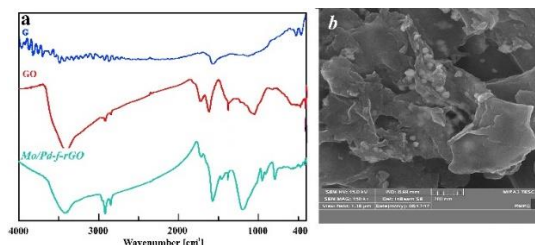


Figure1. (a) FTIR spectra the pristine G, GO and (Pd/Mo-f-rGO) and (b) SEM image of the (Pd/Mo-f-rGO).

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**Application of modified SBA-15 adsorbent with DABCO ligand for solid phase extraction of Cr(VI) ion from water environments**

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Trace detection of heavy metals and their effects is an important subject. Chromium is regarded as being one of the main pollutants in environmental samples. Chromium exists in the environment as Cr(III) and Cr(VI) oxidation states, but Cr(VI) can have acute and chronic toxic including carcinogenic effect. Cr(VI) ion is a well-known and widespread industrial contaminant which inflicts severe health problems to skin, mucous membranes, tooth and respiratory, etc. Meanwhile, the selective determination of Cr(VI) has been a longstanding analytical challenge and is of particular importance due to much higher level of toxicity compared to its counterpart (i.e., Cr(III)) [1-3]. The USEPA has set the concentration of 0.1 mg L<sup>-1</sup> for total chromium in drinking water as “maximum contaminant level goals”, whilst the WHO has established the guideline value of 50 µg L<sup>-1</sup> for Cr(VI) [4].

The crucial issue of the study is synthesis of novel nanocomposite suitable for sorption of selected species of chromium. Modified SBA-15 with 1,4-diazabicyclo[2.2.2]octane (DABCO) demonstrates selectivity toward chromium(VI) ions in the presence of Cr(III) at pH 5. The SBA/DABCO nanocomposite was characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM) and powder X-ray diffraction (XRD). The nanocomposite was used as solid sorbent in preconcentration of Cr(VI) ions from water samples and their determination using flame atomic absorption spectrometry.

The main factors affecting the extraction efficiency such as pH value, sample volume, eluent concentration and volume, amount of sorbent and coexisting ions have been investigated and established. In addition, under the optimal conditions the linear range, limit of detection, enrichment factor and relative standard deviation were found to be 2.0-400.0 µg/mL, 0.05 µg/mL, 83.3 and 2.68 %, respectively. The maximum adsorption capacity calculated based on the Langmuir adsorption model was 25 mg g<sup>-1</sup>. Finally, the method was successfully applied to the separation and preconcentration of Cr (VI) ion from tap, river and wastewater samples.

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**Dispersive liquid-liquid micro-extraction combined with high-performance liquid chromatography-UV-vis detection for the determination of fluorescein in biologic and environmental samples**

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Fluorescein is a pharmaceutical compound and also a dye. The sodium salt of fluorescein, is used extensively as a diagnostic tool in the field of ophthalmology and is used in the diagnosis of corneal abrasions, corneal ulcers, and herpetic corneal infections. In addition, fluorescein can be considered as an environmental pollutant. For example, fluorescein dye solutions are used as an aid to leak detection during hydrostatic testing of subsea oil and gas pipelines and other subsea infrastructure. In this regard, the development of sensitive, selective and green analytical methods for the enrichment, determination and quantification of fluorescein dye is extremely necessary and important from the environmental and toxicological applications point of view. Dispersive liquid-liquid microextraction (DLLME) has become one of the most interesting sample preparation techniques developed in recent years and has been applied to aqueous samples for determining specific groups of pollutants <sup>[1,2]</sup>. However, to the best of our knowledge, the application of this technique for the extraction/enrichment of fluorescein in biologic and environmental samples followed by HPLC-UV-vis detection has not been reported so far.

In this article, a novel extraction methodology based on dispersive liquid-liquid microextraction coupled with high-performance liquid chromatography-UV-vis detection was exploited for sample preparation and subsequent determination of fluorescein in biologic and environmental samples. Extraction parameters such as ionic strength, pH, mixing assistance, the time required, and different variants of emulsion formation were studied and optimized. The HPLC system consisted of the C18 column (250 mm×4.6 mm, 5 μm) with a mobile phase containing acetonitrile: water (40:60 v/v, pH adjusted to 4.0 with ortho-phosphoric acid) at a flow rate of 1.0 mL min<sup>-1</sup> and ambient temperature. UV-vis detection at 494 nm was employed to monitor the analytes. The standard curve was linear within a range of 1.0-5.0 μg mL<sup>-1</sup>. The recovery values ranged from 95% to 100% and the enrichment factor attained was 100-fold. The applicability of the presented method for the analysis of real biologic and environmental samples has also been investigated.

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**solid-phase extraction based on modified mesoporous microspheres for the determination of repaglinide in plasma by HPLC**

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Mesoporous silica particles (MSPs), such as MCM-41 (Mobil Catalytic Material Number 41), and SBA-15 (Santa Barbara Amorphous-15), are solid materials, which are comprised of a honeycomb-like porous structure with hundreds of empty channels (mesopores) that are able to absorb/encapsulate relatively large amounts of bioactive molecules. Their unique properties, such as high surface area, large pore volume, tunable pore size with a narrow distribution, and good chemical and thermal stability of these materials, make them potentially suitable for various applications in many fields of technology such as chemical and pharmaceutical sciences. In general, the surface area of a porous material is higher than the surface of an analogous non-porous material. Thereby the internal surface area is usually much higher than the one contributed by the external surface. The ease of introducing various organic functional groups, either through covalent bonding or electrostatic interactions, provides high level of versatility and many mechanized features to the mesoporous silica materials.

Due to the high pore volume and surface area of MSPs they are especially suitable carrier for the loading of hydrophobic drugs. The present study was to develop MSPs as carrier to load with repaglinide as a poorly water soluble drug. For this propose, SBA-15 was prepared with templating approach. After synthesis of the MSP, the impact of the surface functionalization of SBA-15 with methyl group was investigated on drug loading efficiency of repaglinide.

To investigate the enrichment efficiency of the microspheres, extraction conditions were optimized in the following work. To acquire the maximum extraction efficiency of the target analyt the amounts of MSN microspheres required were optimized first.

For the sake of enhancing extraction efficiency, the selection of extraction time is important after the sorbents are dispersed in to solution. In our study, different extraction time were investigated.

The selection of an appropriate elution solvent is quite important in a SPE procedure. In this study some solvents were examined for improving the extraction efficiency of repaglinide.

The volume of elution solvent and elution time are also important factors to obtain reliable and reproducible analytical results that were investigated.

In optimom condition our loading studies indicated that there was 28 and 75% loading efficiency in the presence of SBA-15 and SBA-CH<sub>3</sub> as carrier. Therefore, the findings clearly showed the substitution of silanol groups with phethyl groups had a positive effect on the loading efficiency (LE). This improvement in LE may be attributed to the hydrophobic interaction between the lipophilic drug repaglinide and the hydrophobic channels of SBA-15.

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**Optimization of solvent composition for dispersive liquid-liquid microextraction and high-performance liquid chromatography based on a fluorescence protocol using fluorescein as a fluorescent tracer**

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Finding a proper solvent composition in a typical extraction procedure or during the chromatographic runs is of great importance because with an optimized composition in a solvent mixture higher extraction efficiencies and better chromatographic separations in a reasonable time can be achieved [1]. Types of solvents which are typically employed in routine extraction or chromatographic experiments are as follows: (1) Nonpolar solvents: these solvents have low dielectric constants (<5) and are not good solvents for charged species such as anions; (2) Polar aprotic solvents: these solvents have moderately higher dielectric constants than the nonpolar solvents (between 5 and 20). They are “aprotic” because they lack O-H or N-H bonds; (3) Polar protic solvents: these solvents all have large dielectric constants (>20) and large dipole moments, but they do not participate in hydrogen bonding (no O-H or N-H bonds). Their high polarity allows them to dissolve charged species such as various anions used as nucleophiles (e.g. CN<sup>-</sup>, HO<sup>-</sup>, etc.). Polar protic solvents tend to have high dielectric constants and high dipole moments. Furthermore, since they possess O-H or N-H bonds, they can also participate in hydrogen bonding. These solvents can also serve as acids (sources of protons) and weak nucleophiles (forming bonds with strong electrophiles). There are two common ways of measuring the polarity in a mixture of solvents. One is through measuring the dielectric constant or permittivity. The greater the dielectric constant, the greater the polarity (water = high, gasoline = low). A second comes from directly measuring the dipole moment.

In this work, a statistical mixture-design technique followed by a fluorescence approach was used to measure the polarity and the subsequent composition in a mixture of solvents (acetonitrile, methanol, water). Firstly, a fluorescent dye (fluorescein) with a fixed concentration was prepared in different solvents and their mixtures as well. Then the fluorescence intensity of each sample was recorded and plotted against diverse solvent compositions. By using statistical approaches and from this plot with a given fluorescence intensity an unknown solvent composition can be extrapolated.

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## Oxidative desulfurization (ODS) of model fuel in supercritical conditions

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In this experiment for High yield oxidative desulfurization of sulfur containing compound such as DBT & BT under catalytic and supercritical conditions, Using Mo/  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> as a catalyst First, Mo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts were prepared using an impregnation method and were characterized using X-ray diffraction and FT-IR. catalytic system Mo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and H<sub>2</sub>O<sub>2</sub> has been found suitable for the deep removal of sulfur in model fuel Among catalysts tested, Mo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> 5% prepared by a conventional impregnation method was considerably active for the oxidation of thiophene, BT and DBT, which could achieve higher than 88.2% conversions at lower reaction temperature-

( $\leq 315$  K). Then, Substrate Dibenzothiophen was respectively dissolved in n-hexane to get model fuels with the sulfur concentration of 1200 ppm (1.2 g/L). A mixture of the catalyst (10 mg), model fuel (15mL), CTAB (3 mg) and deionized water was added into three-necked flask equipped with a cryogenic-liquid con- denser and an air pump. After continuous stirring for 4 h, the resulting mixture was filtered.

The filtrate was quantitatively analyzed by gas chromatography with flame- ionization detection (GC-FID). Then combine Oxidative desulfurization catalytic (ODS) system and Supercritical conditions such as supercritical water (SCW) and supercritical CO<sub>2</sub> of heavy oils reduces sulfur content and decreases average molecular weight, without rejecting carbon as coke products.

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**Multi-response optimization followed by multivariate calibration for simultaneous determination of organophosphorus pesticides in complex matrices extracted by dispersive liquid-liquid micro-extraction and analyzed by gas chromatography**

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Pesticides are materials that they used in agriculture for combat a variety of pests. Many persistent pesticides have been reported as cause of several diseases such as cancer. The U.S. Environmental Protection Agency (EPA) and European Commission (EC) used maximum residue limits (MRLs) to ensure food safety for consumers. Pesticides can be found in different samples such as environmental, vegetables, fruits and dairy products. Due to the complex sample matrices and low concentration of pesticides, extraction step has a very important role [1]. On the other side, various methods have been developed for the determination of pesticides in complex sample matrices such as UV-Vis spectrophotometry, high-performance liquid chromatography (HPLC) and gas chromatography (GC-MS and GC-FID) [2]. In this study, Quick, Easy, Cheap, Effective, Rugged and Safe (QuEChERS) combined with dispersive liquid-liquid micro-extraction (DLLME) has been used for extraction of pesticides in water samples. In this regard, simultaneous determination of 10 pesticides with QuEChERS-DLLME and GC-FID were designed, modelled and optimized using central composite design (CCD), backward multiple linear regression (MLR) and Nelder-Mead simplex optimization [3]. On this matter, 36 experiments for 5 extraction factors in 5 levels were generated. Also, multi-response optimization using Derringer desirability function was used to combine individual models of 10 pesticides and global optimum conditions were obtained which were 0.25 mL of acetonitrile, 39.34  $\mu$ L of chloroform, 25 min of sonication time and 3.72% (w/v) salt in pH 6.7. After optimization of extraction procedure, multivariate calibration model for 10 pesticides was developed using Partial Least Squares (PLS) model in linear dynamic range (LDR) of 0.5–100  $\mu$ g L<sup>-1</sup>. GC-FID profiles were baseline corrected and aligned before PLS modeling. Then, multivariate analytical figures of merit (AFOM) including sensitivity, selectivity and limit of detection (LOD) were calculated [4]. As an instance, the calculated LODs were below the MRLs of 10 pesticides which confirms the validity of the proposed method. Finally, the proposed analytical method was used for identification and quantification of 10 pesticides in real samples (i.e., tap water, milk).

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**Direct electrochemical synthesis of graphene nanosheets on pencil graphite electrode and decorating its surface with poly (L-methionine) for electroanalysis of acyclovir**

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Acyclovir (9-2-hydroxyethoxymethyl guanine, (ACV), as an inhibitor of the replication of herpes viruses, has been used effectively in the treatment of patients with herpes simplex and herpes zoster [1,2]. But due to some adverse neurotoxic and neurotoxic effects, developing sensitive and selective methods for monitoring of its concentration in biological samples is interesting [3].

In the present study, a novel, simple and one spot procedure is reported to produce graphene (Gr) on the surface of a pencil graphite electrode (PGE). The formation of Gr was achieved on the surface of PGE as the working electrode by amperometric method in sulfuric acid solution. The Gr-coated electrode was subjected to electrochemical polymerization of L-methionine resulting a polymer thin film. This modified electrode was applied to determination of ACV. The morphology and structure of the composite film were characterized using X-ray diffraction, electrochemical impedance spectroscopy and Field emission scanning electron microscopy. The results show that Gr nanosheets were successfully synthesized and poly(L-methionine) anchored on the Gr sheets. The stepwise modification of the electrode surface was followed by cyclic voltammetric (CV) using  $[\text{Fe}(\text{CN})_6]^{3-/4-}$  as the probe. The CVs of bare PGE showed a pair of broad redox peaks with  $\Delta E_p$  of 170 mV, but the CVs of the poly (L-methionine)/PGE displayed higher peak currents and smaller  $\Delta E_p$  value (125 mV), and in the case of Gr/PGE the value  $\Delta E_p$  was 110 mV, and the current intensity was extraordinary enhanced with respect to that of unmodified PGE or poly(L-methionine)/PGE. Furthermore, when the poly (L-methionine)/Gr/PGE was used, the peak currents further increased to a certain degree and the  $\Delta E_p$  value decreased to 90 mV, which demonstrated the effective facilitation of electron transfer for  $[\text{Fe}(\text{CN})_6]^{3-/4-}$  due to the combined action of poly (L-methionine) and Gr enhances the conductivity and catalytic activity of the modified electrode. Under the optimized conditions, the electrooxidation of ACV on the poly(L-methionine)/Gr/PGE modified electrode surface was investigated comparatively with Gr/PGE, poly(L-methionine)/PGE and bare PGE. The calibration curve was linear for ACV concentrations from 0.05 to 50  $\mu\text{M}$  with a LOD value of 15 nM observed by differential pulse voltammetry. The application of the electrode for the determination of ACV in blood serum was investigated.

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**Surfactant-enhanced solvent stir bar microextraction coupled with microcell UV–Vis spectrophotometry for trace determination of ammonia in environmental water samples**Sina Davvaji asl<sup>a</sup>, Abbasali Zamani <sup>\*a</sup>, Hamid Badiei<sup>a, b</sup>, Armin Fashi<sup>a</sup><sup>a</sup> Environmental Science Research Laboratory, Department of Environmental Science, Faculty of Science, University of Zanjan, 45371-38791, Zanjan, Iran<sup>b</sup> Department of Chemistry, Faculty of Science, University of Guilan, University of Campus 2, Rasht, Iran\*E-mail: [Zamani@znu.ac.ir](mailto:Zamani@znu.ac.ir)

Ammonia is a significant micro-nutrient in aquatic ecosystems due to its role in the aquatic nitrogen cycle. Nevertheless, ammonia can induce eutrophication of aquatic system with the external discharge of domestic sewage, fertilizers and industrial wastewaters into water sources [1, 2]. Thus, it is considered as a toxic pollutant to fish and diatoms and other aquatic life. However, due to the presence of ammonia at trace concentrations, its analysis is a real challenge for evaluating of biological study in aquatic ecosystems [3]. In this work, preconcentration-determination of ammonia in water samples was performed by combination of surfactant-enhanced two phase solvent stir-bar microextraction (SSBME) and microcell UV–Vis spectrophotometry. To develop this microextraction method, a short length of polypropylene hollow fiber was fixed on a magnetic rotor using a stainless steel wire and used as an extraction device for the preconcentration of ammonia (Fig.1). In this device, the hollow fiber moved along with the magnetic bar in sample solution under external magnetic field on a stirrer. Tetrabutylammonium bromide was added into the donor solution to form an ion-pair with indophenol blue achieved according to the Berthelot reaction. Then, the ion-pair was extracted from donor phase into the acceptor phase impregnated in the pores and lumen of the hollow fiber. Significant parameters affecting the proposed SSBME method such as type and concentration of cationic surfactant, type organic solvent, effect of extraction time, sample volume, ionic strength and stirring rate, were studied and optimized to obtain the maximum preconcentration factor. Under the optimized conditions the proposed SSBME method provided good linearity (1–500 ng mL<sup>-1</sup>), acceptable relative standard deviations (RSDs < 7 %) with preconcentration factor of 200 fold. Finally, the proposed method was successfully applied to monitor trace amounts of ammonia in real sample waters.

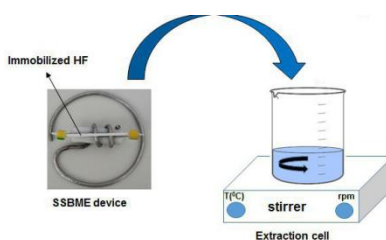


Figure 1: Schematic for device used in SSBME procedure

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**Fabrication of a novel nanostructure electrochemical sensor for determination of tyrosine**

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Amino acids such as tyrosine are the major targets for radical's attack. 4-Hydroxyphenylalanine or tyrosine (Tyr) is a nonessential amino acid and acts as a singlet oxygen quencher. Tyrosine plays an integral role in the synthesis of the neurotransmitter serotonin such as norepinephrine and dopamine (5-HT). Tyrosine and other amino acids play roles in inducing dementia such as Alzheimer's disease. The lack of tyrosine concentration in the body may cause albinism, alkaptonuria, depression, narcolepsy and other psychological diseases while a high level of tyrosine could cause the increase of sister chromatid exchange [1]. Therefore, it is significant to develop a simple, accurate, rapid and inexpensive sensor for the determination of tyrosine. Electrochemical analytical techniques have been a topic of interest to researchers in the biological and environmental analysis, due to simplicity, cost effectiveness, high sensitivity and the possibility of miniaturization. A screen-printed electrode (SPE) is an attractive alternative choice due to their miniaturized size, inexpensive, easy to fabricate, rapid responses and disposable, which makes them especially suitable for on-site analysis [2]. However, the signal to noise of bare electrode is insufficient to determine the trace level of tyrosine. One of the major strategies to enhance the electron exchange in electrochemical sensors and biosensors is to design new sensing layer by combining highly electrocatalytic materials with highly conductive substances. Metal oxide based nanocomposites have wide applications in photocatalysis, gas-sensors, piezoelectric materials, and solar cells due to its features such as photosensitivity, non-toxic and low cost. The combination metals with metal oxide nanocomposites have a significant effect on the catalytic activity due to the interactions and surface reactivity [3]. A simple, selective and sensitive sensor based on La<sup>3+</sup>/Co<sub>3</sub>O<sub>4</sub> nanoflowers modified screen printed electrode (La<sup>3+</sup>/Co<sub>3</sub>O<sub>4</sub> NF/SPE) is introduced for electrochemical determination of tyrosine. Compared with the unmodified electrode, the oxidation peak current significantly improved. Under optimized experimental conditions, the oxidation peak current of tyrosine was linear over a concentration range of  $5.0 \times 10^{-7}$  to  $7.0 \times 10^{-4}$  M with a detection limit of  $4.0 \times 10^{-8}$  M. Moreover, the applicability of the method was demonstrated by the recovery tests of tyrosine in real samples.

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**Highly sensitive determination of dopamine using screen-printed electrode modified with 2D transition metal carbide MXene**

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Dopamine (3,4-dihydroxyphenyl ethylamine, DA), as an excitatory neurotransmitter in mammalian central nervous systems, plays an important role in several physiological activity such as mood, behavior and movement. Abnormal levels of dopamine may lead to neurological diseases, such as Parkinson's disease and schizophrenia [1]. Hence, Sensitive detection of dopamine is of great importance for the understanding and diagnostics of neurological diseases. As compared to other analytical methods, the electrochemical techniques making use of a three electrode system have drawn a particularly considerable amount of attention because of the electroactive nature of dopamine, high selectivity, high sensitivity, low cost, reproducibility, simplicity and short operational duration. Screen-printed electrodes (SPEs), which are fabricated by printing several types of inks on a specific substrate have been considered superior because of the versatile, disposable, inexpensive, good reproducibility of the results, rapid responses to analytes, easy to fabricate, and can be operated over a wide potential range. Such SPEs have been recently employed as diagnostic tools for food poisoning, diseases, and environmental pollutants. In order to improve their electrochemical performance, SPEs have been modified with nanosized materials [2]. MXene, as a new class of two-dimensional (2D) transition metal carbides (or nitrides), has been synthesized by exfoliating pristine  $Ti_3AlC_2$  phases with hydrofluoric acid [3]. A simple, selective and sensitive sensor based on MXene nanosheets modified screen printed electrode (MXene/SPE) is introduced for electrochemical determination of dopamine. Compared with the unmodified graphite screen printed electrode, the modified electrode facilitates the electron transfer of dopamine, since it notably increases the oxidation peak current of dopamine. Under optimized conditions, the modified electrode exhibited a linear response over the concentration ranging from 0.2 to 600.0  $\mu M$ , with a detection limit of 0.06  $\mu M$  (S/N = 3). The proposed sensor exhibited a high sensitivity, good stability and was successfully applied for dopamine determination in dopamine ampoule, with high recovery.

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**Voltammetric determination of carbidopa using a modified glassy carbon electrode with La<sup>3+</sup>/Co<sub>3</sub>O<sub>4</sub> nanocubics**

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Carbidopa (CD) is one of the important catecholamine and it is used in the treatment of Parkinson's disease. Carbidopa is a drug given to people with Parkinson's disease in order to inhibit peripheral metabolism of levodopa. Carbidopa does not cross the blood-brain barrier (BBB) and contributes to the production of effective brain concentrations of dopamine from lower doses of levodopa by inhibiting the peripheral decarboxylation of levodopa to dopamine [1,2]. Therefore, it is very important to establish a sensitive method for detection of carbidopa in pharmaceutical formulations and human serum. Different techniques have been employed for the determination of carbidopa in pharmaceutical formulations. Among these methods, electrochemical techniques offer the opportunity for portable, economical, sensitive and rapid methodologies. Among many electrodes, glassy carbon electrodes (GCEs), which are stable and robust carbon-based electrodes, have been widely used because of their high biocompatibility, low tendency for surface fouling, and relatively low level of residual current over a wide potential range. Thus, the combination of inorganic nanoparticles and sensors is one of the most exciting areas in modern analytical detection development because they offer excellent prospects for designing highly sensitive and selective sensors. As an important p-type semiconductor, cobalt oxide (Co<sub>3</sub>O<sub>4</sub> in particular) has gained increasing attention because of its applications in many fields, such as sensors, gas sensing, catalysis, and lithium-ion batteries. The combination metals with metal oxide nanocomposites have a significant effect on the catalytic activity due to the interactions and surface reactivity [3]. In this study, a new glassy carbon electrode chemically modified with La<sup>3+</sup>/Co<sub>3</sub>O<sub>4</sub> nanocubics was constructed and used for the sensitive electrochemical determination of trace amounts of carbidopa. This electrochemical sensor responds to carbidopa in the wide linear range of 1.0×10<sup>-6</sup> to 7.0×10<sup>-4</sup> M. The detection limit of 7.0×10<sup>-8</sup> M was obtained at pH 7.0. The proposed sensor was successfully applied for the determination of carbidopa in real samples.

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The electrochemical behavior of poly safranin O on MWCNT/CPE modified electrode

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In this study a poly safranin O (SO) film was prepared via electro polymerization technique on multiwall carbon nanotube modified carbon paste electrode (MWCNT/CPE) (Fig. 1) [1]. The effect of pH, MWCNT concentration and safranin O concentration on electrochemical response were explored for optimum analytical performance [2, 3]. The modified electrode exhibited a pair of well defined, quasi-reversible peaks at formal potential ( $E^0$ ) =  $-0.19 \pm 0.001$  V. Ag/AgCl corresponding to the  $SO_{ox}/SO_{red}$  redox couples in the presence of MWCNT and Nafion. The electrochemical parameters such as charge-transfer coefficient and apparent heterogeneous electron transfer rate constant were determined.

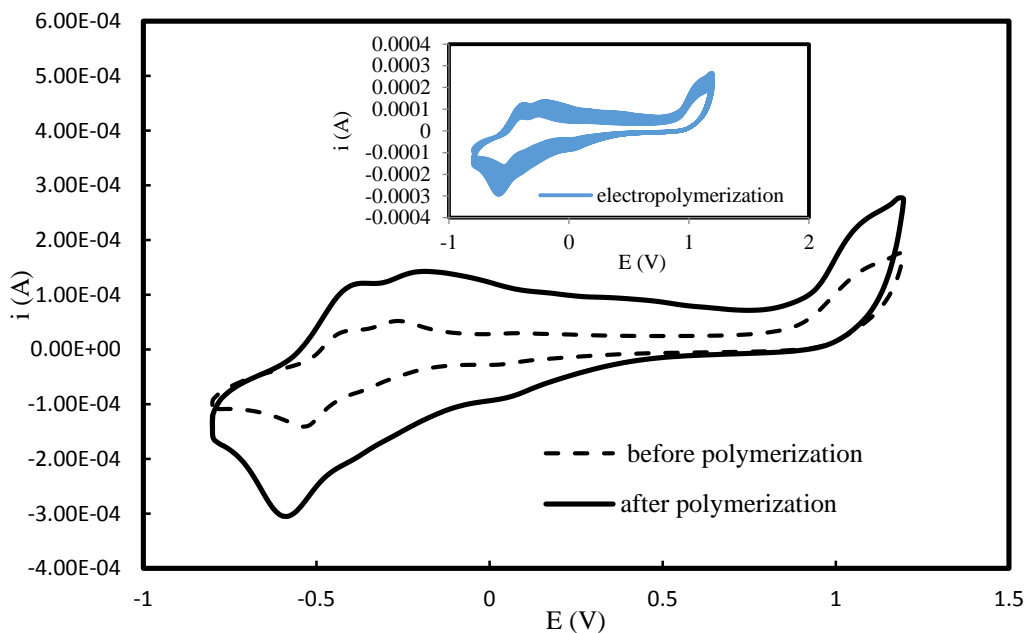


Fig.1

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**Determination of toxic tobacco compounds in urine specimens of 12 smokers in 4 periods after quitting smoking by UPLC-QTOF-MS**

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The World Health Organization reports that there are more than 1 billion smokers in the world. Tobacco products contain a diverse array of chemical carcinogens that cause many types of cancer. There are more than 60 carcinogens in cigarette smoke and at least 16 in unburned tobacco. Among these, tobacco specific nitrosamines (such as 4-(methyl nitrosamino)-1-(3-pyridyl)-1-butanone (NNK) and N'-nitrosornicotine (NNN)), polycyclic aromatic hydrocarbons (such as benzo[a]pyrene) and aromatic amines (such as 4-aminobiphenyl) seem to have an important role as causes of cancer [1]. The trace levels of nicotine and its metabolites have been measured in urine, meconium, hair, saliva or serum. Compared to other human biological samples, collection of urine is non-invasive and comparatively easier and more convenient than other methods [2]. Recently, ultra-high performance liquid chromatography coupled with electrospray ionization quadrupole time-of-flight tandem mass spectrometry (UPLC-QTOF-MS) has been widely applied especially for biological matrices, such as urine, plasma and saliva. The objective of this study was to develop an analytical method for the simultaneous determination and quantification of 9 important tobacco biomarkers, including 4 tobacco-specific nitrosamines such as 4-(methylnitro-samino)-1-(3-pyridyl)-1-butanone (NNK), N-nitrosoanabasine (NAB), N'-nitrosornicotine (NNN) and N-nitrosoanatabine (NAT); 3 aromatic amines such as 2,4-dimethylaniline, 4-aminobiphenyl and 2-naphthylamine; nicotine and cotinine using solid phase extraction followed by an ultra-performance liquid chromatography-tandem quadrupole-time-of-flight mass spectrometry analysis. Limits of detection (LODs) were in the range of 1.6 to 24 ng/g of urine. This analytical method was applied to 12 urine samples (in four periods of times after stop smoking). Nicotine, cotinine and N-nitrosoanatabine (NAT) were detected in urine samples. Nicotine was determined in 6 out of 12 urine samples. Cotinine, the main metabolite from nicotine, was detected in 11 out of 12 urine samples. NAT was detected in 4 urine samples.

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**Development electrochemical sensor based on molecularly imprinted polymer for determination of levodopa**

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Levodopa (3,4-dihydroxyphenylalanine) also called L-dopa, is the precursor required by the brain to produce dopamine, a neurotransmitter. Levodopa crosses the protective blood–brain barrier, whereas dopamine itself cannot. Thus, levodopa is used to increase dopamine concentrations in the treatment of Parkinson's disease (PD), dopamine-responsive and dystonia. However, an excessive amount of levodopa not only helpful but also make serious side effects such as gastritis, paranoia schizophrenia and epilepsy. With dangerous side effects of levodopa with long-term use on human health, this drug should be given an accurate analysis in both pharmaceutical formulations and biological fluids [1]. Forasmuch as levodopa contain phenolic hydroxyl and amino group respectively, which is electrochemically active and can be oxidized. Thus, electrochemical methods because of their good simplicity, sensitivity, relatively fast response, low cost and good stability are the better choice for determination of levodopa. However, the signal to noise of bare electrode is insufficient to determine the trace level of levodopa. To overcome it, molecular imprinted polymer (MIP) is considered one of the best strategy owing to its pre-determined selectivity for an imprinted template. Molecular imprinting is a technique which is used to molecular recognition via self-assembly of functional monomers around a template molecule through the interaction between their functional groups. This technology has been developed for use in sensors since it can provide enhanced selectivity and/or sensitivity. In addition, molecularly imprinted polymers (MIP) benefit from ease of preparation along with good stability in chemical, physical and mechanical properties [2]. A considerable amount of research has been done on MIP based approach for levodopa determination. Levodopa showed a sensitive anodic peak in buffer solution of phosphate (pH=7.0) at the surface of MIP/GCE. The investigation and optimization of the effective factors on the response and electrochemical behavior of target levodopa on the surface of the modified electrode were accurately done. Levodopa response linearly within the range of 0.1-600.0  $\mu\text{M}$  with detection limit of 0.05  $\mu\text{M}$ . The function of this electrode in the determination of biological samples was satisfactory.

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**Application of Molybdenum disulfide Nanosheets for Simultaneous Trace Separation and Determination of Cd(II), Cu(II), Pb(II), Zn(II) and Ni(II) in water samples**

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Molybdenum disulfide ( $\text{MoS}_2$ ) is a type of layered transition metal dichalcogenide. Due to its structural similarities to graphene, it has drawn enormous attention for various applications such as dye sensitized solar cells, supercapacitor, Li-ion battery, hydrogen evolution reaction, photocatalysis for the degradation of organic pollutants, sensors etc.  $\text{MoS}_2$  shows similar physical properties to that of graphene that include high charge carrier transport, high wear resistance, etc. However,  $\text{MoS}_2$  has superior properties over graphene such as low cost, more abundant, tuneable band gap with good visible light absorption capacity. As for the catalytic properties,  $\text{MoS}_2$  has been vastly used as catalysts to remove S and N from crude oils [1-4]. Recently, Nano-sorbents have attracted substantial interest in the scientific community because of their special properties, such as their large surface areas and high adsorption capacity [5].

The purpose of this study is to investigate a new sorbent comprising of  $\text{MoS}_2$  for solid phase extraction and preconcentration of trace amounts of Cd(II), Cu(II), Pb(II), Zn(II) and Ni(II) from environmental samples. The synthesis  $\text{MoS}_2$  nanosheets were characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM), thermogravimetric analysis (TGA), Brunauer–Emmet–Teller (BET) and powder X-ray diffraction (XRD). In the separation/preconcentration step, metal ions are adsorbed onto  $\text{MoS}_2$  nanosheets, eluted by nitric acid and determined by flame atomic absorption spectrometry (FAAS). The main factors affecting the extraction efficiency such as pH value, sample volume, eluent concentration and volume, amount of sorbent and coexisting ions have been investigated and established. Under the optimum experimental conditions, the enrichment factor for above metal ions was found to be 85 approximately. Detection limit (3s) was achieved at 0.5, 3.0, 10.0, 1.3 and 2.5  $\text{ng mL}^{-1}$ , respectively. At the 10.0  $\text{ng mL}^{-1}$  level, the precision (RSD, %) for eight replicate measurements was from 1.0 to 4.0. These results had proved that the proposed method was with good accuracy and could be applied to the analysis of trace metal ions in biological, river water and wastewater samples.

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## On-line micro solid phase extraction of atrazine from real water samples by imprinted silica nanofibers

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Sol composition and ripening condition are two important parameters in silica fibers production through the conventional sol-gel process [1]. In the current study, silica nanofibers were obtained successfully by electrospinning technique and sol-gel formation was performed during this process. Pirzada et al. have reported hybrid silica-PVA nanofibers via sol-gel electrospinning [2]. In this regards, with the aim of increasing the selectivity, we used the molecular imprinted methodology to produce the selective media via sol-gel electrospinning. In this process, sol-gel was formed during electrospinning and then the backbone polymer was removed by heating. To obtain a thin layer of silica nanofiber, the influencing parameters such as backbone polymer types, imprinting time and material ratio were explored. Then, the extraction parameters on online -solid phase extraction were optimized. First, to find the suitable backbone to produce electrospun silica nanofiber the polymer type and concentration were examined and polyamide (PA) showed the best results in electrospinning process and was easily removed by heating. So, the silica precursor was added to the solution of atrazine in acetonitrile (I), and solution of PA in formic acid (II). The ratio of these two solutions for electrospinning was explored, as well. To increase the selectivity and MIP/NIP ratio, the mixture was stored in different times and to let the atrazine template to settle in appropriate spaces. After electrospinning, the PA moiety was removed by heating. To do this, the nanofiber sheet was placed in the oven for 12 h and a control PA nanofiber mat was also fabricated under the same situation. After 2 h, the whole part of PA was quite burnt and disappeared. Finally, the thin silica nanofibers were produced. FT-IR and TGA analyses revealed that the PA is removed after heating and the SEM images indicate the geometry of the silica nanofibers. The extraction efficiency of the electrospun silica nanofibers mat was compared with the same silica precursor sol-gel by two other methods, bulk, and electrochemical synthesis by online -SPE LC-UV method. The data showed higher extraction efficiency for silica nanofibers. The linearity of the analyte was in the range of 6-400 g L<sup>-1</sup>. LOD was found to be 1.8 g L<sup>-1</sup> and the inter- and intra-day RSD% were less than 9.6%. The method was conveniently applied to Zayanderud and tap water samples spiked with atrazine, while the relative recovery percentages for the standard samples were up to 92%.

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An Investigation of electrochemical behavior of indigo carmine on a mesoporous  $Fe_3O_4$  nanoparticles modified carbon paste electrode

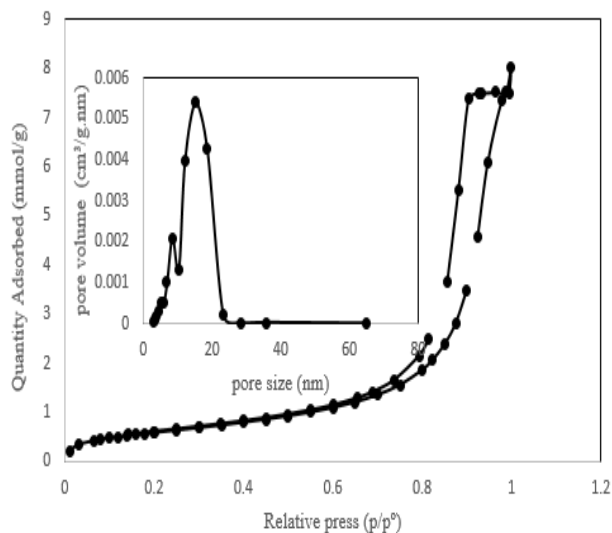
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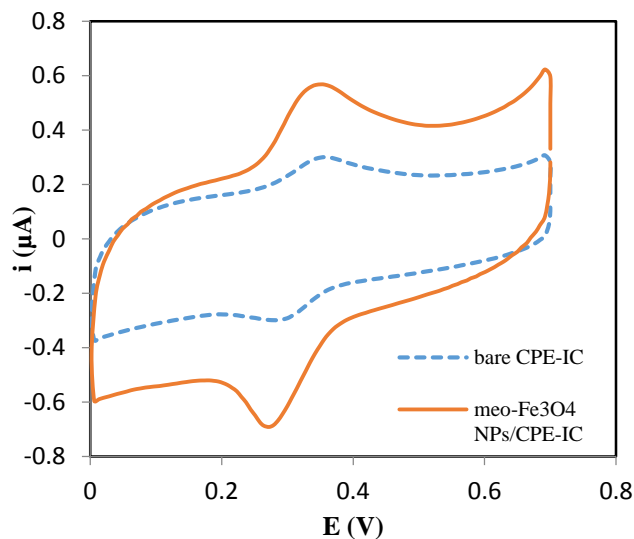
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A new approach for electrochemical study of indigo carmine (IC) was successfully performed on mesoporous  $Fe_3O_4$  nanoparticles (The meso- $Fe_3O_4$ ) modified carbon paste electrode (meso- $Fe_3O_4$ /CPE). The meso- $Fe_3O_4$  nanoparticles were synthesized via solvothermal method. The porosity of nanoparticles was measured by BET method. The obtained meso- $Fe_3O_4$  nanoparticles have pore size of about 16 nm (Fig. 1).

The surface properties of CPE and meso- $Fe_3O_4$ /CPE were examined by cyclic voltammetry (CV) in an electrolyte containing  $K_4Fe(CN)_6^{2/3-}$  as redox probe. For electrochemical study of IC at meso- $Fe_3O_4$ /CPE, conditions such as pore size of the mesopore, pH of the dye solution, temperature, dye concentration and contact time of IC with mesopore were optimized. In Compare with the unmodified CPE, meso- $Fe_3O_4$ /CPE remarkably enhances the redox current of indigo carmine . At the meso-  $Fe_3O_4$ /CPE, the oxidation peak of IC was increased and shifted to negative potential versus at the bare CPE (Fig. 2).



(Fig. 1)



(Fig. 2)

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**aThe discrimination of iron ore concentrates due to their characteristic origin for iron pelletizing and reduction using multivariate pattern recognition analysis**

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Iron ores are rocks and minerals from which metallic iron can be economically extracted. The ores are generally rich in iron oxides, where it can be formed from magnetite ( $\text{Fe}_3\text{O}_4$ ), hematite ( $\text{Fe}_2\text{O}_3$ ), goethite ( $\text{FeO}(\text{OH})$ ), limonite ( $\text{FeO}(\text{OH}) \cdot n\text{H}_2\text{O}$ ) and siderite ( $\text{FeCO}_3$ ). Different compositions of the iron ores as well as other oxides including  $\text{TiO}_2$ ,  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{CaO}$ ,  $\text{MgO}$ ,  $\text{V}_2\text{O}_5$ ,  $\text{P}_2\text{O}_5$ , and  $\text{MnO}_x$  represented different effects on the mechanical and chemical iron products, so, the identification of the origin of the iron ore can be influenced on the pelletizing and reduction processes [1]. The data obtained from x-ray fluorescence spectroscopy, classical determination of iron content, and carbon and sulphur determination by high frequency combustion method with infrared measurement were studied by the multivariate pattern recognition methods including the most usual unsupervised method principal component analysis (PCA) and the supervised methods partial least squares discriminant analysis (PLS-DA) and extended canonical variates analysis (ECVA) [2,3]. In this work, five various iron ore concentrates including Golgohar, Bafgh, Chadormaloo, Kimiamaaden, and Goharzamin were investigated. 350 samples were prepared from these iron ore origins. The dataset was randomly divided into three subsets of training (50% of the samples), evaluation (30%) and test (20%) for classification methods PLS-DA and ECVA. PCA and ECVA were showed their abilities in discrimination of iron ore concentrates. PLS-DA represented so close performances, giving CC% on the training, validation, and test sets in the ranges of 89.4–93.2, 89.1–91.9, and 89.0–91.2%, respectively. These iron ore concentrates were employed in pelletizing and sintering processes by addition of some binders such as limestone, dolostone, olivine and bentonite [4,5]. The iron pellets represented different characteristics and reducibilities because of their compositions. Hence, the pattern recognition was applied as an efficient tool to classify these iron products into various categories based on the initial origins. Accordingly, the reducibility and other mechanical and chemical properties of iron product can be controlled by considering the iron ore composition. Moreover, these properties can be modelled rather than the expecting composition. In conclusion, the merge of raw composition-based data and chemometrics tools was applied to successfully anticipate the final product.

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**Mapping milk samples based on the doses of selected antibiotic residues: Application of pipette tip microextraction using graphene oxide–starch–based nanocomposite**

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Milk is considered as one of the essential nutrients consumed daily. This important food source is easily contaminated *via* various ways one of which is chemical contamination [1].  $\beta$ -lactam antibiotics are modern medicines which have been used often for prevention and treatment of animal husbandry infections as well as growth promotion [2]. Because of the low octanol–water partition coefficient (K<sub>O/W</sub>) values of penicillin antibiotics, the use of polar extractive phase is presumably more logical [3]. Lately, biopolymers have grabbed considerable attentions of the scientific and industrial communities, being an alternative to conventional petroleum-based plastics [4]. In this study, a method is described for the extraction and mapping of three antibiotic residues from cow milk samples using a graphene oxide–starch–based nanocomposite. The prepared nanocomposite was employed as an extractive phase for pipette tip microextraction of antibiotics from cow milk samples. The extracted antibiotics, i.e. amoxicillin, ampicillin and cloxacillin, were subsequently analyzed by HPLC–UV. Important variables associated with the extraction and desorption efficiency were optimized. The implementation of the starch–based nanocomposite in the pipette tip, led to high extraction efficiencies for the selected antibiotics. The penicillin group was validated based on the characteristic performance of the European Commission Decision 2002/657/EC by spiking the selected antibiotics to the blank milk samples. The limits of quantitation for amoxicillin, ampicillin and cloxacillin were 2.7, 3.0 and 5.0  $\mu\text{g kg}^{-1}$  which were lower than the maximum residue limits in the European legislation. The overall obtained results indicate the superiority of the starch nanocomposite performance toward the selected antibiotics. The relative standard deviations of intra and inter–day analysis are less than 3.3 and 6.1%, respectively. Moreover, the mean recoveries of the target penicillin in the real milk samples were in the range of 83.3–105.0%. Statistical and chemometric methods revealed that the clustering of milk samples based on the doses of antibiotic residues was indeed possible.

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## Redox Reaction of Silver Nanoparticles Coated Graphite as an Electrochemical Signature for Determination of Thiopental Sodium

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Thiopental is an ultra-short-acting barbiturate used to induce anesthesia in man and animals. It is used for intensive-care patients with head injuries to reduce intracranial hypertension and is useful to prevent and treat brain ischemia [1]. Different methods for the determination of thiopental sodium have been reported. However, most procedures suffer from the lack in some simplicity, sensitivity, and selectivity. Therefore, it is necessary to develop new methods for determination of thiopental with good sensitivity and selectivity. Among all noble metal nanoparticles, silver nanoparticles (AgNPs) keep on to be of enormous current research attention because of their catalytic properties [3]. AgNP traditionally been explored to employ as catalysts in various reactions and also Ag exhibits the highest electrical and thermal conductivity among all the metals [4]. Based on our knowledge, use of electrochemical sensors for Thiopental determination was rare. In this work, we designed a new electrochemical sensor for the determination of TPS. Some important factors such as pH, ratio of AgNPs-graphite in the electrode, pretreatment potential, and accumulation time were optimized. Under optimized experimental conditions, relationship between current reduction of the electrode and concentration of TPS was linear in range of  $10^{-10}$  to  $5 \times 10^{-6}$  molL<sup>-1</sup>. To investigate repeatability of the method it was tested nine times under the same condition and RSD = 1.24 were obtained for this sensor.

In summary, we have developed a novel electrochemical sensor based on synthesis of AgNPs coated graphite for determination of TPS. The method is simple, time saving, and very sensitive over the reported data. It can be used successfully to assay the drug in dosage form and in biological samples at trace levels.

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## Fabrication of electrochemical sensor based on nano-sized molecularly imprinted polymer for detection of L-Tryptophan

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During the past decade, molecular imprinting technology has become a well-established analytical tool. Non-covalent imprinting, in particular, has found a wide range of applications because of the theoretical lack of restrictions on size, shape, or chemical character of the imprinted molecule. The possibility of tailor-made, highly selective artificial receptors at low cost, with good mechanical, thermal, and chemical properties, makes these synthetic materials appear as ideal chemoreceptors. There are new horizons for the development of a new generation of chemical sensors using these novel synthetic materials as recognition elements [1, 2].

In this study an electrochemical sensor for selective detection of L-tryptophan (L-Tryp) based on nano-sized molecularly imprinted polymer was synthesized at the surface of glassy carbon electrode (GCE). This sensor was created by polymerization of dopamine (DA) as functional monomer and cross linking agent, and L-Tryp as the template. For preparation of molecularly imprinted polymer (MIP), the required precursors including L-Tryp, DA, and phosphate buffer solution were mixed and stirred at room temperature. After centrifugation, it was dried at room temperature for one night. Then it was dispersed in ultrapure water and ultrasonicated for 10 min. Then GCE was coated with 3  $\mu$ L of the composite and dried at room temperature for 30 min.

The obtained product was washed with hydrochloric acid solution and methanol to remove the template L-Tryp [3]. Determination of L-Tryp was directly performed by electro-oxidation process. The surface features of the modified electrode was characterized by cyclic voltammetry (CV), differential pulse voltammetry (DPV). The morphology of the MIP film modified electrode characterized by Fourier transform infrared spectrometer (FT-IR) and X-ray diffraction (XRD).

Some important experimental conditions such as adsorption time, removal time, preconcentration solution pH, were investigated and optimized. Under the optimized conditions the proposed sensor showed a wide calibration range  $10^{-14}$  –  $10^{-8}$  M with improved LOD value of  $5 \times 10^{-15}$  M. Also the MIP-based sensor exhibited good selectivity and repeatability.

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## Sonochemical synthesis of neodymium doped zinc sulfide nanoparticles

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Zinc sulfide (ZnS) nanoparticles have attracted particular attention for properties such as a wide band gap, high UV absorption potential, and high exciting binding energy [1]. Doping with lanthanide metals is a practical way to increase the catalytic activity of ZnS by preventing fast recombination of the electron-hole ( $e^-h^+$ ) pairs [2].

In the current research, a simple sonochemical method was used to preparing neodymium doped zinc sulfide nanoparticles (Nd-doped ZnS). Doped ZnS particles were synthesized by a probe sonicator (60 W–20 kHz, BANDELIN, SONOPULS HD 3200). First, an aqueous solution of  $\text{Na}_2\text{S}$  (100 mL, 0.5 M) was placed in a three-neck round-bottom flask under ultrasonic irradiation and  $\text{N}_2$  gas. After 30 min, an aqueous solution of  $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$  (100 mL, 0.5 M) with appropriate molar ratio of Nd was slowly added to the previous solution, and the obtained mixture was sonicated for 1 h. The white precipitates were collected by centrifugation (Hettich, EBA 20), treated thoroughly with ethanol and deionized water, and finally dried at ambient temperature (25°C).

The prepared samples were characterized for structural, and morphological properties by X-ray diffraction (XRD, X'Pert Pro, Panalytical) and field emission scanning electron microscopy (FE-SEM, SIGMA, Zeiss). The XRD pattern of the Nd-doped ZnS included the characteristic peaks of ZnS without any diffraction peaks from neodymium or other impurities. The intensity of peaks was reduced in the doped sample, which can be explained by the expansion of the ZnS lattice through doping by neodymium due to the larger ionic radius of  $\text{Nd}^{3+}$  (0.983 Å) in comparison with  $\text{Zn}^{2+}$  (0.74 Å). The FE-SEM image of Nd-doped ZnS showed the formation of uniformity and miscibility of nanoparticles with high density spherical shape particles.

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## Synthesis of Ag-ZnS decorated multi-walled carbon nanotubes composite

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In order to increment of the photocatalytic activity, nanosemiconductors can be decorated onto a proper support. Carbonaceous materials such as multi-walled carbon nanotubes (MWCNTs) are good hosts for semiconductors in catalytic reactions because of their sufficient stability, extraordinary structural, electrical and mechanical properties and non-toxicity [1,2].

In this research, Ag-ZnS nanoparticles were synthesized via a simple co-precipitation method and afterwards, Ag-ZnS decorated MWCNTs composite was prepared.

The 0.5 M sodium sulfide aqueous solution was stirred in a three-neck round-bottom flask under the presence of nitrogen gas. Zinc acetate solution (0.5 M) with appropriate molar ratio of AgNO<sub>3</sub> was slowly added to the above solution and stirred for another 30 min at room temperature. The resulting precipitate was collected by centrifugation and rinsed with ethanol and deionized water for several times. Afterward, MWCNTs powder was dispersed in 100 mL of water and sonicated for 15 min. Subsequently, the precipitates coming from the previous stage were added to the MWCNTs suspension under ultrasonic medium until the uniform precipitate was resulted. The resulting product was finally dried at room temperature and thereafter crushed to obtain fine powder.

The prepared Ag-ZnS decorated MWCNTs composite was characterized in detail by X-ray diffraction (XRD, X'Pert Pro, Panalytical) and field emission scanning electron microscopy (FE-SEM, SIGMA, Zeiss). The XRD pattern of the composite included the characteristic peaks of ZnS with slightly lower crystallinity, which revealed that Ag-ZnS nanoparticles were successfully embedded in MWCNTs matrix. Also, according to the FE-SEM image, Ag-ZnS nanoparticles were well distributed in the MWCNTs matrix, which is supported by XRD analysis.

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**Multivariate Curve Resolution-Alternating Least Squares enhanced with Gaussian apodization factor analysis for Columnless gas chromatography ion mobility spectrometry**

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Hyphenated chromatographic techniques have been used to separate and analyze complex samples to reveal the qualitative and quantitative data about eluted components along with their retention times[1]. Notwithstanding, overlapping chromatographic peaks may occur and can really complicate the interpretation and analysis of data[2]. Obtaining appropriate data analysis tools, which focus on the data to detect overlapped/embedded regions and to find the number of pure components that are hidden in these regions, is a problem in common analytical applications. In this paper Data analysis was enhanced with adapted Gaussian apodization factor analysis (GAFA) as a multivariate curve resolution algorithm. A unique Portable Columnless Gas Chromatography Ion Mobility Spectrometer (PCGC-IMS) was designed and fabricated this homemade customized instrument is an alternative to other time consuming technologies for monitoring of organic particles in real samples without sample preparation. GAFA has been developed as an enhanced algorithm to assess the purity of PCGC-IMS data. In GAFA method, submatrices are extracted by Gaussian apodization moving window through weighting the fixed-size moving window via Gaussian formula. Therefore, each submatrix mainly characterizes a spectrum and by performing factor analysis on this Gaussian weighted submatrix, the number of principal components for each evaluated spectrum is determined by Singular value decomposition (SVD)[3]. This precise and quick determination of a rank map is successfully used for extract pure components from PCGC-IMS.

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## Electrosynthesis of Ni<sub>x</sub>Co<sub>y</sub> on porous copper and Its Application for High Performance Supercapacitors

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Supercapacitors with desirable properties such as high power density (ten times more than batteries), fast charge–discharge processes, and excellent cycle life stability are considered as promising candidates for the next generation of energy storage devices [1,2]. Binary transition metal oxides possess higher reversible capacity, better structural stability and electronic conductivity, and have been widely studied to be novel electrode materials for pseudocapacitors [3]. In this study at first a porous Cu platform was prepared by electroless method and then Ni<sub>x</sub>Co<sub>y</sub> was electrodeposited on this porous Cu substrate. Each step of the electrode preparation process was characterized by SEM, BET, and XRD tests. Electrochemical performances were done by CV, constant current charge/discharge and EIS in KOH electrolyte. CV and galvanostatic charge/discharge shows a capacitance of 229 F/g at scan rate of mV/s, high stability and long cycle life of this electrode as a result we could reach from this combination.

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**Modeling and optimizing of adsorption of Reactive Blue B25 on the nickel ferrite magnetic nanoparticles via response surface methodology**

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The discharge of dyes into wastewaters from coloring industries (particularly the textile industry) is one of the major environmental problems, because not only does it damage the esthetic nature of the contaminated water, but also causes inhibitory effect on photosynthesis activity in aquatic systems. In addition, some dyes may degrade into the compounds, causing toxic, mutagenic, and carcinogenic effects on living organisms<sup>[1]</sup>. Therefore, the dye removal from industrial effluents, before being released to the environment is of great importance. The removal of pollutants by adsorption is one of the most attractive techniques for treatment of contaminated water. Recently, magnetic nano-sorbent have gained much more attention because these materials possess the advantages of the nano-scale sorbent and magnetic separation simultaneously<sup>[2]</sup>.

In this study, nickel ferrite (NiFe<sub>2</sub>O<sub>4</sub>) nanoparticles (NFNs) was prepared and used as magnetic nano-sorbent for the adsorption removal of Reactive Blue B25 (RB B25) as a model of azo dye. The NFNs was synthesized by co-precipitation method using nickel nitrate and ferric nitrate<sup>[3]</sup>. Optimization and modeling of the RB B25 using NFNs were performed through the response surface methodology (RSM) based on central composite design (CCD). The structure and morphology of the prepared nano-sorbent were characterized using X-ray diffraction (XRD) and transmission electron microscopy (TEM). Effect of the important factors on the adsorption of Reactive Blue B25 including solution pH, initial concentration of the dye, adsorbent dose, contact time and temperature was considered as input variables for RSM. The analysis of variance showed a high correlation coefficient ( $R^2=0.992$ ) between experimental and predicted response. The removal efficiency of the dye was more than 99 % at the optimum conditions proposed by RSM. Furthermore, the adsorption kinetic studies revealed that the adsorption process followed the pseudo-second-order model. Moreover, adsorption isotherms investigation indicated that the experimental data were well fitted to Langmuir isotherm model and, accordingly, the maximum adsorption capacity ( $q_m$ ) was found to be 79.0 mg/g.

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## Solid-phase extraction to preconcentrate trace amounts of palladium using ZnO nanoparticles

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The determination of palladium in environmental samples is difficult because of the high concentration of interfering matrix components and its low content in the most of samples<sup>[1]</sup>. To solve these problems, preconcentration and separation techniques have been often exploited<sup>[2]</sup>. In this work, a simple method based on solid phase extraction applying zinc oxide (ZnO) nanoparticles and atomic absorption spectrometry was developed for the trace amount determination of palladium (II) in aquatic samples. ZnO nanoparticles were prepared by dissolution–reprecipitation of micro-sized ZnO powder<sup>[3]</sup> and after characterization by SEM, IR and XRD techniques were applied for the solid phase extraction of palladium ions from aqueous solutions. Important parameters influencing the extraction and desorption process including sample pH, desorption solvent and its volume, extraction and desorption time were optimized.

Under optimal conditions, a preconcentration factor of 143 was obtained. The calibration graph showed linearity in the range of 2.49 -70.0  $\mu\text{g L}^{-1}$  of palladium with correlation coefficient of 0.9980. Detection limit based on the  $3S_b$  criterion was 0.74  $\mu\text{g L}^{-1}$  and relative standard deviation for six replicate measurements was found to be 3.8%. ( $n = 6$ ). The developed method was successfully applied to real water samples while the recovery percentages obtained for the spiked water samples were from 93.5 to 101.2 %.

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**Synthesis of cross-linked chitosan-based hydrogel in order to investigation of loading and release rate of hydroquinone**

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Hydrogels are hydrophilic polymers with a three-dimensional network that can absorb and store water and aqueous solutions. These materials are initially anhydrous. But they can absorb aqueous solution several times greater than hydrogel own weight. There are some pores in the hydrogels that can trap the drug and subsequently release the drug through a mechanism that depends on the drug distribution factor. Hydrogel-based drug delivery systems operate on the basis of a kind of stimulus. This can be a physical or chemical stimulus. Physical stimuli, include temperature, current, light, etc. While the chemical stimulant is related to PH, solvent, etc. The small change in ambient conditions such as pH causes large changes in hydrogel structure and its reversibility [1-2].

In this study, chitosan-based hydrogel was cross-linked with glutaraldehyde and the hydroquinone was trapped as a drug into the hydrogel [3]. In order to release the drug, the cross-linked polymer was inserted in the solution at pH 1-12. The concentration of released hydroquinone subsequently was determined using spectrophotometry. The results show that the release of hydroquinone in acidic pHs is greater. This is due to, the amount of water absorption in acidic pHs is higher than that of basic pHs.

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**Chitosan-based hydrogel: synthesis and its application in loadig and release of nile blue**

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Hydrogels are hydrophilic polymers with a three-dimensional network which is capable of absorption and desorption hydrophilic solutions. In general, the rate of release of trapped material inside the hydrogel network is directly related to the rate of diffusion of water into the hydrogel network. That is, the higher the rate of water diffusion into the network, the faster release of the trapped material. The high rate of water diffusion into the hydrogel network causes the flow of water in to the network to be fast and, therefore, the trapped material is release more rapidly from the hydrogel. Chitosan hydrogel is soluble in water and has a positive charge, and this feature is technically important. Because it enables polymers to interact with negatively charged polymers, coarse molecules, and even with some poly-anions in an aqueous medium. A gel is created from these interactions and states of transition [1-3].

PH-sensitive hydrogels were synthesized by grafting acrylic acid monomers onto chitosan in the presence of the cross-linking agent methylene-bis-acrylamide and the thermal primer of ammonium persulfate for controlled release of nile blue. In this research, a pH-sensitive hydrogel was used as carrier of electro-active substance nile blue. The concentration of released nile blue was evaluated utilizing DPV as a sensitive electrochemical method at different pH levels. The synthesized material was inserted at a pH 1 to 12 for a specified period, then the calibration curve was plotted to measure the concentrations of the solutions. The results showed that in acidic PHs the nile blue concentration was higher, indicating that the nile blue release rate was higher in acidic pHs.

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## Determination of proton transfer and the corresponding structures of 2,3-Diamino Pyridine with Benzoic Acid using combined experimental and theoretical approaches

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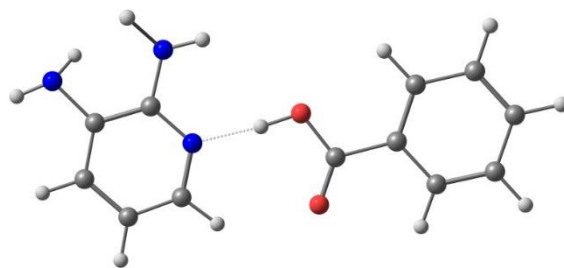
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Noble prize was awarded to founders of Supramolecular Chemistry for the year of 1987. Cocrystal development has attracted huge consideration because of its pertinence in the configuration and development of strong state multi-component frameworks, especially in the field of pharmaceutical science. Cocrystals have gained a lot of recent attention owing to their amenability to design and their ability to tailor physiochemical property. The greatest potential of cocrystals resides in the improvement of physical properties of cocrystals like solubility, dissolution rate, melting point, color, etc. with respect to those of cofomers, Cocrystallization leads to formation of a crystalline complex comprising of two or more molecules bonded together in the crystal lattice through non-covalent interactions like hydrogen

bonding (HB). While, salt formation involves association between two counter ions and also through charge assisted HB. The technique of cocrystallization continues to gain significance for its application to the design of new supramolecular structures with desired functional properties. Various supramolecul

ar architectures comprising acids and a variety of N-containing basic components have been archived recently. Phthalimide derivatives are used as anesthetics, DNA-cleaver agents, tumericidals, optical

brighteners, and dyes [1-3]. In context of previous research work, herein we further extend, report the synthesis and the crystal structures of organic cocrystals of 2,3diamino pyridine with benzoic acid. In followings, using high level TD-DFT calculations, the structural and electronic geometry of 1 have been studied. Finally, electronic transition assignments, vibrational, and frontier molecular orbital (FMO) analysis in ground state have been executed with the aid of DFT/B3LYP/6-311+G(d,p) level of theory.



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**Development of liquid–liquid–liquid extraction clean–up in combination with preconcentration by dispersive liquid–liquid microextraction in analysis of seven pesticides from soya milk**

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Nowadays, the control of pesticide residues in food commodities is a requirement for compliance with the legislation, ensuring the safety of the population and international and national trade [1]. Frequent application of various pesticides simultaneously requires the development of multi–residue analysis methods. The development of such methods is often difficult since the different pesticides from various chemical classes have different physicochemical properties e.g. polarity, solubility, volatility as well as different octanol–water partition coefficients, which make their extraction and analysis difficult. Moreover, the presence of matrix interferences can significantly affect pesticides identification and quantification. Therefore, sample preparation is a crucial step in most analytical procedures. A perfect sample preparation provides not only extraction of the target analytes, but also sample clean–up. It removes the potentially interfering compounds to achieve a sufficient selectivity and sensitivity to guarantee that the detection limits of the method are in agreement with maximum residue limits. Some sample preparation methods have been developed for the analysis of pesticide residues such as liquid–liquid extraction [2] and solid phase extraction [2, 3], which have some drawbacks.

In the present study, a new extraction method based on a three–phase system liquid–liquid–liquid extraction followed by dispersive liquid–liquid microextraction has been developed and validated for the extraction and preconcentration of seven pesticides in soya milk sample. The aim of this work was to develop a sample preparation method in which not only most analytes are transferred from the sample to the extraction solvent but the co–extracted components of the matrix are reduced as far as possible. The extraction mechanism is based on the different affinities of the species from soya milk towards each of the involved phases (aqueous solution, acetonitrile, and *n*–hexane), which provides high selectivity to the process. Most interference co–extracted components such as lipids, free fatty acids, and other hydrophobic compounds are extracted into *n*–hexane and will not be present in the final extract. Effect of various experimental parameters on the extraction efficiency was studied and optimized. Under the optimized extraction conditions limits of detection and enrichment factors for the analytes were obtained in the ranges of 0.11–0.35  $\mu\text{g L}^{-1}$  and 562–933, respectively. The obtained extraction recoveries were between 56 and 93% and the calibration curves were linear in wide ranges with correlation coefficients  $\geq 0.9985$ . Relative standard deviations were less than 7.0% for intra– (n=6) and inter–day (n=5) precisions (at two concentrations of 10 and 50  $\mu\text{g L}^{-1}$  of each analyte). Finally, the proposed method was applied on different soya milk samples and chlorpyrifos was determined in one sample of soya milk at a concentration of  $19 \pm 3 \text{ ng mL}^{-1}$  (n=3).

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**Development of a three-phase system based on liquid-liquid-liquid extraction and its application in sample preparation of different cereals flour samples for the extraction of nine selected pesticides and analysis by high-performance liquid chromatography-diode array detection**

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Pesticides are widely used to protect crops and plants from pests and diseases with the objective of increasing agricultural productivity. But the presence of residues of these compounds in food products may be a risk to consumers health, due to their potential toxicity [1]. Many control authorities have established maximum residue limits or tolerances to protect the environment and consumer health. Nowadays, the control of pesticide residues in food commodities is a requirement for compliance with the legislation, ensuring the safety of the population and international and national trade [2]. Thus, it is of great significance to develop an accurate and reliable analytical method, which is applicable to trace levels of pesticide residues in food and environmental samples. Sample preparation is a crucial step in most analytical procedures. Traditional sample preparation methods such as liquid-liquid extraction [3] and solid phase extraction [3, 4] have some drawbacks.

This work deals with the development of a reliable sample preparation method based on liquid-liquid-liquid extraction combined with dispersive liquid-liquid microextraction and its application in the extraction and preconcentration of some pesticide residues in different cereals flour samples. This method consists of a three-phase system including aqueous phase (sample solution), acetonitrile and *n*-hexane for clean-up and the microextraction method for preconcentration of the analytes before their injection into the separation system (HPLC-DAD). The influence of several variables on the extraction efficiency were investigated and optimized. Under the optimal conditions, extraction recoveries were obtained in the range of 55-90% and the calibration curves were linear in wide ranges with a correlation coefficient  $\geq 0.9987$ . Intra- ( $n = 6$ ) and inter-day ( $n = 5$ ) precisions of the method were satisfactory with relative standard deviations less than or equal to 7.0% at two concentrations of 10 and 50 ng g<sup>-1</sup> of each analyte. Moreover, the detection limits and enrichment factors of the target analytes were obtained in the ranges of 0.16-0.60 ng g<sup>-1</sup> and 221-359, respectively. It was found that the three-phase system was a good clean-up procedure and reduced the risk of potential interferences related to the complexity of the matrix. Finally, the proposed method was applied on different types of cereals including wheat, buck wheat, barley, rice, corn, chickpea, soya, semolina, whole wheat, wheat sprout flours, and wheat grain. Clodinafop-propargyl was determined at the concentrations of  $21 \pm 2$  and  $16 \pm 1$  ng g<sup>-1</sup> ( $n = 3$ ), respectively, in whole wheat and wheat sprout flours.

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## Reduced graphene oxide supported bimetallic Ni-Co nanoparticles as an electrocatalyst for electro oxidation of methanol in alkaline media

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Developments of the fuel cells, batteries, and water electrolyzers which are clean energy conversion and storage technologies, is highly interested subjects for researchers. Because, they can resolve current problems associated with energy security and environmental pollution [1]. Fuel cell technology is developing machinery that can efficiently convert chemical energy into electrical energy with a negligible emission of contaminants. Among different types of fuel cells under development, the direct methanol fuel cell (DMFC) is illustrious by its low operational temperature and suitable fuel feeding. These features permit a potential application to portable electronics such as cell phones, laptop computers, and video camcorders [2]. In the electrochemical oxidation of methanol, the electrode material is clearly an important parameter where a high effective electrocatalyst is needed. Different electrocatalysts based on Pt and Pt-binary electrodes were generally used as a catalyst for the electrochemical oxidation of methanol [3]. Nevertheless, the extensive application of Pt catalyst is seriously limited because of its high cost and easy deactivation from the surface adsorption of poisonous intermediates or reaction products. Applying alloys of low cost metals such as (Fe, Co, Ni, and Cu) can partly solve these problems [4]. Many modified electrodes, in which Ni is used as a structure in their manufacture, can be used as a catalyst in fuel cells. Also, using of graphene nano-sheets as a substrate for deposition of bimetallic nanoparticles make a good nanostructure for catalytic goals.

In this study, we have successfully demonstrated the possibility of fabrication Ni-Co nanoparticles on reduce graphene oxide/carbon paste electrode (Ni-Co/RGO/CPE). After characterization of obtained electrode, prepared electrocatalyst was used for electrocatalytic oxidation of methanol. The results showed that the presence of Ni-Co in the structure of catalyst and application of RGO/CPE as a substrate greatly enhance the electrocatalytic activity towards the electrooxidation of methanol. Cyclic voltammetric responses of various modified electrodes were obtained in NaOH solution pH 13.0 in the absence and presence of methanol. The anodic peak potential of methanol oxidation at the bare CPE is more than 1.1 V, while the corresponding potential at Ni-Co/RGO/CPE is about 0.65 V. On the other hand, the anodic peak current at the surface of Ni-Co/RGO/CPE is greatly enhanced by addition of methanol to the solution, while its cathodic peak current disappears. The chronoamperometry technique was employed for obtaining the diffusion coefficient of methanol and the value of  $8.75 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$  is calculated for it which is comparable with other reports. Also the catalytic rate constant was obtained for the reaction between methanol and Ni-Co/RGO/CPE according to method of Galus as  $1.05 \text{ M}^{-1} \text{ s}^{-1}$ .

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## Optically concentration as new concept for quantitative analysis of nanoparticles

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The unique size-dependent properties of Gold Nanoparticles (GNPs) make them superior and indispensable in many areas from biology to electronics. [1]. This strongly motivates development of trapping and manipulation technologies for metallic particles. The single beam optical trapping was introduced by Ashkin et al. [2]. It refers to a particular geometry where a laser beam is focused through a high numerical aperture objective lens to generate a three-dimensional optical trap by exerting a radiation force to small objects. For a high-gradient light field, two optical forces are exerted on small dielectric particles. The first is a momentum transfer due to scattering of the electromagnetic wave from the particle that pushes the particle and may destabilize trapping. The second is the gradient force on the dipole induced in the particle by the laser electric field. The gradient force depends on both the particle polarizability and the electric-field amplitude [3].

For sufficiently high laser intensities, the gradient force is strong enough to overcome the randomizing effect of brownian motion, thus locally enhancing the particle concentration near the focus. As the intensity of the trapping laser is increased, more particles are pulled toward the focus. an optical trap, in which particles can diffuse into and out of the trap, it is the average particle number density that increases with laser intensity [4]. Ou-yang et al. demonstrated for multiple particles in a single trapping consider both energy of trapping per particle and interaction between the particles [5].

optical concentration of substance in solution is a novel concept for enhancement of analytical sensitivity. In this paper, we investigated optical concentration of gold nanoparticle in the focal region of laser beam. We observed that the optical accumulation of nanoparticles in the trap region increases by the raising of laser intensity and number of gold nanoparticle around the focal region. Thus, increase of the molecules or particles in focal region of laser beam could be used for enhancement of analytical sensitivity. Under optimum conditions, linearly calibration curves in the range of  $7.2 \times 10^8$  to  $1.44 \times 10^{10}$  particle/ml were obtained for gold nanoparticle at laser power of 400 mW, gold nanoparticle size of 100 nm and 40 s after laser beam illuminated.

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**Development of an efficient method for extraction of some widely used pesticides in fruit and vegetable samples prior to their determination by GC-FID**

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Pesticides are chemical compounds with a wide range of physico-chemical characteristics that their consumption in agriculture is increased day by day aiming to combat weeds, fruit diseases, and any other agents that can affect crop quality and yield [1]. Although the use of pesticides has many advantages, however, they can enter the crop matrices and alter them to products that are toxic for human health [2, 3]. These products can cause long-lasting cancer, endocrine disruptors, chronic poisoning, and genetic variation [4]. Therefore, the monitoring of pesticide residues in various food products, especially in fresh fruits and fruit juices is of great importance, because they are unprocessed and consumed by people of all ages, especially children. So, it is critically important to devise facile and highly sensitive analytical methods, which are capable of detecting their trace residue concentrations in food and environmental samples.

In this study, a combination of Quick Easy Cheap Effective Rugged and Safe extraction and dispersive liquid-liquid microextraction has been proposed for the extraction and preconcentration of some extensively used pesticides (diazinon, chlorpyrifos, penconazole, oxadiazon, and diniconazole) from fruit and vegetable samples prior to their determination by gas chromatography-flame ionization detection. In the proposed method, firstly, an aliquant of sample is crushed and its refuse and juice are separated by centrifuging. The juice is transferred to a conical glass test tube. Then acetonitrile as an extraction/disperser solvent is added into the tube containing the refuse. The analyte residues are extracted into acetonitrile after vortexing. The obtained acetonitrile is mixed with an extraction solvent (1, 2-dibromoethane) at  $\mu\text{L}$  level and rapidly injected into the juice. As a result, a cloudy state is formed and the tiny droplets of the extractant containing the extracted analytes are collected at the bottom of the tube after centrifugation. Finally, an aliquot of the sedimented organic phase is removed and injected into the separation system for quantitative analysis. In this study, several significant factors affecting the performance of the introduced method were investigated and optimized. Under the optimum experimental conditions, enrichment factors ranged from 240-375. The relative standard deviations were  $\leq 7\%$  for intra- ( $n=6$ ) and inter-day ( $n=4$ ) precisions at a concentration of  $100 \mu\text{g L}^{-1}$  of each analyte. Limits of detection were in the range of  $0.27-0.48 \mu\text{g L}^{-1}$  in solution and  $0.68-1.2 \mu\text{g Kg}^{-1}$  in the samples. Finally, several fruit and vegetable samples were analyzed by the proposed method and penconazole was found in grape at  $\mu\text{g Kg}^{-1}$  level.

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## Optimization of Reactive Turquoise blue 15 Removal from Aqueous Solutions by Kaolin-Tetrabutylammonium Iodide Using Response Surface Methodology

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Dyes are organic compounds and are resistant against common removal methods and presence of dye wastes in environment causes extensive pollution [1]. Membrane filtration, adsorption, biological methods and advanced oxidation processes have been used to remove of dyes [2]. Among these methods, adsorption is mostly used due to cost-effectiveness and simplicity [3]. Turquoise blue 15 (AT15) is a reactive dye widely used in the textile industry to color natural fibers [4]. In this research modified Kaolin by Cetyl trimethylammonium bromide is used as an adsorbent for the removal of Turquoise blue 15 from aqueous solutions. The modified Kaolin was characterized by Fourier transform infrared spectra (FTIR) and X-ray diffraction (XRD). Response Surface Methodology was used to study the effect of independent variables such as modified Kaolin dosage, Turquoise blue 15 dye concentration, time and initial pH on dye removal efficiency from aqueous solutions. Analysis of variance (ANOVA) suggested that the predicted values were in good agreement with experimental data. Maximum removal was attained as 92.79% at initial pH 4, dye concentration of 60 mg/L, temperature 30 °C with an adsorbent dosage of 3 g/L. At the optimum conditions, experimental and predicted removal of Reactive Blue 21 by modified Kaolin was 93.76% and 91.31%, respectively. Thus, the statistical approach enabled us to predict Turquoise blue 15 removal by modified Kaolin. Also, study of kinetics and adsorption isotherm models of Turquoise blue 15 adsorption onto modified Kaolin showed that the adsorption of study dye onto modified Kaolin was obeyed pseudo-second-order kinetic and Fundlich isotherm models.

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**Photocatalytic degradation of Reactive Blue 21 from aqueous solutions using Zinc oxide**

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Dyes are extensively used in the different industry during dyeing process and the excess dyes are released into the effluent streams as waste after coloring [1]. The released wastes including dyeing are toxic and must be removed from environment [2]. Most of synthetic dyes are resistance to conventional degradation methods [3]. Semiconductor photo catalysis is one of method that has great potential to degradation of aqueous pollutants [4]. In this research Reactive Blue 21 is chosen as a model dye and photo degradation of it was investigated by using the ultraviolet in presence and absence of zinc dioxide. The advantage of using semiconductor in degradation of dye is the mineralization of dyes, without generation of waste [5]. It has been found that the increasing of ZnO dosage and ultra violet intensity due to increase in photo degradation of Reactive Blue 21 dye. Also, more degradation was occurred in basic solution than acidic solutions. The activation energy of photo degradation processes was calculated in the range of 298, 308 and 338 K and was obtained 39.65, 34.65 and 32.54 kJ/mol, respectively.

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**Development of an optical nanosensor based on TGA-stabilized-CdTe embedded in silica molecularly imprinted polymer for the rapid and selective determination of propranolol**

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In this work, a fluorimetric sensor based on molecularly imprinted polymers (MIPs) has been developed for the determination of an important drug, propranolol (PROP).

The World Health Organization has put PROP on the list of essential medicines [1]. PROP most widely used to treat a wide range of different diseases and disorders [2].

MIPs have cavities which are created during polymerization. These cavities are perfectly matched to their template (analyte) regarding shape, size, functional groups and orientation of cavities. MIPs in various fields have received considerable attentions because of their advantages such as ease of production, cheapness, high stability in different experimental conditions (such as temperatures, pH, and toxic environments) [3].

For preparation of the sensor, water-soluble thioglycolic acid stabilized CdTe QDs (TGA-stabilized CdTe QDs), as a probe was synthesized via a refluxing method [4]. Following, reverse microemulsion technique was applied to stabilize a thin silica shell on the surface of the QDs to get QDs@SiO<sub>2</sub> nanocomposites. In the next step, MIPs embedded TGA-CdTe QDs were obtained using 3-aminopropyl triethoxysilane (as a monomer) and tetraethoxysilane (as a crosslinker) In the presence of PROP to produce QDs@SiO<sub>2</sub>@MIPs nanocomposites [5].

Finally, the obtained sensor was used for PROP sensing. At the optimized conditions, a linear dynamic range was obtained from 3.0 to 139 μmol L<sup>-1</sup> PROP with a detection limit as 0.7 μmol L<sup>-1</sup>. The precision of the method for 30.0 and 70.0 μmol L<sup>-1</sup> PROP was obtained as 6.5% and 4.8% (3 replicate detections), respectively. The QDs@SiO<sub>2</sub>@MIPs was successfully applied for the determination of PROP in human plasma samples. Selectivity of the PROP sensor was examined in the presence of some possible interfering substances in human plasma sample. As a result, the proposed PROP sensor exhibited good selectivity for determination of PROP. The proposed method was simple, selective, and cost-efficient for PROP measurement.

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**Identification of crude oils sources based on the analysis of gas chromatographic fingerprints using pattern recognition methods**

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Spills of oil and related petroleum products in the marine environment can have serious biological and economic impacts. There are many oil tankers on the surface of the sea and  $0.68 \times 10^9$  kg crude oil spilled into soil per year [1]. Therefore, oil fingerprinting plays a basic role in source identification of oil spill. Gas chromatographic (GC-MS and GC-FID) and spectroscopic (fluorescence and FT-IR) methods are among the most frequently used techniques for oil fingerprinting. However, the huge amount of produced data are complex and to be analyzed by chemometric methods [2]. Chemometrics provides many tools for pattern recognition, calibration and optimization that can increase the speed of the analysis and allow for more extensive use of the available data in this field. Examples of used chemometric methods for identification of crude oils source are Principal Component Analysis (PCA), parallel factor analysis (PARAFAC), Hierarchical Cluster Analysis (HCA), Partial Least Square Discriminant Analysis (PLS-DA) and Counter propagation Artificial Neural network (CPANN) [3, 4].

The purpose of this study was to provide an update of the state-of-the-art of oil fingerprinting techniques to demonstrate the use of a rapid, inexpensive and useful technique for distinguishing between crude oils. In this regard, a fractionation method based on SARA test [5] was used to divide nine crude oils (obtained from Sharif upstream petroleum institute) into aliphatic (saturate), aromatic, resin and asphaltene. It is necessary to remove the asphaltene fraction before proceeding with chromatography. After fractionation, three fractions of nine oil samples were analyzed by GC-FID and GC-MS. The obtained fingerprints were baseline corrected, aligned and auto-scaled and then analyzed using unsupervised classification methods of PCA and HCA. Evaluation of PCA score plot (explaining 93.69% of variance accounted for three PCs) showed that aromatic fractions belong to three classes and result of HCA with Ward's method confirmed that. The clustering results of aliphatic and resin fractions also showed the presence of 3 classes but due to their different composition, classes were not the same. The results of unsupervised classification were then used a starting point for supervised classification methods of PLS-DA and CPANN. The results of PLS-DA analysis for aromatics showed best discrimination compared to other fractions. The procedure required an initial variable selection step using the variable important in projection (VIP) followed by a PLS-DA model. The optimum number of LVs for aromatic fraction (explaining 93.51 % and 95.87% of variance accounted for three LVs for X- and y-block, respectively) in PLS model was determined using  $R^2$  cross-validation (leave one out cross-validation). The figures of merit for classification of oils were  $R^2$ Cal(0.975 0.972 0.930),  $R^2$ CV(0.712 0.913 0.581), RMSEC(0.0786 0.0699 0.1245), SEN(1.000 1.000 1.000), and Specificity(1.000 1.000 1.000). The CPANN top map of aromatic fractions represented 3 different classes that confirmed the results obtained by PCA score plot, HCA and PLS-DA. The classification figures of merit for CPANN were ERcal(0), ERCV(0.417), accuracy cal(1.000), accuracy cal(0.556), SEN(1.000 1.000 1.000), Specificity(1.000 1.000 1.000). Finally, it is concluded that aromatic fractions were appropriate for identification of crude oils sources.

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**Electrochemical study of 4-*tert*-butylcatechol in the presence of dithiooxamide (rubeanic acid). Electro-organic synthesis of new dithiooxamide derivatives**

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Electrochemistry provides very versatile means for the electrosynthesis, mechanistic and kinetic studies. Electrosynthesis has become more and more important in organic chemistry due to its following characteristics: unique selectivity because of in situ formation of an active species at the interface, inversion in polarity by transfer of electron and variability in product formation by control of potential. The use of water or ionic liquids instead of toxic solvents, room temperature condition, high energy efficiency and using the electrode as electron source instead of toxic reagents are in accord with the principle of green chemistry [1,2].

Dithiooxamide derivatives attract interest as starting compounds for the synthesis of a number of S,N heterocycles [3]. Cyclic voltammogram of 4-*tert*-butylcatechol in the presence of dithiooxamide as a nucleophile confirms the reaction of electrochemically generated 4-*tert*-butyl-*o*-benzoquinone with dithiooxamide. The overall reaction mechanism for anodic oxidation of 4-*tert*-butylcatechol in the presence of dithiooxamide according to spectroscopy data and cyclic voltammetry and coulometry results has reported. The work has led to the development of a facile electrochemical method for the synthesis of new and unique dithiooxamide derivative in good yield and purity.

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**Design and construction of a new configuration of crossed-beam thermal lens spectrometer operating at high flow velocity and its application for Cysteine determination in human serum and saliva**

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Thermal lens spectrometry (TLS) is a high sensitive method for trace determination of non-fluorescent materials [1]. Previous thermal lens spectrometers suffer from operating limitations at high flow velocities, arising from taking the heated element off the probe beam direction which results in a decrease in the thermal lens (TL) signal [2, 3]. Herein, we introduce a new optical configuration of crossed-beam thermal lens in transversal flow mode in which the propagating direction of the probe beam and liquid sample flow azimuth are concentric (CBTC). The system consists of a microfluidic cell with a volume of lower than 3  $\mu\text{L}$ . In the current optical configuration, using 1-(2-pyridylazo)-2-naphthol (PAN) in ethanol as a test solution, by increasing the sample flow velocity and without increasing chopping frequency the reduction in sensitivity is less pronounced. Under 15 Hz chopping frequency, the optimum sample flow velocity is about 2  $\text{cm s}^{-1}$  which is among the highest reported values achieved to date for photothermal lens spectrometers. Although, the system operates at higher flow velocities and lower chopping frequencies compared to the collinear configuration, it provides comparable analytical limit of detection. This optical configuration has been successfully employed for highly sensitive and selective determination of cysteine in human serum and saliva samples through a competitive complexation reaction with Cu-PAN as colorimetric probe. The detection limit of this method (9.5 nM) shows a significant enhancement (726-times) in comparison to UV-vis measurements.

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**Determination of chromate in water samples by flame atomic absorption spectrometry after extraction and preconcentration with an efficient chitosan-based nanocomposite**

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Chromate is placed among the most important environmental pollutants that have changed into a global concern due to their toxicity and carcinogenetic properties. Chromate even in trace amounts accumulate in the body of creatures and their food cycle [1-2]. Therefore, the development of an effective method for preconcentration and determination of chromate in environmental samples is important. In this study, chitosan-based nanocomposites containing zero valence metals such as Cu, Au, Pd, and Pt were individually synthesized [3], and used as a sorbent for the solid-phase extraction and preconcentration of chromate ions from aqueous solutions prior to determination by flame atomic absorption spectrometry (FAAS). The size and morphology of the nanosorbents were characterized via x-ray diffraction analysis, scanning electron microscopy and Fourier transform infrared spectroscopy. The experimental factors affecting the extraction/ preconcentration of the analyte such as pH, amount of nanocomposite, sample volume, type and concentration of eluent and sorption and desorption time were optimized. Under the optimized experimental conditions, the calibration graph was linear in the concentration range of 0.2– 100 ng mL<sup>-1</sup>. The limit of detection and the preconcentration factor are 0.06 ng mL<sup>-1</sup> and 100, respectively. The method was successfully applied to determine chromate in several water samples.

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**Colorimetric sensing of palladium ions based on in situ generation of palladium nanoparticles as an activator for thionine-hydrazine reaction**

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Palladium is a lustrous silver-white transition metal that is used in modern industrial applications including dentistry, jewelry, medical instruments, electrical devices, fuel cell and catalytic converters in automobile nowadays [1-4]. On the other hand, these applications have led to increasing concentration of palladium in the atmosphere and environmental matrices. It is well known that palladium could affect human health. It may cause skin and eyes sensitization and at high concentration level can bind to thiol containing amino acids, proteins, and other biomolecules causing serious physiological disorders. Therefore it is important from analytical viewpoint to monitor palladium concentration in the environment and attentions are made to develop new sensitive method for this purpose.

In this new work, attention has been devoted to in situ generation of palladium nano particles (PdNPs) and its catalytic effect on the reduction reaction of thionine by hydrazine. Upon entrance of Pd<sup>2+</sup> ions into a medium including hydrazine and thionine, Pd<sup>2+</sup> ions were reduced by hydrazine to produce PdNPs which caused depigmentation of thionine by surplus hydrazine. This phenomenon was followed spectrophotometrically by measuring the change in maximum absorbance intensity of thionine (599 nm) versus time. Initially to approve the synthesis of PdNPs, UV-VIS spectroscopy, average particle size and TEM imaging were performed. Then several factors influencing analytical performance of the method such as concentration of reactants and electrolyte, pH of the sample solution and temperature were investigated to achieve the optimum conditions and highest sensitivity. This method showed a linear range from 8-1200 ng mL<sup>-1</sup> concentration of palladium ions with a limit of detection of 6.7 ng mL<sup>-1</sup>. The relative standard deviation was 3.8% and 1.3 % (n=8) for two concentrations of 60 and 300 ng mL<sup>-1</sup>, respectively. The method was successfully applied to the determination of palladium in river water, pond water and soil samples.

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**Effect of temperature on dissociation constant of (+)-(S)-2-(6-methoxynaphthalen-2-yl) propanoic acid in methanol+water binary solvent by potentiometry**

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The dissociation constant is an important physic-chemical parameter of a substance, and the knowledge of this parameter is of fundamental importance in a wide range of applications and research areas. Thus, the dissociation constants of (+)-(S)-2-(6-methoxynaphthalen-2-yl) propanoic acid at 0.1 M (Me<sub>4</sub>NCl) ionic strength and 25, 37 and 45 °C under argon atmosphere in aqueous medium were determined by the potentiometric method using the BEST computer program. Log β values found were 4.4711, 4.423, and 4.3736 for 25, 37 and 45°C respectively. Results show that the logβ values decrease with increasing temperature. This can simply be explained as a result of proton release from ligand [1, 2]. The amount of protons released depends on the strength of the intermolecular hydrogen bond. In other words, it can be said that when temperatures are increased the strength of the intermolecular hydrogen bonds between ligand and solvent molecules is decreased. The thermodynamic parameters such as, Gibb's free energy change (ΔG°), entropy change (ΔS°) and enthalpy change (ΔH°) associated with the dissociation of the ligand were calculated. The negative ΔG° values indicate that dissociation of the ligand process is spontaneous [3]. A decrease in proton-ligand dissociation constant (logβ) with an increase in temperature and the negative value of enthalpy change (ΔH°) for the dissociation suggests that this reaction is exothermic, favorable at lower temperature. ΔS° is positive revealing that entropy is favorable for the dissociation of ligand [4].

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## The 25<sup>th</sup> Iranian Seminar of Analytical Chemistry

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### Solvent effect on stability Constants of (+)-(S)-2-(6-methoxynaphthalen-2-yl) propanoic acid with zinc in different aqueous solution of methanol

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The metal-ligand stability constants of HL ligand, HL= (+)-(S)-2-(6-methoxynaphthalen-2-yl) propanoic acid, with zinc in 50, 60, 70, 80 and 90% (v/v) methanol+water mixtures have been determined at an ionic strength of 0.10 M Me<sub>4</sub>NCI and at 25.0 °C under an argon atmosphere. A potentiometric method was used and the calculation of the stability constants has been carried out using the BEST computer program. Species distribution curves of complexes has been plotted as function of pH using the SPE and SPEPLOT program to visualize the presence of various species in equilibrium in the pH range 2–12. The results are discussed in terms of the effect of solvent on complexation and show that the stability constants of the metal-ligand complex increases with increasing amount of methanol. It is known that the ligand must compete with solvent molecules for the cation in the complexation process. Thus, variation of the solvent is expected to change the apparent binding properties of the ligand. This may be due to the decrease in dielectric constant of the solutions and hydrogen bonding and increase in solvation of protonated species by the organic solvents [1-3]. The different species ML<sub>2</sub>, ML<sub>2</sub>H, ML<sub>2</sub>H<sub>2</sub>, ML<sub>2</sub>H<sub>-1</sub> and ML<sub>2</sub>H<sub>-2</sub> formed depending on pH of solution. The main species formed are ML<sub>2</sub> and ML<sub>2</sub>H<sub>-1</sub> in the pH range of 5-7 and in pH higher than 10, respectively.

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**Determination of methionine using solvent-based de-emulsification dispersive liquid–liquid microextraction coupled with surface plasmon resonance of silver nanoparticles prepared by a bio-stabilizer**

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Methionine, (2-amino-4-(methylthio)butanoic acid), is an essential amino acid with an important role in biological methylation reactions. Methionine is also important in the formation of blood proteins, globulins and albumins helping in the breakdown of lipids and acting as chelating agent for removal of heavy metals from body. This amino acid helps to reduce cholesterol level by increasing lecithin production in liver and is also essential for human growth. Methionine deficiencies have been attributed to toxaemia, muscle paralysis, hair loss, depression, schizophrenia, Parkinson's disease, liver deterioration and impaired growth. Since methionine cannot be synthesized in the body it must be obtained from food supplies and pharmaceutical supplements are commercially available [1, 2]. Thus, the determination of this essential amino acid is very important in the clinical point of view. Due to the excellent LSPR properties of silver nanoparticles (AgNPs) and their color change visualization from yellow to brown by aggregate of AgNPs, they have been considered for colorimetric assays. Surface plasmon resonance (SPR) of dispersed silver nanoparticles in aqueous media depends on their size, shape, aggregation and structure which show very intense colors. Therefore AgNPs can be used as colorimetric probe for chemical or biological sensing [3].

In this study, a solvent-based de-emulsification dispersive liquid–liquid microextraction method coupled with AgNPs as a colorimetric probe was developed for determination of trace levels of methionine. The stable and dispersed AgNPs were synthesized by applying ascorbic acid as reducer and *Stenotrophomonas maltophilia* bacteria as bio-stabilizer and then preconcentrated in organic phase according to a facile dispersive liquid-liquid microextraction procedure based on 1-octanol as extraction solvent and acetone as disperser and demulsifier. The presence of methionine influenced on the intensity of plasmon resonance absorbance peak of AgNPs, which was employed for the spectrophotometric determination of this amino acid. The effect of different variables such as bio-stabilizer amount, ascorbic acid concentration and type and volume of extraction, disperser and demulsifier solvents was investigated and optimized. The calibration curve was linear in the range of 1.7 - 234.6 nM of methionine and limit of detection was 1.0 nM.

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## Application of a new fluorescent Schiff base for determination of cadmium

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Cadmium ion ( $\text{Cd}^{2+}$ ), known as highly toxic heavy metal ion, is frequently used in industrial and agricultural activities, which results in its widespread distribution in environment. Furthermore, its bioaccumulation in the food chain leads to its transportation into the human body, which may cause serious health hazards [1]. Cadmium toxicity is associated with several clinical complications: cancer, liver and kidney dysfunction, increased risk of bone fracture, hypertension, atherosclerosis and severe anemia. Current evidence suggests that exposure to cadmium induces genomic instability through complex and multifactorial mechanisms; there are no proven effective treatments for chronic cadmium intoxication [2]. As such,  $\text{Cd}^{2+}$  contamination has attracted significant attention because of its toxicity and accumulation in human tissues which led to increasing needs to determine even trace  $\text{Cd}^{2+}$  in a variety of matrices [3].

In this study, 1,5-bis(2-hydroxy-3-methoxybenzaldehyde) thiocarbohydrazone (BHMT) as a new and highly intensive fluorescent Schiff base has been introduced for monitoring cadmium ions in aqueous samples. It was synthesized by the reaction of 2-hydroxy-3-methoxy-benzaldehyde with *thiocarbohydrazide* and showed strong fluorescence at 502 nm under excitation wavelength of 380 nm. The synthesized compound was characterized using Fourier-transform infrared (FTIR) and nuclear magnetic resonance (NMR) spectroscopy. It was found that the fluorescence intensity of BHMT decreased with increasing of  $\text{Cd}^{2+}$  concentrations which allows the spectrofluorimetric sensing of  $\text{Cd}^{2+}$ . The effect of important parameters such as acidity or basicity of solution, BHMT concentration was studied and optimized. Under the established optimum conditions, the calibration graph was linear in the range of 10 to 200  $\text{ng mL}^{-1}$  of  $\text{Cd}^{2+}$ . The limit of detection for the target metal ion based on  $3S_b/m$  definition was 2  $\text{ng mL}^{-1}$ . The developed method showed good reproducibility and adequate selectivity, and it was successfully applied to the determination of trace amounts of cadmium in water samples.

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**The Fe<sub>3</sub>O<sub>4</sub> nanoparticle- NaHCO<sub>3</sub>-H<sub>2</sub>O<sub>2</sub> chemiluminescence reaction used for the determination of amoxicillin in pharmaceutical formulations**

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Amoxicillin is a penicillin antibiotic that used to cure bacterial infections in sinuses and the respiratory tract and healing of many different types of dermal and renal infections. They are also used in treating some sexually transmitted diseases. Determination of amoxicillin is very important in the quality control of antibiotic preparations in the pharmaceutical industries [1]. Generally, chemiluminescence (CL) is the generation of electromagnetic radiation through an exothermic chemical reaction. Indeed, it is a favourable detection tool owing to its wide dynamic linear range, high sensitivity, low-cost and simple instrumentation [2]. Several chemiluminescence (CL) systems including luminol–periodate [3], luminol–permanganate [4] and luminol–K<sub>3</sub>Fe(CN)<sub>6</sub> [5] and thiosemicarbazide–H<sub>2</sub>O<sub>2</sub> [1], among others have been developed for the determination of amoxicillin. In this research work, Fe<sub>3</sub>O<sub>4</sub> nanoparticles (NPs) were synthesized by using a quick precipitation method and then characterized by using X-ray diffraction (XRD), Fourier Transform Infrared (FTIR) and scanning electron microscopy (SEM) techniques.

The characterization study revealed that Fe<sub>3</sub>O<sub>4</sub> NPs were spherical in shape and have a narrow size distribution of about 20–40 nm. It was found that the Fe<sub>3</sub>O<sub>4</sub> NPs enhanced the NaHCO<sub>3</sub>-H<sub>2</sub>O<sub>2</sub> CL reaction. Moreover, it was revealed that amoxicillin inhibited the Fe<sub>3</sub>O<sub>4</sub> NPs–NaHCO<sub>3</sub>-H<sub>2</sub>O<sub>2</sub> system. The CL intensity was inversely proportional to the concentration of amoxicillin. Based on these results, Fe<sub>3</sub>O<sub>4</sub> NPs–NaHCO<sub>3</sub>-H<sub>2</sub>O<sub>2</sub> system was used for the developing a new, sensitive, simple and green CL analytical method for amoxicillin. The linear dynamic range, limit of detection and relative standard deviation (RSD%) of the method were  $3.0 \times 10^{-6} - 1.0 \times 10^{-3} \text{ mol L}^{-1}$ ,  $2.9 \times 10^{-6} \text{ mol L}^{-1}$  and 2.41, respectively. The CL method was successfully used for the determination of VPR in pharmaceutical formulations. In addition, the possible mechanism of the Fe<sub>3</sub>O<sub>4</sub> NPs–NaHCO<sub>3</sub>-H<sub>2</sub>O<sub>2</sub> CL reaction was also discussed, briefly.

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## The 25<sup>th</sup> Iranian Seminar of Analytical Chemistry

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### Determination of morphine and codeine in biological samples by high-performance liquid chromatography after simultaneous extraction/preconcentration with a magnetic nano-composite based on reduced graphene oxide and silver nano-particles

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Blood and urine are very useful biological matrices in clinical and forensic toxicology due to their importance for assessing short-term and recent exposure to drugs, respectively [1]. Morphine is a strong opioid used for the treatment of moderate to severe pain. Its use is, however, associated with adverse effects including sedation, nausea, constipation, respiratory depression, and development of tolerance as well as dependence [2]. Plasma morphine concentrations usually range between only 7-100 nM. However, higher concentrations of up to 1  $\mu\text{M}$  have been reported for patients with advanced cancer [3]. Codeine is widely used for the treatment of cough and moderate pain too, so their presence in biological fluids must be often assessed and may be correlated to heroin abuse, particularly in the case of morphine [4]. For this reason, a rapid, simple and sensitive magnetic solid-phase extraction (MSPE) method for the extraction and quantification of the morphine and codeine from biological fluids using high performance liquid chromatography with UV detection (HPLC/UV) was developed and validated. The  $\text{Fe}_3\text{O}_4/\text{rGO}/\text{Ag}$  was synthesized, characterized and used for sample treatment. Nano-magnetic composite morphological and properties were characterized by XRD, FTIR and SEM. The optimizing of the parameters, interaction effect of variables, individually and their interaction effects on the extraction process was evaluated by employing a central composite design. The optimized conditions show the constructed calibration curves are linear in the concentration range of 0.01–10  $\mu\text{g L}^{-1}$  for morphine and codeine with a correlation coefficient of 0.9983 and 0.9976, respectively. The detection limits and quantification limits for morphine and codeine are 0.18, 0.21  $\mu\text{g L}^{-1}$  and 0.61, 0.72  $\mu\text{g L}^{-1}$ , respectively. The morphine and codeine recoveries from different samples (human plasma and urine) are between 97.0 and 102.5 % with relative standard deviations of 1.02–5.10 %.

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**The use of chemometrics methods for analyzing the simultaneous release of drugs from the polymeric substrates**

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Most recently, significant medical advances have been made in the area of drug delivery with the development of controlled release dosage forms using various types of polymers as substrates for drug loading, but these improvements have not been completely defective. The development of mathematical models is widely employed in different disciplines and are very useful in the case of controlled drug delivery systems as this approach enables, the prediction of release kinetics before the release systems are to be realized. Often, it delivers the measurement of some important physical parameters, such as the drug diffusion and the other parameters. (1- 4)

Treximet is a combination drug for the treatment of an acute migraine, Which is a combination of Sumatriptan, and naproxen sodium drugs.

In this study, we used melamine-modified poly(styrene-alt-maleic anhydride) to load and release the so-called drugs. The modified polymer matrices were studied by FT-IR spectroscopy. The release of these drugs was monitored separately and in different pH by the UV-vis spectroscopy. pH=6 is chosen as the optimal pH. In order to study the release kinetics, experimental data obtained from in vitro drug release were approximated by several mathematical models including zero-order, first-order, Hixson-Crowell and Korsmeyer-Peppas to determine the kinetics of drug release from drug delivery systems. The obtained results showed that the Korsmeyer-Peppas model fits well the data of Sumatriptan and Naproxen release. Also it has been shown that the release kinetics for both drugs are similar for simultaneous and single drug release studies and the obtained mathematical models can be used in both situations.

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**Appraisal of changes in groundwater quality of Tasouj aquifer and approaches to improve the quality of water from this aquifer**

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Review of long-term changes in groundwater quality help to understand the quality of aquifer and manage it to improve and stay in good shape. Since the water needed for drinking and farming of Tasouj plain is provided from groundwater resources, it is important to study the process of changes in the quality of these resources. Quality changes of this resources are affected by many factors; one of these factors is the proximity of this aquifer to Lake Urmia and extra withdrawal of these resources in Tasouj aquifer. In this study, changes in Total Solids Solubility (TSS) and its effect on Electrical Conductivity (EC) of groundwater along with existing Chloride, changes in taken samples in the aquifer area during the 10-year period has been studied. The results clearly show the increasing trend of EC in relation to the increase in total soluble materials and the deterioration in groundwater quality. Also, the high correlation coefficient obtained from the comparison of Cl and TDS with EC, which are  $R^2 = 0.94$  and  $R^2 = 0.87$ , respectively, expresses direct impact of water quality of this aquifer to Cl. It is noteworthy that the trend of Cl changes in the aquifer has been rising over the past ten years and gained from 4.69 to 8.36 in the term of the study period. Considering that corrosion of chlorine and strong desire for interaction with metals such as iron, manganese and zinc, Sodium thiosulfate can reduce the high proportion of water-soluble metals by eliminating chlorine.

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**Screen-printed electrodes modified with magnetic core-shell nanoparticles film for detection of chlorpromazine**

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In the present study, magnetic core-shell manganese ferrite nanoparticles (CMNP) as a nanoparticle was synthesized and used for construction of a magnetic core-shell manganese ferrite nanoparticles modified screen-printed carbon electrode (MCSNP-SPCE). Cyclic voltammetry was used to study the electrochemical behavior of chlorpromazine (CPZ) and its determination was conducted by applying square wave voltammetry (SWV). The MCSNP-SPCE in comparison with bare SPCE exhibited enhanced electrocatalytic activity toward the oxidation of CPZ. A single irreversible oxidation peak was observed at a potential of 630 mV and 500 mV on the MCSNP-SPCE and bare SPCE, respectively. Under the optimized conditions, the anodic peak current of CPZ recorded by SWV varies linearly with CPZ concentration in the range 0.25–60  $\mu\text{M}$  with a detection limit of 0.08  $\mu\text{M}$ . The MCSNP-SPCE was used for quantitative analysis of CPZ in tablet and urine samples and the results indicate the feasibility of the amperometric method for CPZ analysis in routine detection..





**Electrochemical determination of acetaminophen by using modified screen printed carbon electrode**

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In the present work, a rapid and sensitive detection of the acetaminophen (AC) based on the modified screen printed carbon electrode (MSPCE) developed. Cyclic voltammetry was used to study the electrochemical behavior of AC and its determination was conducted by applying square wave voltammetry (SWV). The MSPCE in comparison with bare SPCE exhibited enhanced electrocatalytic activity toward the oxidation of AC. A single irreversible oxidation peak was observed at a potential of 590 mV and 480 mV on the MSPCE and bare SPCE, respectively. Under the optimized conditions, the anodic peak current of AC recorded by SWV varies linearly with AC concentration in the range 0.5–220  $\mu\text{M}$  with a detection limit of 0.1  $\mu\text{M}$ . The MSPCE was used for quantitative analysis of AC in AC ampule and AC tablet samples and the results indicate the feasibility of the amperometric method for AC analysis in routine detection.







**Prediction of the sorption coefficient for the adsorption of PAHs on MWCNT based on hybrid QSPR-molecular docking approach**

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In this study, quantitative structure-property relationship (QSPR) methodology and molecular docking employed for modeling of the sorption coefficient ( $\log K_{\text{CNT}}$ ) of 13 polycyclic aromatic hydrocarbons (PAHs) on multiwall carbon nanotube (MWCNT) adsorbent. A molecular docking simulation used to present a reliable and accurate QSPR model with defining the distance and best orientation of PAHs structures on nano-adsorbent. A genetic algorithm-multiple linear regression (GA-MLR) method was employed for implementation of QSPR model. In this model, the square of correlation coefficients ( $R^2$ ) was 0.945 and 0.890, and the root mean square errors (RMSE) were 0.07 and 0.14 for the training and test sets, respectively. Also, inspection to selected descriptors indicates the electrostatic and steric parameters of PAHs are the predominant factors responsible on the  $\log K_{\text{CNT}}$  values. These results can be used for prediction of sorption coefficient of other PAHs by MWCNT and modify the surface of the adsorbent for improving the  $\log K_{\text{CNT}}$ .



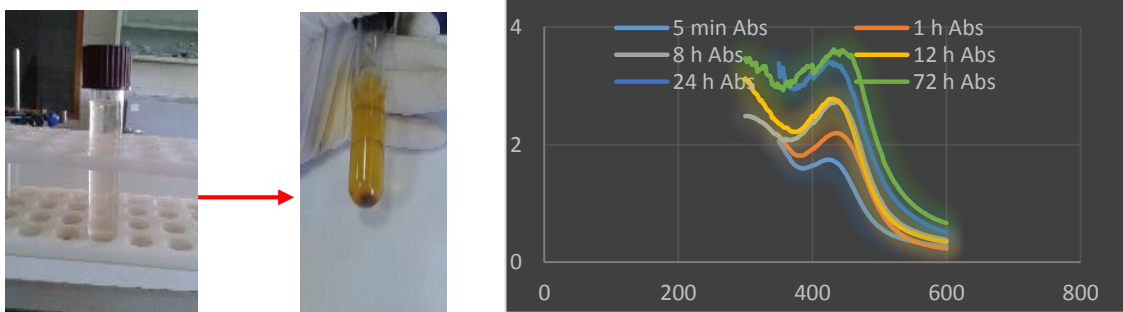
## Green synthesis of silver nanoparticles using a *Lavandula angustifolia* Flowers extract and study of UV-vis spectra of synthesized Ag-NPs in *Lavandula angustifolia* Flowers extract at different times

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Among various metals, silver nanoparticles (AgNPs) are of particular interest due to their remarkable antimicrobial and localized surface plasmon resonance properties, which render them unique properties such as broad-spectrum antimicrobial [1,2]. *Lavandula angustifolia*, known as Spike lavender or Portuguese lavender, is a flowering plant in the family Lamiaceae, The flowers and leaves of this plant are used as a herbal medicine, in the form of a herbal tea [3]. In this paper, a green synthesis route was followed, in order to obtain silver nanoparticles with possible utilization for medical devices. The “Green” synthesis of metallic nanoparticles and investigation of their optical properties has become a useful application between nanoscience and medicine. In this work, silver nanoparticles (Ag-NPs) were successfully prepared through green method by treating silver ions with *Lavandula angustifolia* Flowers extract. Preparation of Ag-NPs in silver nitrate solution (0.001 M) resulted in small and spherical shapes of Ag-NPs with a mean diameter of 50 nm. The formation of Ag-NPs was approved by surface Plasmon resonance (SPR) absorption peaks, using UV-vis spectrophotometer. The obtained curves in Fig display the UV-vis spectra from the *Lavandula angustifolia* Flowers extract Ag-NPs at 40 °C and different reaction times (3 to 72 h) in yellowish aqueous solutions. The existence of a sharp and strong SPR peak at the wavelength of maximum absorbance ( $\lambda_{max}$ ), which was about 436 nm, indicates the formation of Ag-NPs.



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Effect of scaling and normalisation in ranking of metabolites in metabolomics studies

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Metabolomics has been successfully applied in many fields including clinical research, drug discovery, toxicology, and phytochemistry. In all of these methods pathophysiological stimuli or genetic modification is performed on living system and a quantitative measure of the dynamic metabolic response of living systems is made to explain the disease process and mechanism could be investigated in a synthesis induction way[1]. However extracting relevant biological information from large data sets is a major challenge in this field [2]. From data acquisition to statistical analysis, metabolomics data need to undergo several processing steps, which all of them is critical in correct interpretation of data [3]. Prior to multivariate analysis, preprocessing of the data must be carried out to remove unwanted variation such as instrumental or experimental artifacts. In this study effect of scaling and normalization has been investigated by both simulated and 1HNMR nanotoxicometabolomics real data. Different scaling methods such as centering, autoscaling, pareto scaling, range scaling, vast scaling and different normalization methods such as total area normalization, probabilistic quotient normalization, and quantile normalization have been used in this study [1-4]. Finally, it was shown that preprocessing of metabolomics data is an important step prior to statistical analysis and selecting a proper data pretreatment method is a critical step in the analysis of metabolomics data and strongly affects the identification of the most important metabolites in the considered biological system.

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**Two-phase hollow fiber liquid phase microextraction for preconcentration of naproxen prior to UV-Vis spectrophotometry**

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Naproxen (NAP) is a non-steroidal anti-inflammatory drug (NSAID) which is used for the treatment of intense pain and inflammation. Several analytical methods have been published for the determination of NAP in pharmaceutical preparations and biological fluids. These methods included Capillary electrophoresis with electro spray mass spectrometry, HPLC and capillary isotachopheresis. To obtain accurate, reliable and sensitive results, a sample preparation is required prior to detection. The traditional techniques are characterized by long analytical time, manual manipulation of the extracts, large consumption of sample and reagents and produces of large amounts of waste. It has been proved that hollow fiber liquid phase microextraction (HF-LPME) is very useful for extraction of drugs and metabolites from biological matrices and pollutants from environmental samples with simultaneous clean-up of the matrices [1]. HF-LPME, a relatively new miniaturized technique, has high enrichments, simplicity, rapidity and low consumption of organic toxic solvents [2].

The characteristics of NAP show that it has low polarity and consequently has better extraction efficiency in nonpolar solvents. Therefore, a two-phase HF-LPME system has been designed for preparation of pharmaceutical and urine samples followed by spectrophotometric analysis of NAP. The effective parameters of the method, such as extracting organic solvent (acceptor phase), pH of sample solution (donor phase), extraction time, stirring speed, and ionic strength were optimized.

Under optimum experimental conditions, the calibration curve was linear in the concentration range of 0.05–10  $\mu\text{M}$  NAP. Limits of detection and quantification were found to be 0.02 and 0.07  $\mu\text{M}$  NAP, respectively. The method was successfully applied for determining of naproxen in some pharmaceutical and urine samples.

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## Exploratory Analysis of Seized Heroin Samples Using Gas Chromatography and Chemometrics

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Differences in the agricultural conditions, manufacturing procedures, addition of adulterants cause variation in the chemical profiles of a confiscated heroin sample[1]. Chemical profiling and clustering using chemometrics methods have fundamental role in the tactical and strategic intelligence about source production, and transit routes of heroin seized[2,3]. Hence, 459 seized heroin samples-during 2015 and 2016 in Iran were analyzed using GC-FID and then were clustered. Our process has four steps, (a) analysing heroin samples using gas chromatography-flame ionization detector\ gas chromatography - mass spectroscopy and identifying all of volatilized component (b) determining relative peak area of each compound using docosan as the external standard (c) tabulating data set for statistical operations (d) cluster analysis. Principal component analysis (PCA) and projection pursuit (*PP*) as unsupervised exploratory data analysis were incorporated for clustering of aforementioned heroin samples. Projection pursuit (*PP*) is an unsupervised technique that seeks for an interesting low-dimensional linear projections of a high-dimensional data which are useful for clustering. Based on indications, *PP* scores resulted in appropriate separation of clusters/classes within the heroin data which can not be deduced from the PCA scores[4,5]. Finally, clustering of heroin samples reveals four distinct and well-separated groups which are meaningful from origin of production and transit routes point of views. Predicting the origin of seized heroin has primary concern in the tactical and technical investigation. Chemometrics analysis of a heroin data set helps in evaluation for sentencing. This study is useful for the courts concerning the possible links between samples and providing tricky information to assist in the elucidation of drug-dealing networks.

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## Direct Classification of Seized Heroin Samples with FT-ATR Spectroscopy and Multivariate Discriminant Analysis

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Chemical profiles play a very critical role in the clustering/classification of heroin confiscated samples. Classification of heroin helps in the accurate and reliable tactical and strategic investigation on the transit route, geographic origins, and manufacturing process, which are important for forensic and judicial purposes[1,2]. To the customary classification of drugs, a non-destructive, fast, direct, simple, cheap, safe, and free sample preparation steps like attenuated total reflection fourier transform infrared spectroscopy (ATR-FTIR) is proposed. Hence, ATR-FTIR spectra of 69 seized heroin samples were used to build a PLS-DA model. Calibration heroin samples consist of samples from four different seized heroin classes. Each class has its own specific adulterants[3]. One vs. all classification approach was used in this contribution. Additionally, PLS-DA resulted in appropriate modeling of each classes while miss classification rate is acceptable for each of classes. Optimizing PLS-DA model parameters including latent variable resulted in a predictive model not only from internal validation but also from external validation perspective[4,5]. This strategy showed significant potential for exploring adulterants features involved in heroin samples. Finally, this contribution may contribute to paving the way for future studies aiming at identifying heroin networks. These data types are useful as the basis for providing the courts with information concerning the possible links between samples in cases where the charges include supplying and to provide intelligence information to assist in the elucidation of drug-dealing networks. Chemical profiling using ATR-FTIR spectroscopy and chemometrics analyses proved to be an innovative strategy to distinguish adulterants according to treatment.

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## The Whole Cell Sol-Gel Imprinting on Au Interface: A Tool for Detection

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Accurate and fast identification and sensitive detection of microorganisms is required to optimize the clinical management of infected patients, and to limit food poisoning and environmental disasters on a wider range. Molecular imprinting is a method in which an appropriate functional monomer is polymerized in the presence of a template forming covalent or non-covalent bonds with the functional monomer. Afterward, following polymerization process, the template is removed that leaves a space or cavity originally occupied by the template molecule, in its original shape. These cavities due to their steric shape can adopt and bind similar or analogous molecule with pronounced selectivity and sensitivity. The next step in this interesting methodology was to imprint much more complex organic structures such as whole cells in sol-gel matrices, termed macromolecular imprinting. In this work a detection strategy that does not require expensive biological affinity agents and can be tailored at will to any microorganism target with minimal change in the technological approach was developed. This goal was obtained by the development of a bacteria imprinted matrix deposited on gold interfaces allowing the use of electrochemical impedance spectroscopy. We used the potential of microorganism imprinting into sol-gel for the selective capture of pathogens. *Chemically removing the biological template results in complementary cavities that spatially fit and recognized a specific microorganism. Firstly, the non-imprinted and imprinted electrodes have been prepared using sol-gel method. Several microscopic and spectroscopic techniques have been applied for characterization of the prepared electrodes. Finally, electrochemical impedance spectroscopy has been utilized for determination of bacteria in the range of 10<sup>2</sup> CFU/mL-10<sup>6</sup> CFU/mL.*

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## Fluorescent carbon quantum dots for simple and fast detection of Cyanocobalamin

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Vitamin B12 (cyanocobalamin) is a water-soluble vitamin containing a cobalt ion within tetrapyrrole ring and belongs to group B vitamins. This vitamin is an important coenzyme for cell development and growth, and it plays a key role in the normal functioning of the brain and nervous system[1]. Various analytical techniques have been employed for the determination of vitamin B12. However, the applications of these methods are limited due to time-consumption, high cost, the need of sophisticated instrumentations, low reproducibility and insufficient sensitivity[2].

In recent years, considerable attention has been paid to the synthesis and application of carbon quantum dots (CDs), due to their outstanding tunable multi-color photoluminescence (PL) properties, high chemical stability, low toxicity, biocompatibility, and easy functionalization[3]. In this work We testified that N,S-doped CDs can serve as a very effective photoluminescence probe for detection of vitamin B12.

Carbon nanoparticles were synthesized from the mixture of glucose and cysteamine. Glucose served as the carbon source, and the cysteamine provided nitrogen and sulfur. Co-doped carbon dots were characterized by X-ray photoelectron spectroscopy (XPS), transmission electron microscopy (TEM), and Fourier transform infrared (FTIR) spectroscopy techniques.

Briefly, the co-doped carbon dot systems showed quenching of photoluminescence intensity in the presence of vitamin B12. Functional group and doping heteroatoms were impact on the selectivity and sensitivity. The decrease of fluorescence intensity made it possible to analyze vitamin B12 with satisfactory detection limits and linear ranges. The Sterne–Volmer plot showed a linear relationship between  $F_0/F$  and the concentration of vitamin B12 over the range from 0 to 10  $\mu\text{M}$  with a detection limit of 0.07  $\mu\text{M}$ .

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**Developing quantitative structure-retention relationship model to prediction of retention factors of some alkyl-benzenes in nano-LC**

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The present study intends to develop the quantitative structure-retention relationship (QSRR) models to predict the retention factor of some alkyl-benzenes on micro-dispersed sintered nano-diamond (MSND) and silica-gel stationary phases as new and common stationary phase, respectively in normal-phase HPLC. Genetic algorithm-multiple linear regression (GA-MLR) method employed for implementation of QSRR models. The square of correlation coefficient ( $R^2$ ) was 0.997 and 0.961, and the SE was 1.06 and 1.93, respectively for the training and test sets of GA-MLR model on MSND stationary phase. Also, the  $R^2$  was 0.994 and 0.984, and the SE was 0.01 for both the training and test sets of GA-MLR model on silica-gel stationary phase. The statistical parameters and the result of validation tests of these models confirm the fitness, robustness, and predictability of developed QSRR models. The mean effect analysis on the best models introduced the polarizability as the most significant factor that effects on the retention factor of solutes on both studied stationary phases. This similarity confirms the suggestion of MSND as a common stationary phase for normal-phase HPLC. The developed models enable to predict the retention factor of other alkyl-benzenes on both MSND and silica-gel stationary phases on their applicability domain..





**One step ultrasonic synthesis of N,S-co doped carbon dots and their visible-light sensitive photocatalytic ability**

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In recent years, considerable attention has been paid to the synthesis and application of carbon quantum dots (CDs), due to their outstanding tunable multi-color photoluminescence (PL) properties, high chemical stability, low toxicity, biocompatibility, and easy functionalization[1]. The unique PL property of CQDs called by upconversion has been found, which could transfer low energy photon to high energy photon over CQDs by sequential absorbing two or multiple longer wavelength photons[2].

Herein, we report the green synthesis of N,S-CDs via a facile ultrasonic method, which exhibits improved photocatalytic activity for organic dyes (methylene blue) under visible-light irradiation. Carbon nanoparticles were synthesized from the mixture of glucose and thiourea. Glucose served as the carbon source, and the thiourea provided nitrogen and sulfur. Co-doped carbon dots were characterized by X-ray photoelectron spectroscopy (XPS), transmission electron microscopy (TEM), and Fourier transform infrared (FTIR) spectroscopy techniques.

We systematically investigated photophysical properties of CQDs prepared by ultrasonication method, in particular upconversion process under low photons irradiation.

It was demonstrated that compared to CDs, the as-prepared NCDs show prominent photocatalytic property for the degradation of methylene blue (MB) under visible light. The degradation efficiency of MB by N,S - CDs was 4 times higher than that of pure CDs under visible light.

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**9-Methyl Acridine modified silica as Mixed-Mode Stationary Phase of High-Performance Liquid Chromatography for a Wide Range Separation of Compounds**

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The development of novel stationary phases with high separation efficiency has always been the focus point of study. Mixed-mode stationary phases have been proved to be with the merits of a wide range separation of materials [1]. In this work, a stationary phase mixed-mode was prepared from 9-methyl acridine embedded on silica surface to create a multiple separation mechanism in the chromatography column. The 9-methyl acridine was synthesized from diphenylamine, acetic acid in the presence of zinc chloride catalyst. The material was purified by column chromatography [2]. In the making of the stationary phase, the 3-chloro propyl trimethoxysilane was reacted with silica. After completion of the reaction and washing, the excess amount of all methoxyl groups on the silica surface was hydrolyzed using water and replaced with chloro trimethylsilane. Finally, the product made of 9-methyl acridine, is subjected to a reaction with a chlorinated reagent on silica [3]. Since the stationary phase has several effective groups, there will be a multiple interaction mechanism (eg  $\pi$ - $\pi$ , ion exchange, hydrophobic, etc.) between the analytes and the stationary phase. This stationary phase is used to separate samples with different polarity.

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**Developing a point-of-care real-time system for determination of dopamine, ascorbic acid, and uric acid using a modified screen-printed electrode in amicrofluidic chamber**

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A microcontroller based miniature potentiostat (MP) was developed based on Arduino Due and LMP91000EVM to act as a point of care health monitoring device for the first time. A designed syringe pump in tandem with a microfluidic chamber was successfully coupled with the MP to achieve a POC assembly. An SPE-3DG modified electrode was successfully interfaced with the potentiostat for simultaneous determination of UA, DA, and AA in human plasma samples. The voltage, waveform and scan rates were optimized for CV and DPV measurements. GA-PLS and WL-ANN were utilized to resolve overlapped peaks in contrast with time-consuming electrode surface modifications. The method showed better sensitivity in comparison with other methods. 3DG-SPE provides a broad accessible surface and shows remarkable increase in kinetic of electron transfer rate. In addition, it decreases the over potential for oxidation of analytes, which is desirable. Nonlinear methods such as ANN predict concentrations in the mixture slightly better than linear methods like PLS. In contrast, linear methods are simpler in algorithms and codes and also run faster on microprocessors, therefore both methods were performed. The developed miniature potentiostat is capable of detecting AA, DA, and UA at 0.95  $\mu\text{M}$ , 0.12  $\mu\text{M}$ , and 0.20  $\mu\text{M}$  respectively with a linearity of 0.5-2000, 4-4500, 0.8-2500  $\mu\text{M}$  with good determination coefficients. The results were in good agreement with other similar commercial instruments suggest that the developed device could be used as a real-time POC to monitor targeted analytes.





**Rapid determination of nitrate in drinking water based on image processing techniques using a smartphone platform**

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This study presents a portable and low-cost smartphone-based kit for fast nitrate-level-detection in drinking water using a commercially available nitrate indicator and image processing techniques. The colour intensity in photos taken from indicator-added water samples was correlated to the concentration of nitrate ions. Converting Matlab codes to Android platform allowed us to determine the nitrate concentration in water samples using a smartphone. The newly designed technique provided agreeable LOD and LOQ values (respectively 1.50 and 5.0  $\mu\text{g mL}^{-1}$ ), and favourable  $R^2$  (0.995) for matrix-matched calibration in close accordance with UV-visible spectroscopy. The obtained LOQ is well below the maximum residual level for nitrate in drinking water (50  $\mu\text{g mL}^{-1}$ , set by WHO). Field applicability of the smartphone-based technique was investigated by measuring the nitrate level in drinking water samples, collected from forty-two different zones in Tehran and Alborz (central Iran provinces). The results were in close accordance with those achieved from UV-visible spectrometry. Thus, the proposed method, as an alternative technique to expensive and intricate conventional techniques, could be used for rapid determination of the nitrate in drinking water samples.





## Air-Assisted Liquid-Liquid Microextraction Coupled with HPLC for the Determination of Sertraline and Fluoxetine in Biological Samples

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Sertraline and Fluoxetine, are selective serotonin reuptake inhibitors (SSRIs). They exhibit clinical efficacy comparable with classical tricyclic antidepressants, but are devoid of some of the adverse anticholinergic and cardiovascular effects commonly associated with these drugs [1]. Sertraline and Fluoxetine effective drugs in treatment of depression. However, the side effects and clinical response of these drugs are dependent on their concentration in biological samples including plasma and urine. Therefore, monitoring concentration of these drugs are helpful to improve the response and minimize the occurrence of side effects. In the present work, the method consists of air-assisted liquid-liquid microextraction (simple, rapid, sensitive, low cost, and environmentally friendly microextraction method) that coupled with High Performance Liquid Chromatography-Ultraviolet detection, to preconcentration, determination and analysis of Sertraline and Fluoxetine in biological samples [2]. To this aim, in this study a green microextraction method based on DLLME is developed, called air-assisted liquid-liquid microextraction (AALLME). In this method, biological or aqueous sample was transferred into a centrifuge tube with conical bottom. Extraction solvent was added and then the mixture was rapidly sucked into a glass syringe and then was injected into the tube via syringe needle. The extractant was settled down in the bottom of the centrifuge tube after centrifugation. Extractant was withdrawn and injected into the HPLC system for analysis. In order to decrease the toxicity and harmful effects of disperser solvents on operators and environment, air is replaced with disperser solvent. In this study, the effective parameters on extraction efficiency such as type and volume of extraction solvents, number of suction-injection cycle, salt addition and pH are investigated and optimized [3]. According to the test results, the AALLME-HPLC-UV method was successfully applied for extraction and determination of Sertraline and Fluoxetine in the biological sample.

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## Optical Properties of Cu(II) and Co(II) Complexes with One New Chloro Salophen Ligand

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Salophens are one of the oldest class of ligands in coordination chemistry[1]. They are easily prepared from condensation reaction of 1,2-phenylenediamine or their derivatives with salicylaldehyde. Salophen metal complexes are formed by the reaction of both main and transition metals. The preparation method of these complexes is easy and sample. These complexes show extensive applications in several fields. A variety of them exhibit special optical properties [2]. They also found applications as electroluminescent materials and biological activities [3, 4]. Here, we investigate the optical properties of Cu(II) and Co(II) complexes with one new salophen-type ligand by UV/Vis spectroscopy. The ligand is synthesized from condensation reaction between 4-chloro-1,2-diaminobenzene and salicylaldehyde. The complexes are easily prepared from the reaction of ligand and Cu(II) and Co(II) acetate salts. In general, the absorption spectra exhibit intense bands in the region 278-338 nm region which can be related to the  $\pi \rightarrow \pi^*$  and  $n \rightarrow \pi^*$  intra-ligand transitions.  $n \rightarrow \pi^*$  transitions decrease in intensity and shift to shorter wavelengths after complex formation. Moreover the absorption bands between 401- 476 nm is assigned to the metal-ligand charge transfer (LMCT).

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**Sensitive spectrofluorometric determination of hydrogen peroxide and cholesterol using a zirconium-based metal-organic framework as a novel peroxidase mimic**

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The need to develop innovative and reformative approaches for the design of chemical sensors has increased in recent years. It is because of demands for selectivity, stability, and reproducibility. In this respect, nano-mimetic enzymes with their unique features can provide an efficient and convenient platform for chemical sensors. Cholesterol is a construction unit of hormonal system in mammals and also an important component of cell membrane. It plays a vital role in the synthesis of several vitamins, steroid hormones and bile acids. Therefore, the concentration of cholesterol is monitored most often in food and clinical samples [1]. In this study, a simple and one-pot method is developed for the preparation of Zr-based metal-organic framework (MOF) which provides a large surface area and active sites [2]. The obtained MOF exhibits intrinsic peroxidase-like catalytic activity. With the Zr-based MOF as a catalyst, the peroxidase substrate of terephthalic acid (TA) can be oxidized by H<sub>2</sub>O<sub>2</sub> to produce the high fluorescent hydroxyl terephthalate (HTA), which provides a unique strategy for the fluorometric detection of H<sub>2</sub>O<sub>2</sub> and cholesterol. With such a process, H<sub>2</sub>O<sub>2</sub> could be detected with a linear range of 0.1 to 100 μM. Meanwhile, using cholesterol oxidase, sensitive detection of cholesterol is also achieved with a linear range of 0.5 to 200 μM and a detection limit of 0.19 μM. A novel TA/Zr-based MOF system was successfully applied for H<sub>2</sub>O<sub>2</sub> and cholesterol determination in real samples. The unique nature of the MOF makes it promising material for the fabrication of low-cost and high-performance biosensors.

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**Determination of multi-class pesticides using air-assisted liquid-liquid microextraction and dispersive liquid-liquid microextraction; a comparative study**

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Along with a dramatic increase in population, the rise in food products is necessary. Around 20 to 30% of whole agriculture products are lost by pests every year. To overcome this problem, pesticides are used for plagues extermination [1]. Due to pesticides mobility, capability of bioaccumulation and their ability to take part in various physical, chemical and biological processes, they remain in surface, ground waters, and agricultural products [2]. According to some studies, they have unfavorable effects on human health, like an increase in endocrine, developmental, immune, and neuropsychological disorders, great probable of neurodegenerative diseases, especially Parkinson's and Alzheimer diseases, as well as different kinds of cancer [3]. So, presence of pesticides in food chain is an absolute risk for general health and development of efficient methods for determination of them is necessary. Ideal sample preparation methods should be fast, accurate, precise, economic, easy to use, environmentally friendly, compatible with a wide range of analytical instruments, and easy to automate [4, 5]. In this study, two convenient sample preparation methods, air-assisted liquid-liquid microextraction (AALLME) and dispersive liquid-liquid microextraction (DLLME) are developed for the simultaneous determination of multi-class pesticide residues in vegetable and fruit juice samples with gas chromatography-flame ionization detection. The advantages of each method were investigated. In AALLME, fine droplets of an extraction solvent are immediately formed with suction and injection of the mixture of an aqueous sample solution and the extraction solvent into a test tube for several times, while in DLLME, the cloudy solution is formed with the aid of a disperser solvent. The effect of main factors such as type and volume of extraction solvent, salt addition, pH, etc., is studied. Under the optimum conditions, enrichment factors and extraction recoveries are obtained in the ranges of 262–515, 45–438, and 52–103%, 9.2–88% in AALLME and DLLME methods, respectively. Both methods are inexpensive, simple, fast, efficient, reliable, and sensitive, and therefore they are suitable for determination of trace levels of multi-class pesticide residues in fruit juice and vegetable samples.

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**Magnetic solid-phase extraction based on magnetic three-dimensional graphene for determination of nitrite in water samples**

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Graphene (G), a one-atom-thick planar carbon material patterned in a honeycomb lattice form, is a two-dimensional (2D) carbon nanomaterial and has attracted enormous research interest in recent years owing to its intriguing properties. However, due to the strong  $\pi$ - $\pi$  stacking interaction, hydrophobic interaction and van der Waals forces, restacking and aggregation between individual graphene sheets may occur, which may greatly decrease the intrinsic specific surface area of G. In order to overcome the above problems, very recently, Chen et al. have synthesized a three-dimensional interconnected graphene (3D-G) with a foam-like network structure. Since 3D-G has a high surface area, large mesopore volume and three-dimensional nanoporous structure, it might be a promising candidate as an efficient adsorbent for some organic compounds [1].

Nitrite is one of the pollutants found in the atmosphere and natural water and is an important intermediate in biological nitrogen cycle. Traces of nitrite in drinking water may lead to methemoglobinemia in infants and with long term exposure is a possible cancer risk [2].

Magnetic solid-phase extraction (MSPE), as a new mode of SPE, can be carried out directly in the crude sample solution with the magnetic solid adsorbent being added to it and the phase separation can be realized simply by using an external magnet without the need of using additional filtration or centrifugation procedures, which makes separation easier and faster [3].

In this study, a three-dimensional graphene-based magnetic nanocomposite (3D-G-Fe<sub>3</sub>O<sub>4</sub>) was synthesized. Performance of the 3D-G-Fe<sub>3</sub>O<sub>4</sub> was evaluated in magnetic solid-phase extraction of nitrite from water samples. For this purpose, 25 mL of a standard solution (0.2 mg L<sup>-1</sup> of nitrite) or sample was placed into a 50 ml falcon tube. Next, 1 ml HCl (1M) and 1 ml 4-nitroaniline (10<sup>-3</sup> M) were added to the tube in order to form a diazonium salt. After 5 min, 1 ml naphth-1-ol (10<sup>-3</sup> M) and 2 ml NaOH (2M) were transferred into the tube to make the diazonium ion be coupled with naphth-1-ol to form an azo dye that was purple in alkaline solution ( $\lambda_{\text{max}} = 620$  nm). Then, 100 mg adsorbent (3D-G-Fe<sub>3</sub>O<sub>4</sub>) was used for magnetic solid-phase extraction of the product (azo dye). Finally, 0.5 mL acetone was used for desorption of azo dye from 3D-G-Fe<sub>3</sub>O<sub>4</sub>. Several experimental parameters affecting the reaction and extraction efficiencies, such as reagent concentration, the amount of the 3D-G-Fe<sub>3</sub>O<sub>4</sub>, reaction and extraction time, sample pH, salt addition and desorption conditions were optimized. Finally, the proposed method was successfully utilized for the pre-concentration and determination of nitrite ions from different water samples using colorimetric method.

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**On-site determination of nitrite in river-water using a simple homemade light emitting diode based photometer**

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Portable spectrophotometers are of importance in many fields, such as environmental and clinical applications. A cheap, simple, and portable device operated with some ordinary small batteries seems to be a suitable alternative for commercial spectrophotometers. In the design of these spectrometers, compromises are made in the selection of the optoelectronic components to allow for reduced size and cost [1]. Over the last decades, the electronic industries have offered a great variety of devices that are of considerable advantages when applied in chemical instrumentations. These devices could help to overcome the challenges in devising portable colorimeters. Among them, Light emitting diodes (LEDs) received a great interest in the analytical applications and are used as light sources in portable and miniaturized absorption devices. The LEDs are available for almost all the wavelength ranges employed in the analytical spectrophotometers. Since these sources emit light of relatively narrow band widths (20-100 nm) they have been utilized as a monochromatic light source. Another challenge in the development of portable analytical devices is to reduce detector size. Hence, light-dependent resistors, LDR (small, cheap and accessible device) could be a good choice for fabrication of portable colorimeters [2].

In this work, a simple and portable multi-color Light emitting diode based photometer for determination of nitrite ions in river water has been used. The photometer designed employs two red–green–blue (RGB) LEDs as light source and two LDRs as detector. The emission wavelengths and the spectral band width of each emitter are: red, 625 and 25 nm; green, 525 and 40; and blue, 465 and 30 nm respectively. A programmable microcontroller sequentially turns the emitters on, receives the signals followed by calculating the absorbance and displaying it on a liquid–crystal display. For determination of nitrite, p-nitroaniline and naphth-1-ol were used as diazotization and coupling reagents, respectively, to form a colored product (azo dye) [3]. UV- Vis spectrum of the azo dye showed that its maximum absorbance wavelength was 610 nm. So, red light was used in determination of azo dye absorbance that was proportional to nitrite concentration.

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**Electrochemical behaviour of imipramine in the presence of benzenesulfonic acid at glassy carbon electrode**

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Electrochemical methods are widely used for the study of electroactive compounds in pharmaceutical forms and physiological fluids due to their simple, rapid, and economical properties [1]. Among the popular electrochemical techniques cyclic voltammetry (CV) is the most versatile available ones. Under favorable circumstances, CV can also be used for mechanistic studies of systems in which the electron transfer reactions are coupled to chemical reactions, due to the characteristic appearance of cyclic voltammograms associated with different mechanisms [2]. Tricyclic antidepressant drugs (TCAs) are one of the largest groups of drugs for the treatment of psychiatric disorders such as depression. On the other hand, arylsulfonic acids are widely used in the practice of medicinal chemistry, chemical industry, chemical synthesis. The importance of these compounds has motivated us to synthesize new imipramine derivatives via electrochemical oxidation of imipramine in the presence of arylsulfonic acids. The electrochemical oxidation of imipramine have been studied in a range of pH between 1.0 to 9.0 in the presence of arylsulfonic acids as nucleophiles in aqueous solutions by using cyclic voltammetry and constant current coulometry methods. The results indicate that the dibenzazepine derived from oxidation of imipramine participates in Michael type addition reaction with arylsulfonic acids to form the corresponding new sulfone derivatives of imipramine. The present work has led to the development of a facile and environmentally friendly reagentless electrochemical method for the synthesis of some new imipramine derivatives in aqueous solutions with high atom economy, under green conditions.

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**Determination of mercury (II) ions in aqueous solutions by glassy carbon electrode modified with Fe<sub>2</sub>O<sub>3</sub> @ S<sup>2-</sup> NPs**

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Due to the importance of heavy metal ions determination in water samples for quality control in the health, many routine analytical methods have been developed. But, these methods suffer from some disadvantages. They are either time-consuming, or involve expensive procedure and toxic reagents and solvents. Among various analytical methods, electroanalytical methods are rapid, inexpensive and easy to operate. In the present work, a novel modifier, Fe<sub>2</sub>O<sub>3</sub>@S<sup>2-</sup>NPs, for glassy carbon electrode has been synthesized. The synthesized nanocomposite was fully characterized using methods such as Fourier transform infrared spectroscopy, scanning electron microscopy, cyclic voltammetry. Preliminary experiments showed that the nanocomposite has a significant effect on the preconcentration and improvement of the square wave anodic stripping voltammetry (SWASV) signal for mercury (II). Anodic stripping current was obtained at +0.238 V (vs. Ag/AgCl). Various chemical and instrumental parameters which could potentially affect the electrochemical signal were optimized. Under the optimized conditions, a linear calibration curve was obtained for mercury (II) in the concentration range 10 – 380 µg/l with a detection limit of 1.3 µg/l. Furthermore, the method was applied for the determination of mercury (II) ion in real sample with acceptable recoveries and minimal matrix effects. A comparison of figures of merit between the developed method and other previously developed methods showed that a powerful alternative method for the determination of mercury (II) in real samples has been developed.

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**The Individual and Simultaneous Voltammetric Determination of significant biomolecules in pathological and biomedical chemistry ,L-DOPA, L-tyrosine and Uric acid, by Cysteic acid Modified Glassy Carbon electrode**

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In this study a compact and uniform polymeric structure of cysteic acid layer film is immobilized on glassy carbon electrode by electrochemical oxidation of L-cysteine. Then, the nanocomposite modified electrode characterize using field emission scanning electron microscopy (FESEM). Differential pulse voltammetry (DPV) responses was used to estimate the Levodopa (L-DOPA), L-tyrosine (Tyr), uric acid (UA) linear calibration range and the limit of detection individually and simultaneously. Levodopa (L-DOPA), is a biochemical substance, it can prepared via biosynthesis from tyrosine a non-essential amino acid [1]. Tyrosine (Tyr), a non-essential amino acid synthesized from another amino acid that called phenylalanine. Tyrosine also exists in dairy products, eggs, beans and meats. It often added to food products and to pharmaceutical formulations [2]. Uric acid (UA), is an antioxidant that is present in biological fluids like urine and blood serum [3]. Linear relationship is observed in the individually determination in concentration range of 0.35 $\mu$ M to 45 $\mu$ M and 0.6 $\mu$ M to 49  $\mu$ M for L-DOPA and UA. Calibration plot of Tyr consists of two linear ranges from 1.7 to 6 $\mu$ M and from 6 to 50 $\mu$ M. The limit of detection for L-DOPA, Tyr, and UA is calculated to be 0.11, 0.55 and 0.2 $\mu$ M, respectively. It was found that, at cysteic acid/GCE three well separated peaks (0.08, 0.53 and 0.2 mV) were observed corresponding to the oxidation of L-DOPA, Tyr, and UA respectively. So the potential differences were large enough for simultaneously determine of these analytes together. Thus electro-catalytic activity of Cysteic acid/GCE is exploited for the simultaneous determination of L-DOPA, Tyr, and UA by keeping the concentrations of the two analytes constant and varying the concentration of the third analyt. The LODs were evaluated as 0.2, 1.1 and 0.36 $\mu$ M for L-DOPA, Tyr, and UA respectively. In light of efficient and comparable results and efficient electro-catalytic activity the electrochemical sensor can be utilized successfully for the simultaneous determination of the L-DOPA, Tyr, and UA species in real samples.

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**Investigating the amount of elements in some water sources around the city of Urmia and providing a special nano-absorbent for removing Boron from these sources**

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Considering the high importance and the threats of the presence of elements in concentrations excessive levels in drinking water, the optimal limit and permissible limit In drinking water In each country is determined. One of the possible elements In drinking water is Boron, The presence of Boron can cause blood clots and stimulate the eye and cause nausea and vomiting and diarrhea.

In this research, element content of some water resources used in a number of villages around the city of Urmia were investigated, and identified that most of the elements are virtually desirable, and only the Boron element in some sources is more than allowed.

Hence, by stabilization of nanoparticles on activated carbon Using a thermal method, a new nano-absorbent was designed, and to increase the efficiency, tungsten oxide nanoparticles was used. Optimal values, including pH=7.8, absorbent weight 0.07 grams, Collision time 20 minutes, and temp. 40-60 °C has been reached. The removal efficiency was 82% and by partial washing and reuse, efficiency is maintained at an acceptable level. Considering the high capacity of this adsorbent and the concentration of Boron element in the studied resources, utilizing very low amounts of this adsorbent, the amount of Boron element in the studied sources has reached the standard limit of drinking water.

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**Synthesis of new deep eutectic solvent and its application in extraction and pre-concentration of some pesticide residues from honey**

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Pesticides are widely used to protect crops and plants from pests and diseases with the objective of increasing agricultural productivity [1]. Since some pesticides are carcinogenic and some can cause dysfunctions in the nervous and reproductive systems, even at low concentrations, they can be extremely harmful to human health [2]. Due to adverse effects of pesticides on both human health and the environment, their monitoring is a necessity. Pesticides are usually determined by gas chromatography, liquid chromatography, or capillary electrophoresis depending on their polarity, volatility, and thermal stability. However, when their concentrations are low, an enrichment step is usually needed before analysis. Sample preparation is one of the most important steps in each chemical analysis. The aim of this challenging and critical step is to prepurify, concentrate, and transfer the analyte into a form that is compatible with the analytical system. Liquid-liquid extraction (LLE) [3] and solid-phase extraction [4], probably, are the most widely used sample preparation methods for pesticide residues analysis. These techniques are time-consuming, expensive and especially relating to LLE, hazardous to health due to high volume of potentially toxic solvents used [5].

In the present study an LLE combined with a new deep eutectic solvent based dispersive liquid-liquid microextraction (DES-DLLME) was proposed for the extraction and pre-concentration of some pesticide residues in honey. The DES was synthesized using a hydrogen bond donor (dichloroacetic acid) and a hydrogen bond acceptor (menthol). It was used as an extraction solvent. This method consisted of two steps: (i) extraction of the analytes from honey, and (ii) performing DES-DLLME for enrichment of them. In the first step, the selected analytes in honey were extracted into acetone which were used as a disperser in the following DES-DLLME method. Effect of various experimental parameters on the extraction efficiency were studied and optimized. Under the optimized extraction conditions limits of detection and enrichment factors for the analytes were obtained in the ranges of 0.32–1.2 ng g<sup>-1</sup> and 279–428, respectively. The obtained extraction recoveries were between 56 and 86% and the calibration curves were linear in wide ranges with correlation coefficients  $\geq 0.9988$ . Relative standard deviations were less than 7.0% for intra- (n=6) and inter-day (n=5) precisions (at two concentrations of 10 and 50 ng g<sup>-1</sup> of each analyte). Finally, the proposed method was applied on different honey samples and diazinon was determined in one sample at a concentration of  $25 \pm 3$  ng g<sup>-1</sup> (n=3).

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**A new three-components deep eutectic solvent as an extraction solvent in dispersive liquid-liquid microextraction**

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Pesticides are a main group of chemicals which are widely used in prevention or control of fruit diseases or weeds. In spite of many positive effects of the application of pesticides in agriculture, most pesticides are harmful to environment and are known or suspected to be toxic to human. Their adverse effects on human health may include acute neurologic toxicity, chronic neurodevelopment impairment, and endocrine systems or cancer [1]. Thus, developing a fast, simple, sensitive, and reliable analytical method to monitor the residue of pesticides in the environment is of prime importance. Sample preparation is one of the most important steps in an analytical process. For the analysis of pesticide residues, several sample preparation methods have been developed such as liquid-liquid extraction [2] and solid-phase extraction [3] which have some drawbacks. In 2006, Assadi and co-workers introduced a novel liquid phase microextraction technique named dispersive liquid-liquid microextraction (DLLME) [4]. It was proved to be a simple, low-cost, and fast method using the small amount of an extraction solvent and the low sample volume together with high enrichment factor for the analysis of different analytes [5].

In the present study a liquid-liquid extraction combined with a new three-components deep eutectic solvent (DES-DLLME) has been developed, for the extraction and preconcentration of ten pesticides from different aqueous samples. The DES was prepared by mixing dichloroacetic acid, menthol, and n-butanol at 0.5:0.5:1 molar ratio. The DES was mixed with methanol (as a disperser solvent) and the mixture was rapidly injected into an aqueous phase containing the analytes. The obtained cloudy solution was centrifuged and 1  $\mu\text{L}$  of the sedimented phase was injected gas chromatography-flame ionization detector. The influence of several variables on the extraction efficiency were investigated and optimized. Under the optimal conditions, extraction recoveries were obtained in the range of 53–86% and the calibration curves were linear in wide ranges with a correlation coefficient  $\geq 0.9985$ . Intra- (n = 6) and inter-day (n = 5) precisions of the method were satisfactory with relative standard deviations less than or equal to 7.0% (at two concentrations of 10 and 50  $\mu\text{g L}^{-1}$ , each analyte). Moreover, the detection limits and enrichment factors for the target analytes were obtained in the ranges of 0.11–0.23  $\mu\text{g L}^{-1}$  and 1760–2853, respectively. Finally, the proposed method was applied on different samples including tea, rose water, lemon balm, mint, and pussy distillates.

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**Determination of copper in environmental samples by air-assisted liquid-liquid microextraction coupled digital image colorimetric analysis**

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Metal ions currently represent an important threat to both the environment and human health. In particular Cu(II), a key trace element for many biological mechanisms, is listed as a priority pollutant by the Environmental Protection Agency (EPA) and World Health Organization (WHO) which recommends that its concentration in drinking water not exceed 2 mg L<sup>-1</sup> [1]. For this reason, a wide range of methods has been developed for Cu(II) determination ranging from spectrophotometric methods and atomic absorption spectrometry to inductively coupled plasma mass spectrometry [2]. However, several limitations have been associated with these methods including complicated processing, high-cost instruments, and time-consuming operations. Consequently, the detection of metal ions through simple, low-cost methods is highly attractive as they do not involve either the use of costly instruments or complicated operations.

In this study, a rapid, simple and cheap method has been developed based on air-assisted liquid-liquid microextraction (AALLME) coupled digital colorimetry for determination of Cu(II) in different samples. AALLME is similar to dispersive liquid-liquid microextraction but in this method there is no need to use a disperser solvent. In this alternative procedure, an extraction solvent (denser or lighter than water) is transferred into the aqueous sample solution in a conical tube, and the mixture is then repeatedly withdrawn into a glass syringe and pushed out into the tube. By this action, fine organic droplets are formed, and the extraction solvent is entirely dispersed in the sample solution. After centrifugation of the formed cloudy solution, the extraction solvent is settled down at the bottom of the centrifuge tube and used for further analysis [3]. For AALLME, 10 ml of a standard solution or sample containing Cu (II) was placed into a 15 ml centrifuge tube. Next, 1 ml of diethyldithiocarbamate solution (as a chelating agent) and 1 ml of borate buffer (pH = 9.2) were added to the tube in order to form a hydrophobic complex. Then, extraction solvent (1,1,2,2-tetrachloroethane) was transferred into the tube and the mixture was repeatedly sucked into a glass syringe and then injected into the tube. After performing predetermined cycles, the mixture was centrifuged to settle the dispersed droplets of organic phase at the bottom of the tube. Finally, the sedimented phase was analyzed by digital colorimeter. The obtained results showed that the proposed method is powerful in analysis of trace amount of Cu (II) in different samples.

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**Removal Tartrazine dye by Carbon Nanotubes Adsorbent with Response Surface**

**Experimental Design**

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Various liquid dyes waste treatment have been developed. Among these physico-chemical methods like adsorption, electrochemical coagulation and photocatalytic decolourization. Among all these, adsorption is one of the methods, which is gaining attention because of its easy operations and versatility[1]. The purpose of this study was to optimize tartrazine dye removal from aqueous solutions by carbon nanotube using Response Surface Method and Central Composite Design methods. The batch experiment was conducted to evaluate the effects of independent variables such as pH, dye concentration, dose of sorbent and contact time. For the experiment, Response Surface and Central Composite Design methods were applied to evaluate the effects of these variables. Analysis of variance (ANOVA) was used for statistical analysis. The optimum conditions for basic tartrazine dye removal were pH= 8, dye concentration= 23.75, adsorbent dose= 0.016g and contact time= 26.25 min. The verified model is Quadratic and R-squared value of this Study was obtained to be 95.7%, The R-Squared Adjusted was obtained to be 91.0% and The Squared predicted R<sup>2</sup> was obtained to be 70.00%.

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**Evaluate the performance of Carbon Nanotubes in the removal of Tartrazine from aqueous solutions: isotherms and kinetics studies**

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In recent years, with the production and use of increasingly synthesized colors that have a more complex structure than the natural colors, and are much more stable in chemical terms, more attention is paid to their environmental pollution[1]. The purpose of this study, removal of Tartrazine dyes from aqueous solutions dyes by carbon nanotube . The batch experiment was conducted to evaluate the effects of independent variables such as pH, dye concentration, dose of sorbent and contact time .The optimum conditions for basic Tartrazine dye removal were pH= 8, dye concentration= 23.75, absorbent dose= 0.016g and contact time= 26.25 min .Check isotherm and kinetic models showed that the experimental data with the Langmuir adsorption process Tartrazine ( $R^2=0.885$ ) and pseudo-second ( $R^2=0.9996$ ) are correlated.

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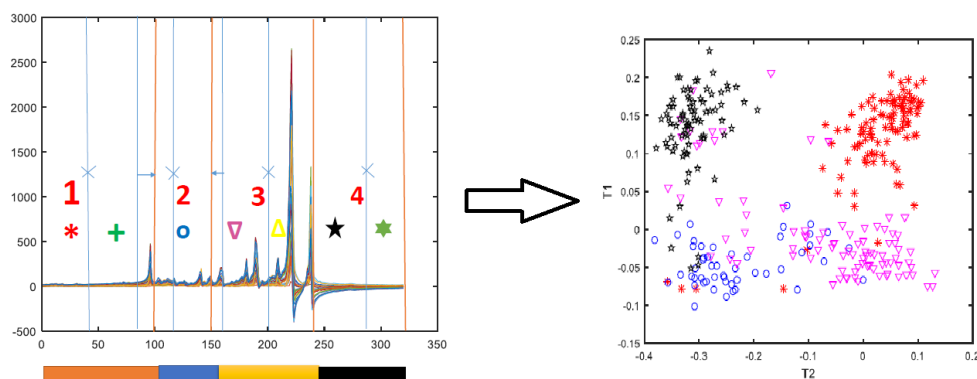
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**Projection pursuit based clustering of NMR variables from metabolic response of Hella cells to silica nanoparticles**Leila Ghiasvand Mohamadkhani<sup>a</sup>, Mohsen Kompany-Zareh<sup>a\*</sup>, Maryam Khoshkam<sup>b</sup><sup>a</sup> Department of Chemistry, Institute for Advanced Studies in Basic Sciences (IASBS), Zanjan 45137-66731;<sup>b</sup> Department of Chemistry, University of Mohaghegh Ardabili, Ardabil

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Exploratory projection pursuit is a set of data analytical techniques for finding “interesting” low-dimensional projections of different multivariate data including NMR [1]. In this work, for the first time, projection pursuit is used for the clustering of NMR data variables. The aim of this work was that which variables or variable regions behave similarly. One of the effective factors in improving the clustering was the change in the size of the bins. Binning is a common technique when dealing with huge NMR data. It is useful for data reduction, solution of peak shift problem, and improvement of sensitivity of quantification [2, 3]. Factors that have been studied to improve clustering efficiency included type of pretreatment and number of factors. However, they showed no effect on the results of the clustering of the variables. Finally the NMR spectra were simply and successfully clustered to different regions without any supervision and additional information. Optimum bin size of about 100 variables per bin was found for obtaining proper information content and clustering results.

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**Preparation of novel fluorescent nanosensor based on ligand capped CdTe quantum dots for Ag (I) detection**

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The use of optical nano-sensors for detection of heavy metal ions based on quantum dots (QDs) is highly significant due to high sensitivity, selectivity and simple of operation [1-4]. In this study, a ligand-capped CdTe QDs as a novel fluorescent nano-sensor was designed for detection of Ag<sup>+</sup> ions in aqueous samples. The surface of the CdTe QDs was modified using a new ligand. The prepared nano-sensor was characterized by transmission electron microscopy (TEM), Fourier transform infrared (FTIR), ultraviolet-visible (UV-Vis) spectrophotometry and fluorescence spectroscopy. The size of the prepared nano-sensor was estimated around 2.5 nm by TEM. Optical properties of produced nanosensor were monitored by UV-Vis spectrophotometry and fluorescence spectroscopy. It was observed that fluorescence intensity of the produced nanosensor quenched selectively by addition of Ag<sup>+</sup> ions in comparison with other metal ions tested. Using ligand-capped CdTe QDs, a rapid and facile analytical method was developed for the determination of Ag<sup>+</sup> with a detection limit of  $6.06 \times 10^{-10}$  mol L<sup>-1</sup>.

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**ZnO nanoparticulates/polyamide nanocomposite coated on cellulose paper as a novel sorbent for ultrasound-assisted thin film microextraction**

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In this work, a novel thin film microextraction (TFME) <sup>1, 2</sup> method was developed using ZnO nanoparticles (ZnO NPs) incorporated into polyamide (PA) nanocomposite. In this regard the ex-situ prepared ZnO NPs <sup>3</sup> was dispersed into PA solution and the obtained solvent blend was deposited onto cellulose paper applying solvent exchange method. The characterization of prepared ZnO NPs/PA nanocomposite was performed applying energy dispersive X-ray spectroscopy (EDX), X-ray diffraction (XRD) and scanning electron microscopy (SEM). The prepared thin film based on ZnO NPs/PA nanocomposite was employed for ultrasound assisted thin film microextraction (USA-TFME) of some organophosphorous pesticides (OPPs) as model compounds including fenthion, chlorpyrifos, fenitrothion, phosalone, edifenphos and ethion in environmental water samples followed by gas chromatography-flame ionization detector (GC-FID) determination. TFME is a relatively new approach based on membrane solid phase microextraction (SPME) in sample preparation techniques which has exhibited more advantages over SPME such as small thickness of the extraction phase, a larger surface area-to-volume ratio, higher extraction rate and shorter equilibration time. Ultrasonic (US) radiation can be used in microextraction techniques as a powerful tool to increase the speed of the mass transfer process of the solutes towards the adsorbent surface <sup>4</sup>, leading to enhance of the extraction efficiency in a shorter duration time <sup>5</sup>. Important parameters influencing the extraction and back-extraction steps of USA-TFME were optimized applying orthogonal array Taguchi design. The developed methods limits of detection (LODs) were in the range of 0.05 to 0.3 ng mL<sup>-1</sup> and its linear dynamic ranges (LDRs) were 0.2-1000, 0.3-1000 and 1-1000 ng mL<sup>-1</sup> for all analytes. The method precision (RSD %) with three replicates experiments was in the range of 2.1 to 9.8% using spiked distilled water (100 ng mL<sup>-1</sup>).

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**Graphene oxide doped polyamide nanocomposite coated on cellulose paper as a novel layered sorbent for microextraction by packed sorbent of organophosphorous pesticides**

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In this work, a novel layered sorbent for microextraction in packed syringe was introduced, which has been prepared by coating the solvent blend of graphene oxide/polyamide (GO/PA) nanocomposite<sup>1,2</sup> (NC) onto cellulose paper through solvent exchange method. Scanning electron microscopy (SEM) was applied to investigate the surface characteristic and morphology of PA and GO/PA coated on cellulose paper. The prepared layered sorbent based on GO/PA nanocomposite was used for microextraction by packed sorbent (MEPS)<sup>3-5</sup> of organophosphorous pesticides (OPPs) including chlorpyrifos, fenthion, fenithrothion, ethion, edifenphos and phosalone in environmental aqueous samples followed by gas chromatography-flame ionization detector (GC-FID) detection. Important parameters affecting the MEPS processes including pH, extraction draw-eject cycles, sorbent layers, desorption solvent volume and desorption draw-eject number were studied and optimized using central composite design (CCD). Based on the method validation, limits of detection (LOD) were in the range of 0.2-1 ng mL<sup>-1</sup>. The method linear dynamic ranges were in 1- 500, 1-1000 and 3-1000 ng mL<sup>-1</sup> for different analytes. The method precision (RSD %) with three replicates determinations were in the range of 2.1 to 11 % for distilled water at the concentration level of 300 ng mL<sup>-1</sup>. The developed method was applied successfully to determine OPP compounds in the river, dam and tap water samples; accordingly, the relative recoveries (RR%) were obtained in the range of 77.8 to 113.3%.

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**Sensitive electrochemical determination of copper (II) based on a glassy carbon electrode modified with ZnO/NiO/montmorillonite**

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Surface modification by nickel oxide and zinc oxide nanostructures and montmorillonite (MMT) on a glassy carbon electrode (ZnO/NiO/MMT-GCE) was employed in the present study as a novel electrode for sensitive determination of trace concentrations of Cu (II). Electrodeposition method has been selected in this study due to many advantages in comparison to other deposition techniques [1-3]. The morphology and properties of electrode surface were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) and Fourier transform infrared spectroscopy (FTIR) techniques. Electrochemical determination of Cu<sup>2+</sup> ions was performed by differential pulse voltammetry. The responses of modified electrode for Cu<sup>2+</sup> was found to be improved significantly in comparison to those obtained using a conventional glassy carbon electrode. Under the optimized conditions the electrode exhibits a linear response to Cu (II) over a wide concentration range ( $5 \times 10^{-7}$  to  $1.0 \times 10^{-4}$  M) with the detection limit of  $1.07 \times 10^{-9}$  M.

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## Exhaustive Study of the Electrodimerization of 2-Mercaptobenzoxazole;

### From Electrochemical Behavior to Electrosynthesis

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Organic compounds possessing S–S bonds, often called disulfides or more specifically disulfanes, have been widely employed in the various fields ranging from biochemistry to industrial chemistry [1]. It is known that the oxidative coupling of the 2-mercaptobenzoxazole (MBO) to the 2,2-disbenzoxazole disulfide (BBOD) passes through a radical path [2,3]. However, there has been a little discussion concerning the electrodimerization of this compound on the various conditions and without paying attention to the significant optimizations. This can be due to the problems caused by the adsorption of thiols and related dimers on the electrode surface. So, the precise and comprehensive electrochemical survey is necessary in order to the better understanding of the proposed mechanisms and the fine electrosynthesis.

Our initial studies showed two essential point; pH–dependent behavior and typical adsorption pattern. At the critical acidic to mild basic conditions, two anodic and one cathodic processes are observed. The MBO undergoes  $1\text{H}^+$ ,  $1\text{e}^-$  oxidation of adsorbed and dissolved forms at the forward and low scan rate. It is leading to the formation of related disulfide (S-S) by dimerization of the electrogenerated thiyl radicals. The typical adsorption peak at the backward scan rate is related to the produced dimer (BBOD) owing to its extremely low solubility, which is easy to understand by the scan rate diagnostic test. At the critical basic conditions, the cathodic adsorption peak has disappeared that can be assigned to the related sulfonate because of over oxidation processes. The pH-dependence, scan rate effect and various solvents have evaluated for obtaining of the optimal condition.

According to the above-mentioned contents, the first aim of this study is the voltammetric analysis as an easy-to-apply electrochemical technique for the oxidation of different thiols in more details in order to shed more lights on the mechanistic aspect of this green electrochemical transformation under various conditions. On the other hand, the obtained optimal parameters will be employed for the electrodimerization of the various type of thiols in the electrosynthesis condition.

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**Synthesis and implementation of gelatin/polyvinylpyrrolidone semi-interpenetrating polymer network scaffold as a biocompatible extractive phase**

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This work introduces a biocompatible gelatin/polyvinylpyrrolidone (PVP) semi interpenetrating polymer network (semi-IPN) scaffold for extraction of contaminants from real samples. Interpenetrating polymer networks, due to their simultaneous possession of two or more polymers, could be preserved characteristics of individual constituent polymers. Choosing appropriate polymers, reagents and their ratio could control IPN different features like porosity, elasticity and swelling [1]. Biopolymers as non-toxic, inexpensive and biocompatible materials have prominent capability for analysis of environmental and biological samples [2]. Gelatin is a protein derived from partial hydrolysis of collagen which because of different reactive functional groups could be interpenetrated within PVP as a biocompatible industrial polymer [3]. Herein, gelatin/PVP semi-IPN scaffolds have been fabricated by freeze drying technique and cross linked with glutaraldehyde to induce a porous structure. The synthesized gelatin/PVP semi-IPN scaffolds were characterized by field emission scanning electron microscopy (FE-SEM), Fourier transform infrared (FTIR) and thermogravimetric analysis (TGA). The proposed scaffold was used as the extractive medium for needle trap device (NTD). The whole method, considered as a green chemistry approach for the determination of chlorobenzene and benzene derivatives of benzene, toluene, ethylbenzene and xylene (BTEX) using gas chromatography-flame ionization detector. The extractive phase performance was checked using different ratios of gelatin and PVP (gel/PVP: 1:0, 2:1, 1:1, 1:2, 0:1). Eventually, the best IPN achieved at the ratio of gel/PVP (1:2) was used as the extractive phase and effects of different parameters containing extraction and desorption time, extraction and desorption temperature, sampling flow rate and salt concentration for BTEX extraction were evaluated.

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**Fabrication of a sensor based upon polyphenylenediamine/NiO/MWCNTs nano-composite for determination of morphine**

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Molecularly imprinted polymers (MIPs) are among artificial selective receptors designed based on molecular imprinting technology which are introduced in 1931 [1]. MIPs are synthesized by copolymerization process of the functional monomers and a cross-linking agent in the presence of template molecules. The extrication of template molecules results in creation of cavities with specific binding sites bearing defined shape, size and functional groups for the analyte. The created cavities are potential to trap the template selectively from the mixtures containing closely related molecules [2].

A morphine-molecularly imprinted polymer (MIP), composed of polyphenylenediamine, nickel oxide/multi-walled carbon nanotube composite and triphenylamine, as cross linker, was synthesized. The deprotection step was done by a mixture of methanol using a soxhlet apparatus for 6 days to extract the sieved particles. Comparison of the cyclic voltammograms of a blank solution with that of a solution containing 250 mg L<sup>-1</sup> of morphine in the buffer 7 (0.1 mol L<sup>-1</sup>) confirmed the complete extraction of the template from the polymer. The prepared MIP was used for modification of carbon paste electrode (CPE) to fabricate a selective morphine electrochemical sensor. Electrochemical behavior of morphine on the investigated modified electrode was studied. This study showed an oxidation peak for morphine at 0.375 V (vs. SCE). The parameters affecting the sensor performance were investigated by using cyclic voltammetry technique. In order to achieve to the optimal MIP-CP composition, various amounts of the prepared MIP was used with 0.01 g graphite, 0.005 g paraffin. The highest anodic peak intensity was obtained by applying a composition of 0.01 g graphite, 0.005 g paraffin and 0.0005 g of MIP, for [reparation of the MIP-CP electrode. The effect of solution pH was investigated by recording the corresponding CVs in the pH range of 2.0–12.0. A maximum peak current was found by adjusting the solution to pH 9.0. The influence of scan rate and the electrode reaction process was studied. Based on the evaluated R<sup>2</sup> values of the plots of I<sub>p</sub>-v and I<sub>p</sub>-v<sup>1/2</sup>, a diffusion-controlled process was suggested for the electrode process. A confirmation for this argument achieved by plotting log I<sub>p</sub> versus log v [3]. This plot for the acquired data was accompanied with a slope of ~0.4, revealing that the role of diffusion is greater than adsorption role. It was confirmed that the anodic peak current increased linearly with the analyte concentration in the range 1.00 – 1500.00 mg L<sup>-1</sup> with a limit of detection 0.01 mg L<sup>-1</sup>. The selectivity of the proposed sensor was tested by determination of morphine in solutions containing some similar structures. The sensor was successfully applied for determination of morphine in some biological samples.

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**Removal methylene blue dye by Absorbent carbon nanotubes with response surface experimental design**

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In industrial water pollution, the color produced by minute amount of organic dyes in water is considered very important because, besides having possible harmful effects, the color in water is aesthetically unpleasant. Colored water can affect plant life, and thus an entire ecosystem can be destroyed by the contamination of various dyes in water. Some dyes are also toxic and even carcinogenic. This dictates the necessity of dye containing water to undergo treatment before disposal to the environment. The conventional methods for color removal are biological oxidation and chemical precipitation[1-3]. The purpose of this study was to optimize methylene blue dye removal from aqueous solutions by carbon nanotube using Response Surface Method and Central Composite Design methods. The batch experiment was conducted to evaluate the effects of independent variables such as pH, dye concentration, dose of sorbent and contact time. For the experiment, Response Surface and Central Composite Design methods were applied to evaluate the effects of these variables. Analysis of variance (ANOVA) was used for statistical analysis. The optimum conditions for basic methylene blue dye removal were pH= 8/5, dye concentration= 12.5, absorbent dose= 0/011g and contact time= 15 min. The verified model is Quadratic and R-squared value of this Study was obtained to be The R-Squared Adjusted was obtained to be 81.52% and The Squared predicted R was obtained to be 27.84%.

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**A simple homemade colorimetric analyzer based on mobile phone for determination of nitrite in different samples**

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One of the trends in modern analytical chemistry is the creation of easy-to-use and universally accessible means of chemical analysis. Nowadays, image analysis based analytical procedures are becoming important because of their ability to perform fast, non-invasive and low-cost analysis on products and processes [1]. Nitrites are widely used as indicators for information about environmental pollution and for food control. The presence of high level of nitrite in drinking water can cause several diseases in human health such as methemoglobinemia and stomach cancer by the production of N-nitrosamines [2].

In this work, an image analysis procedure has been proposed using a homemade colorimetric analyzer. The proposed method is based on the direct acquisition of digital images of the sample or sample extract in a conic tube using a smart phone and a free app to convert RGB-values. For this purpose, a colorimetric analyzer with 10cm high, 15cm wide and 12cm deep was made on which a hole was embedded for inserting 15-ml Falcon polypropylene centrifuge tube with conical bottom. A white light LED lace was placed inside the box. To evaluate the performance of the homemade colorimetric analyzer, nitrite was selected as the model analyte. In order to convert nitrite to a colored product, p-nitroaniline and naphth-1-ol were used. The proposed procedure avoids the drawbacks of UV-vis spectrometric measurements caused by the restricted volume of the sample, such as reduction of the optical path or need for dilution. The proposed procedure was used successfully for determination of nitrite in different environmental samples.

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**Evaluate the performance of Carbon Nanotubes in the removal of methylene blue from aqueous solutions; isotherms and kinetics studies**

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Scientific laboratories, industrial and agricultural wastewaters, rich in organic chemicals, are potential sources of pollution and eutrophication of natural water bodies. It is noteworthy that the number of emerging organic pollutants found in the environment is expected to increase with continually increasing applications of synthetic organic chemicals. Organic pollutants (including phenolic derivatives, polycyclic aromatic compounds, extractants, analytical reagents and dyes) are often found in the environment as a result of their wide laboratories and industrial uses[1-4]. The purpose of this study, removal of Methylene blue dyes from aqueous solutions dyes by carbon nanotube . The batch experiment was conducted to evaluate the effects of independent variables such as pH, dye concentration, dose of sorbent and contact time .The optimum conditions for basic Methylene blue dye removal were pH= 8.5, dye concentration= 12.5, absorbent dose= 0.011g and contact time= 15 min .Check isotherm and kinetic models showed that the experimental data with the Freundlich adsorption process Methylene blue ( $R^2=0.8417$ ) and pseudo-second ( $R^2=0.9941$ ) are correlated.

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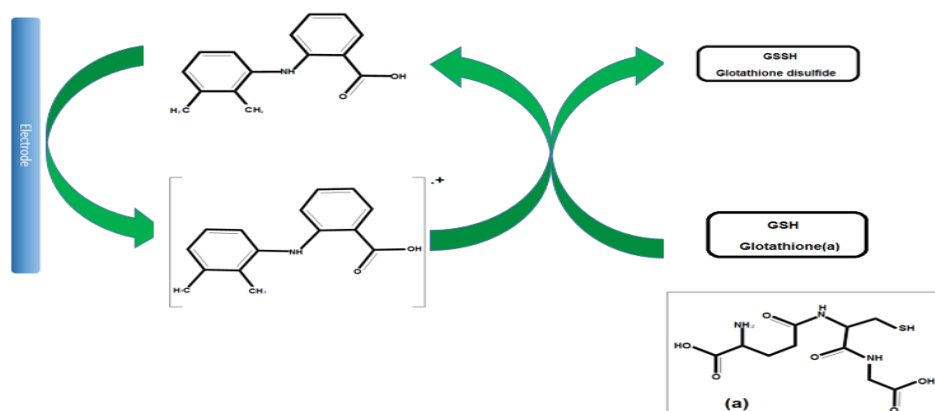
## Electrochemical oxidation of Mefenamic acid in the absence and presence of glutathione and N-acetylcysteine

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Electrochemical methods are widely used for studies on pharmaceutical composition. Mefenamic acid is an anti-inflammatory drug that is used to treat moderate pain and menstrual pain, toothache. It is widely available and present in many prescription and non-prescription medications. The results of a literature survey show that mefenamic acid is metabolized in the body. The product of mefenamic acid oxidation is extremely toxic to the liver. However, under normal conditions product of oxidation is rapidly detoxified by reaction with glutathione. But, in an overdose, cellular glutathione is depleted in the availability of product oxidation cause liver and kidney damage. Mefenamic acid poisoning is treated with N-acetylcysteine. N-acetylcysteine prevents hepatic injury primarily by restoring hepatic glutathione. N-acetylcysteine, which is also a sulfhydryl compound, is thought to act by facilitating hepatic glutathione synthesis or by acting as an alternate substrate for the reaction with the product oxidation. Electrochemical oxidation of mefenamic acid has been studied in presence of glutathione and N-acetylcysteine. Contrary to the previous about mefenamic acid, our results show that product oxidation consumes glutathione stores by catalytic oxidation of it.



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**Chemical nose for discrimination of some ergogenic drugs based on sensor array  
comprised of different metallic nanoparticles**

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Colorimetric sensors based on aggregation of metallic nanoparticles have found extensive applications in detection and determination of various analytes especially drugs of abuse. This is because of their unique characteristics which facilitates their usage for naked eye colorimetric detection. Colorimetric sensor arrays comprised of metallic nanoparticles are suitable analytical tools for detection and classification of different compounds which are based on different interaction of analytes with various metallic nanoparticles for obtaining a specific fingerprint for each analyte of interest in mixture. Combining these sensor array with chemometric techniques like PCA, HCA, LDA... is a good and reliable method for classification and characterization of analytical samples. Ergogenic drugs including salbutamol, atenolol, furosemide, pseudoephedrine ... are most utilized drugs by athletes which besides destructive effects on human health are prohibited by many regulatory bodies so their detection and determination are of importance [1- 4].

In this study a colorimetric sensor array comprised of the combination of four different nanoparticles including Au, Ag, Au@Ag and Ag@Au core-shells is used for classification of some most used ergogenic drugs. The interactions of nanoparticles and drug substances are monitored spectrophotometrically and the effects of drugs on the aggregation behaviour of four nanoparticles are studied based on the extent of the changes in their visible spectra. The obtained data are analyzed using chemometrical classification techniques and the results are used for classification of drugs in blood serum samples. Results showed high efficiency of proposed sensor toward analysis of biological compounds and drugs. Additionally it is possible to modify the constituents of the sensor by different modifiers to achieve high selectivity toward classification of desired analytes.

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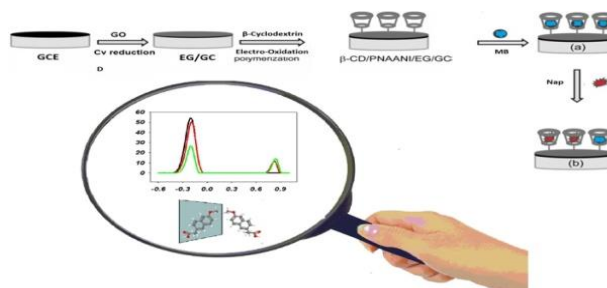


## A Dual-Signalling Electrochemical Recognition of Naproxen Enantiomers Based on Competitive Host-Guest Interaction of a $\beta$ -Cyclodextrin/Graphene modified Electrode

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A novel chiral architecture was fabricated by electrochemically reduction of graphene oxide on the glassy carbon electrode (GCE) and subsequent electro-oxidation of the electrode in a solution of  $\beta$ -cyclodextrin in phosphate buffer solution of pH 6.0. Morphological and electrochemical characterization of the electrode was conducted using scanning electron microscopy (SEM) and electrochemical impedance spectroscopy (EIS). The proposed chiral interface was used for recognition of Naproxen drug enantiomers by a competitive Host-Guest interaction between a probe and naproxen enantiomers which takes place in the interface of electrode. Thanks to the good redox properties and high affinity to  $\beta$ -CD, methylene Blue was used as the electrochemical probe. Due to the host-guest interaction, MB molecule can enter into the hydrophobic inner cavity of  $\beta$ -CD, and the MB/ $\beta$ -CD/ErGO/GCE displays a remarkable oxidation peak due to MB. In the presence of Naproxen, competitive association to  $\beta$ -CD occurs and the MB molecules are displaced by Naproxen, resulting in a decrease in the reduction peak current of MB. However selective binding properties of the electrode toward Naproxen enantiomers, led to different current changes, were further used for discriminating of enantiomes. Effect of different parameters such as concentration of MB and pH of the supporting electrolyte on enantio-selective discrimination was investigated. This approach provided a new available sensing interface to recognize and determine Naproxen enantiomers by electrochemical technology.



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**Removal of ciprofloxacin antibiotic by iron magnetic nanoparticles coated with lignin from hospital wastewater**

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Emerging contaminants in the environment have caused enormous concern in the last few decades, and among them, antibiotics have received special attention. On the other hand, adsorption has shown to be a useful, low-cost, and eco-friendly method for the removal of this type of contaminants from water. An understanding of the interaction mechanisms of antibiotics with environmentally relevant sorbents is important to determine the environmental fate of antibiotics and to develop wastewater treatment strategies. One of the widely used antibiotics is ciprofloxacin (CIP), which has been identified among the top 10 of high priority pharmaceuticals relevant for the water cycle in general[1,2]. Lignin is the second most abundant natural polymer with cellulose being number one, making up to 10–25% of lignocellulosic biomass. Lignin is a three-dimensional, highly cross-linked macromolecule composed of three types of substituted phenols, which include: coniferyl, sinapyl and p-coumaryl alcohols[3]. Iron magnetic nanoparticles ( $\text{Fe}_3\text{O}_4$ ) are used because of their high magnetic properties for separation and biological applications.  $\text{Fe}_3\text{O}_4$  nanoparticles could easily aggregate due to the nanoscale effect and magnetic gravitational effect[4].

In this work lignin coated magnetic  $\text{Fe}_3\text{O}_4$  nanoparticles were used for ciprofloxacin adsorption from aqueous solution.  $\text{Fe}_3\text{O}_4$ @Lignin nanoparticles were prepared and subsequently characterized using FTIR, XRD, SEM, VSM methods. This type of adsorbent is low cost, high efficient and reusable. Also, the parameters of the adsorbent dose, the pH, contact time and adsorption isotherms in the antibiotic removal process were investigated. The maximum removal percentage was obtained 74.5% for adsorption of ciprofloxacin.

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The 25<sup>th</sup> Iranian Seminar of Analytical Chemistry

3-5 September 2018

University of Tabriz



**Azo-Phenol ligand surface-active magnetic graphene oxide nanosheets as solid-phase adsorbents for extraction of cadmium in food samples**

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A sensitive and simple method using azo-phenol ligand functionalized magnetic graphene oxide nanosheets, as an adsorbent, has been successfully developed for extraction and preconcentration trace amounts of cadmium. The prepared nanosheets were confirmed by Fourier transform infrared spectra, X-ray diffraction, vibrating sample magnetometry and transmission electron microscopy. The main factors affecting the recovery such as the sample pH, adsorbent amount, eluent concentration, time of sonication and coexisting ions have been investigated and established. The adsorption equilibrium data obeyed the Freundlich model and the kinetic data were well fitted to the pseudo-second-order model. Thermodynamic studies revealed the feasibility and endothermic nature of the system. Under the optimum conditions, linear calibration curves were established between 1-10000  $\mu\text{g L}^{-1}$ . Detection limit obtained in this way is 0.4  $\mu\text{g L}^{-1}$ . The relative standard deviation (RSD%) was found to be less than 3.32 %. Accuracy of the method was evaluated by the analysis of different food samples; rice, barley, milk and fish. These results demonstrated that the functionalized magnetic graphene oxide nanosheets can be a potential adsorbent for cadmium removal.





## The 25<sup>th</sup> Iranian Seminar of Analytical Chemistry

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### Layered double hydroxide nanosheets deposited diatomite: high performance adsorbent for removal of anionic organic dye

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It would be of significance to design a green composite for highly efficient removal of contaminants. Herein, we fabricated an environmental friendly composite via in situ deposition of positively charged layered double hydroxide (LDH) nanosheets on the surface of the negatively charged diatomite for efficient removal of dye pollutants from aqueous solutions. The resulting LDH/diatomite (LDH/DIA) composites were characterized by X-ray diffraction (XRD), Fourier transformed infrared (FTIR) spectroscopy, scanning electron microscopy (SEM), Energy-dispersive X-ray (EDX), and N<sub>2</sub> adsorption-desorption technique. The adsorption performances of the resulting LDH/DIA composites were evaluated for the removal of anionic tartrazine (TR), and erythrosine (ER) dyes. The adsorption test of dyes demonstrates that the present composite can rapidly reduce the concentration of dyes in aqueous solution from ppm levels to trace levels of  $\leq 1$  ppb. In addition, the adsorption behavior of this new adsorbent fits well with the Freundlich isotherm and the pseudo-second-order kinetic model. Adsorption isotherm studies showed that the maximum adsorption capacities of TR and ER dyes over the LDH/DIA composite were in the sequence 555.56 and 625.23 mg g<sup>-1</sup>, which was much higher than the known adsorbents. Our results suggested that the LDH/DIA have great potential applications as environmentally friendly materials for the treatment of waste water with high concentration of anionic dyes.





Chemiluminescence determination of venlafaxine by using CuO nanoparticles –H<sub>2</sub>O<sub>2</sub>–  
NaHCO<sub>3</sub> reaction

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Venlafaxine (VF) is an arylalkanolamine serotonin–norepinephrine reuptake inhibitor (SNRI) and is used primarily for the treatment of major depression in adults. The chemical structure of VF was shown in Fig.1.

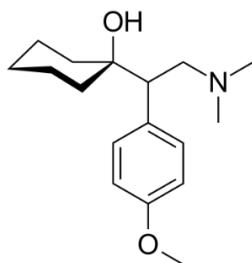


Fig. 1. The chemical structure of venlafaxine

Literature reveals that, several methods including voltammetry [1], high-performance liquid chromatographic (HPLC) [2], liquid chromatography–tandem mass spectrometry (LC–MS–MS) [3], headspace–solid phase microextraction (HS–SPME)– gas chromatography (GC) [4] and nonaqueous capillary electrophoresis– mass spectrometry [5]. However, these methods face the drawbacks of being expensive, laborious and require pre-treatment of the samples. Chemiluminescence (CL) is generally defined as the emanation of light (ultraviolet, visible or infrared) through the process of a chemical reaction. CL detection has advantages including simplicity of operation, low cost of instrumentation, high selectivity, wide dynamic range, reproducibility and rapidity. In this work, CuO nanoparticles (CuO NPs) were prepared by using quick precipitation method. Then, those were characterized by using X-ray diffraction (XRD), transmission electron microscopy (TEM), scanning electron microscopy (SEM) and Fourier transform infrared spectroscopy (FTIR). The results of experiments revealed that CuO NPs amplified the intensity of H<sub>2</sub>O<sub>2</sub>–NaHCO<sub>3</sub> CL system. Moreover, it was found that VF quenched the CuO NPs–H<sub>2</sub>O<sub>2</sub>–NaHCO<sub>3</sub>. Based on these results, a new and sensitive CL method for determination of VF was established. After optimization of reaction condition, the calibration curve was drawn for VF. The liner range and limit of detection of the CL method were  $5.0 \times 10^{-6} - 5.0 \times 10^{-4} \text{ mol L}^{-1}$  and  $4.1 \times 10^{-6} \text{ mol L}^{-1}$ , respectively. The method was successfully exploited for measurement of VF in the pharmaceutical preparations.

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**A new chemiluminescence method for the determination of paracetamol  
in pharmaceutical formulations**

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Paracetamol (acetaminophen, N-acetyl-p-aminophenol, 4-acetamidophenol) is a broadly used minor analgesic. Though it has some cyclooxygenase inhibiting properties, this role is very weak in the peripheral tissues and it has practically no anti-inflammatory action. It is also stated that large doses show adverse effect on the kidneys and liver [1]. The structure of paracetamol was presented in Fig. 1.

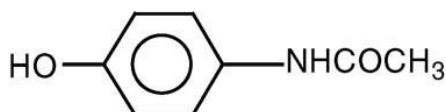


Fig. 1. The structure of paracetamol.

Several chemiluminescence (CL) methods by using different CL reactions including luminol- $\text{Fe}(\text{CN})_6^{3-}$  [2, 3], tris(2,2'-bipyridyl)ruthenium(II)- $\text{KMnO}_4$  [1] and luminol- $\text{KMnO}_4$  [4]. In general, CL methods show many benefits for determination of pharmaceutical including high sensitivity, cost effectiveness, simple sample preparation and instrumentation [1]. In this research work, it was found that the  $\text{Fe}_3\text{O}_4$  nanoparticles (NPs) can increase the intensity of the  $\text{NaHCO}_3\text{-H}_2\text{O}_2$  CL reaction. Moreover, it was found that paracetamol decreased the intensity of the  $\text{Fe}_3\text{O}_4$  NPs- $\text{NaHCO}_3\text{-H}_2\text{O}_2$  system. Based on these results, a new, sensitive, simple CL method was developed for measurement of concentration of paracetamol in pharmaceutical formulations. The linear dynamic range of the CL method was  $1.0 \times 10^{-6} - 1.0 \times 10^{-5} \text{ mol L}^{-1}$ . In addition, the limit of detection (LOD) and relative standard deviation (RSD%) of the method were  $1.2 \times 10^{-8} \text{ mol L}^{-1}$  and 3.2, respectively. The CL method was successfully used for the determination of paracetamol in pharmaceutical formulations. In addition, the possible mechanism of the  $\text{Fe}_3\text{O}_4$  NPs- $\text{NaHCO}_3\text{-H}_2\text{O}_2$  CL reaction was also discussed, briefly. Moreover, it should be mentioned that the  $\text{Fe}_3\text{O}_4$  nanoparticles (NPs) used in this work have average size about 20–40 nm and were synthesized by using a quick precipitation method. Those were characterized by using X-ray diffraction (XRD), Fourier Transform Infrared (FTIR) and scanning electron microscopy (SEM) techniques.

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**A new CuO nanoparticles-enhanced chemiluminescence method****for the determination of cephalixin**Mortaza Iranifam\*, Anis Jafari*Department of Chemistry, Faculty of Science, University of Maragheh, Maragheh, Iran**\*E-mail: MortezaIranifam@yahoo.com*

Cephalexin (Ceph) is a semi-synthetic antibiotic of the cephalosporins group, which can cure a number of bacterial infections. It kills gram-positive and some gram-negative bacteria by interrupting the growth of the wall of bacterial cell. It is an effective broad spectrum antibiotic, which have a structure like to that of the penicillin and is used for patients allergic to penicillin [1]. The chemical structure of Ceph was shown in Fig.1.

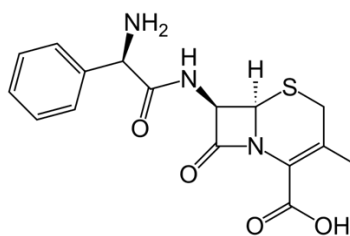


Fig. 1. The chemical structure of cephalixin

Generally, medicines can pollute water sources because of the discharge of chemical industry and hospital wastes into the environment. Most of these chemical compounds may persistent in the environmental waters for a long period of time and can cause harmful effect on aquatic animal organisms and human health. Thus, measurement of pharmaceuticals in water samples is very important. Furthermore, determination of Ceph in pharmaceutical products is very essential process in the quality control of the pharmaceutical industries [2]. In this work, a new and sensitive CuO nanoparticles (CuO NPs)-catalysed  $\text{H}_2\text{O}_2\text{-HCO}_3^-$  system was developed for determination of Ceph. The suggested method was based on inhibitory effect of Ceph on the CL system. The experimental parameters affecting the CL intensity including concentrations of  $\text{NaHCO}_3$ , CuO NPs and  $\text{H}_2\text{O}_2$  were optimized. Under the optimum condition, the calibration curve was plotted for Ceph. It was linear in the concentration of the range of  $5.0 \times 10^{-5} - 1.0 \times 10^{-3} \text{ mol L}^{-1}$ , with detection limit of  $1.2 \times 10^{-5} \text{ mol L}^{-1}$ . In addition, the CuO NPs were synthesized by using quick-precipitation method and characterized by employing X-ray diffraction (XRD) and scanning electron microscopy (SEM) techniques. The method was successfully exploited for measurement of Ceph in the pharmaceutical preparations and tap water.

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## Determination of topiramate based on its enhancing effect on CeO<sub>2</sub> nanoparticles–luminol–O<sub>2</sub> chemiluminescence reaction

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Ceria nanoparticles are one of the most vital nanomaterials for a varied range of applications in catalysts, fuel cell, chemical-mechanical polishing for microelectronics, phosphor/ luminescence, and metallurgical and glass/ceramic applications. These applications are mainly based on cerium's high thermodynamic affinity for oxygen and sulphur, its potential redox chemistry involving Ce(III)/Ce(IV), and absorption/excitation energy bands related to its electronic structure [1]. Newly, much attention has been paid to the CL of nanomaterial systems, to improve the sensitivity and the stability. Semiconducting and metallic NPs used as catalysts in CL reactions have provided new methods to improve the sensitivity and extended new applications of this mode of detection [2]. It is perhaps interesting to mention that topiramate (C<sub>12</sub>H<sub>21</sub>NO<sub>8</sub>S) is an anticonvulsant (antiepilepsy) drug. This medication is prescribed for treatment of diseases such as epilepsy, bipolar disorder, alcoholism, bulimia nervosa, obesity, migraine, post-traumatic stress disorder and mood instability disorder [3].

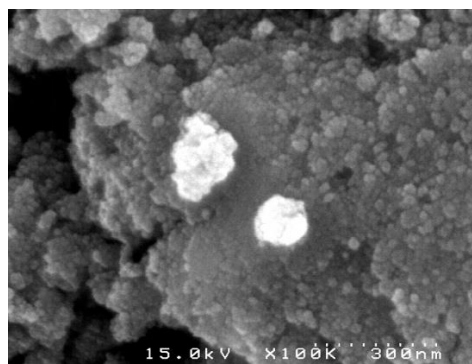


Fig. 1. SEM image of CeO<sub>2</sub> NPs

In this work, CeO<sub>2</sub> nanoparticles (NPs) were prepared by using quick precipitation method and, then, were characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM) (Fig. 1). It was found that CeO<sub>2</sub> NPs present oxidase-like activity and increase the intensity of the luminol-O<sub>2</sub> CL reaction. Moreover, it was found that topiramate could enhance the intensity of CeO<sub>2</sub> NPs-luminol-O<sub>2</sub> CL reaction. Based on these findings, a simple and sensitive CL method for the determination of topiramate was proposed. The linear dynamic range of the CL method for determination of topiramate was  $4.0 \times 10^{-6} - 1.0 \times 10^{-5} \text{ mol L}^{-1}$ , with a limit of detection (LOD) =  $3.9 \times 10^{-6} \text{ mol L}^{-1}$ . The relative standard deviation (RSD%) of the CL method was 1.37% (n = 9). The CL method was used for the measurement of concentration of topiramate in pharmaceutical preparations.

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## Molecularly imprinted polymer based carbon dots as an optical sensor for selective detection of metronidazole

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In this work, a novel selective green and eco-friendly carbon dots (CDs) were synthesized from Eucalyptus leaves as a carbon source via hydrothermal method. The CDs were used as a fluorophore in an optical sensor by joining molecularly imprinted polymers (MIPs) for the detection of metronidazole. The MIPs was prepared via reverse microemulsion method on the surface of the CDs to produce CDs@MIPs.

MIPs have many advantages such as ability to recognize and bind specific target molecules, inexpensive, high stability and easy preparation. For the MIPs preparation, during the polymerization, the target molecule acts as a template to form cavities [1]. The formed molecular cavities in the polymer matrix are sites, which have similar features of physics matched with the target molecules [2]. After polymerization, the template is removed, and binding sites are exposed that are complementary to the template in size, shape, and position of the functional groups.

Metronidazole (2-methyl-5-nitroimidazole-1-ethanol) is a nitroimidazole antibiotic metronidazole. It is a useful treatment of infections due to Bactericides spp. and many anaerobic bacteria. Metronidazole is one of the most commonly used drugs all over the world, one of the top 100 most prescribed drugs in the United States commonly used to treat protozoal diseases counting trichomoniasis, giardiasis [3], and central nervous system diseases [4]. Therefore, measurement of trace amount of metronidazole via sensitive, fast and selective method is very important

In the suggested method, under the optimized experimental parameters such as pH, temperature, amount of CDs@MIPs and time, metronidazole could be detected with a linear dynamic range from 0.08 to 1.0 ng/ml with a detection limit 0.02 ng/ml. The precision of the method for 0.27 and 8.4 ng/ml MTZ was obtained as 3.1% and 2.2% (3 replicate detection), respectively. The selectivity of the sensor was also investigated and the results showed a good selectivity due to the presence of the recognition cavities. Finally, this sensor was successfully applied to metronidazole determination in human plasma sample. This sensor has many advantages for example is green, simple and non-expensive in addition it has good figures of merits such as low detection limit and high selectivity and sensitivity.

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**Easy diagnosis of jaundice: A smartphone-based sensing bioplatfrom using carbon dots embedded in bacterial nanopaper for Point-of-Care hyperbilirubinemia diagnosis**

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Nearly 386,000 babies have been born every day all over the world and about 60 percent of them getting jaundice within the several days of birth. Neonatal jaundice, is a condition that the skin has got a yellow tint and the whites of eyes are turned yellow, due to the accumulation of excess Bilirubin (BL) in blood<sup>1</sup>.

Herein we report a green, low cost and disposable microfluidic nanopaper-based sensor or “lab-on-nanopaper” device for visual determination of BL in human serum samples that monitors Hyperbilirubinemia. Modified bacterial cellulose (BC) nanopapers can be utilized as novel sensing platforms, due to their excellent stability, sustainability and optical transparency<sup>2,3</sup>. The highly photoluminescence (PL) carbon dots (CDs) embedded on BC nanopapers were used as sensing elements. In the presence of BL, quenching of CDs that were excited by an UV-LED ( $\lambda=365$  nm), happened<sup>4</sup>. When BL was exposed to blue light ( $\lambda=470$  nm) a natural photoisomerization happened, therefore the unconjugated BL converted to the conjugated form<sup>5</sup> and the PL of CDs increased. The changes of CDs PL intensity during photoisomerization were used as signal, which can be monitored visually by smartphone camera or fluorometer. The changes were linearly proportional to the concentration of BL in the range of 3-18 mg dL<sup>-1</sup>. The developed sensor was also used for the determination of BL in human blood serum samples with satisfying results. Building upon the use of BC nanopaper as a new platform with unique properties, we believe the lab on nanopaper devices could be considered as a new generation of optical sensors for analysis of (bio)chemical samples.

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## Fluorescence Study of Zn(II) Complexes with Salophen-Type Ligands

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Transition metal complexes with salophen type ligand have attracted enormous attention in coordination chemistry due to their structural liability, unusual configuration and sensitivity towards environment as a functional material [1-3]. They are known to act as an excellent candidate as a luminescent material with possible utilization in solar energy conversion, luminescent sensors, electroluminescent sensors and probes for biological systems [4]. The source of their luminescence is due to the metal to ligand charge transfer (MLCT) excited state, which is usually sensitive to molecular configuration and peripheral ligand. Herein, we investigate the fluorescent properties of two new chloro and bromo salophen ligands and their Zn(II) complexes. The results show the emission of complexes shift to higher wavelengths in comparison with the ligands and about complexes, the emission decreases in intensity.

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**A new and sensitive chemiluminescence method for the determination of fungicide  
tebuconazole in environmental water samples.**

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Tebuconazole (Teb), (RS)-1-p-chlorophenyl-4,4-dimethyl-3-(1H-1,2,4-triazol-1-ylmethyl)- pentan-3-ol) is usually used as a triazolic fungicide. It is used to treat pathogenic fungi on plant in agriculture and on crops like barley, wheat, and peanuts. Teb possess a relatively high soil organic carbon-water binding coefficient and a half-life in soil of 49 – 610 days under aerobic circumstances [1]. The structure of Teb was presented in Fig. 1.

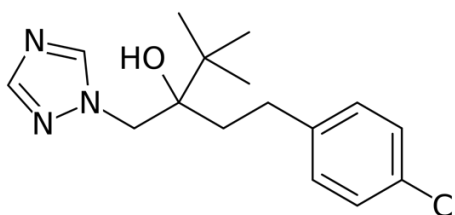


Fig. 1. The structure of Tebuconazole.

So far, various analytical methods including gas chromatography [2], liquid chromatography [3] and electrochemistry [1] have been developed for determination of Teb. In this work, a quick precipitation method was used for synthesis of CeO<sub>2</sub> nanoparticles (NPs). The synthesized CeO<sub>2</sub> NPs were characterized by scanning electron microscopy (SEM) and X-ray diffraction (XRD). It was found that CeO<sub>2</sub> NPs increase the intensity of the luminol-O<sub>2</sub> CL reaction. In addition, it was found that Teb quench the CeO<sub>2</sub> NPs-luminol-O<sub>2</sub> CL reaction and CL intensity was inversely proportional to the concentration of Teb. For finding the reaction condition on which the Teb has highest influence on the CL system, the parameters affecting on the CL system was optimized. Under optimum condition, the calibration curve for Teb was drawn. The linear range, limit of detection and relative standard deviation (RSD%) of the CL method were  $7.0 \times 10^{-6}$  –  $2.0 \times 10^{-4}$ ,  $1.6 \times 10^{-6}$ , 3.42%, respectively. In order to investigate the selectivity of the CL method towards the Teb, the interference study was also carried out. The CL method was successfully used for the determination of concentration of Teb in environmental water samples.

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## Preparation of chitosan/poly vinyl alcohol/nano zinc oxide blend beads for removal of heavy metals from aqueous solutions

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The application of photocatalytic beads in wastewater treatment application has earned attention of many researchers. In this study, the synthesized poly (vinyl alcohol)/chitosan/ nano Zinc oxide (PVA/CS/nanoZnO) beads have been considered as a promising alternative to conventional means of wastewater treatment. The present study has successfully synthesized PVA/CS/nano ZnO beads through simple dropwise method in which varied concentration of CS from 1.0 g to 2.0 g. Solubility and swelling properties investigation of the beads were also performed within the prescribed time of 24h in three different medium which were acidic, distilled water and alkaline solution. Result of solubility test proved that PVA/CS/nano ZnO beads were insoluble only in distilled water and alkaline solution. But, the beads were found to dissolve in acidic solution due to the CS content. Incidentally, the swelling test revealed that increased concentration of CS leads to swelling of beads in distilled water and alkaline solution. Results revealed that beads with the highest CS composition which is 2.0 g recorded 75.1% and 110.7% of swelling in distilled water and alkaline solution, respectively. Meanwhile, beads with the lowest CS composition which is 1.0 g only swell for 70.0% and 95.2% in distilled water and alkaline solution, respectively. As a conclusion, the synthesized beads in this study are feasible to be applied in natural to alkaline environment.

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## The 25<sup>th</sup> Iranian Seminar of Analytical Chemistry

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### The use of chemometrics methods for classification of some soft drink samples by analysis of voltammetric signals obtained from metallic nanoparticle-modified electrodes

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Over the past two decades, interest has increased in using diagnostic methods to analyze analytical responses derived from a set of sensors, which constitute the "electronic tongue". Electronic tongue can be defined as a device from a collection of suitable electrochemical sensors each has different response toward the same sample solution [1]. Researchers are keen on using metal nanoparticles as a modifier in electrochemical assay systems. The combination of electrochemical signals from the constituents of the sensor for a single analyte will form a fingerprint which is unique for any component of the system under study [2-4]. One of the most important uses of chemometrics is to detection and classification of different compounds based on these fingerprints without the use of complex separation methods [5].

In this study an electronic tongue constitutes of a set of glassy carbon electrodes modified with Au, Ag and their core-shell structures was used for classification of some commercial fruit juice samples from different manufacturers. Electrochemical voltammetric measurements consist of successive CV and DPV experiments on the samples that results in a data matrix for each sample which can be used for classification purposes using chemometrics techniques like PCA, HCA and LDA. The obtained results showed the applicability and suitability of proposed method for sensitive and accurate detection and classification of routine samples without any complicated pretreatment and electrode preparation procedures.

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## Synthesis, Characterization and antimicrobial studies of chitosan / poly (vinyl alcohol ) /nano ZnO composite nanofibers

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Nanofibers of (chitosan / poly (vinyl alcohol)/nano ZnO) were prepared by electrospinning method. ZnO nano particles of size (~20 nm) was synthesized and characterized by uv spectroscopy, XRD and infrared spectroscopy (IR).nanofibers were prepared in the varying ratio of chitosan, PVA and nano ZnO.The prepared composite nanofibers were characterized using FT-IR, XRD and SEM studies.The antimicrobial activities of CS/PVA/nano ZnO mats were examined with different bacteria against the measurement of clear zone diameter and found that CS/PVA/nano ZnO mats shows antibacterial activity due to presence of nano ZnO.our researchs suggest that such nano fibers could be used to biomedical applications.

Electrospinning is a simple and a low cost method for formation of nanofibers.nanofibers have interesting specifications such as high pores with very small pore size and very large surface area-to-volume ratio.Therefore, nanofiber can be hope-giving and assured materials for many biomedical applications such as wound dressing, drug delivery, tissue templates,etc.

Chitosan, a (1-4)-linked 2-amino-2-deoxy-D-glucopyranose is obtained from chitin.It is one of the most plentiful natural polysaccharides,due to several unique properties: biodegradability, biocompatibility and antimicrobial properties.It is nontoxic for the human body.chitosan is insoluble in water,and common organic solvents,but it easily dissolves in aqueous inorganic and organic acid media. Since, electrospinning of chitosan itself is difficult, chitosan has been mixed with other synthetic on natural polymers such as PVA and poly (ethylene oxide).PVA is non-toxic, biodegradable and water- soluble synthetic polymer and has been used on vast scale in biomaterial application. During the last few years, Synthesis of nanostructured oxide materials have been acquire significant attention. nano crystalline ZnO is an interesting and promising material for constitutional research and industrial application. Its incomparable optical and electrical properties are useful for gas sensor, solar cells, nano lazars, etc. The surface morphology, crystalline structure, were investigated by scanning electron microscope, X-ray diffractometer (XRD).In this work, we have blended chitosan with PVA for preparing them in to nanofibers and we developed CS/PVA/Nano ZnO nanofiber mats for biomedical applications.[1-3].

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**Vortex assisted dispersive micro solid phase extraction using schiff base ligand anchored nano magnetic iron oxide for preconcentration of phthalate esters and determination by GC-FID**

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Nowadays, phthalate esters (PAEs) are widely used in production of polymer materials; therefore they occur in final products such as plastics, food packages and cosmetics. These compounds undergo emission into the environment and have a negative impact on living organisms [1]. In the present work, a novel nano sorbent was prepared via schiff base reaction between p-dimethylaminobenzaldehyde and Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-NH<sub>2</sub> nanoparticles [2]. The morphology and surface properties of the adsorbent was characterized using Fourier transform infrared spectroscopy, scanning electron microscopy (SEM) and energy dispersive spectroscopy. Modified nano sorbent was successfully applied for dispersive micro solid phase extraction and gas chromatography flame ionization detection (GC-FID) of six types of PAEs including Dimethyl phthalate (DMP), Diethyl phthalate (DEP), Di-n-butyl phthalate (DBP), Butylbenzyl phthalate (BBP), Bis-(2-ethylhexyl) phthalate (DEHP) and Di-n-octyl phthalate (DOP). Several variables affecting the extraction efficiency such as pH, amount of sorbent, extraction solvent type and volume, extraction and desorption time and salt effects were investigated and optimized. The best working conditions were as follows: amount of sorbent, 15 mg; type of solvent, n-Hexane; NaCl concentration, 10 % (w/v); sample volume, 25 ml; Vortex time for adsorbition, 1.5 min; Sonication time for desorption, 2 min; pH, 8.1. Under the optimal conditions the calibration curves were linear in the range of 1- 150 μg L<sup>-1</sup> for DMP, DEHP, DOP and 0.1-200 μg L<sup>-1</sup> for DEP, DBP, BBP. The limit of detections (S/N = 3) obtained in the range of 0.03-0.4 μg L<sup>-1</sup>. Finally, the method was successfully applied for the preconcentration and determination of phthalate esters in bottled water, packaged yogurt and infusion serum with acceptable performance.

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**A highly improved luminol–O<sub>2</sub> chemiluminescence system in the presence of graphene oxide nanoparticles for determination of paracetamol in pharmaceutical formulations**

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Chemiluminescence (CL), as an analytical technique, is based on the measurement of the electromagnetic radiation (usually visible/near-infrared radiation) emitted by a chemical reaction [1]. In recent years, nanomaterials with the unique physical and chemical properties have amplified the CL signal and improved the sensitivity of the various CL detection systems [2]. In this work, graphene oxide (GO) *nanoparticles* (NPs) was synthesized by using the modified Hummer's method [3]. The structural study of GO was performed by ultraviolet and visible (UV-VIS) spectroscopy, X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM) and Fourier transform infrared (FTIR) spectroscopy. It was found that GO NPs possess oxidase-like activity and enhance the intensity of the luminol–O<sub>2</sub> CL reaction. Moreover, in the presence of paracetamol as a target analyte, the improved GO NPs-luminol–O<sub>2</sub> CL intensity was decreased. Accordingly, a novel and sensitive CL method for determination of paracetamol drug was developed. The effect of various chemical parameters on CL intensity were investigated and optimized. Under the optimum conditions, a linear relationship was obtained between the enhanced CL intensity and the concentration of paracetamol in the range of  $7 \times 10^{-6}$  –  $5 \times 10^{-5}$  M with a detection limit of  $8.72 \times 10^{-7}$  M. The relative standard deviation for 5 determinations of  $2 \times 10^{-5}$  M paracetamol is 3.39%. The method was applied to determine paracetamol in several pharmaceutical formulations.

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## Synthesis and Characterization of Nanostructured Polyaniline Doped with Ni<sup>2+</sup> ions

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Conducting polymers are polymers that have conjugated backbone and inherently conduct electricity. Their unique physical and chemical properties; such as conductivity change, conductivity control and dopant exchange; result in applying these intelligent polymers in different chemical and electrochemical areas including batteries, fuel cells, corrosion protection and sensors [1]. Among conducting polymers, polyaniline has received much attention due to its specific properties. To obtain conducting form of polyaniline, doping with Bronsted acids is essential. Doping of polyaniline with Lewis acid and also with transition metal ions have been studied in recent years [2]. In this paper polyaniline nanofibers were synthesized for the first time in the presence of nickel ions, and structural properties of the polymer were investigated by ultraviolet and visible (Uv-vis) and Fourier transform infrared (FTIR) molecular absorption spectrometry, X-ray diffraction (XRD) and field effect scanning electron microscopy (FESEM). Nanostructured polyaniline was synthesized using different percentages of nickel chloride. The FESEM images of the samples indicate the formation of nanofibers similar to polyaniline nanofibers. The XRD pattern reveals the amorphous nature of polyaniline/nickel ion composites. Some of the characteristic absorption bands of polyaniline are shifted in the Uv-vis and FTIR spectra. These observed changes may indicate that Ni<sup>2+</sup> ions interact with nitrogen atoms in the polyaniline chain as dopant. The obtained material can be used for gas sensing applications.

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**A photoluminescence “switch- on” nanosensor composed of nitrogen- doped carbon dots- silver nanoparticles for highly selective and sensitive detection of cysteine**

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Carbon nanodots (CDs) are a new high luminescence class of carbon nanomaterials with the size in the range of units of nanometers. Typically, CDs contain carbon core and many carboxylic groups at their surface, thus imparting them with excellent water solubility and the suitability for subsequent functionalization with various organic, polymeric, inorganic, or biological substances [1]. Isoniazid, pyridine-4-carboxylic acid hydrazide, is an antituberculosis agent, which is usually used to prevent the development of clinical tuberculosis[2]. innovative water-soluble nitrogen-doped carbon dots(N-CDs) with bright luminescence and high quantum yield were synthesized via a simple and straight forward hydrothermal method, using an aqueous solution of isoniazid as a novel N containing single-source precursor. In this paper the interaction of nitrogen-doped carbon dots from isoniazide with silver nanoparticles (AgNPs) was investigated using fluorescence spectroscopy. It was found that AgNPs efficiently quench the fluorescence of N-CDs as a result of fluorescence resonance energy transfer (FRET). thus, a FRET system between nitrogen-doped C-Dots (as the donor) and AgNPs (as the acceptor) was introduced. Moreover, it was found that cysteine could recover the fluorescence of N-CDs due to the competitive adsorption of this compound onto AgNPs. This was exploited to design a simple and selective method for the determination of cysteine in the concentration range from  $3 \times 10^{-8}$  to  $6 \times 10^{-7}$  (mol/lit), with a detection limit of  $3.9 \times 10^{-9}$  (mol/lit).

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**Study of chromium (VI) ion absorption from aqueous solution using activated carbon produced from palm date**

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Water pollution caused by toxic heavy metals constitutes one of the most serious environmental problems. Chromium is one of the toxic heavy metal has been extensively used in industries including electroplating, leather tanning, metal plating, battery and petroleum refining. In aqueous environments chromium exists in two stable oxidation states, trivalent and hexavalent (Cr (III) and Cr (VI)). The Cr (VI) form is considered more toxic than Cr (III) and a suspected carcinogenic material. Hexavalent chromium is very soluble and mobile in the natural environment [1].

There are several strategies for Cr (VI) removal including chemical precipitation, membrane separation, reduction, ion exchange and adsorption [2]. Recently, the adsorption method has promisingly been used for the removal of heavy metals from water and wastewater. This method, compared with other physical and chemical methods, is facile, low-cost, efficient, and easy-design [3].

Activated carbon is widely and successfully used to remove various heavy metals ions from an aqueous solution due to its absorptive capacity. However, this adsorbent poses many restrictions, such as non-renewability of initial materials and high product costs [3]. In order to produce activated carbon, a variety of agricultural materials and wastes can be used. Generally, any inexpensive material that has a large amount of carbon in its structure and a small amount of minerals can be used as raw material for the production of activated carbon. Wood of some plants, charcoal, brown charcoal, lignin, coconut shell, shell fruits such as hazelnuts, walnuts are the most commonly used raw materials to produce activated carbon.

In this study, date *Phoenix dactylifera* was used for the production of activated carbon. Dates were prepare from local formers and then their shells were separated and washed with water to remove excess materials. After washing, date palm (30 g) were placed in an oven at 400 °C for 2 h in order to carbonize the date palm. The resultant activated carbon was characterized by FTIR, SEM, EDAX, and Map techniques. Factors affecting removal efficiency of Cr (VI) ions such as pH, dosage, contact time and initial concentration of Cr (VI) were investigated. The best evaluated pH was 2 for activated carbon.

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**One-step Green synthesis and characterization of highly Luminescent carbon dots from beef as selective and sensitive nanosensors for ketotifen fumarate detection in human fluids**

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Fluorescent carbon dots, a young smart member of the carbon nanomaterial family, were first obtained during purification of single-walled carbon nanotubes in 2004 [1]. They are generally oxygenous carbon nanoparticles with a size of less than 10 nm [2]. In this work, green luminescent water soluble carbon dots (CDs) were synthesized by simply hydrothermal treatment of: beef, shrimp, beef liver and oyster, without using any surface passivating and oxidizing agent or inorganic salt. The application of high fluorescent beef CDs without any surface modification was described as a green, simple, economical method for sensitive and selective determination of ketotifen fumarate. The as prepared CDs exhibit exceptional advantages including considerable fluorescent quantum yield and satisfactory chemical stability. The fluorescence of CDs based nanosensor can be selectively and efficiently quenched by ketotifen fumarate. The linear range of determination of ketotifen fumarate by this nanosensor was  $7 \times 10^{-7}$  -  $5 \times 10^{-6}$  (mol/lit) with a detection limit of  $3 \times 10^{-7}$  (mol/lit). Finally, the proposed method was successfully applied in the determination of ketotifen fumarate in human serum and urine samples with satisfactory recoveries, which suggested that the new nanosensor had great prospect toward the detection of ketotifen fumarate in human fluids.

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## Absorption of methylene blue from aqueous solution using activated carbon/CoFe<sub>2</sub>O<sub>4</sub> magnetic composite

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Colors are one of the most important sources of contamination for water and the environment and their products may be poisonous and carcinogenic to living organisms. It is estimated that synthetic paints are produced annually of about 10,000 tons, and it is estimated that around 1-10% of this amount is evacuated within the environment. Colors are used in various industries such as textiles, paper making, plastics, food, rubber and cosmetics, and they enter the environment through sewage [1]. Colors are generally divided into three categories: (1) anionic (include direct, acid and reactive dyes); (2) cationic (all basic dyes) and (3) non-ionic (disperse dyes and vat dyes). In general, colors are stable over the light, heat, and oxidants and are non-biodegraded. Colors can cause major problems within the environment, because some of them are poisonous, carcinogenic and mutagenic, allergic, cause irritation and gene change in humans[2]. Various physical and chemical methods have been employed for the treatment of dyes, including coagulation, flocculation, precipitation, ozonation, oxidation, photocatalysis, and ultrasound irradiation. Among various methods of dye removal, adsorption has been reported to be the most effective method that provides promising results. Among the adsorbent materials, one of the most extensively explored adsorbents is activated carbon.

In recent years, spinel ferrite nanoparticles have received considerable attention due to their ease of separation under external magnetic fields and large surface area to volume ratio. Among the spinel ferrite compounds, much efforts has been undertaken to synthesis of cobalt ferrite (CoFe<sub>2</sub>O<sub>4</sub>), because of its chemical stability, high mechanical hardness, high magneto crystalline anisotropy ( $k > 10^5$  J/m<sup>3</sup>), and coercivity. Although, its application as an adsorbent material is not yet much explored, recently CoFe<sub>2</sub>O<sub>4</sub> have been used in water purification[3].

In the present work, activated carbon was obtained from apricot leaves and was used to formation of activated carbon/CoFe<sub>2</sub>O<sub>4</sub> nanocomposite. The magnetic composite was used as an adsorbent for the removal of methylene blue dye. As the activated carbon was derived from a natural source it presents an economic and environmental friendly source. Also, the CoFe<sub>2</sub>O<sub>4</sub> nanoparticles help the activated carbon /CoFe<sub>2</sub>O<sub>4</sub> nanocomposite to be easily separated using magnetic fields and shows a cleaning way to dispose the waste. The effect of different parameters such as initial pH and contact time was studied. The results showed that with increasing contact time and initial pH, the removal efficiency of methylene blue from aqueous solution increased.

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**Synthesis and Characterisation of Copper Oxide nanoparticles Prepared by Thermal decomposition Method**

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Schiff bases are formed when any primary amine reacts with an aldehyde or a ketone under specific conditions. Structurally, a Schiff base (also known as imine or azomethine) is a nitrogen analogue of an aldehyde or ketone in which the carbonyl group (CO) has been replaced by an imine or azomethine group. Schiff base ligands are easily synthesized and form complexes with almost all metal ions [1].

Metal oxide nanoparticles have shown their great interest in field of sensing ,optoelectronics ,catalysis and solar cells due to their unique physical and chemical properties differing from bulk. Among all the metal oxides copper oxide nanomaterials have attracted more attention due to its unique properties. Cu<sub>2</sub>O (Cuprous oxide) and CuO (Cupric Oxide) are two important oxide compounds of Copper [2].

The typical preparation of Copper (II) complex, 1 mol of copper nitrate threehydrate Cu (NO<sub>3</sub>)<sub>2</sub>.3H<sub>2</sub>O and 2 mol of salicylaldehyde (C<sub>7</sub>H<sub>6</sub>O<sub>2</sub>) were dissolved in 10 mL of ethanol to form homogeneous solutions. Few drops of ammonia solution were added until pH 6-8. Then thiourea solution was added dropwise to the above solution with stirring. The mixture was allowed to reflux under stirring for 8 h. Copper Oxide CuO nanoparticles were synthesized by the thermal decomposition method. The above complex was grinding steps to ensure the homogenous powder then was heated at 690°C for 2 h in a conventional furnace. The dark precipitate is obtained, filtered and washed with ethanol to remove the impurities, which results the CuO nanoparticles.

In the present paper, we have prepared CuO nanoparticles from Copper (II) Schiff base complex as a new precursor. The complex and CuO are identified by FT-IR spectroscopy, X-ray diffraction (XRD), scanning electron microscopy (SEM), UV-Vis spectroscopy and Conductance measurements.

The typical XRD pattern of the CuO nanoparticles exhibited the monoclinic structure of CuO. FTIR spectra exhibit only two vibrations: occurring at approximately 573 cm<sup>-1</sup> and 637 cm<sup>-1</sup> for the sample, which can be attributed to the vibrations of CuO, confirming the formation of highly pure CuO nanoparticles.

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**Preparation of magnetic molecularly imprinted polymers for selective adsorption of chlordiazepoxide and its determination by HPLC**

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Benzodiazepine drugs (BDs) belong to important and most widely used medicaments that were introduced in the 1960s [1]. They are useful for treating for as hypnotics, anxiolytic-sedative, agitation, anticonvulsive, seizures, instance anxiety, insomnia, muscle spasms and alcohol withdrawal [2]. In this study, the core-shell magnetic molecularly imprinted polymers nanoparticles (MMIPs-NP) were synthesized and then used for extraction and of chlordiazepoxide (CLD) from various samples prior to its determination by HPLC. At first, Fe<sub>3</sub>O<sub>4</sub> nanoparticles were prepared by the coprecipitation method, stabilized with tetraethyl orthosilicate (TEOS) and functionalized with 3-(trimethoxysilyl) propyl methacrylate (MPS). Then MMIPs were synthesized under distillation conditions through precipitation polymerization of methacrylic acid (MAA) as a functional monomer, CLD as a template, ethylene glycol dimethacrylate (EGDMA) as a cross-linking agent and azobisisobutyronitrile (AIBN) as an initiator. The properties of MMIPs are characterized by fourier-transform infrared spectroscopy (FT-IR), scanning electron microscopy (SEM) and X-ray diffraction (XRD). The effective variables on the extraction recovery (ER) such as the amounts of MMIP, time of adsorption, pH and volume of desorption solvent were optimized by central composite design (CCD) combined with desirability function (DF). The extraction conditions were optimized and values of variables were set as 11 mg of adsorbent, 10 min adsorption time, pH = 5.5 and 1.4 mL methanol. The linear response ( $r^2 > 0.998$ ) was obtained in the range of 0.006-10  $\mu\text{g mL}^{-1}$  with detection limit 0.0014  $\mu\text{g mL}^{-1}$  and ER was in the range of 90-96% with RSD <5.0% (n = 3).

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## Chemiluminescence determination of the antioxidant capacity of honey samples and fruit juices using lab-on-a-chip device

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Honey is well-known as a natural and healthy food containing, in addition to sugars, a wide range of substances including flavonoids, phenolic acids and lysozyme with antibacterial and antioxidant activity. Fruits and vegetables partially due to the possessing various antioxidants such as vitamins and polyphenols are very beneficial for the human health [1]. In general, antioxidants can be defined as artificial or natural chemical compounds that their presence even at low-level concentrations can hinder or slow the oxidation of the oxidisable substances [2]. Indeed, antioxidants can protect organisms or non-living systems from the adverse effects of free radical reactions involving reactive oxygen and nitrogen species (ROS and RNS). In general, for expression of antioxidant status and therapeutic potential of a food sample, the terms of “total antioxidant capacity (TAC)” is used. The assessment of TAC is very sample- and method-specific because the reaction mechanisms of TAC determination methods are totally different in terms of types of oxidants, reaction conditions and even results statement. However, the assessment of the TAC under precisely controlled conditions is an outstanding strategy for comparison and ranking of the antioxidant potential of food products. For instance, TAC assessment can be used for evaluating and characterization of honey samples. In general, a variety of methods have been developed for determination of TAC, most of which may fall in one of the three following major categories: (a) spectrophotometry methods: those are mainly based on the reaction of the colored reagents such as 2,2-diphenyl-1-picrylhydrazyl radical (DPPH<sup>•</sup>) radicals with antioxidants, leading to change of the color of reaction solution, (b) electrochemistry methods: those are usually based on the oxidation of antioxidants on the surface of an appropriate working electrode and (c) chemiluminescence (CL) methods: those are generally based on the enhancing or inhibitory effects of antioxidants on the CL reactions. In this research work, a new microfluidic system with chemiluminescence (CL) detection for the rapid assay of the total antioxidant capacity (TAC) of apple and pomegranate juices and honey samples was developed. The method exploited the green and simple CL reaction of  $\text{NaHCO}_3\text{-H}_2\text{O}_2\text{-Co}^{2+}$ . It was found that gallic acid (GA), catechin, caffeic acid, ferulic acid and rutin as selected phenolic and polyphenolic antioxidants could suppress the light emitted from the  $\text{NaHCO}_3\text{-H}_2\text{O}_2\text{-Co}^{2+}$  CL reaction. The CL intensity was inversely related to the concentration of these antioxidants. After optimization of flow rate, concentrations of reagents and pH, the parameters influencing the CL emission, the calibration curve for each antioxidant was drawn. The linear range and limit of detection (LOD) for the antioxidants were as follows: 0.5-3 mg L<sup>-1</sup> and 0.27 mg L<sup>-1</sup> for GA, 0.2-5.0 mg L<sup>-1</sup> and 0.17 mg L<sup>-1</sup> for catechin, 0.03-2.0 mg L<sup>-1</sup> and 0.03 mg L<sup>-1</sup> for caffeic acid, 0.3-2.0 mg L<sup>-1</sup> and 0.23 mg L<sup>-1</sup> for ferulic acid and 0.3-4.0 mg L<sup>-1</sup> and 0.15 mg L<sup>-1</sup> for rutin, respectively. Of the tested phenolic and polyphenolic antioxidants, GA was chosen to state TAC of the apple and pomegranate juices and honey samples as GA equivalents (GAE). Moreover, the correlation study of the MF-CL method with the 2,2-diphenyl-1-picrylhydrazyl radical scavenging capacity assay (DPPH<sup>•</sup> assay) was performed. The results showed very good correlation between MF-CL and DPPH<sup>•</sup> methods. In addition, IC<sub>50</sub> (an amount of antioxidant concentration needed to decrease the CL intensity by 50%) of the fruit juices and honey samples was also calculated.





## Electrochemical synthesis of polypyrrole at a novel 'self-doped' polyaniline modified electrode

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Conducting polymers have received much attention due to their unique physical and chemical properties. Polyaniline, polypyrrole and polythiophene are the most studied conductive polymers [1]. In the present research, a new approach is described for electrosynthesis of polypyrrole (PPy) on a polyelectrolyte modified electrode. The electrode was modified by water soluble conducting polymer, poly(2-methoxy aniline -5- sulfonic acid) (PMAS). Modified electrode was prepared by direct drop casting of 10 microliters of a PMAS solution (0.1-5%, w/v) on a glassy carbon electrode. The electrodeposition of the polypyrrole material is enhanced by the presence of the electrically conducting PMAS polyelectrolyte dopant, which functions as a molecular template providing supramolecular pre-ordering as well as simultaneously facilitating charge transport during electrodeposition. Electrochemical experiments showed that even at very low concentrations of pyrrole monomer (0.025 M), an adherent, uniform and stable polypyrrole film is deposited on electrode surface. Post synthesis cyclic voltamograms of polypyrrole showed characteristic redox pairs of electroactive polypyrrole. The method has the advantage of minimizing the amount of PMAS and monomer for deposition of a desirable conducting polymer film.

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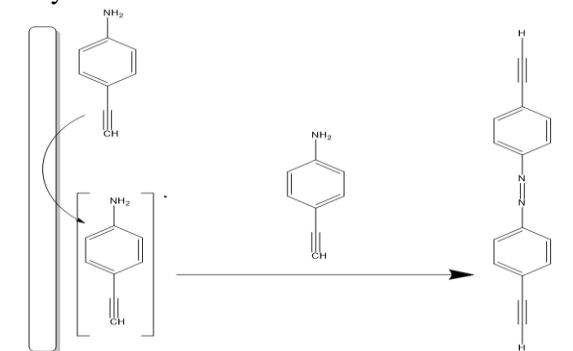
## Electrochemical behaviour of 4-ethynylaniline and synthesis of diazo compound

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Aniline and phenylacetylene and their derivatives are important compounds in chemical industries. P-ethynylaniline has the amino and ethynyl substituents which classified as the electron-donating group [1]. Due to the stability, simple and effective preparation, easy to control over surface coverage and density, aromatic diazonium salts has been used to functionalize solid interface. This approach, popularly known as electrografting, uses diazonium salts that are electrochemically reduced in order to generate reactive radicals. These radicals enable covalent binding to the electrode surface [2, 3]. Diazonium salts are highly **useful intermediates** in the synthesis of a large variety of aromatic compounds. These can be used to prepare many classes of organic compounds. Aryl azo compounds are brightly coloured and are useful as dyes and pigments so are classified as azo dyes. In this work we study the electrochemical behaviour of 4-ethynylaniline, using cyclic voltammetry and coulometry at controlled potential technique at the surface of glassy carbon at various scan rate and pH. Electrochemical behavior of 4-ethynylaniline was studied in acetonitrile at the different scan rate. The results revealed that it had an irreversible redox reaction. The diazo compound was synthesis by oxidation of 4-ethynylanilin at the specific pH in the divided cell using controlled potentials coulometry.



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## Synthesis of a novel cross-linked graphene aerogel/Yb<sub>2</sub>O<sub>3</sub> NPs composite as high performance supercapacitor

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Supercapacitors or ultracapacitors as energy storage devices have benefits in comparison to the batteries such as higher power densities, fast charging/discharging rates, and long cycle life. Among various supercapacitor electrode materials, pseudocapacitive transition-metal oxides and 3D porous structures exhibited much higher energy density than that of electrochemical double layer capacitive carbon materials due to their very high surface area and fast mass transport [1]. In present work, cross-linked graphene aerogel (GA) and its composite with transition metal oxide nanoparticles (GA/Yb<sub>2</sub>O<sub>3</sub>) were synthesized through a one-step hydrothermal manner by using p-phenylenediamine, graphene oxide and ytterbium salt [2-3]. GA/Yb<sub>2</sub>O<sub>3</sub> characterized by FE-SEM, XRD, and FTIR techniques. The specific surface area was calculated from the Brunauer-Emmett-Teller (BET) plot of the nitrogen adsorption isotherm. The supercapacitive behavior of GA/Yb<sub>2</sub>O<sub>3</sub> electrode investigated by using cyclic voltammetry (CV), continuous CV (CCV), galvanostatic charge/discharge (GCD) and electrochemical impedance spectroscopy (EIS) techniques in 1 M Na<sub>2</sub>SO<sub>4</sub> solution. According to the GCD studies, nanocomposite indicates enhanced supercapacitive performance, where it has capacitance of 510 at 0.8 A/g and high energy density of 53 Wh/Kg. GA/Yb<sub>2</sub>O<sub>3</sub> exhibits an efficient supercapacitive performance due to the presence of efficient graphene/transient metal oxide-based electrode material. Also p-phenylenediamine as a crosslinker considerably improved supercapacitor behavior of nanocomposite. In fact, cross-linked structures provides large inter-sheet spacing for transferring the ions quickly and increasing the electroactive material–electrolyte interface area which results excellent performance of the electrode materials.

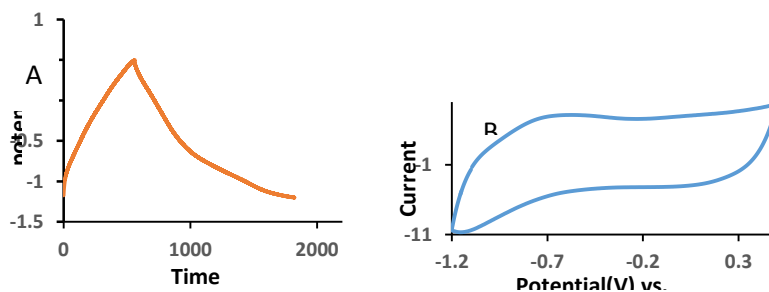


Fig1. (A) GCD of GA/Yb NPs at the current density of 0.8 A/g. (B) CV of GA/Yb NPs at the scan rate of 10 mV/s.

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**The effect of current density on the morphology, structure and purity of Dy/TiO<sub>2</sub> nanostructures that produced through electrochemical technique.**

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DyTiO<sub>2</sub> powders were synthesized by electrochemical method under mild conditions without any hard templates and surfactants. In this paper, DyTiO<sub>2</sub> was galvanostatically deposited from low temperature methanol bath on a steel substrate by electrogeneration of base. Samples were synthesized by electrochemical method and the effect of different current densities on morphology, structure and purity of synthesized powders will be described. SEM analysis revealed that the resulted material has a spherical morphology with a homogenous distribution.

In this paper, galvanostatic electrodeposition was used to prepare Dysprosium Titanate powders applying current density of 25 mA Cm<sup>-2</sup>. Fig.1 showed the spherical nanosize structure of the sample. Fig.2 depicts the XRD Patterns of the synthesized sample. We can observe the Dy<sub>2</sub>TiO<sub>5</sub> peaks in the pattern. As well Peaks of Fe can be obtained from the pattern.

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**Synthesis and characterization of magnetic chitosan-poly (acrylic acid) hydrogels as drug delivery system for 5-fluorouracil**

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Hydrogels are three-dimensional polymer networks that are able to retain a large amount of water in their swollen state. Hydrogels have become very popular due to their unique properties such as high water content, softness, flexibility and biocompatibility. These compounds have tendency to absorb water due to the presence of hydrophilic groups such as  $-SO_3H$ ,  $-CONH_2$ , and  $-CONH$ . Gels can be hydrated in a variety of proportions, which in some cases it reach more than 1500-2000 percent by weight of polymer, and it can be due to the nature of the aqueous medium and the polymer structure [1]. Medications or electrophobic species are trapped in the pores structure of the hydrogels and released from their structure based on a mechanism that depends on the spreading coefficient of the drug or the electroactive species [2].

Hydrogel-based drug delivery systems are divided into two major groups: 1. Systems with time control. 2. Release systems due to the presence of a stimulus. Environmentally sensitive hydrogels, known as smart systems, are divided into three sub-branches: 1. Release system with physical stimulation such as temperature, electrical current, light and pressure. 2. Release system with chemical stimulation such as pH, the composition of solvents, ions, and special interactions that lead to identify the molecules. 3. Release systems with other stimuli [3].

Magnetic chitosan-poly (acrylic acid) hydrogels were synthesized and used as drug delivery system. The chemical structure and surface morphology of the magnetic chitosan-poly (acrylic acid) hydrogels were studied by FTIR, SEM, and XRD, techniques. The swelling properties of the hydrogels were investigated in pH 1.2 and 7.4 buffer solutions. 5-fluorouracil (5-FU) was selected as an anti-cancer model drug. The pH-responsive release was verified by in vitro release test at pH 1.2 and 7.4.

The obtained results showed that the swelling ratio of hydrogels increased by decreasing of the pH from 7.4 to 1.2. The releasing behavior of 5-FU to the hydrogels, indicated that chitosan-poly (acrylic acid) hydrogels had better drug releasing under acidic conditions.

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**A simple and sensitive chemiluminescence method for determination of atenolol**

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Atenolol, [4-[2-hydroxy-3-isopropyl-aminopropoxy]-phenyl-acet- amide], is a  $\beta$ 1-receptor antagonist belonging to the category of  $\beta$ - blockers that is widely used in the treatment of varied cardiovascular disorders like cardiac arrhythmia, angina pectoris, and systematic hypertension. It is in the list of banned drugs due to misuse as doping agents in sports, because of its soothing result [1]. Literature survey reveals that several analytical methods including gas chromatography–mass spectrometry [2], spectrophotometry [3], amperometry [4], differential pulse voltammetry [5] and chemiluminescence (CL) [1], among others, have been developed for determination of atenolol. In this work, CuO nanoparticles (CuO NPs) were made by using quick precipitation approach. Then, those were characterized by using X-ray diffraction (XRD) (Fig. 1a), scanning electron microscopy (SEM) (Fig. 1b), transmission electron microscopy (TEM) (Fig. 1c) and Fourier transform infrared spectroscopy (FTIR).

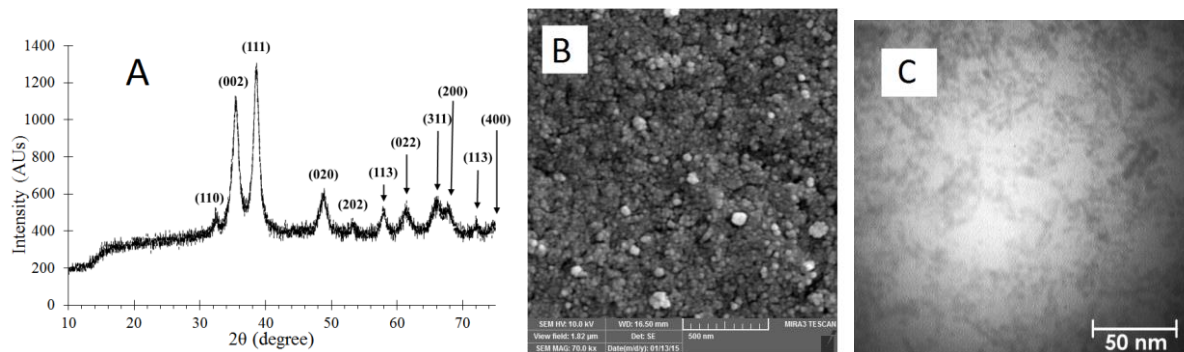


Fig. 1. (A) XRD pattern, (B) SEM image and (C) TEM image of CuO NPs.

The results of experiments indicated that CuO NPs improved the intensity of  $\text{H}_2\text{O}_2$ – $\text{NaHCO}_3$  CL system, remarkably. Furthermore, it was indicated that atenolol suppressed the intensity of CuO NPs– $\text{H}_2\text{O}_2$ – $\text{NaHCO}_3$ . Based on these findings, a CL method for determination of atenolol was developed. The linear range and limit of detection of the CL method were  $2.0 \times 10^{-5}$ – $9.0 \times 10^{-4}$  mol  $\text{L}^{-1}$  and  $1.0 \times 10^{-5}$  mol  $\text{L}^{-1}$ , respectively. The method was successfully applied for quantification of atenolol in the pharmaceutical preparations.

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**Determination of organic sulfurcontaminants using hollow fiber-protected liquid-phase microextraction coupled with gas chromatography**

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A simple and solvent-minimized sample preparation technique based on hollow fiber-protected liquid-phase microextraction has been developed for extraction of fifteen organic sulfur compounds (OSCs) from aqueous samples. Analysis of the extracted OSCs was performed by gas chromatography equipped with mass spectrometry (GC-MS) and/or flame photometric detectors (GC-FPD). Three  $\mu\text{L}$  of organic solvent located in the lumen of hollow fiber was used to extract OSCs from an 8 mL of aqueous sample. Several parameters influencing extraction efficiency such as salt concentration, stirring speed, temperature, sample volume, organic phase volume and extraction time were studied and optimized using super-modified simplex method.

Under optimized conditions (extraction solvent (toluene) Extraction time (15 min ), salt addition (4 % w/v), stirring rate (1200 rpm), sample volume (8 ml SV), organic solvent volume (3.3  $\mu\text{l}$ ) and extraction temperature (35°C)) the limits of detection (LODs) varied from 0.1 to 8.7  $\mu\text{g L}^{-1}$  and 0.7 to 99.4  $\mu\text{g L}^{-1}$  for GC-FPD and GC-MS, respectively. The calibration graphs were linear over three orders of magnitude for most of the studied OSCs. The relative standard deviations (RSDs) for inter- and intra-day analysis were in the range of 5 to 10%, and the relative recoveries of the analytes from the three different real water samples were better than 83%. The results were compared with those obtained using direct single drop microextraction (Direct-SDME) and headspace single drop microextraction (HS-SDME) methods. The proposed method is reliable and can be considered useful for routine monitoring of the OSCs in surface water samples.

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## Synthesis of Dysprosium by Cyclic Electrochemical Method

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Control rods are one of the most important components in nuclear reactors that is used to compensate for the fuel consumption and adjust the reactor. Boron carbide and boron steel have been used for control rods. Among all compositions, Dysprosium Titanate powders and ceramics have been used as shielding materials such as control rods [1]. Electrochemical method is an easy and economical method which carried out in low temperatures. In this paper, DyTi<sub>2</sub>O<sub>5</sub> have been prepared by cyclic galvanostatically electrochemical experimental method.

DyTi<sub>2</sub>O<sub>5</sub> was obtained by cyclic cathodic electrodeposition from an additive free 0.005 M Dy (NO<sub>3</sub>)<sub>3</sub> and TiCl<sub>4</sub> bath. The bath temperature was 0 °C. The electrochemical cell included a cathodic steel substrate centered between the two parallel graphite anodes. Also a power supply was used to generate the electric pulses. Deposition experiments were followed up in galvanostatic mode at current density of 25 mA.Cm<sup>-2</sup>, duty cycle of 0/75 for 42 minutes. After the sample dried out, the deposit was scarpred from the cathode and calcinated in 600 °C. Crystal structure of and morphological characterization was explored by SEM.

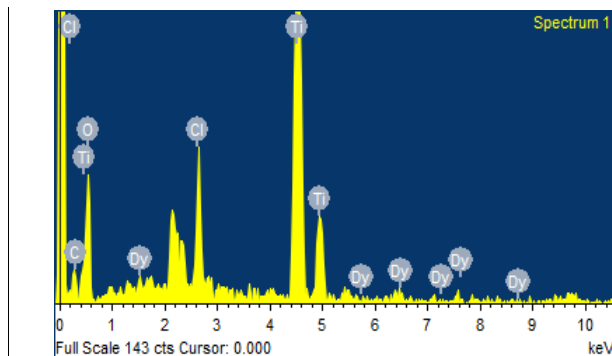


Fig.1 EDAX image of the synthesized material. We can observe Dy and Ti contents in the composition.

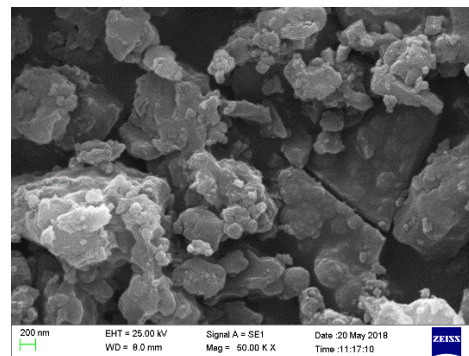


Fig.2 SEM images of the prepared sample





## The 25<sup>th</sup> Iranian Seminar of Analytical Chemistry

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### Preparation and Characterization of $\gamma$ - Alumina Nanoparticles

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Metal complexes of Schiff base derived from the reaction of substituted salicylaldehydes with aliphatic and aromatic amines represent a series of compounds containing nitrogen, sulphur and oxygen ligand donor atoms that has been widely studied. Over the past few years, there have been many reports on their applications in biology including antibacterial, antifungal, anticancer, antioxidant, anti-inflammatory, antimalarial and antiviral activity[1,2].

In the past few years, much attention has been focused on the research field of nano-crystalline oxide materials, both because of their fundamental importance and the wide range of potential technological applications. Alumina exists in a variety of metastable structures including  $\gamma$ -,  $\eta$ -,  $\delta$ -,  $\theta$ -,  $\kappa$ - and  $\chi$ -alumina, as well as its stable  $\alpha$ -alumina phase. Among these transitions,  $\gamma$ -alumina is one kind of extremely important nanosized materials. It is extensively used as catalyst, catalytic supports and adsorbents [3].

Alumina  $\text{Al}_2\text{O}_3$  nanoparticles were synthesized by the thermal decomposition Method. To preparation of Alumina (III) complex, 1 mol of Aluminum nitrate  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  and 2 mol of salicylaldehyde ( $\text{C}_7\text{H}_6\text{O}_2$ ) were dissolved in 10 mL of ethanol to form homogeneous solutions. Few drops of ammonia solution were added until pH 6-8. Then thiourea solution was added dropwise to the above solution with stirring. The mixture was allowed to reflux under stirring for 8 h. The above complex was grinding steps to ensure the homogenous powder then was heated at  $820^\circ\text{C}$  for 3 h in a conventional furnace. The white precipitate is obtained, filtered and washed with ethanol to remove the impurities, which results the  $\text{Al}_2\text{O}_3$  nanoparticles.

In the present paper, we report the synthesis of Al(III) salicylidenic schiff base complexes derived from thiourea and studied by elemental analysis (CHNS), FT-IR, UV-Vis spectroscopy, conductance measurement and magnetic moment. Then  $\text{Al}_2\text{O}_3$  nanoparticles were synthesized from Al(III) Schiff base complexes by solid-state thermal decomposition method and identified by FT-IR spectroscopy, X-ray diffraction (XRD) and scanning electron microscopy (SEM). The mean size of as-prepared  $\text{Al}_2\text{O}_3$  nanoparticles was around 17 nm from Debye-Sherrer equation. Range of particles size is 51nm and porous structured nanoparticles metal-oxide confirmed.

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### Removal of Amido black 10B through adsorption–photocatalytic degradation synergistic effect of doped Cr- ZnO/CDs nanocomposites under solar light

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In this work, chromium doped ZnO/carbon dots (Cr-ZnO/CDs) nanocomposite was used for removal of Amido black 10B (AB) through adsorption–photocatalytic synergistic effect. In order to synthesis of the novel nanocomposite, in the first step, a green strategy have been successfully applied for the synthesis of carbon dots (CDs) from pine leaf, based on hydrothermal treatment [1]. The as-synthesized CDs exhibited many advantages including high fluorescence intensity, water solubility, non-toxic and eco-friendly. In the next step, Cr-ZnO/CDs nanocomposite was synthesized using the facile one-step hydrothermal method. One of the great advantages of this method is that the synthesis was carried out at lower temperature (at 100°C) than other methods [2]. The CDs and Cr-ZnO/CDs nanocomposite were characterized using X-ray diffraction (XRD), Raman spectrometer (Raman), energy dispersive X-ray (EDX), Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM) and UV-vis spectrophotometry.

The photocatalytic degradation and adsorption effects of Cr-ZnO and Cr-ZnO/CDs nanocomposites on AB (as a sample), which is an amino acid staining azo dye, were investigated. The results indicated that the CDs had a significant influence in improving the effectiveness of Cr-ZnO nanocomposite. Removing of AB, as a pollutant from water, was performed by dual-functionality properties of Cr-ZnO/CDs nanocomposites. This nanocomposite can adsorb a high percentage of the dye and then degrade the remaining dye by its own photocatalytic property. In this way, this nanocomposite can remove nearly 100% of the dye. The effect of experimental variables such as pH, amount of the nanocomposite and dye concentration on the dye removal were investigated. The results showed that Cr-ZnO/CDs nanocomposite, under optimum conditions, even is capable to removal of the dye concentrations higher than 100 ppm. Also, this nanocomposite can be eliminated other azo dyes such as methyl orange (MO) and congo red (CR). Under the optimal conditions, about 98% of AB was removed rapidly (less than 10 min) by the Cr-ZnO/CDs nanocomposite from wastewater in room temperature [3]. This composite can recovery in alkaline media for reusing.

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## The 25<sup>th</sup> Iranian Seminar of Analytical Chemistry

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### Solid phase synthesized N-doped carbonic supported manganese oxide as electrocatalysts for oxygen reduction reaction (ORR) in neutral media

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Poor kinetics of the oxygen reduction reaction electrocatalysts (ORR) at neutral pH and low temperatures can hinder the performance and development of fuel cells under these conditions [1]. A viable approach for reducing costs, while enhancing ORR, is the use of platinum group metal (PGM) free catalysts. Previous literature reports have shown that PGM-free catalysts obtained by supporting transition metal, such as Fe and Co, on different carbon supports can be used as cathode achieving an electrochemical performance comparable to that of Pt [2]. In fact, there are two possible ways of oxygen reductions that can take place: oxygen can be reduced to water by direct 4-electron pathway or to peroxide by 2-electron pathway. For achieving high power performance in MFCs and avoid peroxide formation, the direct 4-electron pathway is a mandatory requirement of ORR catalysts [3]. Also, thanks to low cost, natural abundance, environmental friendly nature, and good electrochemical properties, electrode materials based on manganese dioxide ( $\text{MnO}_2$ ) have been tested for ORR catalysts [4]. In this work, a novel multivalent  $\text{MnO}_x$  supported on nitrogen doped carbon and reduced graphene oxide (C(N)/  $\text{MnO}_x$ -SP, rGO(N)/  $\text{MnO}_x$ -SP) was synthesized via a solid state method. The cathodic oxygen reduction reaction (ORR) in neutral media was improved by modified electrode with manganese based catalysts. The synthesized catalysts were characterized by X-ray diffraction (XRD), Raman spectroscopy, field emission scanning electron microscopy (FE-SEM), X-ray photoelectron spectroscopy to reveal their crystalline structure, morphology and chemical composition. Electrolytic behavior of prepared materials for ORR performance was measured by cyclic voltammetry, linear sweep voltammetry and electrochemical impedance spectroscopy. C(N)/  $\text{MnO}_x$ -SP showed good performance toward oxygen reduction with 4-electron pathway dominantly. As such it can be selected as an air breathing cathode to be applied in microbial fuel cells which operate in neutral media. These results indicate that the representative sample is a good candidate to be used in practical MFC applications owing competitive price and good performance ORR process.

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## The 25<sup>th</sup> Iranian Seminar of Analytical Chemistry

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### Evaluation of mesoporous silica nanomaterial for extraction of chlordiazepoxide from aqueous samples; central composite design

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Chlordiazepoxide (CLD) belonging to benzodiazepines category has medicine properties such as antianxiety, sedative, anticonvulsant, and muscle relaxant. This drug inhibits monosynaptic and polysynaptic reflexes by inactivity neuronal transmitters or by blocking excitatory synaptic transmission. The drug may also directly depress motor nerve and muscle function [1]. For these reasons, the development of highly sensitive and selective methods for analysis of BDs in complicated matrices is of great interest to clinicians and forensic toxicologists[2]. A new extraction method, based on dispersive mesoporous silica-ultrasound assisted microextraction, was used for the preconcentration of the chlordiazepoxide (CLD) in the water samples prior to high performance liquid chromatography (HPLC). The properties mesoporous silica (MCF-NH<sub>2</sub>) nanomaterial are characterized by FT-IR, SEM, and BET. This nanomaterial showed great adsorptive ability towards the CLD. The effective variables such as pH, the amount of adsorbent (mg), adsorption time (min), and Volume of desorption solvent (mL) are investigated by central composite design (CCD) were combined by a desirability function (DF). At optimum conditions, the method has linear response over 0.004–10  $\mu\text{g mL}^{-1}$  with detection limit between 0.005  $\mu\text{g mL}^{-1}$  with relative standard deviations (RSDs) less than 5% ( $n=3$ ). The method has been successfully applied for the determination of the CLD in the water samples.

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## A new chemiluminescence method for determination of oxcarbazepine using cerium oxide nanoparticles

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Oxcarbazepine (10,11-dihydro-10-oxo-5H-dibenzo- [b,f]azepine-5-carboxamide, OXCBZ, Fig. 1) is a new antiepileptic medicine, presented onto the market in the Nineties. OXCBZ is structurally related to carbamazepine, of which it is a keto-derivative. These medicines are highly lipophilic and neutral at most pH values, and are used mainly for the cure of partial seizures and generalised tonic-clonic seizures [1].

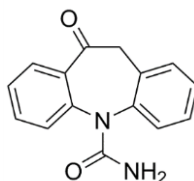


Fig. 1. Chemical structure of OXCBZ

Recently, rare earth oxide nanoparticles have found many applications because of their attractive structural and optical properties with wonderful luminescence efficiency in the visible region. Luminescence performance of rare earth oxides is mainly stem from the partially-filled 4f electronic shell. Between rare earth oxides, cerium oxide nanoparticles (CeO<sub>2</sub> NPs) are interesting compounds for many possible uses for example solid state electrolyte for electrochemical tools, catalyst for automobile exhaust, sun screen for UV absorbents, luminescent materials, gas sensors, polishing materials, and oxygen storage capacity [2]. In this work, we used CeO<sub>2</sub> NPs for enhancing chemiluminescence (CL) reaction of luminol-O<sub>2</sub>. Moreover, it was found that OXCBZ decrease the intensity of CeO<sub>2</sub> NPs-luminol-O<sub>2</sub> CL reaction such that there was linear relationship between the CL intensity and concentration of OXCBZ. After optimization of CL reaction conditions, the log log calibration curve (log[CL peak intensity] vs. log[OXCBZ]) was constructed for a series of seven standard solutions in the range of  $1.0 \times 10^{-6} - 6.0 \times 10^{-5} \text{ mol L}^{-1}$ . The relative standard deviation (RSD) of the CL method calculated by nine replicate measurements of  $6.0 \times 10^{-5} \text{ mol L}^{-1}$  OXCBZ was 4.79%. The CL method was used for the measurement of concentration of OXCBZ in pharmaceutical preparations. The utilized CeO<sub>2</sub> NPs were prepared by exploiting a quick precipitation technique and were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM).

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## Sonocatalytic Degradation of Methyl Orange Using Zinc Sulfide Carbon Nanotubes

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Dye sewage is dangerous problem in our environmental aquatics that cause generation of harmful effects for living organism. In this work, because of simplicity, easy operation, high efficiency and no creating secondary pollutants, ultra sound radiation applied for degradation of a synthetic dye, methyl orange using zinc sulfide nano particles decorated on carbon nanotubes as nanocatalyst. ZnS/CNTs prepared by co-precipitation of carbon nanotubes and zinc acetate. Methyl orange (MO) is a cationic dye that used widely in some medical uses, coloring paper, dyeing cottons, wools, coating for paper stocks and etc. For achieving highest degradation efficiency several parameters such as pH, amount of nanocatalyst, initial dye concentration and time were evaluated and optimized. Results showed that highest degradation efficiency (100%) obtained at 0.3 gr of nanocatalyst while initial dye concentration is 30 mg.L<sup>-1</sup> at pH, 2. Comparison of several methods for degradation of methyl orange showed feasibility of applied method. In addition, reusability of nanocatalyst was suitable for degradation of MO in real wastewater samples

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## Determination of Carbamazepine in Urine and Water Samples using Functionalized Metal-Organic Framework as Sorbent

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A stable and porous amino-functionalized zirconium-based metal organic framework (UiO-66-NH<sub>2</sub>) containing Missing Linker Defects was prepared, and fully characterized by FTIR, scanning electron microscopy (SEM), powder X-ray diffraction (PXRD), and N<sub>2</sub> adsorption/desorption isotherm. The Zr-MOF was then applied as an adsorbent in pipette-tip solid phase extraction (PT-SPE) of carbamazepine. Important parameters affecting extraction efficiency such as pH, sample volume, type and volume of eluent, amount of adsorbent, and number of aspirating/dispensing cycles for sample solution and eluent solvent were investigated and optimized. The best extraction efficiency was obtained with 5 mg of sorbent at pH 7.5, and 10  $\mu$ L of eluent solvent when 100  $\mu$ L of sample solution was used. Linear Dynamic Range (LDR) was obtained between 0.1- 50  $\mu$ g. L<sup>-1</sup> and Limit of Detection (LOD) for 10 measurement of blank solution was 0.05  $\mu$ g. L<sup>-1</sup>. This method was successfully applied for extraction of carbamazepine in urine and water samples. The strategy combined the advantages of both PT-SPE and Zr-MOF-NH<sub>2</sub> material such as fast and easy operation, low cost, less solvent consumption, large porosity, and large specific surface area.

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**A simple hyphenated method by ultrasound assisted extraction-magnetic solid phase extraction coupled with gas chromatography for determination of caffeine in food samples**

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A simple and efficient extraction method composed of ultrasound assisted extraction (UAE)-Magnetic solid phase extraction (MSPE) combined with gas chromatography system was applied for extraction and determination of caffeine in food samples. Three dimensional graphene-Fe<sub>3</sub>O<sub>4</sub> nanoparticles was successfully synthesized and used as adsorbent in MSPE step. The properties and morphology of synthesized adsorbent were characterized by Fourier transform-infrared spectroscopy (FT-IR), scanning electron microscopy (SEM), VSM, XRD, Raman spectroscopy, BET and BJH methods. The influence of main parameters affecting the extraction efficiency such as temperature, ultrasound time, the amount of nanoparticles (adsorbent), pH, amount of salt concentration and desorption condition were investigated and optimized. Under the optimized experimental conditions, the figure of merit results showed excellent linear dynamic range (0.5-500 µg mL<sup>-1</sup>), with determination coefficient (R<sup>2</sup>) higher than 0.996 and limits of detection (LOD) of 0.1 µg mL<sup>-1</sup> (S/N = 3). Intra- and inter-day relative standard deviations (RSDs) were less than 5.9 and 7.1 % (n = 5), respectively. The method was successfully applied for determination of caffeine in different food samples including teas (green, black, oolong and tea bag), coffees (coffee bean, espresso, cacao powder and Nescafe coffee) and chocolate (white chocolate, 52 and 72% dark chocolate).





## Cobalt Metal Organic Framework as Sorbent for Fast Determination of Bisphenol A in Juice and Drinking Water Samples by Pipette tip Solid Phase Extraction

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Cobalt metal organic framework (Co-MOF) was prepared and used for solid phase extraction of Bisphenol A (BPA). Synthesis of Co-MOF was performed with rapid ultrasound assisted method by using of cobalt nitrate and pyridine 2, 6-dicarboxylic acid dissolved in ethanol. Micro solid phase extraction (Micro-SPE) applied in pipette-tip as micro column for extraction and determination of BPA. All parameters that influenced extraction efficiency such as pH, sample volume, amount of Co-MOF, type and volume of eluent, number of draw/ eject cycles for sample and eluent and effect of temperature were tested and optimized. Results showed that best extraction efficiency obtained at pH 3, 150  $\mu\text{l}$  of sample volume, 3 mg of adsorbent and 10  $\mu\text{l}$  of methanol. Numbers of draw/ eject cycles for both sample and eluent were 7 cycles. Limit of detection (LOD) and limit of quantification (LOQ) of this method were 0.07 and 0.3  $\mu\text{g l}^{-1}$  while linear dynamic range (LDR) was 0.3 to 300  $\mu\text{g l}^{-1}$ . This method applied successfully for determination of BPA in 7 canned food and drinking water samples.

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**The use of red mud nano-particles for the removal of methylene blue and Eriochrome Black T from polluted waters**

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Organic compounds especially dye materials are considered as an emerging environmental problem due to their continuous input and persistence into the aquatic ecosystem even at low concentrations [1]. Using red mud as unconventional adsorbents for water and wastewater treatment purposes are motivated by the fact that red mud is a fine-grained mixture of oxides and hydroxides, capable of removing several contaminants, as well as being widely available [2]. In the present study, the adsorption of organic dyes, Methylene Blue (MB) and Eriochrome Black T (EBT), from aqueous solutions was investigated using low-cost, natural, and reused adsorbent, Red Mud, as an ideal alternative to the current expensive methods of removing organic pollutant compounds from wastewater. The adsorption studies were carried out under various parameters, such as pH, sorbent dosage, contact time, and initial dye concentration in batch experiments and one at a time procedure. The experimental results show that the percentage of adsorption increases with an increase in the adsorbent dosage, contact time, and initial dye at beginning the process. The maximum adsorption occurred at the pH value of 7 for Methylene Blue and Eriochrome Black T. Adsorption kinetic data were properly fitted with the pseudo-second-order kinetic model. The experimental isotherms data were analyzed using Langmuir, Freundlich and Tempkin isotherm equations. The Tempkin and Freundlich model obtained the best fit for EBT and MB, respectively. Maximum sorption capacity was 2.41 mg/g for Methylene Blue and 0.91 mg/g for Eriochrome Black T.

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**Preparation and comparison fluorescence sensor based on molecularly imprinted polymers carbon dots and molecularly imprinted polymers polymer dots for detection of acetamiprid**

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This study defined the design, development and Comparison of molecularly imprinted polymers of carbon dots (CDs) and polymer dots (PDs) for measure acetamiprid. PDs were prepared by a one-step aqueous synthetic way from ascorbic acid and diethylenetriamine at room temperature. That also CDs were prepared by hydrothermal method at 180 °C. These particles are characterized by means such as FE-SEM, FTIR, DLS, XRD, UV/Vis and fluorescence that quantum yield of PDs 47% and CDs 8%. At the next step, a thin padding of silica was covered, by reverse microemulsion Method, on the Outer environment of PDs and CDs. at the end, molecularly imprinted polymer inside it PDs and CDs were obtained. Other variables affecting the fluorescence peaking were optimized by design expert software. The results illustrate that the considered method for PDs had wide dynamic range 0.08-101 nmol L<sup>-1</sup>, good accuracy and detection limit 0.024 nmol L<sup>-1</sup>, also CDs had Thin dynamic range 0.12-2.19 nmol L<sup>-1</sup> and detection limit 0.031 nmol L<sup>-1</sup>.

The response of the optical sensor on usual specimens in water and Fruitage was considered. The consequence certified the well selectivity of the sensor for the evaluation of acetamiprid.

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**Applying chemometric methods studying multidimensional data is transforming them into multiparty data and analyzing them with MCR-ALS in order to measurement of Furosemide drug in actual samples based upon studying its degradation**

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Measurement of medical materials in aqueous media are generally performed with difficult procedures including extraction from high volumes of water followed by tedious derivatization and measurement steps with different methods. Gas and liquid chromatography coupled with mass spectroscopy are among the examples [1]. These techniques need very specific equipment, long times and high costs. Therefore, application of methods with less expensive devices, desirable sensitivity, and high rate and accessibility such as spectrophotometry are ideal solutions. The data obtained from spectrophotometric-kinetic methods were of second order which make it possible to analyze the data in the presence of unknown interfering species. By using rate differences in the destruction of furosemide in the presence of interfering drug and spectrophotometric-kinetic data obtained during the destruction process of oxidants such as chlorine and studying the creation and selection of optimum conditions in terms of drug concentration and oxidant and pH of the reaction medium, simultaneous measurement and recording of 2D spectrophotometric-kinetic data can be performed providing second order algorithms for data analysis. In this work, Using MCR-ALS chemometric method and applying non-negativity and unimodality constrains in both concentration and spectrum dimensions and by comparing results obtained by applying more constrains such as equality constrains in concentration and/or spectrum dimensions as well as applying trilinearity constrains, the responses were improved [2-5]. destruction of Furosemide drug under optimum conditions gave linear rang of ( $5 \times 10^{-7}$ -  $2 \times 10^{-5}$ ) and using MCR-ALS technique, simultaneous drug measurements are possible without the need for knowing interfering species.

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**Applying chemometric methods studying multidimensional data is transforming them into multiparty data and analyzing them with MCR-ALS in order to measurement of Rizatriptan drug in actual samples based upon studying its degradation**

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Spectrophotometric-kinetic technique is a strong method for the investigation of drug destruction in the presence of oxidants [1]. In a spectrophotometric-kinetic measurement, it is common to order the obtained matrices along time dimension. One method for studying multidimensional data is transforming them into multiparty data and analyzing them with MCR-ALS (Multivariate Curve Resolution- Alternating Least Square) method. To do so, multidimensional data-construction matrices are aligned in the direction of one dimension of the matrices. By using rate differences in the destruction of Rizatriptan in the presence of interfering drug and spectrophotometric-kinetic data obtained during the destruction process of oxidants such as chlorine and studying the creation and selection of optimum conditions in terms of drug concentration and oxidant and pH of the reaction medium, simultaneous measurement and recording of 2D spectrophotometric-kinetic data can be performed providing second order algorithms for data analysis. In this work, Using MCR-ALS chemometric method and applying non-negativity and unimodality constrains in both concentration and spectrum dimensions and by comparing results obtained by applying more constrains such as equality constrains in concentration and/or spectrum dimensions as well as applying trilinearity constrains, the responses were improved [2-3]. destruction of Rizatriptan drug under optimum conditions gave linear rang of ( $5 \times 10^{-7}$ -  $2 \times 10^{-5}$ ) and using MCR-ALS technique, simultaneous drug measurements are possible without the need for knowing interfering species.

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**A sensitive colorimetric method for detection of uric acid based on the formation of gold/silver core-shell nanorods**

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Gold nanorods (Au NRs), as an important class of anisotropic NPs, have received increasing attention in recent years due to their high chemical stability and unique optical properties that is strongly dependent on their size and aspect ratios [1].

In this work, by using Au NRs a simple and sensitive colorimetric method has been developed for detection of uric acid in biological samples. Au NRs were synthesized by a silver ion-assisted seed mediated method and their interaction with uric acid and silver ions was studied. Uric acid can reduce  $\text{Ag}^+$  to Ag on the surface of Au NRs to form Au core–Ag shell nanorods. This leads to a blue-shift in longitudinal surface plasmon resonance band of Au NRs. The influence of various parameters such as incubation time, pH, concentrations of Au NRs, silver ions and buffer was studied. Based on the correlation of Au NRs LSPR wavelength with the concentration of uric acid, a method for colorimetric determination of uric acid in the concentration range of 0.1-1.0  $\mu\text{M}$  with a detection limit 0.065  $\mu\text{M}$  and RSD of 3.2% was developed. The method was applied for analysis of human plasma and urine samples.

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**Highly Safe and Selective Liquid-liquid Micro-Extraction of Cobalt (II) Ions from aqueous samples with N, N'-disalicylidene-3, 4-diaminotoluene (H<sub>2</sub>dst) Dissolved in synthesized Supra Molecular Solvent**

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The separation of heavy metals from aqueous regions such as industrial and environmental waste waters has important aspects in the environmental and economic topics. The most applicable methods for the metal ions extraction from industrial waste waters are the liquid-liquid extraction and micro-extraction by organic solvents. In comparison of water-immiscible supra molecular solvents (SUPRAs) with other ordinary organic solvents used in the LL- extraction processes, SUPRAs possess some advantages such as: friendly environment, non-flammability, tunable polarity in dissolving the solutes with different polarities and high extraction capability of analysts in small volume of SUPRA. In this paper, the possibility of selective extraction of Cobalt (II) ions with SUPRAs composed of vesicles of decanis acid was studied. For this purpose, the extraction processes of Cobalt (II) ions from its aqueous solution alone and also its aq-solution mixture with other ions into SUPRA were investigated. The metal ions concentrations were determined by the flame atomic absorption spectroscopy. In order to achieve the selective extraction of Cobalt (II) ions into SUPRA, the presence of some Co<sup>2+</sup> selective ligands such as: Bis (2-ethylhexyl) phosphate (D2EHPA),  $\alpha$ -Nitroso- $\beta$ -naphthol, N, N'-disalicylidene-3, 4-diaminotoluene (H<sub>2</sub>dst) dissolved in SUPRA were investigated. The results showed that H<sub>2</sub>dst was the best and chose as the selective ligand dissolved in SUPRA for the Co<sup>2+</sup> extraction. In comparing of Co<sup>2+</sup> extraction into SUPRA alone with its extraction into the solution of ligand (H<sub>2</sub>dst) in SUPRA, the results showed that the later was made significant increasing in Co<sup>2+</sup> extraction percentage (about 50%). So, the experimental conditions for the selective separation of Cobalt (II) ions into the liquid phase composed of ligand H<sub>2</sub>dst dissolved in SUPRA were optimized. Under optimal conditions, 25ml of 1.5ppm Co<sup>2+</sup> at pH 5, 10<sup>-2</sup> M of H<sub>2</sub>dst dissolved in 710  $\mu$ l SUPRA as a selective liquid phase for Cobalt (II) ions extraction and 10min extraction time at 25°C, quantitative extraction of Co<sup>2+</sup> ions was observed about 99.21%  $\pm$  0.064 (n=10). To evaluate the selectivity of Cobalt (II) ions extraction, the separation processes were carried out from aqueous solutions containing Co<sup>2+</sup> ions and other cations such as: Na<sup>+</sup>, K<sup>+</sup>, Fe<sup>+3</sup>, Mg<sup>+2</sup>, Sb<sup>+3</sup>, Cu<sup>+2</sup>, Ni<sup>+2</sup> and Pb<sup>+2</sup>. The results showed that the efficiency of Cobalt (II) ions extraction towards Na<sup>+</sup>, K<sup>+</sup>, Fe<sup>+3</sup>, Mg<sup>+2</sup>, Sb<sup>+3</sup> and Pb<sup>+2</sup> ions were more significant than its extraction efficiency towards Cu<sup>+2</sup> and Ni<sup>+2</sup> ions. Also the matrix effect on Co<sup>+2</sup> extraction efficiency into the liquid phase composed of H<sub>2</sub>dst dissolved in SUPRA was investigated. So, 1.5ppm of Cobalt (II) cation solution was spiked into Lead and Zinc flotation plant waste water. The results showed that the extraction efficiency of Co<sup>+2</sup> ions from the matrix was highly selective and quantitative, about 96.64 $\pm$ 0.051 (n=10).





**Fabrication a new modified electrochemical sensor based on GO/AgCo dendritic nanoparticles, [PMIM] Br ionic liquid for anticancer drug, imatinib determination**

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Imatinib, is a specific inhibitor of the BCR-ABL tyrosine kinase, platelet-derived growth factor receptors, and the receptor kinase c-KIT. This drug has made progress in chronic myeloid leukemia (CML) and gastrointestinal stromal tumor (GIST) treatment [1]. A novel electrochemical sensor was fabricated for determination of anticancer drug, imatinib (IMA). First GO/AgCo nanoparticles with dendritic morphology were synthesized by a facile method and then the nanocomposite of GO/AgCo and [PMIM] Br ionic liquid was prepared to modify a pencil graphite electrode [2]. The formation of GO/AgCo was characterized using transmission electron microscopy (TEM) and energy dispersion spectroscopy (EDS). The surface morphology of the modified electrode was characterized by scanning electron microscopy (SEM). Electrochemical methods including cyclic voltammetry (CV) and square wave voltammetry (SWV) were used to study the electrochemical behavior of IMA. The effect of several relevant operating parameters was investigated and they were optimized. Under the optimized experimental conditions, the calibration curve was linear within the concentration ranges of 0.05  $\mu\text{M}$  to 60  $\mu\text{M}$  of IMA with a limit of detection (LOD) of 0.015  $\mu\text{M}$ . The proposed sensor was successfully employed for the direct determination of IMA in urine sample.

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## The 25<sup>th</sup> Iranian Seminar of Analytical Chemistry

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### Extraction and identification of a plant toxic protein (abrin) by Liquid Chromatography Tandem Mass Spectrometry

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The aim of this work was unequivocal identification of abrin that is a dangerous plant toxin, in 6 unknown samples that were sent for analysis. Abrin lethal dose is 0.1–1  $\mu\text{g}/\text{kg}$  body weight so due to the potential misuse as a biothreat agent, abrin is in the focus of surveillance. Therefore a reliable and fast identification of toxin in potentially contaminated environmental or clinical samples at low level, is of great importance [1, 2]. The most reliable technique for unequivocal identification of abrin, is detection of its specific peptides after enzymatic digestion, using liquid chromatography tandem mass spectrometry technique and MRM method and also measuring the activity of sample to ensure that the protein isn't denatured and acts properly in the body. Abrin is a 60 kDa, natural toxic protein isolated from beans of the tropical and subtropical leguminous plant *Abrus precatorius*. It has two A-chain and B-chain with a disulfide linked heterodimeric chains. The B-chain binds to cell surface receptors and facilitates a transport of the A-chain across the cell membrane. The A-chain is not active until it is internalized by the cell, where halts protein synthesis by removing an adenine within the  $\alpha$ -sarcin site on the large (28S) ribosomal subunit, which results in failure of protein synthesis and death. There are some unique peptides after digestion in both chains that are specific for this protein and can be used for identifications [3].

In this work, after extraction of abrin from sample, enzymatic digestion (trypsin) and clean-up, 3 unique peptides from A-chain (T2A, T3A, T7A) and 2 unique peptides from B-chain (T3B and T4B), were identified using LC-MS/MS technique and MRM method in 2 contaminated samples with abrin concentration about 100 ppm, successfully. Also the activity assay was done by adding a RNA substrate (GCGCGAGAGCGC) to the sample and measuring the released adenine by LC-MS/MS and results showed that they were active.

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**Determination of Penicillamine using CPE modified with 4,4'-Biphenol and MWCNTS**

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Penicillamine (PA) is a strong chelating agent and can react with the majority of heavy metal ions. The outstanding metal binding capability is reflected in the pharmaceutical importance of PA [1]. Multi-walled carbon nanotubes (MWCNTs), which is a nanomaterial, is now in mass production because of its excellent mechanical and electrical properties [2]. In this work, a carbon paste electrode modified with MWCNTS and 4,4' biphenol was prepared and applied for the determination of d-penicillamine. It was found that under an optimum condition (pH 7.0), the oxidation of d-penicillamine at the surface of such an electrode occurs at a potential about 340 mV. The diffusion coefficient ( $D = 1.23 \times 10^{-5} \text{ cm}^2/\text{s}$ ) and the electron transfer coefficient ( $\alpha = 0.52$ ) for d-penicillamine oxidation were also determined. linear dynamic range of 1  $\mu\text{M}$ -700  $\mu\text{M}$  and detection limit of penicillinamine was obtained 0.219  $\mu\text{M}$ .

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### 3<sup>rd</sup> Official OPCW Biomedical Proficiency Test: Verification of Nerve Agents Exposure in Human Plasma by Gas and Liquid Chromatography-Tandem Mass Spectrometry

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The purpose of this study was to analyse human plasma samples for the protein adducts (or biomarkers) with different analytical methods for the presences or absence of nerve agents exposure. Organophosphorus Nerve agents (OPNAs) including tabun (GA), sarin (GB), soman (GD), cyclosarin (GF), and VX target the enzyme Butyrylcholinesterase (BuChE) and albumin to cause acute toxicity [1-2]. Albumin is abundant protein in blood and is a good target protein to investigate exposure to nerve agents. It can be phosphorylated by OPNAs on the tyrosine residue [3]. In this Biomedical Proficiency Test, plasma samples (6 × 5 mL vial with codes P301-P306) received 5 March, 2018 from Organisation for the Prohibition of Chemical Weapons (OPCW) Laboratory (Rijiswijk, The Netherlands), were analyzed for verification of a human exposure to nerve agents. The spiking protocol was kept unknown for participating laboratories. Laboratories are encouraged to identify nerve agents aged and/or non-aged adducts of BuChE and/or albumin with two techniques such as GC-MS/MS and LC-MS/MS. When tandem mass spectrometric identification is performed by multiple reaction monitoring (MRM) using GC or LC-MS/MS, the data from at least two diagnostic precursor-product ion transitions corresponding to the chemical of interest must be recorded. The signal-to-noise ratio for each diagnostic ion must be  $\geq 5:1$ .

BuChE activity was measured spectrophotometrically using an Ellman assay as a preliminary test to diagnose exposure to OPNAs. Fluoride regeneration method (6 M potassium fluoride) and clean-up with HLB solid phase extraction step identified Fluorotabun (Ethyl N,N-dimethylphosphoramidofluoridate) released from the protein using GC-MS/MS (+CI) in MRM with two ion/transition  $m/z$  156→128 and 110 and GC-HRMS (EI) in selected ion monitoring (SIM) with two ions with exact mass of 126.01140 and  $m/z$  155.05109. Totally protein precipitation, enzymatic digestion with Pronase E, clean-up with 10KD MWCO Identified the Ethyl N,N-dimethylphosphoramido-tyrosine (GA-Tyr) using LC-MS/MS (+ESI) in MRM with two ion/transition  $m/z$  317→226 and 198. BuChE from plasma purified with Sepharose Q fast flow gel (anion exchange)-procainamide affinity gel chromatography and digestion with pepsin, clean-up with C18 solid phase extraction identified the two modified aged nonapeptide adduct FGES(Ethyl phosphate)AGAAS and FGES(Phosphate)AGAAS using LC-MS/MS (+ESI) in MRM with two ion/transition  $m/z$  904→778 and 673 and  $m/z$  876→778 and 673 respectively, that all of results unambiguously verified samples to contaminated with Tabun. Reference chemicals (own synthesis) were used for the comparison to the data obtained with the test samples. The plasma samples with code P301 and P306 identified as blank sample. The Defense chemical research laboratory (DCRL) identified all the spiked chemicals (Tabun) in the concentration range of 10-60  $\mu\text{g L}^{-1}$  in plasma samples P302, P303, P304 and P305 correctly with sufficient analytical data and obtained maximum score A in the Third Official OPCW Biomedical Proficiency Test.

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**Gold Nanoparticles@ $\beta$ -Cyclodextrin@Nanodiamond Crowned Nanoporous Gold DVD Platform as a Disposable Electrochemical Sensor for Detection of Bisphenol A**

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Bisphenol A is an important endocrine disruptor and leads to a considerable risk on human health and ecosystem<sup>[1]</sup>. Because of its widespread use in industrial and household applications, it has become a worldwide concern in recent decades<sup>[2]</sup>. Therefore, development of reliable analytical methods for detection of trace levels of Bisphenol A in different matrices is of critical importance. Herein, a disposable electrochemical sensor constructed from a gold DVD (GDVD) platform crowned with gold nanoparticles@ $\beta$ -cyclodextrin@nanodiamond is proposed for detection of Bisphenol A. The electrode is prepared in five successive steps. First, a silver nanofilm is electrodeposited on the GDVD platform. Then, the silver film is replaced galvanically with gold and selective etching of silver is carried out by nitric acid and ammonia to obtain a nanoporous gold film. Thereafter,  $\beta$ -cyclodextrin stabilized gold nanoparticles and an aqueous nanodiamond dispersion are drop casted at the as-prepared platform, respectively. The characterization of the electrode surface at each stage was performed using scanning electron microscopy and atomic force microscopy. Also,  $\beta$ -cyclodextrin stabilized gold nanoparticles was characterized using UV-Vis spectrophotometry, transmission electron microscopy, and dynamic light scattering. Electrochemical oxidation behavior of bisphenol A at the surface of the modified electrode was investigated using cyclic voltammetry which showed an irreversible oxidative wave with decreased oxidation overpotential and increased current response compared to the bare GDVD electrode. Linear sweep voltammetry was used for quantitative measurements after careful optimization of influential operating conditions. The reproducibility of the method defined as RSD% was obtained to be 4.01%. The analytical applicability of the proposed sensor was demonstrated by determination of bisphenol A in water and beverages. The cheap disposable GDVD platforms removes the concerns about the memory effects and tedious solid surface polishing.

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**Identification of Saffron Volatile Components from 34 Different Geographical Regions of Iran by Headspace Solid Phase Microextraction (HS-SPME) Gas Chromatography/Mass Spectrometry**

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Saffron is one of the most expensive and valuable food spices. Iran is the first country in the field of saffron production (>90%), followed by Greece, Morocco, India, Spain and Italy [1]. Iranian saffron has a special place in the world. In this research the volatile compounds of saffron from 34 different geographical regions of Iran were analyzed by HS-SPME-GC-MS [2]. Saffron samples were collected and prepared according to standard procedure. Headspace solid phase microextraction is a simple, rapid, affordable, high sensitive and solvent-free technique which integrates sampling, extraction and concentration of volatile compounds before their GC/MS analysis [3]. Saffron samples were collected and prepared according to standard procedure. In this study 90 compounds were identified which is much more from previous works. Identification of volatile compounds was made by comparing their mass spectra with the mass spectra of two libraries (Nist05a, Wiley275) and also the literature. For each peak the Kovats retention index was also determined and the value was compared with those reported in the literature. The chromatograms of 34 different regions were studied and some of the results are:

The highest amount of total volatile compounds is related to south Khorasan and the minimum amount of total volatile compounds belongs to Gonabad in Razavi Khorasan and then to Qom. The maximum amount of safranal is related to Khorasan province and Zirkooh in south Khorasan has the highest value. The minimum amount of safranal belongs to Gonabad, Zanjan and Arak respectively. The maximum amount of  $\alpha$ -isophorone, 2,2,6-trimethyl-1,4-cyclohexanedione and 4-ketoisophorone belong to south Khorasan. Arak, Zanjan, Gonabad and Kermanshah have the minimum amount of  $\alpha$ -isophorone respectively. The minimum amount of 4-ketoisophorone belongs to Arak, Gonabad and Zanjan respectively. The minimum amount of 2,2,6-trimethyl-1,4-cyclohexanedione is related to Arak, Zanjan, Gonabad and Qom respectively. In Estahban in the Fars province  $\alpha$ -isophorone was the major component and its amount was more than safranal. In Jajerm in the north Khorasan province 4 isomers of megastigma were observed. The amount of 2(5H)-furanone was very low in some regions.

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**Synthesis and investigation of electrocatalytic effect of Ag@pt core-shell nanoparticles supported on carbon nanotubes (CNTs) and modifier for determination of hydrazine**

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Hydrazine and its derivatives are widely used in chemical and pharmaceutical industries. They are mainly used as antioxidants, explosives, fuel cells, pesticides, herbicides, dyes and synthesis of insecticides. Despite this advantage, hydrazine is a toxic material. Therefore, an easy and sensitive analytical method for detection of hydrazine is warranted [1-2]. The electrochemical methods using chemically modified electrodes (CMEs) have been widely used as sensitive and selective analytical methods for the detection of the trace amount of important compounds [3]. In the present research, derivative pyrazole as modifier was synthesized in the laboratory of yazd university and characterized by spectroscopy techniques. The Electrochemical behavior of modifier was investigated. A pair of reversible peaks are observed at  $E_{p,a}=0.185V$  and  $E_{p,c}=0.100V$  versus SCE, and  $\Delta E_p=(E_{p,a}-E_{p,c})$  was  $0.085V$ . An Ag@pt nanoparticles core-shell supported on carbon nanotubes (Ag@pt NPs/CNT/CS) was synthesized by a colloidal method and a chemical reduction method with sodium borohydride and ethylene glycol as reducing agents [4]. Mixture of modifier and Ag@pt NPs/CNTs/CS with mass ratio 3:1 was prepared. Then,  $3\mu L$  of solution drop casting on glassy carbon electrode and at room temperature was placed to dry. In this research, electrocatalytic activity of Ag@pt NPs/CNT/CS/glassy carbon electrode (GCE) has been studied by cyclic voltammetry (CV), chronoamperometry (CHA) and differential pulse voltammetry (DPV). It has been found that under optimum condition (pH=8) in cyclic voltammetry, the oxidation of hydrazine occurs at a potential about 180 mV less positive than that of as unmodified glassy carbon electrode. The dynamic linear range, current sensitivity and detection limit for hydrazine were evaluated by DPV. The detection limit of hydrazine was  $0.1\mu M$ . Some advantages of using the modified electrode are ease of preparation, potential window, and ease of modification, excellent electrical conductivity and increasing the surface of the electrode. The sensor produced good sensitivity, selectivity and reproducibility and stability properties.

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**Facile synthesis of uniform nanoporous CuCo<sub>2</sub>S<sub>4</sub> hollow microspheres as a novel electrode material for high-performance supercapacitors**

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Today Among the various energy storage devices supercapacitor (SCs) possessing higher energy density than conventional capacitors, more power densities than Li-ion batteries high safety long cycle life, less thermochemical heat generation and easy mode of operation and integration have been attracted much more attention for application in various portable devices. Recently metallic sulfides (such as NiCo<sub>2</sub>S<sub>4</sub>, MnCo<sub>2</sub>S<sub>4</sub> etc.) have been intensely applied as electrode material due to greater electrical conductivity than metal oxides. It is accepted that by substituting oxygen with sulfur possessing lower electronegativity can effectively facilitate the electrons transfer in electrodes and consequently enhance electrical conductivity power performance of the electrodes. Herein, for the first time we developed a new electrodes from nanoporous CuCo<sub>2</sub>S<sub>4</sub> hollow microspheres with an average diameter of around 500 nm and evaluated their electrochemical properties for high-performance supercapacitor. These hollow microspheres were synthesized through facile and low cost two-step hydrothermal method.

The crystalline nature, nanoporous structure and hollow interior of the microspheres were characterized by X-ray diffraction (XRD), Brunauer–Emmett–Teller (BET), and transmission electron microscopy (TEM) techniques. Electrochemical evaluation of the as-prepared CuCo<sub>2</sub>S<sub>4</sub> electrodes was performed by galvanostatic charge-discharge and cyclic voltammetry (CV) the electrodes exhibited a high specific capacitance of 1576 F g<sup>-1</sup> at a current density of 2 A g<sup>-1</sup>, excellent good rate capability, and an remarkable cycling stability of 91% after 5000 cycles.

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**Determination of dihydronicotinamide adenine dinucleotide (NADH) using a carbon paste electrode modified with graphite nanoparticles and modifier**

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The electrochemical oxidation of dihydronicotinamide adenine dinucleotide (NADH) to the corresponding oxidized form (NAD<sup>+</sup>) in aqueous solution has received considerable attention. However, direct electrochemical oxidation of NADH at a bare platinum electrode requires a high (>1 V) overpotential. The overpotential for NADH oxidation could be reduced by using a mediator [1-3].

In this present work, we prepared a modified carbon paste electrode by using 2((7-(2,5-dihydrobenzylideneamino) heptylimino) methyl) benzene-1, 4-diol (DHB) modifier and graphite nanoparticles for NADH detection. Modifier synthesized in our laboratory and characterized by spectroscopy techniques. The Electrochemical behavior of DHB was investigated. The anodic and cathodic peak potentials appeared at 0.185 and 0.132 V (vs Ag/AgCl/KCl 3.0 mol/L), respectively, and  $\Delta E_p$  was 0.053 V.

The electrochemical response characteristics of the modified electrode toward NADH were investigated by cyclic voltammetry (CV), chronoamperometry (CHA) and differential pulse voltammetry (DPV) techniques. All the optimum condition, the concentration of NADH in 0.1M phosphate buffer solution at pH=7 was performed. Based on CV method the redox properties of the modified electrode at various scan rates were investigated. The affecting parameters such as pH, amount of modifier and nanoparticles content were optimized. The dynamic linear ranges, current sensitivity and detection limit for NADH were obtained by DPV technique. Under the optimized conditions, the oxidation peak current of NADH showed linear dynamic range (12.0-5000.0  $\mu\text{mol/L}$ ) with a detection limit of 6.0  $\mu\text{mol/L}$ .

The advantages of this fabricated sensor include a low detection limit, good stability and reproducibility.

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## Fabrication of nano-geopolymer filter cartridge for treatment of polluted aqueous solutions with Methylene blue

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Methylene blue (MB), a cationic dye, is commonly used in textile manufacturing as a colorific agent for different tissues [1]. Several researchers are attempting for the removal of MB due to its harmful impact on health [2-3]. Fixed-bed adsorption methods have been used for confirming the ability of new synthesized adsorbents. In this study, nano-geopolymer filter was fabricated with combination of Kaolin, sodium hydroxide, sodium silicate and water and then prepared slurry was molded into a ring-disk shape (5 cm in diameter, 0.2 cm thickness). Functional groups and morphological structure was fully characterized by Fourier transform infrared spectroscopy, field emission scanning electron microscopy, transmission electron microscopy, Brunner, Emmett, and Teller analysis and energy-dispersive X-ray spectroscopy. Then the media used for filtration were ring-disk shaped nano-geopolymer net. The effects of pH, contact time, dye concentration, sample volume and flow rate are all taken into consideration in detail under ambient conditions. The time-dependent experimental studies showed that the adsorption quantity of methylene blue increases with initial concentration, pH and adsorbent dosage. The study parameters influencing the adsorption processes show that nano-geopolymer filter removed 92% of the MB (initial concentration 10 mg/L) from 100 mL of water with a pH = 6 after 5 min. The adsorption equilibrium and kinetics were studied for experimental data. From these results, it can be considered that the fabricated nano-geopolymer filter from Kaolin sample tested herein is effective in the removal of MB from aqueous solutions and may be used as an alternative to high-cost commercial adsorbents. The filter cartridge made from the nano-geopolymer rings is very resistant and its materials are not dispersed in water.

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**Preparation of optical sensor based on biodegradable polymers for determination of cations.**

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The development of a novel green optical pH sensor for a wide range pH values is described based on the immobilization of (rubiatictroom, sour tea, barberry, blackberry) extract on an optically transparent agarose biopolymer.

(rubiatictroom, sourtea, barberry, blackberry) is famous in Iran. The anthocyanins of (rubiatictroom-sour tea-barberry and blackberry) were extracted and used as a suitable dye for the preparation of a pH optical sensor, by its immobilization on a transparent agarose film. In an optimized coupling, pH of 11 for rubiatictroom, pH of 2.45 for sourtea, pH of 7.5 barberry, solution with primary pH for blackberry, and a dye concentration of 100 mg L<sup>-1</sup>, a sensitive sensor with long term stability was obtained. The sensors responds rapidly to the pH changes in a range of 1–12 with a response time of 5.0 min and repeatability better than %0.3 (RSD). The sensors were mounted in the quartz cells and successfully applied for pH monitoring. No evidence of leaching of the dye or any signal drift was observed.

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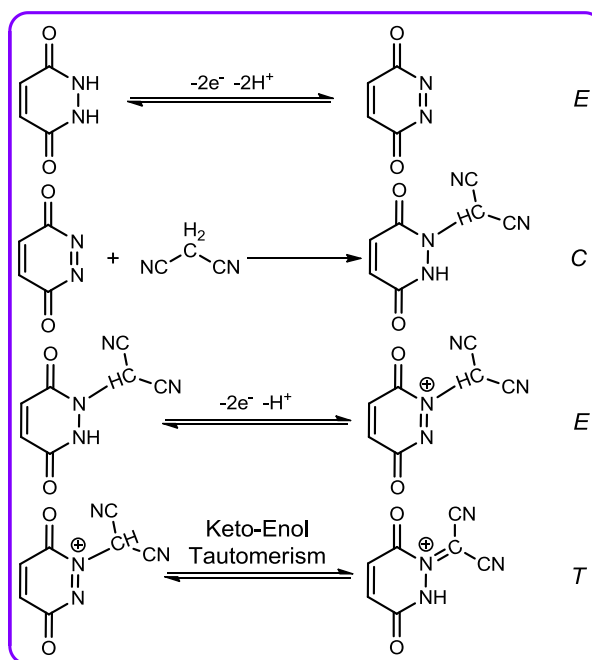
## Electrochemical oxidation of 1,2-Dihydroxyppyridazine-3,6-dione in the presence of malono nitrile

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1,2-Dihydroxyppyridazine-3,6-dione (3,6-dihydroxyppyridazine) is a plant growth regulator and used extensively in agriculture as a major commercial herbicide and as suppression of sprouting of vegetable and stored food crops, control of sucker growth on plant, retardation of flowering and prolongation of dormancy period [1]. In previous work, the electrochemical behavior of 1,2-dihydroxyppyridazine-3,6-dione on glassy carbon electrode in aqueous and some organic solvents was investigated. The results indicate that the electrochemically generated pyridazine-3,6-dione is unstable and via oxidative ring cleavage converts to maleic acid [2]. In this work, electrochemical oxidation of 1,2-dihydroxyppyridazine-3,6-dione has been studied in the presence of malononitrile in aqueous solution using cyclic voltammetry as a diagnostic technique. The results showed that the electrochemically generated pyridazine-3,6-dione participates in Michael type addition reaction with malononitrile via an *ECET* mechanism and is converted to the corresponding new dicyanide derivatives. In this work, some new dicyanide derivatives are provided with high yields in aqueous solutions, without toxic reagents and solvents at a carbon electrode in an undivided cell using an environmentally friendly method.



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## The 25<sup>th</sup> Iranian Seminar of Analytical Chemistry

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### **Preparation of modified carbon-ceramic electrode, based on ionic liquid and Pd nanoparticles supported on porous silicon and its application for simultaneous electrochemical determination of some pharmaceutical compounds**

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Pd nanoparticles were supported on the surface of porous silicon (PSi) powder by a simple in-situ redox reaction between Pd<sup>2+</sup> and PSi, in hydrofluoric acid solution. Pd/PSi nanocomposite as a new electro catalyst is used in modified carbon ionic liquid electrode and has synergetic effect on the oxidation of acetaminophen and mefenamic acid. Several techniques were applied to study of morphological, chemical and electrochemical properties of the prepared nanostructure were distinguished using X-ray diffraction spectroscopy, energy dispersive X-ray spectroscopy (EDX), Fourier-transform infrared spectroscopy (FT-IR), cyclic voltammetry (CV). The high electrochemical activity, fast electron transfer rate, high surface area and good antifouling properties of this nanostructure enhanced the oxidation peak currents and reduced the peak potentials of ACT and MFA at the surface of the proposed sensor. Simultaneous determination of ACT and MFA was carried out using differential pulse voltammetry (DPV). A linear range of 0.1–30  $\mu\text{mol L}^{-1}$  was achieved for ACT and MFA with detection limits of 32 nM and 37 nM, respectively. Finally, the prepared electrochemical was applied to determination of ACT and MFA in real samples such as blood serum and pharmaceutical compounds with proper results.





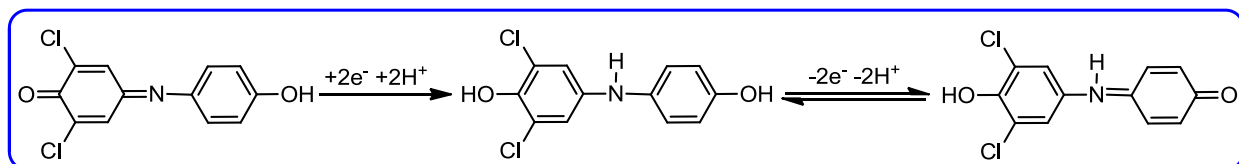
## Electrochemical behavior of 2,6-dichlorophenol-indophenol in aqueous solutions

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2,6-Dichlorophenolindophenol is part of the Hill reagents family, which has been widely used as a redox dye in determination of the rate of photosynthesis [1], vitamin C [2] and NADH [3]. It has also, acid-base indicator properties. Its color is red in acidic media and blue in alkaline media [4]. So, it is used as indicator in various acid-base titrations. The absorption spectra of the acidic and basic forms of the indicator are presented. Therefore detailed mechanistic information is important in the understanding of the stability and identifying the intermediates structure resulting from the oxidation/reduction of this compound. In this work we study the electrochemical behavior of 2,6-dichlorophenol-indophenol using cyclic voltammetry technique at the surface of glassy carbon at various scan rate and pH in aqueous solutions. According to voltammetric data, we propose the following Scheme for the electrochemical oxidation/reduction of 2,6-dichlorophenol-indophenol in aqueous solutions.



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## The 25<sup>th</sup> Iranian Seminar of Analytical Chemistry

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### Application of Microchip Capillary Electrophoresis – Electrochemical Detection (MCE-EC) for separation and determination of Acetaminophen and Codeine

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Since the initial description of the “Lab-on-a-Chip” concept, there has been an explosion of interest in the development of analytical systems utilizing the microchip format, so called micro-total analysis systems ( $\mu$ TAS). Microfabricated systems have numerous advantages like increased precision and accuracy, automation, reduced solvent waste, portability, high speed and disposability<sup>1</sup>. There are various materials used in the fabrication of  $\mu$ TAS like Glass, PDMS, PMMA, Quartz and etc<sup>2</sup>. Various detection systems like UV-Vis Spectroscopy, electrochemical, MS spectroscopy, Conductometry and etc were used in the detection systems<sup>3</sup>. These devices can be used in different fields such as environmental monitoring, biomedical and pharmaceutical analysis, clinical diagnostics, and forensic investigations<sup>4,5</sup>.

In the present study, separation and determination of Acetaminophen and codeine were investigated on the microchip capillary electrophoresis-electrochemical detection (MCE-EC). The MCE-EC device consists of SU-8/Glass and three Pt electrodes as substrates and electrochemical detection system, respectively. Dimensions of Channel were 20 (H)  $\times$  50 (W)  $\mu$ m with 4 and 1cm for the electromoving and side channels long, respectively. Analytes were loaded in the sample reservoir and injected to the channel by applying of appropriate voltage to the same reservoir and then the switcher applies definite voltage to the buffer reservoir. Analytes moved to the end of the channel less than one minute. It is notable that 2-(N-morpholino)ethanesulfonic acid (MES) was used as running buffer.

Parameters that affected the separation and detection were investigated, including injection time and voltage, strength of separation field, detection potential, pH and concentration of running buffer. Optimized conditions were 5s, +750 V, +1000 V, +1.1 V vs. Pt reference electrode, 7 and 20 mM MES buffer, respectively. After method developing, analytical features including linearity, precision, accuracy, LOD and LOQ were studied.

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**A highly sensitive chemiluminescent probe for detection of glutathione based on gold nanostar@reduced graphene oxide composite**

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Gold nanostars (GNSs) are particularly interesting class of plasmonic particles. They consist a near-spherical core and multiple branches with sharp tips, which create lots of “hotspots” and enhance the local electromagnetic fields strongly [1,2]. Here we describe for the first time, the application of GNS@rGO in CL and demonstrate their remarkable enhancing effect on luminol-IO<sub>4</sub><sup>-</sup> reaction. This enhancement was supposed to result from the unique catalytic action of GNS@rGO, which leads to the acceleration of reactive oxygen species generation. It was also found that a remarkable increase in the CL intensity of GNS@rGO-luminol-NaIO<sub>4</sub> system occurs in the presence of glutathione (GSH). Based on this observation, a simple and highly sensitive CL probe was developed for detection of GSH. With the optimum conditions chosen, the calibration curve exhibits linear range from 1.0 nM to 1.0 μM for GSH with a detection limit of 0.2 nM. The developed nano sensor was applied to the detection of GSH in human plasma samples with satisfactory results.

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**A colorimetric method for determination of Selenium based on surface Plasmon resonance properties of silver nanoprisms**

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Silver nanoprisms are one of the most important anisotropic metal nanoparticles which have attracted tremendous attention due to their unique optical properties [1]. One of the unique features of Ag NPs which is extensively applied to establish analytical sensor is surface Plasmon resonance (SPR). This feature of metal NPs is affected by various structural and environmental parameters such as size, shape, architecture, composition of nanoparticles spacing between nanoparticles and their surroundings. Recently, due to exceptional optical, surface and structural properties of anisotropic noble metal NPs, the colorimetric methods based on these NPs have attracted considerable attention [2]. Herein we report on a novel plasmonic probe for detection of ultra-trace amounts of Se(IV) based on morphological transformation of silver nanoprisms (AgNPRs). This nano particles were synthesized in a mild condition and characterized by UV-Vis absorption spectroscopy and transmission electron microscopy (TEM). It was found that in the presence of Se(IV), SPR peak of AgNPRs at 720 nm shifts to lower wavelengths and the color of solution changes from light blue to violet. This is due to the shape transformation of AgNPRs to nanodisks which is proved by TEM images, and results from the etching of corners of NPRs by selenite ions. Based on this phenomenon, a sensitive colorimetric probe was developed for determination of Se(IV) in the concentration range of 2.5-100  $\mu\text{g L}^{-1}$  with a detection limit of 1.2  $\mu\text{g L}^{-1}$ . The developed method was applied for the analysis of water and food samples.

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**A comparative study of two urea functionalized metal organic frameworks for phenol sensing**

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Two pillared metal-organic frameworks containing urea functional groups were synthesized by a sonochemical method and characterized by scanning electron microscopy, X-ray powder diffraction, IR spectroscopy and elemental analysis. The time of sonication and concentration of starting materials have been optimized to synthesize nanoparticles of TMU-31 and TMU-32. These two frameworks are interesting candidates for a comparative fluorescence study. Thus, their potential abilities for phenol sensing were investigated. This investigation revealed the prominent roles of hydrogen bond donating urea groups inside the pore cavity in the ability of these structures in phenol sensing.

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**Development of a new hyphenated sample preparation method in combination with GC–MS for extraction and determination of some tricyclic antidepressants in biological fluids**

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Tricyclic antidepressants (TCAs) are one of the classes of psychopharmaceuticals which still are widely used for the treatment of various forms of depression and psychological disorders [1]. TCAs inhibit the reuptake of neurotransmitters by impeding serotonin and norepinephrine transporters [2]. Generally, therapeutic drug monitoring is becoming highly important as it can help for effective control of pharmacotherapy and drug poisoning in clinical pharmacology and forensic sciences. This point is more important in the case of TCAs because of their narrow therapeutic range. The concentrations of these drugs in human biological fluids are at very low levels and mainly determined by chromatographic methods [3, 4]. In most cases, an additional step termed as sample preparation which includes extraction, preconcentration, and cleanup is mostly required for pharmaceutical analysis due to the inherent complexity of the biological fluids. In this study, dispersive solid phase extraction coupled with deep eutectic solvent-based air-assisted liquid-liquid microextraction has been developed and applied to the extraction and preconcentration of some tricyclic antidepressant drugs in human urine and plasma samples prior to their determination by gas chromatography–mass spectrometry. In this method, firstly, a sorbent is added into an alkaline aqueous sample and dispersed by vortexing. By this action the analytes are adsorbed onto the sorbent. Then the sorbent particles are isolated from the aqueous solution by centrifugation. Afterward, a synthetic deep eutectic solvent is used to desorb the analytes from the sorbent. Subsequently, the supernatant solution is removed and added into an alkaline deionized water placed into a test tube with conical bottom. The resulting mixture is rapidly sucked into a glass syringe and then is injected into the tube. This procedure is repeated for several times, and a cloudy solution consisting fine droplets of deep eutectic solvent dispersed into the aqueous phase is formed. After centrifuging the obtained cloudy solution, the tiny droplets of the extractant containing the extracted analytes are settled at the bottom of the tube. Finally, an aliquot of the extractant is taken and injected into the separation system for analysis. Several significant factors affecting the performance of the proposed method were evaluated and optimized. Under the optimum extraction conditions, the method showed low limits of detection in the ranges of 8–15 and 32–60 ng L<sup>-1</sup> in urine and plasma, respectively. Enrichment factors were obtained between 163 to 193 in urine and 65 to 77 in plasma for the analytes. Extraction recoveries were in the range of 65–77%. The relative standard deviations of the proposed method were ≤ 6% for intra- ( $n=6$ ) and inter-day ( $n=4$ ) precisions. Finally, the applicability of the introduced method was investigated by analysis of the selected drugs in different patient's biological fluids.

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**A fluorescent probe based on S,N- carbon dots – MnO<sub>2</sub> nanosheets for determination of quercetin**

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Ultrathin two dimensional MnO<sub>2</sub> nanosheets have several interesting physicochemical properties such as high extinction coefficient, rich redox chemistry, high colloidal stability and good biocompatibility which make them an excellent quencher in fluorescence sensing platform [1,2].

In this study, a turn-on fluorescent probe based on the effect of MnO<sub>2</sub> nanosheets on the fluorescence of sulfur and nitrogen co-doped carbon dots (S,N-CDs) is reported for detection of quercetin. The fluorescence of S,N-CDs, a novel classes of highly luminescent nanomaterials, efficiently turns off in the presence of MnO<sub>2</sub> nanosheets due to the formation of carbon dots–MnO<sub>2</sub> nanocomposite. By adding quercetin to the solution of S,N-CDs–MnO<sub>2</sub> nanosheets, the fluorescence of S,N-CDs is partially recovered as a result of its reaction with MnO<sub>2</sub> nanosheets. Under the optimum conditions, the recovered fluorescence intensity displays a linear relationship with the concentration of quercetin in the range of 2.5–30 μM with a detection limit of 0.7 μM. The method was applied for analysis of water samples with satisfactory results.

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### 3-Methyl pyridine as extraction solvent and chelating agent in extraction and preconcentration of some heavy metals in aqueous samples based on heat-induced homogeneous liquid-liquid extraction

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Heavy metal ions are present in relatively low concentrations in the environment. They are widely used in many industries. Cobalt and nickel are typical metal ions in environmental samples and have important roles in many physiological functions. However, high concentrations of these metal ions may be toxic and lead to side effects [1, 2]. Prior to assess low concentration, performing separation and preconcentration techniques are compulsory to eliminate or minimize matrix effects which leads to low detection limit and improved sensitivity of detection techniques towards metals.

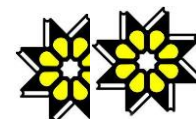
Homogeneous liquid-liquid extraction (HLLE) is based on the usage of a low dielectric constant organic solvent such as acetonitrile, methanol, acetone, etc., which is soluble in water. An agent is utilized as a phase separation phenomenon in a homogeneous solution to produce two distinct phases. In this method an analyte (organic / inorganic compound) in the homogeneous aqueous solution is extracted in the separated organic phase. In HLLE the contact area between the phases is practically infinitive compared to liquid liquid extraction and dispersive liquid liquid microextraction facilitating fast mass transfer. Moreover, it possesses the advantage of having a short extraction time with a high enrichment factor due to the absence of obstacles from surface contact between the organic phase and the aqueous phase during extraction. Picoline (PL) is soluble in water at low temperatures while its solubility in water is decreased by heating. Therefore heating can be used as phase separation agent to form a two-phases system from a homogenous solution containing water and PL.

In the proposed method, initially to 5 mL standard solution or real sample (pH= 5) in 8-mL glass tube,  $\mu\text{L}$ -level PL was added to form cation-PL complexes in a homogeneous solution. Then 0.9 g sodium chloride was added to the solution. After manual shaking, the tube was placed in a water bath with 70°C for 6 min. A cloudy solution was formed due to the decrease of PL solubility at 70°C compared to room temperature. After centrifugation for 5 min at 5000 rpm, the fine droplets of PL (extraction solvent) containing the formed complexes were collected as the upper phase. In order to investigate the extraction efficiency of the method, the collected phase was removed and injected into GFAAS.

Under the optimum conditions the calibration curves were linear in the ranges of 10-150 ng L<sup>-1</sup>. Repeatability of the proposed method ranged from 3-5% (n=6, C=100 ng L<sup>-1</sup>). Moreover, the detection limits of the selected analytes were obtained in the range of 4-7 ng L<sup>-1</sup>. Finally, the proposed method has been successfully applied for the simultaneous analysis of the selected analytes in environmental water samples.

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**Aptamer-based assay of ractopamine in human biofluids using thiolated GQDs-chitosan biocompatible nanocomposite modified gold nanostructures: The effect of size and morphology of nanoparticles on the efficient of apta-assay**

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A representative biosensor contains three components: a biological sensing element, a transducing element, and a display. The sensing element primarily defines the selectivity and sensitivity of the biosensor. To date, many different types of biological components (enzymes, antibodies, or DNA/RNA) have been employed for highly selective responses to specific analytes. A typical electrochemical biosensor makes use of an electrode surface as the platform to immobilize biological sensing components (e.g., antibodies or aptamers), for which the analyte-binding event is monitored based on electrical current variations[1]. Aptamers are single stranded DNA or RNA molecules with high specificity to various ligands. Biosensors based on DNA or RNA aptamers (aptasensors) represent new type of the sensor that utilize unique properties of artificial receptor-aptamers. Aptasensors are of considerable interest due to their application in detection practically unlimited kind of compounds[2].  $\beta$ -agonists are phenylethanolamines with different substituent groups on the aromatic ring and the terminal amino group, including Ractopamine (RAC), Clenbuterol (CLB), Salbutamol (SAL), Phenylethanolamine (PHL), Procaterol (PRO) and so on[3]. In general,  $\beta$ -agonists are applied as bronchodilators for the treatment of human pulmonary disease and asthma[4]. Now  $\beta$ -agonists and their analogous are illegally used in animals as growth promoters to increase the daily gain. However,  $\beta$ -agonists can be accumulated in animal and be easily stored in human tissues after meat consumption, and result in many serious health problems with symptoms such as palpitations, tremors and tachypnoea[5]. Therefore, establishing a sensitive, rapid and convenient analysis method for detection of  $\beta$ -agonists is great significance for food safety and human health control.

In this study, an electrochemical aptasensor based on thiolated graphene quantum dot (GQD), chitosan (Cs), and gold nanoparticles (Au NPs) has been developed for sensitive detection of ractopamine human biofluids. A layer-by-layer strategy were used for the preparation of nanocomposite (GQDs-CS-Au NPs). The prepared interface were utilized for immobilization of specific aptamer. The RAC aptamer was attached on Au NPs of the composite membrane via Au-S bond. Surface morphology of the sensor was studied using field emission scanning electrode microscopy (SEM) and energy dispersive spectroscopy (EDS). The signal for the determination of ractopamine was recorded using differential pulse voltammetry (DPV) at the optimized conditions.

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**A post synthetic modified metal organic framework based fiber coating for solid phase microextraction of organophosphorus pesticides**

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Separation and extraction processes are usually required prior to the instrumental analysis either due to low analytes concentrations or/and sample complexity. Solid phase microextraction (SPME) is a fascinating, sensitive and rapid method which has been successfully applied for the sampling, pretreatment and preconcentration analysis of a wide variety of compounds, in both headspace (HS) and direct immersion (DI) modes. In this methodology, sampling, extraction, preconcentration and sample introduction are combined in one step and usually needs no desorbing solvent <sup>[1, 2]</sup>.

Metal organic frameworks (MOFs) have emerged as a new class of porous crystalline materials that are based on the coordination of metal ions or clusters with bi-or multidentate organic linkers. MOFs, due to their outstanding properties such as high surface area, great potential for post synthetic modification (PSM), uniform structure cavities and high hydrothermal stability have been developed in research areas including catalysis, sensing, gas storage and drug delivery <sup>[3]</sup>. In the current work, a chromium based MOF (MOF1) was synthesized with hydrothermal method and then modified with acetic anhydride in a PSM process to achieve MOF2 <sup>[4]</sup>. Both MOFs were fabricated, as SPME fiber coatings, via sol-gel methodology on the stainless steel substrate and after conditioning, they were examined for the extraction of some organophosphorus pesticides including diazinon, fenthion, profenophos, ethion, and phosalone in DI mode. The fiber coating based on MOF2 was superior extraction capability and selected for the following experiments. Influencing parameters affecting the DI-SPME analysis and gas chromatography-mass spectrometry (GC-MS) procedure such as desorption time (5 min) and temperature (260 °C), extraction time (20 min) and temperature (25 °C), ionic strength (0 w/v % NaCl) and sample stirring rate (1000 rpm) were investigated and optimized.

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**An Electrochemical Sensor for Determination of Sulfamethazine Based on C<sub>3</sub>N<sub>4</sub>-Chitosan NanoComposite Film Modified Glassy Carbon Electrode and Application in Biological and Pharmaceutical Samples**

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The C<sub>3</sub>N<sub>4</sub>-chitosan composite film modified glassy carbon electrode was fabricated and used to determine sulfamethazine. In pH 5.3 phosphate buffer solutions, the redox peak currents of sulfamethazine increased significantly at C<sub>3</sub>N<sub>4</sub>-chitosan composite film modified glassy carbon electrode compared with bare electrode and chitosan modified glassy carbon electrode, indicating that C<sub>3</sub>N<sub>4</sub> possessed electrocatalytic activity towards sulfamethazine. The experimental conditions were optimized and the oxidation mechanism was discussed. Under the optimal experimental conditions, the oxidation peak current was proportional to sulfamethazine concentration in the range from 0.8-54 μM with the correlation coefficient of 0.9930. The detection limit was 0.4 μM (S/N=3). Using the proposed method, sulfamethazine was successfully determined in serum sample, tablets and urine, suggesting that this method can be applied to determine sulfamethazine in pharmaceuticals.

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**Improvement of a selective modified electrochemical aptasensor using Amino-rGO/ Ionic Liquid/Mesoporous Silica Nanoparticle for the ultrasensitive detection of lysozyme protein**

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An aptamer-based method is described for electrochemical determination of lysozyme. A screen-printed electrode was modified with a nanocomposite composed of Amino-reduced graphene oxide (Amino-rGO), Ionic Liquid (IL) and Mesoporous Silica Nanoparticle (MSN). The composition of the nanocomposite (Amino-rGO/IL/MSN) warrants a high surface-to-volume ratio, high conductivity, high stability, and great electrocatalytic activity. This nanocomposite provides a suitable site for better immobilization of aptamers due to the existence of many amino groups. In addition, this nanocomposite allows considerable enhancement of the electrochemical signal and contributes to improving sensitivity. The amino-linked lysozyme aptamers were immobilized on the nanocomposite through covalent coupling between the amino groups of the aptamer and the amino groups of the nanocomposite using glutaraldehyde (GLA) linker. Using the obtained data from differential pulse voltammetry (DPV) and EIS techniques, two calibration curves were drawn. The anti-lysozyme aptasensor proposed has two very low LODs. These measures are 2.8 and 1.1 fmol L<sup>-1</sup> within the wide detection ranges of 15 fmol L<sup>-1</sup> to 10 nmol L<sup>-1</sup>, and 10 fmol L<sup>-1</sup> to 100 nmol L<sup>-1</sup> for DPV and (electrochemical impedance spectroscopy) EIS calibration curves, respectively.

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**A new chemiluminescence system based on nitrogen-sulfur doped carbon quantum dots for highly sensitive detection of uric acid in human plasma and urine samples**

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Carbon quantum dots (CQDs) are a fascinating class of luminescent nanomaterials that comprise discrete, quasi-spherical carbon nanoparticles with sizes below 10 nm. They typically display high quantum yield fluorescence with interesting behavior.

Recently nitrogen-sulfur doped carbon quantum dots (N,S-CQDs) have been introduced and attracted considerable interest in various areas [1]. In this work, N,S-CQDs were prepared by a hydrothermal method and characterized by fluorescence spectra and transmission electron microscopy. The effect of as-prepared CQDs on the chemiluminescence (CL) of colloidal MnO<sub>2</sub>-luminol system was investigated. The results showed that N,S-CQDs remarkably increase the intensity of CL emission. Moreover, the effect of uric acid on the S,N-CQDs–MnO<sub>2</sub>-luminol CL system was studied and found that the CL intensity of this system is significantly declined by uric acid. Based on this finding a sensitive and selective method was developed for detection of uric acid. The calibration curve was linear in the concentration range of 0.05 to 1.0 μM. The method was successfully applied to the determination of uric acid in human plasma and urine samples.

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## Survey of Colloid Silver Stability for LSPR Spectrum in Determination of Dextrose with Nanoparticles synthesis Method

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In a green chemistry method, determination of dextrose with a method based on silver nanoparticles (AgNPs) formation was investigated. Colloid silver nanoparticles were synthesized in the natural polymeric matrix of gelatin. The localized surface plasmon resonance (LSPR) Spectrum were characterized with UV-Vis spectroscopy.

Stability of silver nanoparticles was investigated for standard sample with concentration 0.02 M of dextrose at intervals of 20 to 280 min. No changes in the LSPR situation showed the stability of the nanoparticles. Also, the stability was studied in a period of three months. Samples were stored at room temperature and the UV-Vis spectrum was obtained in the range of 300 to 800 nm after the formation of colloid silver yellow and after a day, three days, six days, thirty days, sixty to ninety days. The results, were not showed any significant differences in position and the symmetry of the absorption peak at the time was mentioned. Figur (1-2) confirms the lack of significant changes in absorbance intensity and wavelength of maximum during stability of three month for nanoparticles made. In addition, stability of silver nanoparticles was monitored through UV-Vis spectrophotometer at time intervals of 20,40,60,80,100,120,140,160,180,200,220,240,260 and 280 min .

The results confirm the lack of significant changes in absorbance intensity and maximum wavelength during the stability period of three months for nanoparticles made. There is no shift in the maximum absorbance. Incremental changes of absorbance over time is probably due to aggregation. [1-3]

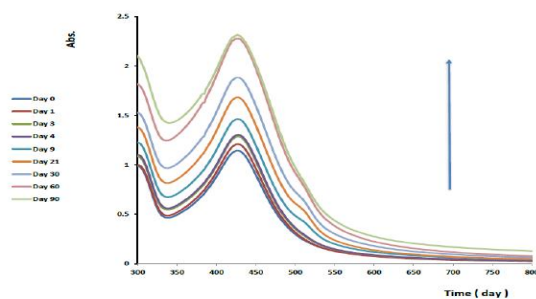


Fig.1. Stability for LSPR spectrum in standard sample after 280 min.

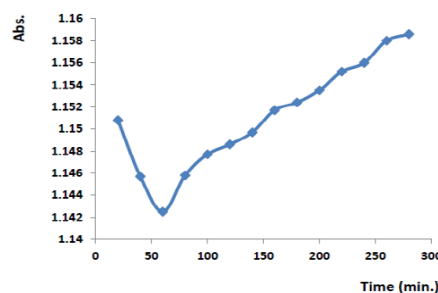


Fig.2. Stability of silver nano particles in standard sample

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## Synthesis of nanocomposites based on polyaniline and natural wool for removal of methylene blue dye from aqueous solution

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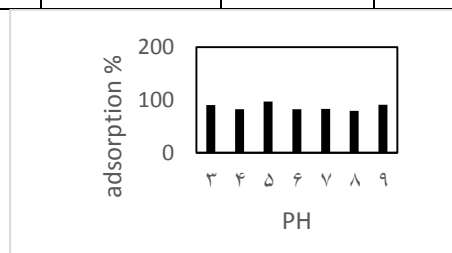
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Dyes containing industrial wastewater have become an important contamination because of exploitation in various industries such as textile, chemical, refineries and plastic industries [1]. Due to its simplicity, flexibility and low cost, the attraction is one of the most up-to-date technologies and the use of adsorbents has attracted much attention [2].

The nanocomposites was synthesized by graft polymerization of aniline on the modified sheep wool in various ratios of polyaniline to wool. The synthesized nanocomposites were tested for removal of color from aqueous environments. The typical color was methylene blue [3]. The best results was obtained in methylene blue dye. For comparison unmodified natural wool was tested for removal of selected dye for demonstration of nanocomposites efficiencies. The results were summarized in table 1. Fig 1 shows the percent of adsorption at different PH. Studies on pure wool and polyaniline-modified wool on methylene blue showed that the removal rate in the presence of pure wool is about %38 and the modified wool is %97 at pH = 5. The prepared nanocomposite was characterized by FT-IR, SEM , TGA and Raman spectroscopy.

Table 1. adsorption of wool modified by polyaniline and pure wool to remove the methylene blue from water

	PH=5	Time= 30 min	Temperature= 20°	Potential= 1
polyaniline-modified wool	%96.93	%92.43	%90.35	% 17.78
pure wool	%38.87	% 12.82	%24.13	%0



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**Electrochemical determination of metronidazole on a graphene based carbon ionic liquid electrode modified with silver nanoparticles and its application to pharmaceutical analysis**

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Electrochemical determination of metronidazole (MET) using graphene modified ionic liquid electrode (graphene/CILE) is described by using cyclic and differential pulse voltammetries at physiological pH 6.5. An increased peak current with a shift of peak potential to less positive value was observed using graphene modified carbon ionic liquid electrode (CILE) as compared to CILE. The effect of pH, scan rate and analyte concentration has been examined. Under the optimum conditions the peak current was linear to the concentration of metronidazole in the range  $2.0 \times 10^{-7}$  to  $1.7 \times 10^{-5}$  mol.L<sup>-1</sup> for graphene/CILE and the detection limit was found to be  $1.0 \times 10^{-7}$  mol.L<sup>-1</sup>. The method was successfully used to determine the content of MET in the pharmaceutical preparations and human serum sample.

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**Preparation of modified electrode by Ag nanoparticles in graphene oxide substrate and its application in glucose analysis in real samples**

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Due to the pivotal role of glucose in physiological processes, much effort has been devoted to the development of highly sensitive and selective, low cost and reliable methods for detecting glucose in food and biological matrices. Many electrochemical techniques have been developed to detect glucose [1-3].

A non-enzymatic glucose sensor based on pencil graphite electrode (PGE) modified by Ag nanoparticles decorated reduced graphene oxide (Ag(NP)/rGO-PGE) was prepared. The prepared Ag(NP)/rGO exhibited a nano porous structure by scanning electron microscopy (SEM). Cyclic voltammetry at Ag(NP)/rGO-PGE showed the immobilized Ag(NP)s were highly stable in alkaline solutions and had high electrocatalytic activity toward glucose oxidation. Using amperometry, the detection limit of [0.09 ( $\pm$ 0.003)  $\mu$ M] and concentration sensitivity of [2295 ( $\pm$ 3.2)  $\mu$ A mM<sup>-1</sup>cm<sup>-2</sup>] for glucose was obtained at optimum conditions. The applicability of the sensor was evaluated to determine the glucose concentration in real samples. The preparation of Ag(NP)/rGO-PGE was reproducible, very simple, fast and inexpensive for practical application.

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## Ligandless green effervescence-assisted dispersive liquid-liquid microextraction method for trace analysis of Co(II) and Ni(II)

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Heavy metal ions are present in relatively low concentrations in the environment. They are widely used in many industries. They are important pollutants in environment due to their toxic effect on human health. Cobalt and nickel are typical metal ions in environmental samples and have important roles in many physiological functions. However, high concentrations of these metal ions may be toxic and lead to side effects [1, 2]. Prior to assess low concentration, performing separation and preconcentration techniques are compulsory to eliminate or minimize matrix effects which leads to low detection limit and improved sensitivity of detection techniques towards metals.

In conventional dispersive liquid-liquid microextraction, an extraction solvent is dispersed into an aqueous sample solution with the aid of a disperser solvent [3]. The presence of relatively high volume of the disperser solvent makes the aqueous phase relatively nonpolar and results in an increased solubility of the target lipophilic analytes into the aqueous sample solution leading to relatively low extraction efficiency.

Ligandless gas-disperser liquid-liquid microextraction followed by graphite furnace atomic absorption spectrometry detection has been developed for the extraction and preconcentration of cobalt and nickel from aqueous samples. In the proposed method, initially a solid mixture of phthalic acid and sodium bicarbonate is placed in the bottom of a conical and dried glass test tube. Then  $\mu\text{L}$ -level of 1,1,2,2-tetrachloroethane as an extraction solvent is added to the tube. An aqueous solution of the analytes is transferred into the tube. The reaction between phthalic acid and sodium bicarbonate is immediately occurred, and the produced  $\text{CO}_2$  leads to dispersion of the extraction solvent as tiny droplets into the sample and subsequent extraction of the analytes. The cloudy solution is centrifuged and the sedimented phase is analyzed by the analytical method.

Under the optimum conditions the calibration curves were linear in the range of 20-300  $\text{ng L}^{-1}$ . Repeatability of the proposed method, expressed as relative standard deviation, ranged from 3-5% and 4-7% for intra- and inter-day ( $n=6$ ,  $C=50 \text{ ng L}^{-1}$ ) precisions, respectively. Moreover, the detection limits and enrichment factors of the selected analytes were obtained in the ranges of 6-12  $\text{ng L}^{-1}$  and 193-198, respectively. The accuracy of the developed procedure was checked by analyzing NRCC-SLRS4 Riverine water as a certified reference material. Finally, the proposed method has been successfully applied for the simultaneous analysis of the selected analytes in environmental water samples.

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**A highly sensitive hydrogen peroxide amperometric sensor based on (Ag–Pd NPs)/  
polypyrrole modified glassy carbon electrode**

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Herein, the polypyrrole decorated with gold–silver nanoparticle (Ag–Pd NPs) nanocomposite modified glassy carbon was used for the determination of hydrogen peroxide. Electrochemical experiments indicated that the proposed sensor possesses an excellent sensitivity toward the reduction of hydrogen peroxide. The resulting sensor exhibited a good response to hydrogen peroxide over linear range from 0.05 to 90.0  $\mu\text{M}$  with a limit of detection of 0.02  $\mu\text{M}$ , good reproducibility, long-term stability and negligible interference from ascorbic acid, uric acid and dopamine. The proposed sensor was successfully applied to the determination of hydrogen peroxide in human serum sample. Pd-Ag nanoparticles; Polypyrrole; Hydrogen peroxide; Electrochemical sensor

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**Highly sensitive non-enzymatic electrochemical glucose sensor by periodic mesoporous organosilica /Ni (II) modified glassy carbon electrode**

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A novel non-enzymatic glucose sensor based on PMO-supported nickel ion (PMO-Ni (II)) nanomaterial was successfully prepared. The electrocatalytic activity of prepared modified electrode towards glucose oxidation was investigated by cyclic voltammetry and amperometric methods in alkaline solution. The amperometry results revealed that the prepared sensor exhibited a good response to glucose with a wide linear range from 0.1  $\mu\text{M}$  to 14 mM and with a low limit of detection of 0.015  $\mu\text{M}$ . The PMO-Ni (II) modified glassy carbon electrode exhibited good reproducibility, long-term stability and negligible interference from uric acid, dopamine, and ascorbic acid. The PMO-Ni (II) modified glassy carbon electrode showed good activity towards glucose oxidation in human serum samples with low overpotential, avoiding interference.

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**Extraction and preconcentration of cadmium and zinc cations using ligandless green effervescence-assisted dispersive liquid-liquid microextraction performed in a**

**narrow-bore tube**

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Although heavy metal ions are present in relatively low concentrations in the environment, in recent years, with an increase in city development and industry, they have been widely used in many industries. Among the heavy metals, cadmium and lead are potentially toxic, have no known biological function to living organisms and probably cause damages to human health even at low levels. Therefore they are of primary interest in environmental quality, waste, and food [1,2].

Dispersive liquid-liquid microextraction (DLLME) is based on a ternary component solvent system. Operation simplicity, rapidity, low cost, and high enrichment factor are some of the DLLME advantages. In conventional DLLME, an extraction solvent is dispersed into an aqueous sample solution with the aid of a disperser solvent. The presence of relatively high volume of the disperser solvent makes the aqueous phase relatively nonpolar and results in an increased solubility of the target lipophilic analytes into the aqueous sample solution and relatively low extraction efficiency. Developing a reliable and environmentally friendly DLLME method in a narrow-bore tube combined with AAS for the extraction, preconcentration, and determination of Cd(II) and Pb(II) in aqueous samples was aimed.

In the proposed method 25 mL deionized water containing Cd (II), Pb(II), and extraction solvent was poured into a narrow bore tube (25 cm × 12 mm i.d.) which its head was the funnel shaped and its end was connected to a ground glass joint. It is noted that the optimized amount of phthalic acid and sodium bicarbonate were mixed and placed into the end glass vessel. In contact with the aqueous solution, an acid-base reaction between phthalic acid and bicarbonate was rapidly occurred and the resulted CO<sub>2</sub> led to dispersion of the extraction solvent as tiny droplets into the aqueous solution, and a cloudy state was formed. Finally, after a short time phase separation and collection of the organic phase on the surface of the aqueous phase was occurred.

The proposed method made possible the determination of the analytes in the ranges of 1.0-20 µg L<sup>-1</sup>. The accuracy of the developed method was verified by analyzing a certified reference material, namely SPS-WW2 Batch 108. Relative recoveries (80-96%, obtained at three fortification levels) confirmed the usefulness of the method for analysis of the analytes in the environmental water samples. The method was shown to be fast, reliable, and environmentally friendly with low organic solvent consumption.

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**Synthesis of different morphologies of silver nanoparticles and studying of their catalytically properties by optical methods**

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Silver nanoparticles due to their special optical, electrical and catalytic properties, which are related to their shape, size and chemical surface, have vast applications in various sections of science and industries. So, beside the control over their size, control of their shape is also necessary [1]. Among nanoparticles, silver nanoparticles with features such as; electronic conductivity, high temperature stability, chemical stability, high catalytic activity, anti-bacterial properties and low cost are a suitable choice for applications in a wide range of industries [2]. Silver nanoparticles significantly enhance the peaks in optical systems, which leads to the increment of these system's efficiencies in measurement and detection of various materials. Several methods are used for synthesis of nanoparticles in different shapes and sizes [3]; laser erosion, thermal decomposition of microwave with reverse micelle sol-gel, sonochemical reduction, photochemical reduction and chemical reduction. In this study, different morphologies and sizes of silver nanoparticles, through variations in the experiment conditions, were successfully synthesized. Distribution and morphology of the particles were determined by SEM, DLS and UV-Vis tests. Catalytic properties of silver nanoparticles were evaluated in quantitative luminescence interactions. Based on the results, by reducing the size of the nanoparticles the intensities of the peaks of quantitative luminescence are increased. The best size and morphology were chosen based on the comparison of peak's intensities in quantitative luminescence system.

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**Simultaneous determination of penicillamine and adrenaline at a carbon paste electrode modified with reduced graphene oxide and Bisbenzoylacetone-ethylenediimine Cobalt (II) by using MCR-ALS approach on the square wave voltammetric signals**

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Penicillamine as a pharmaceutical of the chelator class is mainly used for the treatment of rheumatoid arthritis and mercury poisoning. <sup>[1]</sup> Also, it is classified as a chelating agent which is significant in treating some diseases such as Wilson's disease. <sup>[2]</sup> Therefore, the trace determination of this compound is very important. Adrenaline is a catecholamine which is important in the functioning of the central nervous system as well as renal, hormonal, and cardiovascular systems. <sup>[3]</sup> Due to this fact that there are many life phenomena which are related to the concentration of Adrenaline in the blood, the quantitative determination of Adrenaline in different human fluids is a significant method for making diagnoses and controlling medicines. <sup>[4]</sup>

In the present work, we prepared a carbon paste modified electrode with Bisbenzoylacetone-ethylenediimine cobalt (II) (CO (II) - BBE) and reduced graphene oxide (Co (II)/RGO/CPE) as an electrochemical sensor for electrochemically sensitive and selective detection of penicillamine in the presence of adrenaline. The results showed that Co (II)/RGO/CPE had high electrocatalytic activity for the electrooxidation of penicillamine in aqueous buffer solution (pH = 7.0). The electrocatalytic oxidation peak currents increase linearly with Penicillamine concentrations over the concentration ranges of 0.5-104.5  $\mu\text{M}$  using square wave voltammetric method. Under the optimum conditions, the detection limit for Penicillamine was obtained to be 0.168  $\mu\text{M}$ . The modified electrode was used for the determination of Penicillamine and adrenaline simultaneously in real sample. Since two materials have close oxidation peaks, the obtained square wave voltammetric (SWV) signals indicated overlap at the modified electrode. So, to solve this problem a suitable chemometric method of multivariate curve resolution based on the alternative least squares (MCR-ALS) was used. As known, MCR-ALS is useful tool for resolution of different species present in the equilibrium systems. It let us to extract the concentration profile and pure spectra in a mixture from a set of spectra with various composition. <sup>[5]</sup> Using this chemometric method led to solving the overlapping SWV signals of penicillamine and adrenaline and consequently simultaneous determination of their binary mixtures.

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**Removal of Pb(II) ions from aqueous solution using aminated magnetic graphene oxide nanoparticles**

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With the development of industry, heavy metal pollution has become a severe environment issue [1]. Hence, they are needed to remove from the environmental and biological samples. Lead ion is very harmful to most organisms due to its toxicity and carcinogenicity [2]. Therefore, it is important and necessary to separate lead ions from aqueous solutions. Adsorption is a simple, economically and fast method for removing heavy metals from various wastewaters. In recent years, graphene oxide (GO) has been used as an excellent adsorbent material due to its unique properties [3]. GO has very high surface area and a large number of carboxyl, carbonyl, hydroxyl and epoxy groups, which can be used as anchoring sites for metal ions. However, GO is difficult to separate from aqueous solution due to its hydrophilic nature in the adsorption process. The dispersion of magnetic nanomaterial on GO sheets is very important because it combines easy phase separation and advantages of high adsorption rate [4]. Ethylenediamine (EDA) is low cost, low toxicity and contains two amino groups that can form stable chelates with metal ions. Therefore, grafting ethylenediamine to GO-based materials may increase their adsorption ability. In this study, we attempted to prepare a kind of GO based composite named EDA-GO@Fe<sub>3</sub>O<sub>4</sub> (EDA-MGO) with high sorption capacity in comparison with the similar adsorbents, which can be used in wastewater treatment. The aims of this research are to: (1) synthesize and characterize magnetic adsorbent (EDA-MGO) and apply it for removing Pb(II) ions from aqueous media; (2) evaluate the effects of operational parameters on Pb(II) removal such as effect of pH, time, sorbent dose, and temperature; (3) apply kinetics and isotherm models for modelling the adsorption experiments. The results demonstrated that EDA-MGO is a rapid, regenerable and more sustainable sorbent for Pb(II) and thus a promising material for metal ion decontamination. The synthesized nanomaterial and its lead chelates were characterized by FT-IR, gravimetry, UV-Vis spectroscopy, scanning electronic microscopy (SEM) and atomic absorption spectroscopy (AAS) techniques.

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## Modification of bentonite surface with magnetite nanoparticles for removal of Reactive yellow dye from aqueous solutions

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Clay minerals are among the mostly used minerals in numerous applications. The term bentonite as an aluminium silicate compound is used in the industry for clays mostly composed of smectite group minerals. Nano-sized materials have superior physical and chemical properties due to their mesoscopic and surface effects. Recently, magnetite nanoparticles ( $\text{Fe}_3\text{O}_4$  MNPs) have been intensively investigated because of their superparamagnetic, non-toxicity, high coercivity, low Curie temperature and biocompatibility properties [1].

The present study deals with the development of an innovative cost effective bentonite adsorbent modified with  $\text{Fe}_3\text{O}_4$  MNPs for the removal of Reactive yellow anionic dye from aqueous samples. For this propose, bentonite/ $\text{Fe}_3\text{O}_4$  nanocomposites were synthesized via a co-precipitation method with addition of ammonium hydroxide to a solution of  $\text{Fe}^{2+}/\text{Fe}^{3+}$  in the presence of bentonite [2]. The structure, magnetic property and morphology of the prepared composite were investigated by Fourier transform infra-red spectroscopy (FT-IR), vibrating scanning magnetometer (VSM), X-ray diffraction (XRD) and scanning electron microscope (SEM) instruments, respectively. Experimental factors affecting the removal of Reactive yellow dye such as pH, ionic strength, adsorbent dosage and contact time were studied using orthogonal array design ( $\text{OA}_{16}$ ). Under the optimum conditions (solution pH= 8.5, NaCl concentration: 0.1 mol  $\text{L}^{-1}$ , contact time: 40 min and adsorbent dosage: 0.1 g), the removal efficiency higher than 86% was obtained. The adsorption kinetic was studied using two different concentrations of Reactive yellow (15 and 100 mg  $\text{L}^{-1}$ ) via four kinetic models including pseudo-first-order, pseudo-second-order, intra-particle diffusion and Elovich models. The data were obeyed from pseudo-second-order kinetic model ( $R^2 = 0.9997$ ,  $q_e = 24.69$  mg  $\text{g}^{-1}$ ). Also, three well-known isotherm models (Langmuir, Freundlich and Tempkin) were studied in the optimized conditions. Finally, the applicability of magnetite modified bentonite composite for removal of Reactive yellow dye from real aqueous samples was successfully investigated. The results indicated that modification of bentonite surface by magnetite generates an adsorbent with suitable adsorption capacity for removal of dyes like Reactive yellow from aqueous solutions.

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**Synthesis of magnetite graphene oxide nanocomposite for removal of  
Congo red from aqueous samples**

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Graphene is a kind of novel and interesting carbon material that has attracted remarkable attentions from both the experimental and theoretical scientific communities in recent years. In addition to being the principle component of the most carbon based nanomaterials, graphene also exhibits extraordinary properties, such as excellent mechanical, electrical, thermal, optical properties and very high specific surface area [1]. Magnetite graphene oxide ( $\text{Fe}_3\text{O}_4/\text{GO}$ ) shows very interesting properties including high stability, large surface area and strong magnetic behavior that make it suitable as a useful adsorbent for simple and rapid separation of chemicals from aqueous solutions [2].

In the present study, graphene oxide (GO) was prepared from graphite according to a modified Hummers' method by addition of  $\text{KMnO}_4$  and  $\text{H}_2\text{O}_2$  to a solution containing graphite and  $\text{H}_2\text{SO}_4$  in the presence of  $\text{NaNO}_3$  [3]. After that, the synthesized GO was used for preparation of  $\text{Fe}_3\text{O}_4/\text{GO}$  nanocomposite by addition of  $\text{Fe}^{3+}/\text{Fe}^{2+}$  solution to a 4 M ammonia solution in the presence of GO. The synthesized  $\text{Fe}_3\text{O}_4/\text{GO}$  nanocomposites were characterized by FT-IR, DRS, XRD, SEM and VSM instruments and were used for removal of Congo red dye from aqueous samples. The experimental parameters affecting the removal efficiency were optimized using Taguchi Fractional factorial design method and 100% removal efficiency was obtained at optimum conditions. In order to study the kinetic and isotherm of dye adsorption, pseudo-first-order, pseudo-second-order, intra-particle diffusion and Elovich kinetic models as well as Langmuir, Freundlich and Tempkin isotherm models were studied in optimized conditions. Langmuir isotherm ( $R^2=0.9601$ ) and pseudo-second-order ( $R^2=0.9959$ ) models were proved to be the best in describing the adsorption isotherm and kinetic, respectively. The reusability experiments show that adsorbent has a recycling capability up to twenty times. Finally, the applicability of proposed adsorbent for removal of Congo red from several aqueous real samples was investigated and satisfactory results were obtained. The results showed the synthesized  $\text{Fe}_3\text{O}_4/\text{GO}$  nanocomposite has capabilities such as easy and rapid separation from sample and high potential in removing Congo red, so, it can be introduced as an appropriate adsorbent for removal of this pollutant from water and wastewaters.

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**Green synthesis of carbon dots and then functionalization with silver nanoparticles as a turn-off probe for highly selective and sensitive detection of chlorpromazine and histidine**

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Fluorescent carbon dots (CDs) are a type of novel nanomaterial that possess good photostability and low Toxicity [1]. the preparation of fluorescent carbon dots and their applications have expanded rapidly, with new types are constantly emerging[2]

Chlorpromazine (CPZ) is one of phenothiazines with high biological importance which sensitive and accurate methods are needed to monitor it in pharmaceuticals and biological fluids [3]. In this work we develop a simple, rapid, selective and sensitive method for determination of Chlorpromazine. In this study, we developed a simple, green and one-step method to generate C-dots from inexpensive broad beans through a one-step heating reaction. The as-prepared CDs exhibit good water-solubility. Carbon dot nanoparticles were characterized by transmission electron microscopy (TEM), UV-vis spectroscopy and photoluminescence (PL) emission spectroscopy. The generated C-dots can be used as sensing probes for chlorpromazine determination. Under the optimum conditions, The fluorescent CDs probe demonstrated a wide linear range between 50 nM and 118 nM and the detection limit was 31 nM. Furthermore, chlorpromazine was determined by this method in human urine samples with satisfactory results. furthermore, the strongly fluorescent carbon dots were modified with Ag nanoparticles (CD-AgNPs). The results showed that the fluorescence of the CD-AgNPs could be quenched effectively by histidine. This was exploited to design a simple and selective method for the determination of histidine in the concentration range from 60 to 300 nM, with a detection limit of 40 nM. The method presented here is simple, rapid, inexpensive, sensitive and suitable for practical application.

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Using octadecylsilane coated iron oxide magnetic nanoparticles as adsorbent  
for removal of dicyclohexyl phthalate

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Today, magnetite nanoparticles ( $\text{Fe}_3\text{O}_4$  MNPs) are widely used in various fields such as, biomedical, drug delivery, catalysis and magnetic separations. They showed broad applications for isolation and pre-concentration of some target analytes. However, naked  $\text{Fe}_3\text{O}_4$  MNPs are very likely to be oxidized and aggregate and are not suitable for extraction or removal of chemicals. Therefore, it is necessary to protect these MNPs with proper organic or inorganic groups to improve their surface as a selective and applicable adsorbent. Normally, coating with silica is viewed to improve the stability and prevent oxidation of the  $\text{Fe}_3\text{O}_4$  MNPs [1].

In the present study, magnetic  $\text{Fe}_3\text{O}_4@SiO_2$  NPs functionalized with octadecyl groups ( $\text{Fe}_3\text{O}_4@SiO_2-C_{18}$ ) were synthesized, characterized and employed as powerful nano sorbent for removal of dicyclohexyl phthalate (DCP) from aqueous solutions. For this purpose, after chemical synthesis of  $\text{Fe}_3\text{O}_4$  NPs via co-precipitation method, a silica layer was coated on the surface of NPs to form  $\text{Fe}_3\text{O}_4@SiO_2$  NPs and subsequently, octadecyl silane groups were chemically synthesized on the  $\text{Fe}_3\text{O}_4@SiO_2$  surface using octadecyl trichlorosilane. The structure, magnetic property and morphology of the prepared NPs were investigated by FT-IR, DRS, VSM, XRD and SEM instruments. The results showed the good functionalization with a nanometric size of synthesized particles. The experimental factors affecting the DCP adsorption including solution pH, ionic strength, adsorbent dosage and contact time were studied via orthogonal array design ( $OA_{16}$ ) using 50 mL solution containing  $50 \text{ mg L}^{-1}$  DCP and optimum values were determined with UV-Vis spectrophotometer. In order to study the kinetic and isotherm of adsorption, four kinetic models (pseudo-first-order, pseudo-second-order, intra-particle diffusion and Elovich) and three well-known isotherm models (Langmuir, Freundlich and Tempkin) were studied in the optimized conditions. The results showed the high adsorption efficiency (>95 %) in a short time. Finally, the applicability of proposed adsorbent for removal of DCP from real water samples was examined and satisfactory results were obtained.

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**Rapid, Sensitive and trace analysis of Ceftriaxone using highly fluorescent carbon dots synthesized by hydrothermal method from Chicken meat, and modification of this nanoprobe with silver nanoparticles as a novel highly Sensitive “Turn-On” Fluorescent probe for morphine Sensing**

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Carbon dots (CDs) have attracted considerable attention recently because of their good stability, low cytotoxicity, high biocompatibility and flexibility in surface functionalization compared to those of organic fluorophores and semiconductor quantum dots [1-3]. Ceftriaxone (CFX) is a semi-synthetic antibacterial antibiotic that is a derivative of the third generation of cephalosporins. High-performance liquid chromatography is the method most commonly used for the determination of CFX. In this work a simple, rapid, selective and sensitive method was proposed for determining of ceftriaxone. Morphine (MRF) is a powerful narcotic analgesic and highly addictive. It is used primarily to treat both acute and chronic severe pain. It is also used for pain due to myocardial infarction and for labor pains [4].

In this report, a novel fluorescent sensing Carbon dots (CDs) was synthesised by a simple, green, and low-cost method using a one-pot hydrothermal treatment of chicken meat. The as-prepared carbon dot has exceptional advantages including high fluorescent quantum yield and satisfactory chemical stability. The synthesized CDs were characterized using various techniques as transmission electron microscopy (TEM), UV-Visible spectroscopy and photoluminescence spectroscopy. More strikingly, as-synthesized CDs generate strong response to ceftriaxone and gives rise to the fluorescence quenching. This phenomenon was used to develop a fluorescent method for facile detection of ceftriaxone with a linear range from 0.9 to 140 nM and a detection limit of  $4.4 \times 10^{-10}$  M, and further extended to measure urine samples with satisfactory recoveries. Eventually, carbon dots-modified silver nanoparticles (CDs-Ag NPs) were successfully prepared for rapid and selective determination of morphine. The CDs-AgNPs fluorescent probe illustrates a linear detection range towards morphine from 0.04  $\mu$ g/ mL to 0.40  $\mu$ g/ mL with the detection limit of 0.003  $\mu$ g/ mL. The results showed that this probe is facile, rapid and offers high sensitivity, selectivity, repeatability and sustainability.

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**Controlled gentamicin delivery via biocompatible system: mesoporous silica nano rods(MSNRs) which capped with zinc sulfide quantum dots(ZnSQDs).**

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In this project we design a controlled drug delivery system for gentamicin. Gentamicin is a widely used antibiotic for most infections and has a high potential for treating various types of infections. Because of the importance of this drug, we decide to design a green drug delivery system that is be able to get the right amount of drug at the right time to the target tissue. It has been tried to use completely green materials and biocompatible materials for the drug delivery system. The nanosized rods made from silica were selected and, after functionalized the surface of these nanorods, high-yield gentamicin was loaded. Then, loaded nano rods were capped with zinc sulfide quantum dots and release of drug studied as a function of time in stimulated buffer of human fluid body. We use of uv-vis spectrophotometry method to detect gentamicin release amount.

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**Glycine capped gold nanoparticles for detection of *Pseudomonas aeruginosa* by ELISA and UV-Vis spectrophotometry**

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*Pseudomonas aeruginosa* is a common bacterial, opportunistic and gram negative bacterium that infects people with poor immune systems and often causes hospital infections and pandemic and general infections. *Pseudomonas aeruginosa* is currently the most common and deadliest cause of death among various factors in hospital infections. *Pseudomonas* has a higher relationship with *Staphylococcus aureus* and other gram-negative bacteria than with deaths from blood-borne infections. Even a small number of these rod bacteria (about 10-100) can form colonies in the colon and cause patients with poor immune systems to develop severe illnesses. In the food experiments, the World Health Organization (WHO) has identified the concentration of *Pseudomonas aeruginosa* as an indicator of water contamination and water quality determinations. Therefore, the early diagnosis of *Pseudomonas aeruginosa* is very important [1, 2]. In this work, we have designed a novel method for the synthesis of alginate-AuNPs functionalized by glycine, in order to detect and measure *pseudomonas aeruginosa*. The AuNPs were synthesis with slowly and dropwise adding of proper amounts of borax solution into the mixture of alginate-AuCl<sub>4</sub><sup>-</sup> as the base matrix. The characteristics of the synthesized alginate-AuNPs was studied by TEM, particle size analyser and UV-Vis spectrophotometry. The effect of various parameters on the measurement of *Pseudomonas aeruginosa* such as the capping time of gold nanoparticles by glycine, Glycine consumption time and concentration was studied and optimized. The absorption spectra showed that the maximum wavelength of capped nanoparticles was 535 nm. Under the established optimum conditions, the calibration curve was linear in the range of 0.1-3.3 McFarland ( $r=0.9981$ ) with a detection limit of 0.0976 McFarland. The relative standard deviation for 0.9 and 1.5 McFarland of *Pseudomonas aeruginosa* was 4.71 and 2.11 % (7 replicate measurements). The sensing system was successfully applied for the determination of *Pseudomonas aeruginosa* in various samples. This measurement process was fast, easy and without using any toxic or harmful materials and solvent, relative to the other usual methods of *Pseudomonas aeruginosa* measurement.

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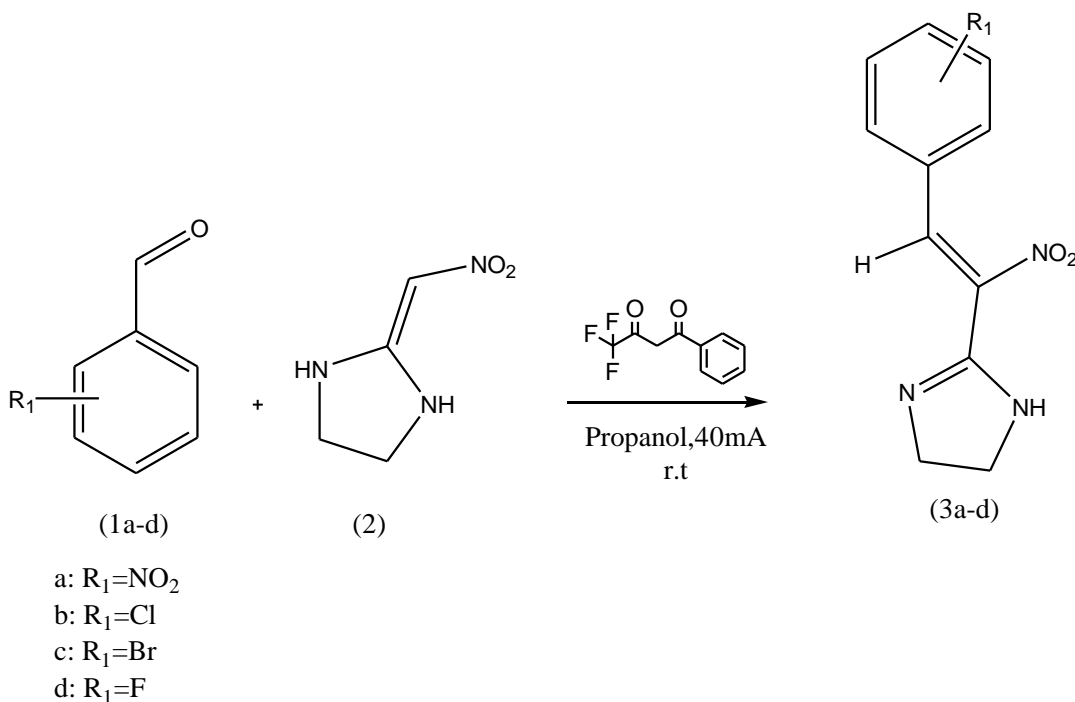
## Electro synthesis of nanosized particles of imidazole by 2-Nitromethylene-imidazolidine and aromatic aldehydes

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Nowadays electro-synthesis is used as a new green methodology for elimination of hazardous reagents, green environment applications, elimination of dangerous substances, treatment of pollutions, and atom economy. In this method, electrons act as catalysts and since electrons are clean and renewable reagents, this methodology can be used to replace toxic or dangerous oxidizing or reducing reagents [1]. In addition, size reduction of products helps to improve bioavailability, surface area or viscosity, the rate of absorption, uniform mixing and drying and also improves dissolution rate [2, 3]. Organic electro-synthesis as a new facile and green method was applied for synthesis of imidazole derivatives via Knoevenagel condensations of aromatic aldehydes and 2-Nitromethylene-imidazolidine in propanol and an undivided cell in the presence of sodium bromide as an electrolyte at room temperature. In this study the anion of 1-Benzoyl-3,3,3-trifluoroacetone which was produced by anion of propanol leads the Knoevenagel condensation.



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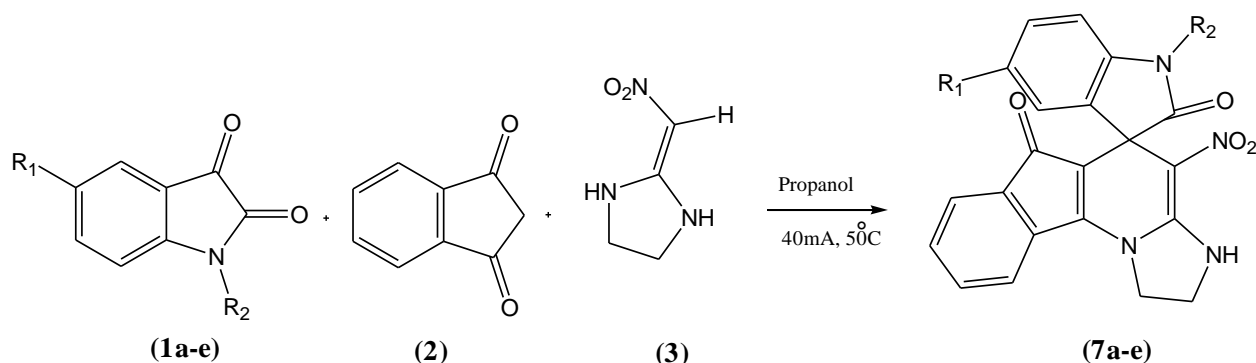
**Organic electro-synthesis as a new facile and green method for One-pot synthesis of nano size particles of dihydro pyridines derivatives via a multi component reaction**

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An electrochemical strategy is presented in order to synthesize nanoparticles of dihydro pyridines, by an electro-generated base from propanol anion in a one-pot, three-component reaction. This reaction includes the condensation of isatin derivatives, 1,3 indandione and 2-Nitromethylene-imidazolidine in an undivided cell in the presence of sodium bromide as an electrolyte at 50°C. The protocol has the advantages of easy work-up, high yields, wide application scope, and an environmentally benign procedure compared with the reported methods [1-2]. In addition, size reduction of products by this method helps to improve solubility and bioavailability, reduce toxicity, enhance release, and provide better formulation opportunities for drugs [3-4].



- a: R<sub>1</sub>=H R<sub>2</sub>=H  
 b: R<sub>1</sub>=Cl R<sub>2</sub>=H  
 c: R<sub>1</sub>=Br R<sub>2</sub>=H  
 d: R<sub>1</sub>=NO<sub>2</sub> R<sub>2</sub>=H  
 e: R<sub>1</sub>=H R<sub>2</sub>=CH<sub>2</sub>Ph

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**Determination of benzene homologues in environmental water samples by hollow-fiber liquid membrane-protected solid-phase microextraction based on Aluminum based metal-organic framework-polymer monolith fiber**

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A new rapid, simple and effective cleanup procedure is demonstrated for the determination of benzene homologues (Benzene, toluene, chlorobenzene, ethylbenzene, trimethylbenzene, styrene, and *p*-xylene) in water samples by using hollow-fiber liquid membrane-protected solid-phase microextraction (HFLM-SPME) based aluminum terephthalate metal-organic framework (MIL-53(Al)) incorporated capillary monolithic fiber and gas chromatography–flame ionization detector (GC–FID). Main aim this study is fabrication of a novel aluminum terephthalate metal-organic framework (MIL-53(Al)) incorporated capillary monolithic fiber via polymerization for the extraction of benzene homologues in water samples. In this technique, a MIL-53(Al) incorporated monolith fiber was protected with a length of porous polypropylene hollow fiber membrane which was filled with water-immiscible organic phase. Subsequently the whole device was immersed into water sample for extraction. Methacrylic acid (MAA), ethylene glycol dimethacrylate (EGDMA) and azo (bis)-iso butyronitrile (AIBN) was used as functional monomer, cross-linker and initiator respectively to prepare the MIL-53(Al) incorporated monolith fiber. The Al-MOF-polymer was characterized using fourier transform infrared (FTIR) spectroscopy, powder x-ray diffraction (XRD), scanning electron microscopy (SEM) and SEM-energy-dispersive x-ray spectroscopy (SEM-EDS) to clarify the crystalline structure retained as well as the homogeneous dispersion of Al-MOF (MIL-53) in polymer monolith. The developed Al-MOF-polymer (MIL-53) monolithic fiber was evaluated according to its extraction recovery of benzene homologues. Several parameters affecting the extraction recoveries of benzene homologues using fabricated Al-MOF polymer (MIL-53) monolithic fiber including desorption temperature and time, organic solvent, volume organic solvent, sample solution pH, ionic strength, extraction time and stirring rate were investigated and optimized. Under the optimal conditions, the method detection limits ( $S/N = 3$ ) were in the range of 0.03–0.07 ng mL<sup>-1</sup> and the limits of quantification ( $S/N = 10$ ) between 0.08 and 0.15 ng mL<sup>-1</sup>. Relative standard deviations for intra-day and inter-day precisions were 4.8–9.0% and 4.9–8.1%, respectively. Subsequently, this procedure was successfully applied with satisfactory results to the determination six benzene homologues in waters samples. The relative mean recoveries of in waters samples ranged from 92.0% to 101.0%.

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**Fabrication and characterization of magnetic metal–organic framework nanocomposites as solid-phase microextraction fibers coupled with high-performance liquid chromatography for determination of non-steroidal anti-inflammatory drugs in biological fluids and tablet formulation samples.**

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A novel solid-phase microextraction (SPME) fiber based on a glass tube coated with  $\text{Fe}_3\text{O}_4/\text{Cu}_3(\text{BTC})_2$  magnetic metal –organic formwork nanoparticle nanocomposite was prepared by sol–gel technique. The  $\text{Fe}_3\text{O}_4/\text{Cu}_3(\text{BTC})_2$  nanocomposite were synthesized by a simple hydrothermal reaction and the resultant powder was mixed with sol–gel precursors to prepare sol–gel solution of the  $\text{Fe}_3\text{O}_4/\text{Cu}_3(\text{BTC})_2$  coating material. The prepared  $\text{Fe}_3\text{O}_4/\text{Cu}_3(\text{BTC})_2$  was deposited on surface of glass tubes as new substrate with a simple method. The results revealed that this procedure was a simple and reproducible technique for the preparation of SPME fibers coated with magnetic nanoparticles. The  $\text{Fe}_3\text{O}_4/\text{Cu}_3(\text{BTC})_2$  nanocomposites was characterized using fourier transform infrared (FTIR) spectroscopy, powder x-ray diffraction (XRD) and scanning electron microscopy (SEM). Than this nanocomposite as novel solid-phase microextraction (SPME) fiber combined with high-performance liquid chromatography (SPME–HPLC) was applied for the determination and quantification of nonsteroidal anti-inflammatory drugs (NSAIDs) (nalidixic acid, diclofenac, naproxen and ibuprofen) in biological fluids including serum, plasma and human urine. To found optimum extraction condition, the influences of effective variables were investigated using one-factor-at-a-time experiments and then, the significant variables were optimized by using a Box–Behnken design (BBD) combined with desirability function. Under optimized conditions, calibration graphs of NAL, DIC, NAP and, IBU were linear in a concentration range of 0.1–400  $\mu\text{g L}^{-1}$  with correlation coefficients more than 0.9966. Limits of detection and quantification were in the ranges of 0.03–0.05  $\mu\text{g L}^{-1}$  and 0.12–0.18  $\mu\text{g L}^{-1}$ , respectively. This procedure was successfully employed in determining target analytes in spiked plasma, serum samples and human urine samples; the relative mean recoveries ranged from 94.0 to 99.0%. The new approach offers an attractive alternative for the analysis of selected drugs from biological samples, providing several advantages including fewer sample preparation steps, faster sample throughput and ease of performance compared to traditional methodologies.

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**Rank Annihilation Factor Analysis for estimating of Förster Resonance Energy Transfer (FRET) profile in hybridization studies**

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Förster resonance energy transfer (FRET) is a mechanism describing energy transfer between two light-sensitive molecules (chromophores) labeled as suitable donor or acceptor. A donor chromophore, initially in its electronic excited state, may transfer energy to an acceptor chromophore through non-radiative dipole–dipole coupling when the distance between them is close enough to energy transfer occurs. This distance dependence means that FRET data provide valuable information about the structure and conformation of bio-macromolecules and their interactions including protein-protein interactions, protein–DNA interactions, and protein conformational changes. The FRET efficiency is measured through spectral changes and used to identify interactions between the labeled complexes and hence accurate resolution of the chromophores spectral profiles is of importance. There are several ways of measuring the FRET efficiency by monitoring changes in the fluorescence emitted by the donor or the acceptor [1, 2].

In this work a new solution for accurate extraction of FRET profiles and consequently determination of FRET efficiency is proposed. Rank Annihilation Factor Analysis [3, 4] was used in two modes for eliminating the donor and acceptor pure contributions from data and accurate profile related to component (hybrid component making FRET phenomenon) retained. The efficiency of proposed method was evaluated by simulating several datasets at different degrees of spectral overlapping and in the presence of noise. The advantage of the proposed method is its simplicity toward the extraction of true FRET profiles of desired component from a complex data without need to complicated chemometrics analysis.

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**Fabrication of a modified and flexible plastic-based graphite electrode and its application for determination of some drug compounds in biological samples**

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In the recent years many efforts have been focused on the miniaturization and pliability of electrochemical systems for use in electrochemical sensors, biosensors or energy storage devices using inexpensive, inert and flexible substrates for fabrication of electrodes with desired shapes including plastic or paper [1, 2]. Carbonaceous materials like carbon nanotubes, carbon black and graphite are the most attractive choices for these applications because of the ease at which the electrode can be prepared, its stability and also good electrochemical properties of carbon including high conductance and chemical inertness which can be further modified by different modification techniques for achievement of a good and reliable electrochemical signal toward analytes [3]. There are many reports in the field of the home made plastic or paper-based electrodes for electronic, electrochemical or wearable devices [3-5].

Herein we demonstrate the fabrication of a modified graphite electrode with desired shape and size based on a non-conductive plastic substrate which can be used in various electrochemical applications. The electrode was activated using electrochemical pretreatment and some modifications were performed for achievement of high surface area and electrocatalytic activity toward analyte determination. The effects of some parameters including pH and scan rate on the electrode response were studied and optimized. The prepared electrode was used for determination of some drug components in pharmaceutical preparations and real biological samples. Linear calibration curve and low limit of detection obtained. The efficiency of method was further evaluated with recovery experiments. Results showed the suitability of prepared electrode in the fast, inexpensive and accurate electrochemical determinations.

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## A novel plastic-based graphite mesh electrode for spectroelectrochemical determination of drug substances in pharmaceutical preparations

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Spectroelectrochemistry is an old field in analytical chemistry and yet a new one as well which not only can get the information about the electrochemical behavior of an analyte, but also its spectroscopic characteristics on the modified or even unmodified transparent working electrodes including mesh electrodes or semiconductor oxides like ITO or FTO [1]. It is new because of its potential ability to combine with chemometrics for analysis of the huge amounts of obtained data with intrinsic trilinearity [2]. Various types of transparent electrodes were used and it seems that the mesh electrodes consisting of carbon materials like graphite or carbon nanotubes due to their facile preparation and modification could best comply the requirements provided that the electrode substrate itself does not participate in electrochemical reaction otherwise there will be the risk of electrode deterioration. In some cases, this will necessitate the use of inert or even non-conductive substrates for electrode fabrication like paper or plastic-based devices [3, 4].

In this study a new plastic-based transparent carbon mesh electrode was fabricated using graphite as carbon source and after electrochemical activation was modified with graphene oxide or graphene quantum dots for further electron transfer enhancements. Spectroelectrochemical studies was performed using electrochemical techniques in combination with UV-Vis spectroscopy for analysis and determination of some drug compounds in biological samples and pharmaceutical preparations with standard addition method. The effective parameters including pH and potential scan rate were investigated and optimized. The obtained three-way data were analyzed with chemometrics techniques. The accuracy of method was further ascertained by recovery experiments.

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## The 25<sup>th</sup> Iranian Seminar of Analytical Chemistry

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### Mean centering of ratio spectra for estimating of Förster resonance energy transfer (FRET) profile

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In general, "FRET" refers to situations where the donor and acceptor proteins (or "fluorophores") are of two different types. In many biological situations, however, researchers might need to examine the interactions between two or more proteins of the same type or indeed the same protein with itself, for example if the protein folds or forms part of a polymer chain of proteins or for other questions of quantification in biological cells. Obviously, spectral differences will not be the tool used to detect and measure FRET, as both the acceptor and donor proteins emit light with the same wavelengths and this leads to rank-deficiency in measured data [1-3]. There are several methods for measuring the FRET efficiency by monitoring changes in the fluorescence emitted by the donor or the acceptor with the aim of revealing the conformational changes in protein hybridizations.

In this work a new simple solution for accurate extraction of FRET profile and consequently determination of FRET efficiency is proposed. Mean centering of ratio spectra [4, 5] was used in two directions on unfolded excitation-emission data matrix obtained for different concentrations of components for eliminating the donor and acceptor pure contributions. The accurate profile related to hybrid component making FRET phenomenon retained. The method was applied on several simulated data matrices in the presence of noise with different degrees of spectral overlapping to evaluate its efficiency toward extraction of true FRET profiles. The effect of unknown interferent on the obtained responses was also tested.

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**Cobalt ferrite nanoparticles decorated on exfoliated graphene oxide, application for amperometric determination of NADH and H<sub>2</sub>O<sub>2</sub>**

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Here, cobalt ferrite nanocomposite decorated on exfoliated graphene oxide (CoFe<sub>2</sub>O<sub>4</sub>/EGO) was synthesized. The nanocomposite was characterized by different methods such as X-ray diffraction spectroscopy, scanning electron microscopy, energy dispersive X-ray diffraction microanalysis, FT-IR, Raman spectroscopy and electrochemical methods. The CoFe<sub>2</sub>O<sub>4</sub>/EGO nanocomposite was used to modify glassy carbon electrode (GCE). The voltammetric investigations showed that CoFe<sub>2</sub>O<sub>4</sub>/EGO nanocomposite has synergetic effect towards the electro-reduction of H<sub>2</sub>O<sub>2</sub> and electro-oxidation of nicotinamide adenine dinucleotide (NADH). Rotating disk chronoamperometry was used for their quantitative analysis. The calibration curves were observed in the range of 0.50 to 100.0 μmol L<sup>-1</sup> NADH and 0.9 to 900.0 μmol L<sup>-1</sup> H<sub>2</sub>O<sub>2</sub> with detections limit of 0.38 and 0.54 μmol L<sup>-1</sup>, respectively. The repeatability and reproducibility of the electrochemical sensor for NADH and H<sub>2</sub>O<sub>2</sub> analysis were studied too. The selectivity of the electrochemical sensor was investigated. The new electrochemical sensor was successfully applied for the determination of NADH and H<sub>2</sub>O<sub>2</sub> in real samples with satisfactory results.





**Simultaneous extraction and determination of carbonyl compounds in ozonated water samples via derivatization using hollow fiber liquid phase microextraction followed by gas chromatography-electron capture detection**

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Ozonation is regarded as the most popular and effective oxidation process in waste water treatment technology. Ozone reacts with natural organic substances present in water to produce a number of corresponding by-products [1]. The common by-products are short-chained carbonyl compounds such as aldehyde and ketones [2-4]. They are highly volatile and can cause severe respiratory and health-related problems [5]. The present study has centered on the development of a sensitive and reliable HF-LPME method for the GC-ECD quantification of PFBHA-oxime derivatives of selected carbonyl compounds generated following ozonation of the waste water samples. Screening and optimization of the parameters affecting the HF-LPME procedure such as temperature of solution, stirring rate, extraction time, salt addition and pH of solution was performed by a fractional factorial design and a subsequent central composite design (CCD). Under the optimal conditions (sample solution temperature, 50°; stirring rate, 1000 rpm; pH, 5; salt addition, 4% w/w; and 40 min, extraction time), limits of quantification and dynamic linear ranges of 10-25 ng/ml and 10–500 ng/ml were obtained for the studied carbonyl compounds, respectively. The relative standard deviations (RSDs %) representing the precision of the method were in the range of 4.2-13.8 based on the average of five measurements. Accuracy of the method was also tested by the relative recovery experiments on spiked samples, with results ranging from 87 to 115 %. Finally, the method proved to be simple, rapid, and cost-effective for routine screen of carbonyl compounds in highly complicated ozone-treated waste water samples.

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**Implementation of an ultrasonic assisted  $\mu$ -dispersive solid phase extraction method for the trace analysis of lead in aqueous and urine samples**

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Lead is defined as heavy metals which is generally considered to be widely distributed and abundant in environmental water samples as well as being biologically significant as a toxic substance [1,2]. Herein, an amino-tagged silica-based nano sorbent (MCM-41-NH<sub>2</sub>) was applied as a complexing agent for the effective ultrasonic assisted  $\mu$ -dispersive solid phase extraction of Pb from various water samples [3]. The sorbent was successfully synthesized and subsequently characterized by scanning electron microscopy, X-ray diffraction and Fourier-transform infrared spectrometry. The analyte was extracted by the nanosorbent through complex formation. Once the extraction of analyte was completed, the target ion was desorbed from the sorbent and detected by AAS. Various factors affecting the extraction and desorption of the analytes were investigated in detail and the optimum conditions established. Under the optimum conditions, the calibration curves were linear over the concentration range of 1-25 ng/mL, and based on a signal-to-noise ratio of 3 (S/N = 3), the limits of detection were determined to be 0.5 ng/mL for the analyte. To test the extraction efficiency, the method was applied to various real fortified water and urine samples. The average relative recoveries obtained from the fortified real samples varied in the range of 90-112% with relative standard deviations of 4.9-8.8%.

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**Dispersive solid-phase extraction of selected nitrophenols from environmental water samples using a MOF-based nanosorbent**

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Metal-organic frameworks (MOFs) are a class of porous materials with great potentials in separation via extraction [1, 2]. Amongst the common extraction techniques, dispersive solid-phase extraction (d-SPE) as a rapid and simple technique has gained a great deal of interests in analysis of environmental samples [3, 4]. This study has centered on the establishment of an efficient and reliable analytical extraction method leading to an accurate trace determination of a class of compounds with high toxicity and extremely slow degradability, namely nitrophenols. In addition, an efficient extraction followed by determination of nitrophenols at trace level in environmental samples is of great importance for raising public health awareness and prevention of compounds-related human diseases. The above objectives was achieved via a four-stage route as follows: First, the synthesis a proper nano-adsorbent (UiO-66-NH<sub>2</sub>, metal-organic framework) through a number of chemical reactions. Second, the structure confirmation of the as-prepared sorbent using X-ray based analytical instruments was made. Third, the optimization of the dispersive solid phase extraction process for finding out the optimal extraction conditions was performed. Finally, the validation of the method of analysis followed by the implication of the method for analysis of the targets in real environmental samples including waste water, surface water was made. Under the optimal extraction conditions, the calibration curves for the analytes were linear over the concentration range of 1-250 ng/L. The accuracy of the method was tested by the relative recovery experiments on the fortified real samples with the results falling within the range of 90 to 116 %, while the corresponding precisions varied in the span of 3.9-12.5%. Based on a signal-to-noise ratio of 3 (S/N=3), the method detection limits were determined for the target analytes.

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**Trace measurement of Hg(II) levels in aquatic environment using an imido-based nanomagnetic sorbent**

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Hg(II) has been regarded as one of the most hazardous substances because it may cause several health problems in humans and environmental samples [1, 2]. Therefore, an efficient extraction method leading to the determination of Hg(II) levels in various seems to be vital [3, 4]. In this research work, a nanomagnetic imide-based sorbent was synthesized through an imide-formation reaction and subsequently used as magnetic solid phase extracting agent for AAS measurement of Hg(II) concentration in several aquatic samples. It is noted that the nanosorbent was previously characterized by scanning electron microscopy, energy dispersive X-ray, X-ray diffraction and Fourier transform Infra-red techniques. Various factors affecting the sorption and desorption of the target ion were investigated and the optimized conditions were then applied for the trace detection of Hg(II). The calibration curve was linear over the concentration range of 0.5-25  $\mu\text{g L}^{-1}$ . The obtained assay accuracy in real sample analysis was in the range of 85-112%, while the precision varied in the range of 3.9-7.8%. Finally, the introduced method was successfully applied for the determination of low levels of Hg(II) in various real samples such as river, well and tap water.

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**Ultrasonic assisted dispersive micro-solid phase extraction based on modified magnetic-MCM-41 as a new extraction method for removal and trace detection of nickel ions in food and water samples**

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Due to carcinogenicity of the nickel, International Agency for Research on Cancer (IARC) classified nickel as a definite human carcinogen [1]. Nickel level in tap water is generally under 10.0 µg L<sup>-1</sup> [2]. The UK drinking water threshold for nickel is 20.0 µg L<sup>-1</sup> [3].

Advance instrumental techniques such as ICP-MS, ICP-AES, AAS, etc. [4], has been widely applied for measuring heavy metals at trace levels in different matrices. However, the major difficulties with the mentioned methods are small amount of targets concentration and matrices effect [5]. Sample preparation step before analyzing the targets is necessary to overcome the mentioned troubles. Applying various nanosorbents in dispersive micro solid-phase extraction (D-µSPE) procedure is becoming more popular due to its many advantages, e.g. rapid interaction of nanomaterial and target ions, and the shorter time necessary for sample preparation rather than classical solid-phase extraction (SPE).

Ultrasonic assisted dispersive micro-solid phase extraction with a new magnetic material using pyridine functionalized magnetic nanoporous sorbent was utilized for trace detection of nickel ions. Magnetized nanoporous silica (MCM-41) was modified with pyridine groups and the structured of prepared magnetic nanoporous sorbent was confirmed using Fourier transformed infra-red Spectroscopy (FTIR), X-ray diffraction analysis (XRD), thermogravimetric and differential thermal analysis (TGA/DTA) and transmission electron microscopy (TEM). Pre-concentrated nickel using the mentioned sample preparation procedure was monitored by graphite furnace atomic absorption spectrometry at ng L<sup>-1</sup> concentrations. Relative standard deviation and method detection limit for nickel monitoring under optimized conditions by UA-D-µSPE was found to be < 6 % and 0.008 µg L<sup>-1</sup>, respectively.

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## The effects Ni /Pt functionalized on the electrical behavior of the (6,0) zigzag GaNNTs: A NMR study

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In this research the effects of Ni and Pt atoms functionalized on the structural, electrical and optical behaviour of the (6,0) zigzag Gallium nitride nanotube (GaNNTs) are investigated by using density functional theory at the B3LYP/lanl2dz level of theory. At the first step, the structures of GaNNTs & Ni(Ga), GaNNTs&Ni(N), GaNNTs& Pt(Ga) and GaNNTs& Pt(N) are optimized, and then the structural, quantum and nuclear magnetic resonance parameters of system are calculated by using above level of theory. The chemical shielding tensors in principal axes system (PAS) are converted to measurable NMR parameters, chemical shielding isotropic (CSI) and chemical shielding anisotropic (CSA) by Eqs 1 and 2[1-3].

$$CSA(ppm) = \sigma_{33} - (\sigma_{11} + \sigma_{22}) / 2 \quad (1)$$

$$CSI(ppm) = (\sigma_{11} + \sigma_{22} + \sigma_{33}) / 3 \quad (2)$$

The calculated results demonstrate that with functionalizing Ni and Pt atoms on the surface of Ga and N atoms of nanotube the structural, electrical and optical parameters of nanotube alter significantly from original state. On the other hand with functionalizing Ni and Pt atoms the CSI values of Ga and N atoms increased significantly from original values, and so the electron charges around nanotube increased due to donor electron effect of Ni and Pt atoms. This result confirms that the activity and conductivity of nanotube increase. The quantum parameters such global hardness and gap energy of system decrease. The calculated results confirm that the Ni&Pt functionalized GaNNTs can be used as electrical detector and sensor.

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**Application of an inorganic-organic hybrid material as the efficient electrochemical sensor for ultra-trace detection of cadmium ions**

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In recent years, the pollution of natural water by the release of heavy metals has attracted great consideration because of high pernicious and bioaccumulation factor in the food samples [1]. Cadmium, as one of the highly toxic heavy metal, has become widespread as an outcome of many industrial and agricultural applications [2]. Cadmium has been identified as a harmful environmental contaminant known to generate highly toxic effects on different organs and systems of animals and humans [3]. The maximum contaminant level (MCL) permissible by the American Environmental Protection Agency (USEPA) in drinking water is 10  $\mu\text{g L}^{-1}$  to enable sample protection of human health [4]. According to the increasing use of cadmium in the industrial and its serious hazardous effects on human health, wide studies have been carried out on the development of methods for determination of Cd(II). Therefore, it is desired to design selective, simple, eco-friendly and efficient methods for the monitoring of Cd(II) in environmental and biological samples [5].

In the present work modified siliceous mesocellular foam with dithizone was used as a sensitive electrochemical sensor for ultra-trace detection of Cd<sup>2+</sup> ions in environmental water samples. The present material used as the electrode material was characterized by scanning electron microscopy, Fourier transform infrared spectrometry, nitrogen adsorption-desorption examination, thermal evaluation and elemental analysis. The introduced modified electrode combined with differential pulse anodic stripping voltammetry was used as the simple and applicable electrochemical method for ultra-trace detection of Cd<sup>2+</sup> ions. The strong interaction of cadmium ions with active sites of dithizone in the porous of prepared electrochemical material and its reduced at a negative potential (-0.9 V) was applied for preconcentration of target on the electrode surface. For analysis of target ions at ultra-trace levels, the reduced cadmium ions were oxidized by differential pulse anodic stripping voltammetry.

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**Reduced graphene oxide stabilized copper nanoparticles for electrochemical sensing of acyclovir using rosemary extract**

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In this work, in situ green synthesis of reduced graphene oxide decorated copper nanoparticles (RGO-CuNPs) and copper nanoparticles (Cu NPs) was done via the reduction of aqueous  $\text{Cu}^{2+}$  of Cu (0) by using rosemary leaf extract. The use of rosemary leaf extract is economic, easy access and friendly environment. Flavonoids in rosemary leaves work as a reducing and fixing agent. X-ray diffraction (XRD), Fourier transformed infrared (FT-IR) spectroscopy, Scanning electron microscopy (SEM), and Transmission electron microscopy (TEM) were used for characterizing of the morphology and structure of the Cu NPs and Cu/RGO nanocomposite. Also, the synthesized Cu NPs and Cu/ RGO nanocomposite were successfully used to modification of a carbon paste electrode. Two methods for surveying of the oxidation reaction were cyclic voltammetry and chronoamperometry. The altered electrode showed high catalytic activity toward electro-oxidation of the acyclovir with a cyclic mediation electron-transfer process. The electrocatalytic activity of the Cu/ RGO- CPE was greater than that of the Cu – CPE. This is mainly due to the really large surface area and higher electrical and ionic conductivity of Cu/ RGO. The amperometric procedure was successfully progressed for the determination of the catalytic rate constant and diffusion coefficient of the acyclovir. The rate constant of the electrocatalytic oxidation of acyclovir was  $1.8 \pm 0.03 \times 10^5 \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  and the electron-transfer coefficient was  $4 \pm 0.05 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ . Furthermore, the synthesized Cu NPs and Cu/ RGO nanocomposite by this way are completely durable and can be guarded below an inert atmosphere for too many months.





## In-tube liquid phase microextraction; a novel sample preparation technique

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Clean-up and preconcentration of samples are spent more than 80% of analysis time and significant amount of the target analytes can be lost during these steps and lead to noticeable errors in the final result. So sample preparation is a critical part in most analytical procedures [1]. Application of microextraction methods in determination of analytes is more common [2, 3].

In this study, a new sample preparation technique named in-tube liquid phase microextraction (IT-LPME) has been reported. In this method an injection port of high performance liquid chromatography (HPLC) and a stainless steel tube (like a loop of injection port of HPLC; volume about 20  $\mu\text{L}$ ) are used. When the injection port is in the load state, sodium hydroxide solution (0.2 M) is passed through the stainless steel tube. Then 1 mL of an organic solvent (e.g. n-hexane) containing ionisable compounds (previously extracted from 10 mL acidic aqueous sample) is passed through the tube. In this step, a thin layer of aqueous solution of sodium hydroxide is remained (adsorbed) onto the inner wall (inner surface) of stainless steel tube. So the ionisable compounds are back-extracted into the aqueous layer. The injection port is changed to the inject state and the extracted compounds enter into the HPLC column by mobile phase for further separation and determination.

The performance of IT-LPME is illustrated by the extraction of some anti-inflammatory drugs (naproxen, diclofenac, and ibuprofen) in water as model compounds. Some important parameters such as the material, length, internal diameter and volume of the tube, concentration and volume of sodium hydroxide solution, type and volume of organic solvent, etc. were investigated. Under the optimum extraction conditions the enrichment factors were 57, 168, and 200 for naproxen, diclofenac, and ibuprofen, respectively. The linear ranges of the calibration curves were 1-500  $\mu\text{g L}^{-1}$  for naproxen and diclofenac, and 20-10000  $\mu\text{g L}^{-1}$  for ibuprofen. The detection limits were 0.3, 0.2, and 5  $\mu\text{g L}^{-1}$  for naproxen, diclofenac, and ibuprofen, respectively. The overall extraction time was about 5 minutes. This technique is simple, fast, low cost, having high enrichment factors, and needs low sample volume. Also it is available to all laboratories even with low facilities.

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**A novel ultra-sensitive neural stem cells -based biosensor for subattomolar potentiometric detection of mercury ions using array system**

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In this study for the first time the direct potentiometric detectability of mercury ions with detection limit as aM ( $10^{-18}$  M) concentrations without any preconcentration, any analyte recycling, or electrocatalytic signal enhancement will be studied in detail [1]. To reach this aim, a programmed switching system will be combined with an array of potentiometric sensors consisting of fifteen potentiometric sensors is connected immediately to a pH/potentiometer and a data processor (PC) to sequentially acquire the potential corresponding to water sample mixtures [2]. The acquired potentials are recorded and saved on the PC and will be as input variables for the sub aM concentration of Hg<sup>2+</sup>, in elementary and complex mixtures. Selectivity for a certain ion selective sensor is greatly related to the ionophore used. Due to the existence of sulfur donor atoms in stem cells biosensor, which is a soft base, in the structure of different proteins of stem cells, its interaction with some mercury ions was studied in aqueous solution. The results showed that neural stem cells have special interaction with Hg<sup>2+</sup> ions. For this purpose, effect of some ion blockers such as calcium blocker seems to be an important probe for evaluation of probable the mechanism during selective mercury detection and determination [3].

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**Application of a novel layered by layered graphenized graphite/ Graphene oxide@polyaniline nanocomposite coating for solid phase microextraction of Organophosphorus pesticides from food and environmental samples**

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An in situ facile layered by layered graphenized graphite/ Graphene oxide@polyaniline nanocomposite (GG/PANI@GO) coating for solid phase microextraction (SPME) was proven successfully by electrochemical methods for determination of some Organophosphorus pesticides (OPPs) in food and environmental samples. The SPME is a simple, fast, sensitive, solventless, easy automation and cost-effective sample preparation technique which combine sample clean-up, extraction, pre-concentration and sample introduction into one step [1]. An ideal fiber for SPME application should have some general properties including: high adsorptive capacity, good thermal, mechanical and chemical stability, low cost, reproducibility and ease in preparation and finally, the ability to extract various classes of compounds with different polarities [2]. Conducting polymers are multifunctional materials with various interesting properties. The electrochemical synthesis of conductive polymers offers high purity, uniformity of deposits, good control of the film thickness, and rate of deposition and oxidation state of the polymer by controlling the electrochemical conditions [3]. In this study a fiber coated with a layered by layered graphenized graphite/ Graphene oxide@ polyaniline nanocomposite (GG/PANI@GO) using electrochemical methods were applied for extraction of the OPPs, as the model analytes. Organophosphorus pesticides have been increasingly used to control pests and prevent diseases that affect various crops, such as fruits, vegetables and cereals. Many of these compounds are highly toxic and pose Significant negative risks to human health and the environment. Therefore, in order to ensure environmental and health safety, it is necessary to develop effective methods to monitor OPP residues in the environment and food [4]. The new studied fiber have large specific area, high chemical stability, good extraction efficiency and low cost. Six important parameters, affecting the extraction efficiency of OPPs, including: adsorption and desorption times, extraction solvent, pH, stirring rate and salt content of the sample were evaluated. Under experimental optimized conditions, the calibration curves are linear ( $R^2 \geq 0.995$ ) and the limit of detection(S/N=3) were  $\leq 1 \mu\text{g L}^{-1}$  for different OPPs. The applicability of the proposed method was evaluated by the extraction and determination of OPPs from several food and environmental samples.

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**Magnetic Fe<sub>3</sub>O<sub>4</sub>–chitosan nanoparticles as a new sorbent for removal of Carmoisine from aqueous solutions**

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The current study aims at investigating the potential of magnetic chitosan nanoparticles (CS@Fe<sub>3</sub>O<sub>4</sub>) cross-linked by sodium tripolyphosphate (STPP) for the removal of Carmoisine from aqueous solutions. The prepared CS@Fe<sub>3</sub>O<sub>4</sub> was further characterized upon their physicochemical properties using SEM, EDX, FT-IR, vibrating sample magnetometer (VSM) and Zeta potential.

Magnetic nanoparticles (MNP) have been opened up an entirely new field of application according to their specific properties (non-toxicity, nano sizes, etc.) in environmental and biomedical sciences. In comparison with many other polymers, the chitosan backbone contains a number of free amine groups, which allow binding of many agents [1, 2]. Carmoisine, an acidic azo dye, was used as a model to investigate the adsorption properties of CS@Fe<sub>3</sub>O<sub>4</sub> nanoparticle sorbent. Batch adsorption studies were carried out and the effect of experimental parameters such as pH, initial concentration, sorbent dosage, exposure time, and temperature on uptake of Carmoisine dye were investigated. Dye concentrations in the supernatant solutions were measured using a UV-Vis spectrophotometer. Complete removal was observed when a dye solution with the initial concentration of 50 mg.L<sup>-1</sup> was treated by 8 mg of the used adsorbent at pH value of 4 at 298K. The adsorption of Carmoisine on studied MNP at different temperatures was studied as a function of contact time (5–40min) in order to determine the equilibrium time; experiments were conducted at 298, 303, and 313K in an isothermal water bath shaker with initial dye concentration of 40 mg/L. The results indicated that the contact time is needed for dye solution with initial concentration of 40 mg/L to reach equilibrium was 30 min. Carmoisine adsorption isotherms carried out at 298K and equilibrium isotherm data were fitted to Langmuir and Freundlich equations and constants of isotherm equations were determined. Furthermore, pseudo-first and second-order kinetic models were also used to analyze adsorption kinetics [3].

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## Synthesis of Mg/Ag orthophosphate and its application in photocatalytic degradation of methylene blue and bisphenol A

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These days one of the most important problems in cleaning waste water up is degrading carcinogen compounds like bisphenol A. However, Silver Orthophosphate (SO) is one of the best active semiconductors in photocatalytic degradation of pollutant; it's still a little use due to the high price of silver [1]. In this research, was synthesized new composition of SO with magnesium, which has high photocatalytic activity and low cost, by co-precipitation method [2]. This composition was tested in degradation of methylene blue and bisphenol A. Methylene blue degraded above 90% in 60 minutes and bisphenol A degraded above 70% in 140 minutes.

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## Electrochemical behavior hydrazine at a modified glassy carbon electrode by pyrazole derivative

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Hydrazine is the simplest diamine, a highly reactive base, and a reducing agent. Hydrazine and its derivatives are broadly utilized in applications including fuel cells, catalysts, blowing agents, corrosion inhibitors, antioxidants, pharmaceutical intermediates, pesticides, plant-growth regulators, and dyes in addition to their use as starting materials in the synthesis of some insecticides and photography materials [1]. Moreover, hydrazine is a high energy molecule which can be used as a fuel in explosives and rocket propulsion systems [2]. Despite the widespread use of hydrazine and its derivatives in various fields, they are highly toxic and their exposure to human could cause a serious damage to the central nervous system, liver, lungs and kidneys [3]. Therefore, simple, sensitive and selective monitoring of hydrazine and its derivatives is a vital of interest in different industries [4].

In this paper, pyrazole derivative (P), was prepared and used to modification of glassy carbon electrode (GCE) to determination of hydrazine. The voltammetric oxidation of hydrazine was investigated at a P/GCE electrode using cyclic voltammetry (CV), differential pulse voltammetry (DPV), chronoamperometry (CA) and electrochemical impedance spectroscopy (EIS). The oxidation process was irreversible over the pH range studied (pH 4-11) and exhibited a diffusion-controlled behavior. In the range of  $0.5 \times 10^{-6}$  to  $1.6 \times 10^{-3}$  M, the current measured by differential pulse voltammetry presents a good linear property as a function of the concentration of hydrazine with a detection limit of 75 nM with good selectivity and sensitivity. The modified electrode showed good stability and repeatability.

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**Fluorimetric Determination of Ibuprofen in Real Samples by a New Two liquid-phase Microextraction Method**

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Ibuprofen (IBU) is one of the most frequently administered nonsteroidal analgesic, antipyretic, and anti-inflammatory drugs (NSAIDs) with properties mainly used for suppressing inflammatory processes, treating allergies and reducing pain [1]. It is applied orally, rectally or by injection and to a large degree also dermally as an ointment. In recent years, ibuprofen and the other NSAIDs have also been found as environmental contaminants in sewage, surface, ground, and drinking water samples [2-4]. Heberer and Reddersen reported amounts of these drugs in environmental water samples up to  $\mu\text{g L}^{-1}$  [2]. Considering that these substances are present in the environment at trace concentrations and in complex matrices, suitable preparation techniques need to be applied to the samples in order to isolate and preconcentrate the analytes prior to their determination [4]. In the present research, a new, speed, inexpensive and very simple preconcentration and sample preparation method based on two liquid-phase microextraction was used for the extraction of trace amounts of ibuprofen from real water and biological hair samples prior to spectrofluorometer. The proposed modified extraction method was used in this work is based on filtration of a non-homogeneous mixed solution of an aqueous sample and the organic extraction solvent with the ordinary filter papers. On the other hand, by using an innovative simple method, the internal volume of the quartz microcell was decreased and so, the used volume of the organic extraction solvent reduced as much as possible. The parameters influencing the extraction efficiencies including kind of the extracting solvent, microextraction time, the volume of the aqueous sample solution (donor phase), the volume of extraction solvent (acceptor phase), the stirring speed, the effects of pH and salt were optimized in this modified method. Under the optimal conditions, the obtained enrichment factor is above 80. By plotting fluorescence emission of the standard solutions versus various concentrations of the analyte, calibration curve is obtained which show that the linear ranges of  $0.0007\text{-}1.5 \mu\text{g mL}^{-1}$  with correlation coefficient ( $r$ ) of 0.9945 for ibuprofen. The precision of the method was calculated as relative standard deviation (RSD %,  $n=5$ ) in three different concentrations and were 5.8. The limit of detection (LOD) and also, the the limit of quantitation (LOQ) were calculated theoretically and the obtained values were 0.0002 and  $0.0007 \mu\text{g mL}^{-1}$ , respectively. Finally, the proposed microextraction method was used for the extraction of the analyte from environmental water and biological samples and the calculated relative recoveries were all above than % 85.

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The 25<sup>th</sup> Iranian Seminar of Analytical Chemistry

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**Comparison of Directly Suspended Drop Microextraction with Dispersive Liquid-liquid Microextraction Method for Extraction of an Antidepressant Drug in Biological Samples Prior to UV-Vis Spectrophotometer**

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Depression is one of the serious global economic problems because the patients often lose the ability of working. In addition, depression may ultimately result in suicide [1]. The depression treatment includes various forms of psychotherapy as well as pharmacotherapy with antidepressant drugs. Tricyclic antidepressants (TCAs) are a group of important drugs that are widely used for the treatment of this psychiatric disorder. Sometimes, they are encountered for emergency toxicology screening, forensic medical examinations and drug-abuse testing [2-4]. Due to the complexity of biological samples, the sample pretreatment process has become the bottleneck in method development and sample analysis in many cases [5]. The main aim of this research is using two different preconcentration and sample preparation methods: directly suspended drop microextraction and air-dispersed liquid-liquid microextraction methods which are coupled with UV-Vis spectrophotometer for the analysis of doxepin in biological samples. Several important parameters which influence the extraction efficiencies of these two microextraction methods, such as kind of the extracting solvent, volume of the aqueous sample solution (donor phase), volume of the organic extraction solvent (acceptor phase), pH of the donor phase, salt effect, extraction time, stirring rate and number of the air injection were investigated. Under the optimal conditions the enrichment factors were above than 30. The linearity of the methods has been investigated between the ranges of 0.005-1.5 and 0.003-1  $\mu\text{g mL}^{-1}$ . The precisions of two methods which are based on the average relative standard deviations are lower than 6, for three different concentrations of the analyte. Finally, the proposed methods were applied for the determination of doxepin in biological samples including urine and human plasma under the optimal conditions and the reasonable relative recoveries were obtained which are above 88%.

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## The 25<sup>th</sup> Iranian Seminar of Analytical Chemistry

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### Detection and determination of Zn (II) and Copper (II) cations by an effective solid phase extraction method (SPE) coupled by flame atomic absorption spectroscopy (FAAS) using dissolvable (nitrile acetic acid-nickel)-layered double hydroxide

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Zn (II) cation ( $Zn^{2+}$ ) and Copper (II) cation ( $Cu^{2+}$ ), the required micro nutrient elements for organisms, plays an essential role in many biological processes, including oxygen transport, Enzyme catalysis, DNA and RNA synthesis, as well as cellular metabolism [1-3].

In this work, a simple, rapid and efficient method has been developed for extraction, and preconcentration of copper and iron ions in water samples by solid phase extraction coupled with flame atomic absorption spectrometry (FAAS). The metallic ions in the aqueous were complexed with nitriloaceticacid-nickel-layered double hydroxide (NTA-Ni-LDH) [4]. NTA-Ni-LDH was successfully synthesized and characterized and then used as dis-solvable sorbent in dispersive solid-phase extraction to pre-concentrate and separate  $Cu^{2+}$  and  $Fe^{3+}$  from aqueous phase due to the larger formation constant with NTA compared to  $Ni^{2+}$ .

The individual and interactive effect of process variables (pH, salt effect, extraction time, extraction temperature and absorbent amount) on the simultaneous extraction of cations were studied. The results showed that, temperature, pH, absorbent amount and time have significant effect on the extraction efficiency of copper and iron simultaneously. The experimentally obtained data were analyzed by analysis of variance (ANOVA) and second-order polynomial models. The developed models were predictive and good with high coefficient of determination ( $R^2$ ) values (more than 0.95). An optimization study using Derringer's desired function methodology [5] was performed and the optimal extraction conditions were found to be extraction temperature of 35°C, time of 30 min, adsorbent dosage of 3 mg, 0% (w/v) salt effect and pH of 6.5.

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**Investigation of Fe@Fe<sub>2</sub>O<sub>3</sub> /three dimensional graphene composite as cathode electrode for the electrochemical removal of organic compounds from contaminated water**

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One of the main current worldwide concerns is the growth of water pollution by organic compounds arising from many industrial, agricultural and urban human activities. A large variety of electrochemical advanced oxidation processes (EAOPs) have been recently developed to remove organic pollutants from wastewaters [1]. Nowadays, research on advanced oxidation processes (AOPs) have become a hot topic. These technologies have been shown to be able to oxidize efficiently most organic pollutants until mineralization to inorganic carbon (CO<sub>2</sub>) [2]. Graphene is the most recent member of the family of multi-dimensional graft carbon material [3]. Materials based on graphene and graphene oxide have a two-dimensional structure. For this reason, despite having a high surface area, they still cannot have high efficiencies for different processes [4]. In the present study, a 3D graphene loaded with Fe@Fe<sub>2</sub>O<sub>3</sub> (Fe@Fe<sub>2</sub>O<sub>3</sub>/3D-GO) core-nanowires was used as a cathode electrode in the electro-Fenton process. In the first step, 3D graphene was prepared by graphene oxide using a hydrothermal method with an improved Hummers method. Then it was transformed into a three-dimensional graphene composite Fe@Fe<sub>2</sub>O<sub>3</sub>, and properties of the composite were characterized by XRD, FT-IR, BET and SEM analysis. The amount of electrogenerated H<sub>2</sub>O<sub>2</sub> on the surface of this electrode was investigated, too. The performance of the prepared cathode electrode was studied using LSV and CV analyzes. The effect of operational parameters such as applied current, initial pH and initial pollutant concentration were studied in an attempt to reach higher degradation efficiency.

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## Solid-phase microextraction of PAHs from water samples using mesoporous carbon nitride coating

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Solid-phase microextraction (SPME) has been widely applied in environmental, food, clinical and biological analysis since the pioneering work of Pawliszyn and Arthur in the early 1990s [1]. This technique is a solvent-free and green equilibrium-based sample pretreatment method that integrates sampling, isolation and enrichment into one step. The extraction ability of SPME is primarily determined by the nature of the sorbent coated on the fiber. Therefore, the development of novel coatings is a key focus for current research on SPME [2]. Carbon-based nano materials have been used to form a sorption layer on SPME fibers. Their affinity for relatively strong sorption of organic pollutants, combined with other properties (very large specific surface, durability, chemical and thermal stability), make them promising options that can be applied in SPME as adsorbents. Fullerenes, carbon nanotubes (CNTs), graphene, ordered mesoporous carbon (OMC) and their functionalized forms are good SPME coatings [3].

Carbon nitrides (CNs) are fascinating materials with unique properties including semi-conductivity, high hardness, chemical robustness and high chemical, thermal and mechanical stability. These properties make it popular in many fields, such as water splitting, sensor, and NO decomposition and hydrogenation reactions [4]. The in-built N-rich functional groups and electronic delocalization properties endow graphitic carbon nitride (g-CN) with complex sorption mechanism, containing complexation, hydrogen bond, redox reaction,  $\pi$ - $\pi$  conjugation, hydrophobic effect, acid-base reaction and electrostatic interaction [5].

Herein, an MCN with a highly ordered mesoporous structure and a very large Brunauer-Emmett-Teller (BET) surface area ( $503 \text{ m}^2 \text{ g}^{-1}$ ) has been coated on the surface of stainless steel wire to prepare highly sensitive SPME fiber. The SPME-GC-MS method showed low detection limit ( $0.2 \text{ ng L}^{-1}$  to  $2 \text{ ng L}^{-1}$ ), wide linear range ( $2 \text{ ng L}^{-1}$  to  $2000 \text{ ng L}^{-1}$ ) and good recoveries in extraction and determination of PAHs in real water samples. The relative standard deviations (RSDs) for the six replicated tests using a single fiber ranged from 3.2% to 7.1%. The fiber to fiber reproducibility for three parallel fibers ranged from 5.4% to 9.7%

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## Synthesis of Samarium Molybdate Nanoplates and its application in construction of Electrochemical Sensors based Graphene Quantum Dots for Catecholamine drugs determination

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Levodopa (LD) is one of the commonly prescribed medications used in combination with other medications in Parkinson disease. Carbidopa (CD) and Entacapone (EN) together with levodopa causes a longer effect of levodopa in the brain<sup>[1]</sup>. LD, as one of the catecholamines is the intermediate precursor of the neurotransmitter dopamine. Unlike dopamine, LD easily enters the central nervous system<sup>[2]</sup>. In this work, due to the importance of these drugs, a novel modified nanocomposite electrode based on Sm<sub>2</sub>(MoO<sub>4</sub>)<sub>3</sub> nanoplates and Graphene Quantum Dots (GQDs) was introduced for determination of LD and CD. A facile one pot precipitation method was used for the preparation of the used nanomaterials. The synthesized nanoplates were characterized through FT-IR, XRD, EDX, FESEM and Zeta potential technique, also the highly conductive synthesized GQDs were characterized through TEM. Next, Sm<sub>2</sub>(MoO<sub>4</sub>)<sub>3</sub> nanoplates was used as modifier in a carbon paste electrode (CPE). The characterization of modified electrodes accomplished by FESEM, EDX and EIS. Then the surface of the modified CPE was coated by GQDs in a drop wise manner. Finally, the electrode was used as an electrochemical sensor in determination of LD and CD by Differential pulse voltammetry technique. The possibility of analyzing LD and CD, separately and simultaneously is investigated. Electrochemical tests showed that because of unique properties of GQDs, such as large surface area, facile electronic transport and high electrocatalytic activity and synergic effect between GQDs and Sm<sub>2</sub>(MoO<sub>4</sub>)<sub>3</sub> nanoplates, the final modified electrode exhibited highly enhanced electrochemical performance of LD electrooxidation in comparison with the modified electrode just by Sm<sub>2</sub>(MoO<sub>4</sub>)<sub>3</sub> nanoplates. It showed an excellent electrocatalytic activity toward LD with a lower overvoltage. This sensor is sensitive for the determination of LD through electrooxidation of phenolic functional group in a supporting electrolyte 0.1 M PBS solution (pH 6.5) while has no sensitivity to determine the amount of CD. The primary fabricated electrode modified with Sm<sub>2</sub>(MoO<sub>4</sub>)<sub>3</sub> nanoplates was also evaluated for the simultaneous determination of LD and CD in a supporting electrolyte 0.1 M PBS solution (pH 9.0 and pH 3.0 respectively). Under the selective conditions, the detection limit of proposed modified electrode was 0.02 nM for LD (LOQ = 0.08 nM) and detection limit of primary modified electrode was 0.05 nM for CD (LOQ = 0.15 nM) based on S/N = 3. The linear dynamic range of determinations were as follows: 1 × 10<sup>-4</sup>–1 × 10<sup>3</sup> μM for LD and 1 × 10<sup>-4</sup>–1 × 10<sup>2</sup> μM for CD. Also in determination of CD, EN does not interfere. For evaluating the validity of the suggested method, human plasma samples were analyzed and it is potential for use in clinical research. Reproducibility, stability, low detection limits, wide dynamic linear ranges and long life-time are some of the advantages of the recommended sensor in this investigation.

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**Ultrathin nanosheets of Ni-Co-Fe layered double hydroxide as a novel binder-free electrode for fabrication of a high-energy and flexible asymmetric supercapacitor and water splitting**

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Discovering efficient energy conversion and storage technologies has become one of the grand challenges in an era where energy plays an essential role in our everyday lives. The demand for renewable and clean energy from the sun and the wind is rapidly increasing. However, their intermittent nature necessitates the development of efficient energy storage devices that can deliver energy at any time and place.[1] Batteries and supercapacitors are the two major energy storage devices, and the direct storage of solar energy into the chemical bonds ( $H_2 + O_2$ ) is another potential solution. Supercapacitors with high power density, superior rate capability, rapid charging/discharging rate, long cycle life (>100,000 cycles), and low maintenance costs have attracted a great deal of attention from both industry and academia.[2,3] On the other hand, the electrochemical splitting of water into hydrogen and oxygen is one of the most promising approaches for converting the energy harvested from renewable sources into clean fuels.[4] Therefore, the development of multifunctional energy harvesting and storage devices in which supercapacitive energy storage and electro-catalytic water splitting are integrated into a single device is of considerable interest.

In this study we propose a fast, simple and scalable approach for the synthesis of Ni-Co-Fe layered double hydroxide (LDH) mesoporous nanoplatelets on a Ni foam substrate. Ni-Co-Fe LDH is a promising active electrode material for both electrochemical energy storage and electro-catalytic oxygen evolution reaction (OER). A supercapacitor based on Ni-Co-Fe LDH exhibits a high specific capacitance of 2460 F  $g^{-1}$  (2460 mF  $cm^{-2}$ ) at a discharge current density of 1.0 A  $g^{-1}$  (1.0 mA  $cm^{-2}$ ), with an excellent rate capability. An asymmetric supercapacitor based on Ni-Co-Fe LDH as the positive electrode and activated carbon as the negative electrode displays an operating potential window of 1.5 V, excellent cycle life, an ultrahigh specific energy of 57.5 Wh  $kg^{-1}$  and outstanding specific power of 14.95 kW  $kg^{-1}$ . As an OER electro-catalyst, Ni-Co-Fe LDH exhibits remarkable performance with a low overpotential of 207 mV to afford 10 mA  $cm^{-2}$ , much better than that of the most previously reported electro-catalysts. This active electrode material based on earth-abundant species opens new prospects for the design and fabrication of highly efficient multi-functional energy storage and conversion systems.

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## Selective and sensitive electrochemical determination of Ni(II) based on ion imprinted polymer technology

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Selective recognition of metal ions is a real challenge for a large range of applications in the analytical field (from extraction to detection and quantification). For that purpose, ion-imprinted polymers (IIPs) have been increasingly developed. IIPs are a new category of polymeric materials to produce polymers with ionic memory through the polymerization of appropriate monomer in the presence of specific ion that act as a template. The subsequent discharge of target ions form identification sites in ion imprinted polymers which selectively rebind to the desired ions (target) [1, 2].

With progress of mining industry, plating and other industrial activities, heavy metals are widely found in water resources which can harm human health and the environment at low concentrations. Pollution with heavy metals not only affects the agriculture products, but also impresses the quality of atmosphere and the safety of humans and animals through the food cycle. Environmental pollution that caused by heavy metals is a lasting process [3]. Nickel is one of heavy metals, although it is assumed as an fundamental element in body because of its activator role for several enzymes [4], excess amount of nickel is toxic. It can increase risk of lung cancer, cardiovascular disease, neurological deficits, and high blood pressure. In addition it is one of many carcinogenic metals known to be an environmental and occupational pollutant. Therefore, it is necessary to accurately determine low concentrations of nickel in environment and natural water resources [5]. Therefore, electrochemical determination of Ni(II) using Ni(II) imprinted poly dopamine film at the surface of glassy carbon electrode was performed. The Ni (II) – imprinted PDA/GCE sensor showed faster binding kinetics and higher selectivity to template Ni(II). Differential pulse anodic stripping voltammetry (DPASV) was used for Ni(II) determination in Britton- Robinson buffer solution and some parameters such as volume of polymer drop on electrode surface, pH of Ni(II) solution, pre concentration time, Ni(II) ions reduction potential and time and Britton- Robinson buffer's pH were optimized. The calibration graph is linear in the range of 1-25  $\mu\text{M}$  of Ni(II) with a correlation coefficient of 0.9987 and the limit of the detection for (S/N=3) was 0.85  $\mu\text{M}$ . Finally this sensor was used for Ni(II) determination in different water and tea samples.

**Keywords:** Electrochemical determination, ion imprinted polymer, water analysis, tea samples,

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**Methacrylic acid functionalized magnetite nanoparticles for the removal of Toluidine blue dye from aqueous solutions**

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Due to the importance of water and the growing need to the clean water, different chemical and biological methods have been developed to purify it [1]. Adsorption methods are considered as one of the effective methods for elimination of many of pollutants from water and wastewaters. In this study, magnetite nanoparticles (MNPs) were chemically synthesized by addition of ferric and ferrous salts (2:1) to ammonia solution under N<sub>2</sub> gas protection and stirring at temperatures higher than 80 °C. The synthesized nanoparticles were functionalized by methacrylic acid to improve its adsorption ability. Characteristics of synthesized MNPs were done using FESEM, FT-IR, XRD, and VSM instruments. The effects of experimental variables affecting the removal of toluidine blue including contact time, pH, adsorbent dose and ionic strength were evaluated using Taguchi orthogonal array method. The optimum conditions for toluidine blue dye removal were obtained as pH=7, contact time: 30 min, adsorbent dose: 0.1 g L<sup>-1</sup> and ionic strength: 0.05 M. Pseudo first order, pseudo second order, intraparticle and Elovich kinetic models as well as Langmuir, Freundlich and Tempkin isotherm models were investigated. The results showed that the experimental data were correlated with Langmuir adsorption isotherm ( $R^2 > 0.972$ ) and pseudo-second order kinetic ( $R^2 > 0.998$ ) models. To evaluate the efficiency of the method in removal of toluidine blue, three different real samples including tap water, sea water and well water were examined and the results showed removal efficiencies higher than 95%. The results showed magnetite nanoparticles functionalized by methacrylic acid have the potential to remove toluidine blue dye from aqueous solutions. Also, their separation from the solution is fast and simple using an external magnetic field.

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**Studies of Polyaniline Thin Layer Presence in Electrocatalytic Properties Pt-Sn/GC Electrode Modified by MWCNT for Methanol Oxidation**

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The direct methanol fuel cell has been designated as a candidate for electric power sources. The methanol oxidation reaction (MOR) by itself is rather slow and requires active catalytic sites for adsorption and oxidation of methanol, As well as oxidation and repulsion of the adsorbed intermediates [1]. In this way one of the major efforts in fuel cells catalysts research is to improve the electrocatalytic activity for methanol oxidation and methanol tolerance as well as to reduce the cost of these electro catalysts [2]. Platinum\_ based catalysts supported on carbons have recently been reported to play a very important role in catalyzing MOR. Polyaniline (PANI) with porous structure and high surface area is a particularly attractive material as catalyst support [3].

Electrocatalytic activities Pt and Pt\_Sn nanoparticles supported on Multiwall carbon nanotubes and Vulcan carbon were examined for methanol oxidation reaction. The Pt/C, Pt\_Sn/C, Pt/MWCNT, Pt\_Sn/MWCNT catalysts were synthesized using a deposition\_ reduction technique with sodium borohydride. The electrocatalysts were characterized by EDS, XRD, FESEM and cyclic voltammetry. From the XRD patterns, the Pt(220) peak of the PtSn/C, PtSn/MWCNT catalysts shift slightly to lower  $2\theta$  values with increasing Sn compared with that of the Pt/C, Pt/MWCNT catalysts, suggesting the alloy formation. The Pt\_Sn/MWCNT electrocatalyst with an atomic ratio Pt/Sn (3:1) in MOR exhibited a higher forward peak current density and a lower peak potential during cyclic voltammetry compared to other electrocatalysts. Then the effect of glassy carbon electrode (GC) surface modification by a thin layer of polyaniline was investigated. The results showed that in present a thin layer of polyaniline and platinum-tin electrocatalytic particles supported on multiwall carbon nanotube (GC/polyaniline/Pt-Sn/CNT) the oxidation of methanol in aqueous acid media is considerably enhanced.

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**Micro-solid-phase extraction of diazepam and oxazepam from wastewater and biological fluids based on miniaturized pipette-tip method and electrospun nanofibers as an efficient sorbent**

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Nitrazepam and oxazepam belong to a major class of pharmaceuticals named benzodiazepines. Benzodiazepines are widely consumed as anticonvulsants, central muscle relaxants, minor tranquilizers, sedative hypnotics, and anxiolytic agents, however, they induce many unwanted side effects, including drug dependency, impaired memory and concentration, depression, and loss of balance. Overdoses of these drugs can cause acute symptoms; therefore, it is desirable to monitor their concentrations in the biological fluids [1]. Pipette tip solid-phase extraction (PT-SPE) method is a miniaturized form of SPE. In this method, the pipette tip with a small outlet diameter requires tiny amount of sorbent to be used and the PT-SPE setup has low solution consumption. By using this approach, a large number of reusable SPE tips can be prepared simultaneously [2]. Electrospinning is a technology that can produce ultrathin nanofibers economically, and has features such as extremely long lengths, a high surface area to volume ratio, a small pore size, and high porosity. The use of electrospun nanofibers with mentioned properties allows for a reduction in sorbent mass in sorption studies [3]. In this work, a self-assembly of miniaturized pipette-tip-based solid-phase extraction for the coextraction of diazepam and oxazepam was developed with electrospun nanofibers used as sorbents. The electrospun nanofibers were characterized by SEM, TEM, XRD and FTIR analysis. The results showed that the pipette-tip-based solid-phase extraction was effective in extracting of target analytes in the pH ( $\approx 8$ ). The investigation also revealed that the optimum mass of electrospun nanofibers sorbent was 10 mg and 4 aspirating/dispensing cycles gave the maximum recovery of target analytes with 250  $\mu\text{L}$  propanol/methanol as the best eluting solvent. Under the optimum conditions linear dynamic ranges were achieved in the range of 1.0–1000  $\mu\text{g L}^{-1}$  with coefficients of determination  $>0.999$ . Relative standard deviations ( $n = 5$ ) of  $<11\%$  were obtained. Moreover, the performance of the present method was studied for the extraction and determination of diazepam and oxazepam in wastewater and biological fluids and satisfactory results were obtained.

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**The study of application of polyamide membrane modified with polydopamine**

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Membrane separation processes play a very important role in the separation industry. Microfiltration, ultrafiltration, nanofiltration, reverse osmosis (RO) are widely used membrane separation processes, and their difference is based on separation mechanisms and size of the separated particles [1]. For example, polyamide membrane used for the separation of pharmaceutical compounds from aqueous streams [2]. In the present study, a commercial polyamide membrane was modified via surface coating of polydopamine (PDA). It is well-known that a tightly adherent PDA layer can be generated over a wide range of material surfaces through a simple dip-coating process in dopamine aqueous solution [3]. PDA modified polyamide membranes can be made according to the requirements for the separation of organic matter by the addition of supplementary materials. The resulting PDA coating is prone to condensation of the organic compound because of its robust reactivity. In the condensation of L-cysteine on the PDA modified polyamide membrane, the interaction effects of L-cysteine and polydopamine occur. The condensation of L-cysteine was recorded by spectroscopic and spectrophotometer curves and membrane surface properties were characterized through scanning electron microscopy (SEM). The results showed that modification enhanced the surface hydrophilicity and condensation of L-cysteine.

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## Investigation of parameters affective on MFC operation

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Bioenergy is a renewable energy that plays an indispensable role in meeting today's ever increasing energy needs. Unlike biofuels, microbial fuel cells (MFCs) convert energy harvested from redox reactions directly in to bioelectricity. MFCs can utilize low-grade organic carbons (fuels) in waste streams[1]. In recent years, MFCs have also been used in the electrolysis mode to produce bioproducts in laboratory tests. Micro organisms actively catabolize substrate, and bioelectricities are generated. MFCs could be utilized as power generator in small devices such as biosensor. Besides the advantages of this technology, it still faces practical barriers such as low power and current density. In the present article different parts of MFC such as anode, cathode and membrane have been reviewed and to overcome the practical challenges in this field some practical options have been suggested MFCs research has intensified in the past decade and the maximum MFCs power density output has been increased greatly and many types of waste streams have been tested[2]. However, new breakthroughs are needed for MFCs to be practical in wastewater treatment and power generation beyond powering small sensor devices. To reduce capital and operational costs, simple and robust membrane less MFCs reactors are desired[3]. This review is an update on the recent advances on MFCs designs and operations.

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**Increasing the solar energy absorption by using self-cleaning glass surface coatings to improve the efficiency of solar cells**

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Among renewable energies, using photovoltaic systems to convert solar energy into electricity without noise, toxin production and release of greenhouse gases has become increasingly important. Despite the advances in solar cell technologies, these cells are diversely used on building roofs in urban areas, which exposes them to problems such as rapid deposition that reduces light transmittance and cell efficiency.<sup>(1)</sup> The upper layer of solar cells consists of a glass surface with various applications.<sup>(2)</sup> The present study aimed to enhance the self-cleaning ability of the anti-reflection layer containing titanium dioxide nanoparticles for the glass surface of the solar cells, which has photocatalytic properties. The surface was prepared by the nanosol/immersion method. After calcination at the temperatures of 400 to 550 centigrade for an hour, the surface was placed in a methylene blue solution (concentration of 30  $\mu$ M) and exposed to ultraviolet light for 90 minutes. Using an ultraviolet-visible spectrometer, the level of self-cleaning and removal of organic contaminants (methylene blue) of the two surfaces were compared and measured against the glass without surface based on its absorption at the wavelength of 665 nm. In addition, the reduction of light transmittance was evaluated. Also, analysis of the changing nature of the nanoparticle was performed by an X-ray diffraction (XRD) device, and morphology of the surface and cross-sections of the films by a scanning electron microscope (SEM).

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## Investigation of the elimination of Acid Red 74 from wastewater by the rounded cones of *Cupressus arizonica*

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Water is one of the most important factors for the survival of human life and living creatures. Water pollution is a big threat and a worldwide concern. Some of the most hazardous pollutants of water are different dyes which enter water sources from various industries like textile and leather. Researchers are trying to prevent this from happening as far as possible. Organic colors are an important group of dyes. Because in addition to contamination, they reduce the penetration of sunlight into the water and threaten the life of aquatic plants by disrupting photosynthesis. Organic colors are almost strong and resistant to biological degradation [1]. When entering the human body, they can be regarded as a potential or probable carcinogen and totally endangers human life and environment [2]. The common decolorization methods for synthetic dyes are adsorption, coagulation, flocculation, microbiological or enzymatic decomposition, membrane filtration, ion-exchange, oxidation and advanced oxidation [3]. Among all these methods, adsorption has its own advantages and can be effective for wastewater treatment [4]. Some of the agricultural products which have few or no special usage can be utilized as cheap adsorbents for removal of dyes from water. They are inexpensive, freely available, abundant, having a simple application, high efficiency and green chemistry. [5]

*Cupressus arizonica* is widely cultivated as an ornamental tree. It is native to the southwestern United States but the seeds are sown in different countries such as Iran. In the present study, the ability of the rounded cones of *Cupressus arizonica* in adsorption and elimination of the acidic red color from the aqueous solution has been investigated. For preparing adsorbent, rounded cones were picked up and ground properly. Then the powder was boiled in deionized water for 3 times and then immersed in acidic solution in order to be eliminated from some contaminants. In the next step, it was immersed in deionized water for several times until the solution pH became neutral. Finally, it was dried in an oven in 95°C for 24 hours. After all, the powder was ready to be used in wastewater treatment process. To optimize the treatment efficiency, different parameters like the amount of adsorbent, the concentration of dye solution, pH and adsorption time were studied. The results showed that, as the amount of adsorbent and adsorption time increases, the removal efficiency is enhanced. Furthermore, the obtained data revealed that, as the pH and concentration of dye solution decreases, the elimination efficiency of color from the aquatic solution is increased. As a conclusion, the outcome of the wastewater treatment experiments in the optimum conditions demonstrated that the adsorbent can eliminate the pollutant up to 99% from the contaminated water.

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**Determination of phthalate esters in water by headspace solid phase microextraction using covalent organic framework-based nanocomposite as advanced coating coupled to gas chromatography-mass spectrometry detector**

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Phthalate esters (PEs) are a class of synthetic chemicals which have been used on a large scale since the 1950s, comprise a large number of compounds, and now are frequently used in plastic production industries to enhance the flexibility of the materials. Several phthalates have been identified and classified as endocrine disruptors possibly associated with known estrogenic and anti-androgenic activity [1].

Covalent organic frameworks (COFs) are a new type of porous materials purely constructed with organic building blocks [2]. Characteristic in tunable functionality, regular pore structure, and high surface area make COFs as useful adsorbent in microextraction techniques.

In the present work, COF nanocomposite was coated on etched stainless steel and evaluated as a novel headspace solid phase microextraction (HS-SPME) fiber coating for extraction of ultra-trace amounts of PEs. Determination of PEs were performed by gas chromatography coupled with mass spectroscopy (GC-MS). Important parameters which have effect on extraction efficiency such as extraction time, extraction temperature, salt concentration, and stirring rate were optimized. To evaluation of the method performance the extraction of the PEs, limit of detection (LOD), linear range (LR), coefficient of determination (R<sup>2</sup>), relative standard deviation (RSD), and extraction efficiency (EE) were studied in distilled water under optimum extraction conditions. The obtained relative recoveries show this procedure is a reliable method for extraction and determination of PEs in water.

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**Separation and determination of anionic surfactants by polymeric nanofibers as a micro-solid phase extraction and optimization of extraction conditions using response surface methodology**

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Anionic surfactants are currently the types most used, being incorporated in the majority of detergent and cleaning-product formulas in daily use [1]. But these kind of compounds cause water pollution of water supply source, such as rivers and lakes, and attract as one of the factors which affect natural ecosystem then determination of their concentration is important [2].

In this study we use polymeric nano-fibers prepared by the electrospinning method as a micro-solid phase extraction ( $\mu$ -SPE) for extraction, purification and preconcentration of Sodium dodecyl sulfate (as a sample of anionic surfactants). Characteristics of the fibers were inspected by Energy dispersive spectroscopy (EDAX), scanning electron microscopy (SEM), and Fourier-transform infrared spectroscopy (FT-IR).

The amount of anionic surfactants was measured by UV-Vis spectroscopy using Methylene Blue based on the formation of the ionic pair anionic surfactant-methylene blue and the extraction of the ion pairs and measuring the absorbance at 654 nm.

The effective factors on extraction were optimized by response surface methodology (RSM). The optimum conditions included pH 9, 0.5 mL for elution solvent volume and 0.0636 grams of sorbent.

Under the optimized conditions, the method showed linearity with correlation coefficient of  $>0.995$ . Also Relative standard deviation was calculated 0.66%.

Furthermore, the proposed method was successfully applied to the quantification of residual anionic surfactants in the surfaces of dishes washed with dishwasher and hand wash.

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## A Simple and High Efficient Direct Glycerol Fuel Cell with Cu-Nanoparticles Incorporated Polymeric Film Modified Electrode

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Development of alternative low temperature power source is an important and interesting subject for researchers in the world. Direct alcohol fuel cells (DAFCs) have attracted considerable interest in their application alternative power sources for portable consumer electronics and even automobiles [1]. Among the different alcohols, glycerol has attracted more interest in recent years, due to its lower toxicity, renewability from biomass, and relatively high theoretical energy density as compared to other alcohol fuels [2]. The non-Pt-based nanoparticles are commonly used as electrocatalysts in the fuel cells due to low cost, relatively abundant material and suitable catalytic activity [3]. Copper (Cu) is one of the most commonly used non-Pt transition metals and is used to manufacture the electrocatalysts that are found in numerous electrochemical systems, such as rechargeable batteries, supercapacitors and fuel cells. In fuel cells field, there are few reports about the electrooxidation of alcohols on the Cu and Cu-based nanoparticles.

Hereupon, in this work, a promising electrocatalyst was developed based on a layer process by electropolymerization of methyl orange (MO) on the surface of glassy carbon electrode (GCE) as a proper polymeric framework for deposition of Cu nanoparticles (CuNPs) for the first time. The prepared electrocatalyst was characterized by XRD, SEM, EDX and electrochemical techniques. Then, the cyclic voltammetry and chronoamperometry approaches were employed to characterize the electrocatalytic activity of the present nanoparticles modified electrodes toward the oxidation of glycerol in 1.0 M NaOH solution. Electrochemical studies demonstrate that this CuNPs/PMO/GCE catalyst could have both superior electrocatalytic activity and stability for glycerol oxidation, confirming that CuNPs/PMO/GCE should be a good material for supporting the catalyst. The results obtained at optimized conditions have highlighted the excellent electrocatalyst activity of CuNPs/PMO/GCE in terms of specific peak current density and onset potential. Also, the CuNPs/PMO/GCE kept initial performances over 100 voltammetric cycles. For CuNPs/PMO/GCE, kinetic parameters such as the electron transfer coefficient ( $\alpha$ ) and the number of electrons involved in the rate determining step ( $n_a$ ) for oxidation of glycerol at the CuNPs/PMO/GCE surface were calculated.

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## Epinephrine Electrochemical Sensor Based on L-Methionine Film/ZnO Nanoparticles in Carbon Paste Electrode

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One example of neurotransmitters considered is epinephrine (EP), also known as adrenaline. EP as a neurotransmitter is synthesized biologically in the adrenal medulla and sympathetic nerve terminals. It has a key role in the functioning of central nervous system (CNS), renal, hormonal, and cardiovascular system [1]. Numerous diseases are related to the concentration of EP, such as Parkinson's disease, Alzheimer's disease, hypertension and multiple sclerosis [2]. Furthermore, EP is used as a drug to treat bronchial asthma, organic heart disease, anaphylaxis, anaphylactic shock and superficial bleeding. Several methods have been reported for EP analysis [3] and due to electro active nature of EP, it can also be determined electrochemically. Therefore, it is necessary to effectively enhance the sensitivity of electrochemical sensors for medical applications.

This paper demonstrates a new modified carbon paste electrode fabricated from l-methionine film /ZnO NPs, by cyclic voltammetry that the whole procedures take only several minutes and can be used for quantification of EP in different real samples. Combination of the benefits of both polymer/ZnO NPs and CPE, enhanced the electrocatalytic activity and voltammetric performance of the fabricated sensor for the oxidation of EP. The surface and electrochemical characterization of the modified electrode was investigated by field emission scanning electron microscopy (FESEM), chronocoulometry (CC), cyclic voltammetry (CV) and differential pulse voltammetry (DPV). In the optimized conditions, the presented sensor is able to detect the concentration range of 0.5–12.4  $\mu\text{M}$  with a limit of detection of 40 nM. The presented methodology possesses a reliable reproducibility, repeatability and stability in biological samples. These results proved that the composite has a hopeful capacity in electrochemical sensors development. The developed electrochemical sensor was successfully employed for the determination of analytes in real samples with satisfactory results.

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**Electrooxidation of glucose on nanoporous MCM-41-cryptand-Pd modified carbon paste electrode in alkaline solution**

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Mesoporous silicate, MCM-41, is a member of a new family of mesoporous molecular sieves, M41S, invented by researchers in 1992 [1]. The most interesting feature of MCM-41 is its regular pore system which consists of hexagonal array of unidimensional, hexagonally shaped pores. The pore diameter of MCM-41 is systematically between 2-10 nm [2].

In this study, a new nanoporous Pd-cryptand complex anchored onto MCM-41 was synthesized through a simple method and its morphology and spectral characters was studied. The electrocatalytic properties of modified carbon paste electrode (CPE) with MCM-41-cryptand-Pd toward electrooxidation of glucose in alkaline solution were investigated. It was confirmed that the application of modified CPE significantly reduces the oxidation potential of glucose about 250 mV as well as increasing oxidation currents. The proposed electrode was successfully used as a new and efficient sensor for determination of glucose in various samples.

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**A Voltammetric Sensor for Determination of Morin at Stacked Cu Nanoparticles Immobilized on L- Arginine Film Nanocomposite Modified GCE**

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Metallic nanoparticles (MNPs) have also drawn particular attention due to their high surface area, effective mass transportation, catalytic properties and control over local microenvironment [1, 2]. Conductive polymers have attracted attention as a proper choice for the modification of electrodes' surfaces. Among different methods for preparing polymer-modified electrodes, electropolymerization is a good choice to immobilize the polymer, as the film thickness and its permeation characteristics can be controlled. Formation of metal nanoparticles (MNPs) in a polymer matrix is a popular tool for design of metal nanoparticles and polymers frameworks (MNPPFs). Properties of polymer can be greatly altered by incorporating MNPs [3]. To obtain MNPPFs with well-defined and reproducible properties, one should achieve suitable control over MNPs growth, particle size distribution, and particle–interface interactions.

In this work, a sensitive and convenient electrochemical sensor based on stacked arginine film and copper nanoparticles composite modified glassy carbon electrode was developed for the determination of morin. Electrochemical investigation of the modified electrode are achieved using cyclic voltammetry, differential pulse voltammograms. The effect of several experimental variables, such as pH of the supporting electrolyte and number of electropolymerization cycles were optimized by monitoring the CV response of the modified electrode toward morin. Under the optimized conditions, a significant electrochemical improvement was observed toward the electrooxidation of morin on the modified electrode surface relative to the unmodified electrode. The oxidation peak current of morin was proportional to its concentration over the range from 0.2 to 9.8  $\mu\text{M}$ . The limit of detection was evaluated to be 0.16  $\mu\text{M}$ . The developed nanosensor was applied to the samples of juice for determination of morin with high sensitivity and high selectivity.

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## Removal of Neutral Red from Aqueous Solution by Ni/Al Layered Double Hydroxide (LDH)

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Sorption is a common treatment for removing organic pollutants from the natural environments [1]. Dyes and pigments are widely used, mostly in the textiles, paper, plastics, leather, food and cosmetic industry to color products. Most of the dyes, such as neutral red, are toxic and must be removed before discharging into receiving streams since their effluents can reduce light penetration and photosynthesis. Neutral red is a cationic dye that is used extensively for nuclear counterstaining in biological research [2]. Neutral red attracts noteworthy attention to innovate effective techniques for its removal.

Layered double hydroxides (LDHs), which first were reported in the mid-19<sup>th</sup> century, are mixed-metal hydroxides that consist of octahedral double hydroxyl layers with exposed positive surface charges and interlayer anions [3]. LDHs have biological, pharmaceutical, and environmental applications [4]. The general known formula of LDH is  $[M_{1-x}^{2+} M_x^{3+}(\text{OH})_2]^{x+} A_{x/m}^{m-} n\text{H}_2\text{O}$ , where  $M^{2+}$  and  $M^{3+}$  are divalent and trivalent cations, respectively, each with an ionic radius similar to that of  $\text{Ni}^{2+}$ . Among the various types of LDH species, a hydrotalcite-like compound consisting of an Mg Al-, Ni Al-, or Mg Ni Al- $\text{CO}_3$  double hydroxides with carbonate as interlayer anions, is commonly used for a variety of applications. However, they seem to be less effective at binding hydrophobic organic compounds (HOCs), such as pesticides or phenols, because of their strongly hydrophilic surface.

Hence, current study was devoted to synthesize Ni/Al LDH via free hydrothermal method. As-obtained Ni-Al LDH was used to investigate their applications as an adsorbent for the adsorption of neutral red from aqueous solution. Effects of various experimental conditions such as pH, contact time and initial dye concentration, on the adsorption were evaluated through a batch equilibrium technique. In addition, the adsorption isotherms, kinetics and thermodynamics have been performed. The results are promising for further application of magnetic hollow spheres as an efficient low cost and recyclable adsorbent for dye removal.

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## Highly Sensitive Detection of Isoniazid at a Glassy Carbon Electrode Utilizing Ternary Nanohybrid of Graphene Oxide Nanosheets- Glycine- Copper Nanoparticle

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In the present investigation a new electrochemical sensor based on copper nanoparticles for detection of isoniazid (INZ) has been developed. Copper nanoparticles/glycine/graphene oxide nanosheets (GONs) modified glassy carbon electrode (CuNPs/glycine/GONs/GCE) was prepared by using dripping well-dispersed graphene oxide nanosheets, electropolymerized poly glycine (p-Gly) followed by electroplating of metallic copper nanoparticle film. The CuNPs/glycine/GONs modified glassy carbon electrode has excellent electrocatalytic ability for the electrooxidation of isoniazid. Scanning electron microscopy and energy dispersive X-ray spectrometry were used for the characterization of the prepared film. The process of oxidation and its kinetics were established by using cyclic voltammetry, chronoamperometry and differential pulse voltammetry (DPV) techniques. The results indicate that CuNPs/glycine/GONs can facilitate the electrochemical oxidation of isoniazid with great decrease of overpotential in pH 7.0 phosphate buffer solution. The proposed biosensor provides excellent performance towards the determination of isoniazid with acceptable linear response ranges from 0.2 to 60  $\mu\text{M}$  with the limit of detection (LOD) of 6.07  $\mu\text{M}$ . Studies show the facts that oxidation of INZ occurs through a four proton transferring mechanism and endures a limitation, considered to be depended on generation of  $\text{N}_2$  as the final oxidation product [1, 2]. The diffusion coefficient of  $3.65 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$  for isoniazid was also estimated using chronoamperometry study. The CuNPs/glycine/GONs modified electrode displayed good storage stability, excellent reproducibility toward the sensing of INZ. The utility of this modified electrode was demonstrated for the determination of INZ in solid pharmaceutical formulations. The results of the analysis suggest that the proposed method has promise for the routine determination of isoniazid in the products examined.

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## Highly Sensitive Determination of Hydrogen Peroxide Employing Copper Nanoparticles Decorated Neutral Red Film on a Glassy Carbon Electrode

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Hydrogen peroxide ( $H_2O_2$ ) is a very simple molecule in nature but has been widely used in pharmaceutical, clinic, environmental, mining, textile, paper, food manufacturing and chemical industries because of its strong oxidizing and reducing properties [1, 2]. This work describes a convenient and effective strategy to construct a highly sensitive amperometric biosensor for the detection of  $H_2O_2$  based on neutral red (NR) and Cu nanoparticles (CuNPs) nano composite. Scanning electron microscope (SEM) image showed that the neutral red have been electropolymerized on the GCE and the Cu nanoparticles were immobilized as spherical particles on the polymer surface. The electrochemical performance of the sensor for detection of  $H_2O_2$  was investigated by cyclic voltammetry and chronoamperometry techniques. The modified electrode exhibits an enhanced electrocatalytic property, low working potential, high sensitivity, excellent selectivity, good stability, and fast amperometric sensing of hydrogen peroxide. The detection limit of the electrochemical sensor using the CuNPs/PNR/GCE for  $H_2O_2$  determination was calculated to be  $1.5 \times 10^{-7}$  M, which was even superior to some noble metal-decorated  $H_2O_2$  sensors. The effective coupling of NR and CuNPs boosted significantly the electroanalytical performance by providing more active area for analyte interaction, thereby allowing more rapid interfacial electron transfer process. These studies revealed that the novel Cu NPs/PNR/GCE sensor could be a potential candidate for the detection of  $H_2O_2$ .

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## A simple dispersive micro-solid phase extraction method based on magnetic MIL-101(Cr)@MWCNTs for the simultaneous determination of phthalates and parabens

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Phthalic acid esters (PAEs), widely known as phthalates, are among the compounds that are attracting a high interest nowadays as a result of the high production of plastics worldwide. In this sense, PAEs are widely used as plasticizers in the manufacture of plastics to provide the necessary flexibility for their correct handling. Apart from that, they also have an extensive variety of industrial, agricultural and domestic applications [1]. The analysis of PAEs in food matrixes has attracted much attention because of their potential risk for humans' health, including fertility and growth problems [2]. In particular, their analysis in drinking water or beverages, especially those commercialized in plastic bottles, is of importance as a result of the high human consumption and their already mentioned negative effects for health [3]. Parabens (alkyl and aryl esters of p-hydroxybenzoic acid) are a group of widely used ingredients that act as an antifungal and preservation agent in processed food, cosmetics, and pharmaceuticals. Owing to their attractive features such as broad-spectrum, antimicrobial activity, low cost, water solubility, and chemical and thermal stability in a wide pH range, parabens are popular preservatives in consumer products. The extensive applications of parabens containing compounds have increased worldwide concerns about them because of their potential to disrupt endocrine function. Furthermore, parabens have been found in a small number of breast tumor tissues. Thus, some simple, sensitive, and fast methods are needed to determine trace amounts of parabens in different matrices [4]. In this study, an easy and fast dispersive micro-solid phase extraction (D- $\mu$ -SPE) method was developed for coextraction of target analytes. Magnetic MIL-101(Cr)@MWCNTs was synthesized and used as an efficient sorbent in D- $\mu$ -SPE method. The synthesis of MOF was confirmed by Fourier transform infrared spectroscopy, X-ray dispersive spectroscopy, thermogravimetry analysis, scanning electron microscopy, transition electron microscopy, vibrating sample magnetometry and X-ray diffraction. The method is easily operated, benefits from good reproducibility values, low detection limit with wide dynamic linear range, and acceptable extraction recovery. Due to the magnetic property, the phase separation was convenient and rapid for D- $\mu$ -SPE procedure. The opted conditions were: pH of the sample, 8; MOF amount, 11.5 mg; sorption time, 13.5 min; salt concentration, 10% w/v; sample volume, 18 mL; type and volume of the eluent, acetonitrile, 100  $\mu$ L; elution time; 2 min. Under the optimum conditions detection limits and linear dynamic ranges were obtained in the range of 0.12-0.43  $\mu$ g L<sup>-1</sup> and 0.5-1000  $\mu$ g L<sup>-1</sup>, respectively. Relative standard deviations (n = 5) were in the range of 1.5%-5.6%. Eventually, the synthesized magnetic MOF was successfully applied for the coextraction and determination of target analytes in various real samples with satisfactory results.

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## Evaluation of some dental materials used for root endcapping in terms of releasing lead, arsenic, and chromium in plasma

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The aim of this study was to evaluate the presence of lead, arsenic and chromium toxic metals in 4 dental materials with titles A(Angelus MTA), B(Endo sequence root repair material), C(Bio-dentine) and D(CEM Cement), made by Brazil, USA, France and Iran, respectively. High Performance Liquid chromatography, Atomic Absorption and Inductively Coupled Plasma Mass Spectrometry was used for metal determination. First, a 10 ppm solution of CrCl<sub>2</sub> in doubled distilled water was used to determine the HPLC method. According to the results, for C18 column an appropriate elution solvent was ammonium acetate with a pH of 6, together with methanol, flow rate was 0.7 ml/min and  $\lambda = 221\text{nm}$ . Arsenic and lead were measured by atomic absorption spectrometry. Inductively coupled plasma mass (ICP-Mass) and Energy-dispersive X-ray spectroscopy (EDAX) was used for confirming the results. For this purpose several blocks of Teflon were prepared with a hole of 2 mm in diameter and 2 mm in length. For each of the 4 dental materials, one block was took and filled by it and therefore it was placed in contact with the Liquid Simulator [SBF] away from light and in a sealed container at a temperature of 37 °C. Finally, the amount of released heavy metals from any of the dental materials mentioned above was investigated. The results showed that all three materials A, B and C had toxic metals such as lead, chromium and arsenic, and the released chromium content was obtained in C> B> A, respectively. Also, for D (construction of Iran), there was no release of lead, arsenic and chromium.

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## Antioxidant activity of chitosan and effect of molecular weight and pH

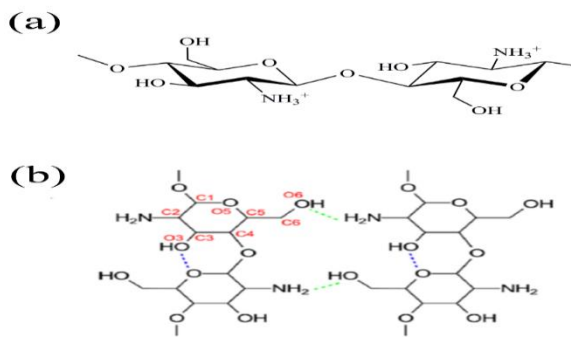
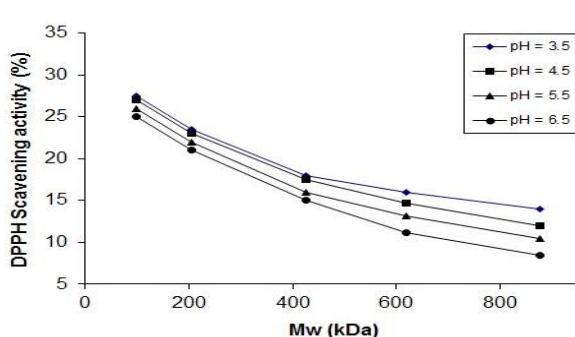
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The antioxidant activity of chitosan with different initial molecular weights were evaluated by the radical scavenging activity method using 1,1-diphenyl-2-picrylhydrazyl (DPPH) at different pHs. Fig.1 shows the antioxidant activity of chitosan with different initial molecular weights at different pHs. Scavenging activity of DPPH radical decreased with the increasing of molecular weights of chitosans and antioxidant activity is directly affected by the amount of molecular weights. The results showed that the antioxidant activity of chitosan with different molecular weights depend on the pH values and CS5 (M=98 kD) has the highest antioxidant activity at pH=3.5 and CS1 (M=876 kD) has the lowest antioxidant activity at pH=6.5. These results are possibly due to the low-molecular weight chitosan has lower H bonds than medium and high-molecular-weight chitosan, and with decreasing of intermolecular interaction (Van der Waals) and hydrogen bonds in low Mw, the lone pair of electrons or hydrogen compounds from C–O and N–H may be more available[1]. The effect of pH on the antioxidant activity is probably because of the scavenging mechanism of chitosan that free radical can react with the residual free amino (-NH<sub>2</sub>) groups to form stable macromolecule radicals, and the -NH<sub>2</sub> groups can form ammonium(-NH<sub>3</sub><sup>+</sup>) groups by absorbing a hydrogen ion from the acidic solution [2]. At low pH these amino (-NH<sub>2</sub>) groups are protonated, making chitosan a cationic polyelectrolyte but, at neutral and high pH, deprotonation of amino groups enables the formation of intermolecular hydrogen bonds and concomitant dehydration of the internal region of the associated chains leading to gelation. Intramolecular hydrogen bonding between the hydroxyl O3 and ring O5 atoms confers rigidity to a single chitosan chain, while intermolecular hydrogen bonding between the amine N and hydroxyl O3 as well as O6 atoms is responsible for the selfassembly and the anti-parallel packing of the chains in the crystalline domains [3]. The chemical structure of chitosan at low pH (a) and Chitosan structure with intra- and intermolecular hydrogen bonds at neutral and high pH (b) are shown in Fig.2.



**Fig. 1.** Variation of antioxidant activity of chitosan with various initial molecular weights at different pH values at 25 °C. **Fig.2.** The chemical structure of chitosan at low pH (a) and chitosan structure with intra- and intermolecular hydrogen bonds at neutral and high pH (b)

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**Monitoring of some pesticides in farmers saliva and exhaled breath condensate using deep eutectic solvent- based liquid-liquid microextraction and GC-MS**

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Pesticides are organic or inorganic compounds which are extensively used in agriculture worldwide [1]. Commonly, these compounds are highly toxic and stable in the environment. Generally, pesticides were transferred to the human's body indirectly by consuming foods and drinking waters contaminated with these compounds [4]. But farmers have direct contact with pesticides in period of agriculture activities. Due to toxicity of the pesticides their monitoring is needed in biological fluids. Different biological samples were investigated in several studies such as blood, plasma, urine, saliva, and exhaled breath condensate (EBC). The major aim of the present study was the development of an LPME method performed in a new extraction vessel using a lighter than water green DES for the extraction and preconcentration of some mostly used pesticides in farmer's saliva and EBC samples and their determination using gas chromatography–mass spectrometry (GC-MS). The microextraction method was performed in an extraction vessel fabricated in our laboratory. It was firstly cleaned with deionized water and then washed with acetone to remove possible impurities adhered to inner wall of the glass and glass filter. Then, 5 mL of aqueous standard solution (spiked with the analytes at 10 ng mL<sup>-1</sup>, each analyte) or diluted saliva or EBC sample (see Sec. 2.3) containing 0.25 g NaCl (5%, w/v) was transferred into the device on the on the glass filter. The prepared menthol: phenylacetic acid (41 μL) was transferred into the narrow tube of the device and it was forced to pass through the glass filter using air stream with a flow rate of 2 mL min<sup>-1</sup> for 2 min. In this step, the DES was dispersed as fine droplets and moved up with the aid of air bubbles due to its low density and the analytes were extracted into the extraction solvent. After collection of the extraction solvent on the top of the sample solution a portion of the DES was removed by a capillary tube and 1 μL of the extraction solvent was injected into the GC–MS system. Validation of the method showed, limits of detection and quantification at the ranges of 2–17 and 10–85 ng L<sup>-1</sup> in saliva and 7-59 and 35-295 ng L<sup>-1</sup> in exhaled breath condensate, respectively. Extraction efficiency of the present method, expressed as extraction recovery for the target analytes, was in the range of 79–97%.

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**Dispersive liquid phase microextraction method performed in a home-made device using menthol based lighter than water deep eutectic solvent in extraction of some pesticides in farmer urine and plasma samples followed by gas chromatography-mass spectrometry**

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Pesticides are chemical compounds that are intended to control weeds, insects, herbs and pests [1]. These compounds are used on large scale in agricultural activities. The pollution of environmental compartments involves a serious risk to the environment and to human health as well, due to either direct exposure or residues in food and drinking water [2]. The pesticides risks to human health have been widely evaluated, but their risks to farmer health are one subject that has so far received little attention. This is true in developing countries the major pesticide users are farmers [3]. In this work, a new disperser-less and centrifuge-less dispersive liquid phase microextraction performed in a home-made extraction device has been developed for the extraction and preconcentration of some pesticides in plasma and urine samples followed by gas chromatography-mass spectrometry. For this purpose, a U-shaped glass device with a glass filter was designed and a new deep eutectic solvent lighter than water was used as an extraction solvent. The extraction solvent was forced to pass through the glass filter under air stream and it was dispersed as tiny droplets in whole parts of the aqueous solution placed on the filter. By this action the analytes were extracted into the fine droplets of the extraction solvent. The produced droplets of the extraction solvent went up through the solution and collected on the aqueous phase without centrifugation. Under the optimum extraction conditions, the method showed low limits of detection in the ranges of 2–17 and 4–36 ng L<sup>-1</sup> in urine and plasma, respectively. Extraction recoveries were in the range of 79–97%. Enrichment factors were obtained from 379 to 485 in urine and 158–194 in plasma. Finally, plasma and urine samples of farmers were successfully analyzed using the proposed method.

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## The 25<sup>th</sup> Iranian Seminar of Analytical Chemistry

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### Development of microwave-assisted liquid-liquid extraction combined with lighter than water in syringe dispersive liquid-liquid microextraction using deep eutectic solvents; Application in extraction of some herbicides from wheat

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Herbicides are the compounds that are mainly used to stopping and destroying the growth of weeds and unwanted vegetations [1]. The use of herbicides in agricultural and non-agricultural activities is developing to control weeds and in this way different compounds are tested to obtain high efficiency in weeds control [2]. Several forms of herbicides including liquids, granules, and fumigation are used in agriculture. In most cases herbicides are used in liquid formulations and they are added to soil before cultivation stage [3]. Therefore, the herbicide residues have been found in a lot of agriculture products. According to these regulations, the residue of the herbicides should be controlled. In this work, a deep eutectic solvent-based microwave-assisted liquid-liquid microextraction method followed by gas chromatography-mass spectrometry has been reported for the extraction and preconcentration of seven herbicides from wheat samples. The analytes are extracted into a water-miscible deep eutectic solvent under microwave irradiations and then the extractant is used as a dispersive solvent in the following dispersive liquid-liquid microextraction method. In this method, ChCl: phenol and ChCl: butyric acid deep eutectic solvents are used in the first and second steps mentioned above, respectively. After that, the mixture is dispersed into deionized water placed into a syringe with a retracted plunger. By this action, ChCl: butyric acid was dispersed in whole parts of the solution. To break up the cloudy state, acetonitrile is added and the collected organic phase is used in determination system. Low limits of detection and quantification in the ranges of 1.6-12, and 5.5-42 ng kg<sup>-1</sup>, relative standard deviations  $\geq 6.1\%$  (at a concentration of 50 ng kg<sup>-1</sup>, each analyte) and extraction recoveries and enrichment factors in the ranges of 69-94% and 345-470, were obtained, respectively, under optimal conditions. Lastly, some wheat samples were analyzed and diclofob-methyl was found in two samples.

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**Homogeneous liquid-liquid extraction performed in narrow tube followed by in-syringe dispersive liquid-liquid microextraction based on deep eutectic solvents; Application in extraction and preconcentration of some herbicides from tea**

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In recent years, deep eutectic solvents (DESs) engrossed more attentions in analytical chemistry [1]. DESs generally are formed from two compounds which they are hydrogen bond donor (HBD) and hydrogen bond acceptor (HBA). By mixing HBD and HBA, hydrogen bonding interaction is occurred and a mixture with low melting point (near to room temperature) is prepared [2]. These solvents are considered as a suitable replacement for traditional extraction solvent due to their low toxicity, high biodegradability, and extraction capability. Simple preparation of DESs and availability of different compounds in synthesis of them expand their use as solvents in many fields. Sample preparation methods are one of the main fields which are involved with DESs [3]. The usage of DESs as acceptor phases in extraction methods attracts more attentions in the recent years. A homogeneous liquid-liquid extraction performed in narrow tube coupled to in-syringe dispersive liquid-liquid microextraction based on deep eutectic solvent has been developed for the extraction of some herbicides from tea samples. The deep eutectic solvent used in homogeneous liquid-liquid extraction is a water-miscible solvent which is used as a dispersive solvent in the next step. In this method, firstly, sodium chloride as a separation agent is filled into the narrow tube and the tea sample is placed on top of the salt. Then a mixture of deionized water and deep eutectic solvent is passed through the tube. In this procedure, the deep eutectic solvent (ChCl: phenol) is realized as tiny droplets in contact with salt. They go up through the tube and collected on top of the remained solution. By passing the droplets from the tea layer placed on the salt layer, the analytes are extracted into them. After collecting the solvent as separated layer, it is removed and mixed with another deep eutectic solvent (ChCl: butyric acid) and the mixture is dispersed into deionized water placed in a syringe. After adding acetonitrile to break up the cloudy state, the collected organic phase is injected into gas chromatography-mass spectrometry. Under optimal conditions, low limits of detection and quantification in the ranges of 2.6-8.4 and 9.7-29 ng kg<sup>-1</sup>, respectively, were obtained. Relative standard deviations lower than 7% express an acceptable repeatability for the present method. The extraction recoveries and enrichment factors in the ranges of 70-89% and 350-445 were obtained, respectively.

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**Multi residue determination of pesticides in cow milk using deep eutectic solvents-based  
dispersive liquid–liquid microextraction**

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Milk and its processed products have an important role in human food chain. They are a well supply of fat, protein, carbohydrate, and minerals which are provide many essential needs of human [1]. However, they can be indirectly contaminated with different pollutants *via* infected feed, water, and air [2]. Among these compounds pesticides have attracted main concern owing to their extensive application in farming. The presence of pesticide residues in some foods such as milk may be key risk to human health due to their possible toxicity [3]. Therefore many control establishments have advised some arrangements to prevent contamination of milk samples. A dispersive liquid–liquid microextraction method based on deep eutectic solvents has been developed for simultaneous determination of some pesticides including carbaryl, hexythiazox, pretilachlor, iprodione, famoxadone, sethoxydim and fenazaquin from milk samples. In this method, deep eutectic solvents prepared from ethylene glycol: choline chloride and p–chlorophenol: choline chloride are used as dispersive and extraction solvents, respectively. For this purpose, the analytes are extracted from milk samples into ethylene glycol: choline chloride in the presence of sodium chloride and after centrifugation the collected phase is mixed with p–chlorophenol: choline chloride (as the extraction solvent) and injected into deionized water. The cloudy solution is centrifuged and the sedimented phase is injected into gas chromatography–flame ionization detector. Under the optimum extraction conditions, low limits of detection and quantification within the ranges of 0.90–3.9 and 3.1–13 ng mL<sup>-1</sup> were achieved, respectively. Precision of the method expressed as relative standard deviation was in the ranges of 4.2–5.3 and 4.8–6.9 for intra– and inter–day (n=5) precision, respectively, at a concentration of 50 ng mL<sup>-1</sup> of each analyte. Extraction recoveries and enrichment factors were 64 and 89% and between 320 and 445, respectively. Lastly, several milk samples were successfully analyzed using the proposed method.

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**Determination of plasticizers in aqueous samples using simultaneous homogeneous liquid–**

**liquid and dispersive liquid–liquid microextraction and GC–MS**

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The alkyl or aryl esters of 1,2-benzenedicarboxylic acid commonly known as phthalate esters (PEs), and di-(2ethylhexyl) adipate (DEHA) are used as plasticizers in order to improve the flexibility of various polymers. Also, PEs and DEHA are used in several industrial sectors such as paints, cosmetics, glues, photographic films, insect repellents and etc [1]. Due to wide applications of these chemical compounds, the production amount of them is several million tons per year. The migration of PEs and DEHA from plasticized products into the environment and foods consumed by human due to not covalently bounded of these compounds to plastics can constitute a great menace to the environment and human health [2]. It was shown that PEs are estrogenic, carcinogenic, and have an endocrine disruption activity [3]. So, their determination in environmental matrices and human body has attracted great importance among the researchers. Now, mostly chromatographic techniques such as gas and high-performance liquid chromatography are used for analysis of PEs [4, 5]. But, due to trace concentrations of these compounds in real samples and in order to obtain the reliable results performing a sample preparation procedure before chromatographic techniques is essential. In the present work, a green mode of simultaneous homogeneous liquid–liquid microextraction and dispersive liquid–liquid microextraction assisted by sodium sulfate has been developed for the extraction and preconcentration of some phthalate esters and di-(2-ethylhexyl) adipate from different aqueous samples prior to their determination by gas chromatography–mass spectrometry. In this method, an appropriate mixture of sodium sulfate solution (phase separation agent and disperser solvent) containing *iso*-propanol (extraction solvent) is rapidly injected into an aqueous solution containing sodium sulfate and the selected analytes. By this action the extraction solvent is dispersed as fine droplets into the aqueous phase. After centrifuging the extractant containing the extracted analytes is collected on the surface of the aqueous phase. Under the optimum conditions, limits of detection and quantification were obtained in the ranges of 14–33, and 47–110 ng L<sup>-1</sup>, respectively. The extraction recoveries and enrichment factors of the selected phthalate esters ranged from 79–94% and 395–470, respectively. The relative standard deviations were  $\leq 7\%$  for intra- (n=6) and inter-day (n=4) precisions at a concentration of 250 ng L<sup>-1</sup> of each analyte.

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**Application of molecular imprinted polymers based stir bar for selective extraction and pre-concentration of carbamazepine in biological samples**

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Carbamazepine (CBZ), 5-H-dibenze[b,f]azepine-5-carboxamide, is the most frequently prescribed first-line drug for the treatment of simple and complex partial seizures and psychiatric diseases [1]. It is almost completely metabolized in the body and only small traces are excreted unchanged in urine. The pharmacokinetic characteristics of CBZ are complex; there is no simple relationship between the dose of CBZ and concentration of the drug in body fluids. Therapeutic concentrations have been reported to be 2–12 µg/ml, although considerable variations may arise [2]. As we know, analysis of most of drugs in the biological samples are challenging due to the complexity of these matrices. The presence of endogenous interferences, such as proteins in plasma, serum and inorganic salts in urine demands sample pretreatment prior to the analytical determination. So, the sample preparation procedures are an undeniable step in drug analysis [3, 4].

In this work, we synthesized and developed a selective molecular imprinted polymer (MIP) based stir bar for pre-concentration of low level of CBZ in biological samples especially urine and serum. The capability of the developed selective stir bar for pre-concentration of CBZ as an analyte, were investigated with a magnetic solid-phase extraction method. In this method, a stir bar coated with polyamide was placed in the 2 mL sample solution containing CBZ in desired concentration and the sorption was carried out for 20 min while stirring at 900 rpm. After extraction, the stir bar was removed from the sample solution with tweezers and the analyte desorbed into 500 µl vial containing 10% (v/v) acetic acid/methanol. Desorption of the CBZ was performed stirring for 15 min. 50 µL of the extract solution were injected into the HPLC-UV system. Chromatographic separation was achieved in approximately 10 min on a reversed-phase C18 column using a ternary mixture of potassium dihydrogen phosphate buffer (pH 6.0)/acetonitrile/2-propanol (63:22:15, v/v) as the mobile phase, at a flow rate of 1.0 mL/min. The UV detector was set at 220 nm. Calibration curves were linear with regression coefficients greater than 0.992 over the concentration ranges 0.1–12 µg/mL for CBZ. Applying this adsorbent enables access to accurate and precious information about CBZ levels in the body fluids and it seems to be a simple and suitable tool for routine therapeutic drug monitoring.

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**Liquid phase microextraction based on deep eutectic solvent for extraction of agrochemical pesticides by gas chromatography**

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In the present work, a new class of solvent in the name of Deep eutectic solvent (DES) were synthesized and used as an extraction solvent in a headspace single drop microextraction method for the preconcentration and extraction of triazole pesticides from real sample by gas chromatography-flame ionization detection using choline chloride and 4-chlorophenol as deep eutectic solvent. Extraction was carried out by a hanging micro drop. The significant parameters HS-SDME process (type of solvent, drop volume, stirring speed, extraction temperature, sample pH and extraction time) were optimized. The limit of detection (LODs) calculated between 100 and 0.001  $\mu\text{g mL}^{-1}$  with the relative standard deviation (RSD%) ranging from 4.3 to 8.2.





**Synthesis of Magnetic graphene Oxide/Soluble egg protein (GO-SEP/Fe<sub>3</sub>O<sub>4</sub>)  
Nanocomposite and its application in removal of heavy metals from water**

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Removal of toxic heavy metals from water samples is an important environmental challenge [1-2]. In this work GO-SEP/Fe<sub>3</sub>O<sub>4</sub> is used as a bio-sorbent for the removal of Hg<sup>2+</sup>, Pb<sup>2+</sup>, Cd<sup>2+</sup> and Sb<sup>2+</sup> from water. The effects of contact time, pH, Temperature, initial metal concentration, and amount of adsorbent on the adsorption process were studied. The time required for the removal of metal ions was about two hour. Effective removal of metal ions was demonstrated at pH values of 4-8. The maximum adsorption capacities of Hg- GO-SEP/Fe<sub>3</sub>O<sub>4</sub>, Pb- GO-SEP/Fe<sub>3</sub>O<sub>4</sub>, Sb- GO-SEP/Fe<sub>3</sub>O<sub>4</sub> and Cd- GO-SEP/Fe<sub>3</sub>O<sub>4</sub> were 8.77 mmol g<sup>-1</sup>, 12.20 mmol g<sup>-1</sup>, 25.10 mmol g<sup>-1</sup> and 4.05 mmol g<sup>-1</sup>, respectively. Metal adsorption onto GO-SEP/Fe<sub>3</sub>O<sub>4</sub> was evaluated by Langmuir and Freundlich isotherms. Results indicate that the Langmuir isotherm model is the most suitable one for the adsorption process using water.

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## A Highly Sensitive Electrochemical Determination of Eletriptan at $\beta$ -Cyclodextrin and Graphene Oxide Nanosheets Modified Glassy Carbon Electrode

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Eletriptan (ELT) is a novel, orally active, selective serotonin 5-HT<sub>1B/1D</sub> receptor agonist and is second generation antimigraine drug [1]. Eletriptan is used for the treatment of acute migraine headaches. Its pharmacological effects include the constriction of cerebral blood vessels and neuropeptides secretion blockade which eventually relieves the pain [2, 3].

This paper reports a sensitive and selective ELT sensor was developed by utilizing poly ( $\beta$ -cyclodextrin) ( $\beta$ -CD)/ Graphene Oxide Nanosheets (GONs) composite. The composite material was characterized using scanning electron microscopy. The functionalization of GONS with  $\beta$ -CD was scrutinized by varying the content of the  $\beta$ -CD material. Interestingly, the synergistic electrocatalytic activity was examined at different  $\beta$ -CD loadings functionalized GONs in the sensitivity for the detection of ELT. The process of oxidation and its kinetics were established by using cyclic voltammetry, chronoamperometry and differential pulse voltammetry (DPV) techniques. The electrochemical response is adsorption controlled and irreversible in nature involving one electron accompanied by a transfer of one proton. Under the best experimental conditions, the sensor exhibited a linear response to ELT from 0.1  $\mu$ M to 63  $\mu$ M, with a limit of detection of 36 nM, one of the lowest achieved up until now. The reproducibility, repeatability and stability of the sensor were examined and are superior to those reported in the literature using similar architectures for ELT sensors. The proposed method was successfully applied for determination of the ELT in human blood serum and urine sample with a good selectivity and suitable recovery.

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## Electrochemical Determination of Valtrex Utilizing Carbon Paste Electrode Modified with Polymeric Film/ZnO Nanoparticles

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Valaciclovir (valtrex) is an antiviral drug used in the management of herpes simplex and herpes zoster. Valaciclovir is the L-valyl ester of acyclovir, which is rapidly converted to acyclovir after oral administration by first-pass metabolism in the liver. Valaciclovir has the same mechanism of action, antiviral spectrum, and resistance profiles as acyclovir with bioavailability [1]. From the electrochemical point of view, only one study has been made on this compound [2]. So the electrochemical determination of the present drug is favorable due to its simplicity, portability, fast responses, good sensitivity and high selectivity.

In our present investigation, the poly (L-methionine)/ZnO nanoparticles based electrochemical sensor was fabricated by the electropolymerization of L-methionine on the surface of ZnO nanoparticles immobilized onto the carbon paste electrode (CPE). The developed electrochemical sensor was abbreviated as poly (L-MeT)/ZnO NPs/CPE. This electrochemical sensor shows an excellent electrochemical activity towards detection of Valacyclovir (VALA). The surface morphology of different modified electrodes was studied by the help of scanning electron microscopy (SEM). The limit of detection (LOD) values for VALA was determined using the differential pulse voltammetry (DPV) with the calculated value of 1.3  $\mu\text{M}$ . The effect of pH, scan rate and concentration of VALA were studied in detail. The presented methodology possesses a reliable reproducibility, repeatability and stability in biological samples. The obtained results suggest that the fabricated composite chemical sensor poly (L-MeT)/ ZnO NPs/ CPE has satisfactory electroanalytical performance. The proposed electrode was successfully applied for VALA determination in pharmaceutical formulations with promising results.

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**Waste Management and Chemical Test Methods For Designating Dangerous Waste In  
Chemical Laboratories  
(A glimpse into the conservation and Restoration laboratories of Historical and Cultural  
relics)**

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Dealing correctly with laboratory wastes is an important issue for all who manage or are employed in chemical laboratories. This Note outlines best practice in managing wastes from chemical laboratories in the context of relevant statutory controls. It stresses both the need to assess the risks to health or safety in handling wastes, and the need to protect the wider environment. Laboratory waste management is a broad subject. This Note does not pretend to be a full or definitive guide nor does it address issues such as microbiological or medical wastes. The environmental impact caused by teaching and research with regard to chemical waste is of increasing concern, and attempts to solve the issue are being made. Education and research-related institutions, in most laboratory and non-laboratory activities, contribute to the generation of small quantities of waste, many of them highly toxic. The management of hazardous chemical waste at the Universities and research centers consists of the collection, storage, and on site comingling of waste generated in laboratories and other campus facilities. So in this paper briefly describes the function and responsibility of each group and its relation to hazardous chemical waste management. In an effort to create a more effective, cost efficient and environmentally friendly waste management system on campus, we are proposing the following procedures for the disposal of hazardous chemical laboratory waste.

-What are wastes?

- Types of laboratory waste

- Dangerous Waste Designation

- Analytical Test Methods

-Preparing a Waste Management Plan(A methodological guidance note)

- Procedures for laboratory chemical waste disposal

This article presents Waste classification, sampling, analysis and an assessment of the problem and identifies possible solutions, indicating pertinent laws, directives and guidelines; examples of institutions that have implemented protocols in order to minimize the generation of waste; harmonization of procedures for waste management and waste minimization procedures such as reduction, reuse and recycling of chemicals. Also, a glimpse into the process of classifying, identifying, and transferring standard wastes from Research institutes of conservation and restoration of historical monuments will be addressed. The success of the management system depends on cooperation between the research community and Environmental Health and Safety (EH&S). All laboratory personnel should use this manual to help classify chemical waste and determine the appropriate route of disposal for that waste.

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**Extraction and spectrophotometric determination of some parabens using air-assisted liquid-liquid microextraction based on solidification of floating organic drops and its optimization by chemometrics methods**

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This study addressed an air-assisted liquid-liquid microextraction method coupled with a multivariate calibration method, namely partial least square (PLS). This method was developed for the extraction and simultaneous determination of ethylparaben (EP) and propylparaben (PP) via a spectrophotometric approach. Because of the reproductive and endocrine toxicity for parabens from food, therefore, it is critical to develop sensitive, simple and rapid methods for the determination of trace parabens [1]. Spectrophotometric methods combined with multivariate data analysis have developed as rapid, inexpensive and favorable tools for qualitative analysis [2]. In this work, a two-step microextraction method was used. In the first step analytes were extracted from acidic aqueous solution into dodecanol, as an organic solvent and the second step, the analytes were simultaneously back-extracted into an alkaline aqueous solution. The high absorption signal of dodecanol was the main reason to perform this back extraction [3]. The effects of different parameters such as extraction solvent volume, ionic strength of aqueous solution, pH, number of extraction cycles, and aqueous sample volume were investigated and optimized using (CCD) as the experimental design and analysis. Finally, a multi response optimization approach based on a desirability function (DF) of the factors was employed to simultaneously maximize the response factors (extraction efficiency of parabens).

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**Mediatory determination of antihypertensive drug nifedipine on glassy carbon electrode modified with novel ferrocene based ionic liquid**

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Ionic liquids (ILs) are liquids containing solely ions with melting points lower than 100 °C<sup>1</sup>. One of the attractive attributes of ILs is the potential to generate a wide range of types of ILs with fine-tuned physicochemical properties by the combination of various cations with anions, along with rational functionalization of ions<sup>2</sup>. The idea of task-specific ionic liquids (TSILs) carrying specific functionality tailored for certain applications has become more popular, and an impressive catalog of TSILs with pendant acid, base, alcohol, or ether groups on one (or both) of the ions are recently synthesized<sup>2</sup>. Ferrocene is an organometallic compound which has been used as an effective redox mediator for the electrocatalytic oxidation of various substrates due to its unique electrochemical behavior<sup>3</sup>. Therefore, combination of unique characteristic of ionic liquids and ferrocene by synthesizing ferrocene based ionic liquids could be beneficial. Nifedipine, known as a calcium channel blocker, is widely used in the treatment of cardiovascular diseases such as hypertension and angina pectoris. However, high doses are toxic and can result in heartbeat, nausea, vomiting, etc, so the sensitive and accurate detection of nifedipine is required. Recently, electrochemical methods were proved to be effective for nifedipine determination<sup>4</sup>.

In the present study, the N-(1-methyl imidazolium)-propyl ferrocene sulfonamide tetra fluoroborate ionic liquid was synthesized and applied for surface modification of glassy carbon electrode. Then, this modified electrode was used for mediatory electrochemical determination of antihypertensive drug nifedipine. Cyclic voltammetry was explored to investigate preliminary experiments, optimization of effective parameters on electrode performance and studying kinetic parameters of modified electrode. By using hydrodynamic amperometry as sensitive method the calibration curve was plotted in the concentration range of 3 nM to 110 nM. The detection limit was calculated as 1 nM based on signal to noise ratio of 3. Lastly, the present method was applied to determine nifedipine in urine and plasma samples which was taken from patients who was administrated nifedipine tablet and satisfactory results were obtained with good accuracy.

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## Electrochemical determination of acetaminophen drug on sol-gel electrode modified with Fe<sub>3</sub>O<sub>4</sub> nanoparticles

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Acetaminophen (paracetamol, N-acetyl-p-aminophenol) is a well-known drug which has extensive applications in pharmaceutical industries. It is an antipyretic, non-steroidal anti-inflammatory drug. It is the preferred alternative to aspirin, particularly for patients who cannot tolerate aspirin. and its use is one of the most common causes of poisoning worldwide. and analgesic compound that has high therapeutic value. It is also used as a precursor in penicillin, and as stabilizer for hydrogen peroxide, photographic chemical, etc. It is a suitable alternative when the patients are sensitive to aspirin. At the recommended dosage, there are no side effects. However, overdoses of acetaminophen cause liver and kidney damage and may lead to death. It is suspected that a metabolite of acetaminophen is the actual hepatotoxic agent. <sup>1</sup>

Magnetic nanoparticles have been intensively studied due to the fact that they can be used in a wide range of application such as clinical diagnosis, mineral separation, magnetic storage devices, absorption of microwave radiation, magneto-optic materials, and microwave filters. Among magnetic nanoparticles, magnetite (Fe<sub>3</sub>O<sub>4</sub>) is a metallic mineral with the most powerful magnetism among transition metals such as nickel (Ni), cobalt (Co), and zinc (Zn). <sup>2</sup> Fe<sub>3</sub>O<sub>4</sub> nanoparticles are easily oxidized and aggregated in aqueous system. In order to fulfil application requirements of Fe<sub>3</sub>O<sub>4</sub>, surface modification is needed. Surface modification by coating is one way to protect Fe<sub>3</sub>O<sub>4</sub> from oxidation and reduce interparticle magnetic forces so improve the dispersibility of nanoparticles in solution and protect the Fe<sub>3</sub>O<sub>4</sub> nanoparticles in a state of dissolution acid. Fe<sub>3</sub>O<sub>4</sub> is easy to aggregate and has bad dispersion stability because of its magnetism. <sup>3</sup>

In the present study, the sol-gel electrode modified by Fe<sub>3</sub>O<sub>4</sub> was explored to detect acetaminophen. Cyclic voltammetry was applied to investigate preliminary experiments, optimization of effective parameters on electrode performance and studying kinetic parameters of modified electrode. By using hydrodynamic amperometry as sensitive method the calibration curve was plotted in the concentration range of 0.3 μM to 90 μM. The detection limit was calculated as 0.1 μM based on signal to noise ratio of 3. Lastly, the present method was applied to determine acetaminophen in phosphate buffer at PH~7 in serum samples which was taken from patients who was administrated acetaminophen tablet and satisfactory results were obtained with good accuracy.

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## 2-Pyridine Carboxaldehyde Hydrazone Ligand and its Complexes: Synthesis and Electrochemical Characterizations

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In this work from the reaction of 2-pyridine carboxaldehyde hydrazone ligand (HL) with Nickel (II), Cobalt (II), Manganese (II) and Vanadate ions new complexes were formed as  $\text{Ni}(\text{C}_{13}\text{H}_{11}\text{N}_3\text{O}_2)_2$ ,  $\text{C}_{26}\text{H}_{22}\text{O}_4\text{N}_6\text{Co}_2\text{Cl}_2$ ,  $\text{C}_{13}\text{H}_9\text{O}_2\text{N}_3\text{MnCl}_2$ ,  $\text{C}_{13}\text{H}_{10}\text{N}_3\text{O}_4\text{V}$ , respectively. These complexes are characterized and identified with x-ray diffraction, elemental analysis and spectroscopic methods. These complexes generally crystallize in monoclinic and triclinic systems and space groups of P21/c and P-1[1]. The electrochemical responses of the ligand HL and its complexes were studied by recording the cyclic voltammograms (CV) in the potential range of +1.0 V to -1.0 V[2]. The CV of ligand and its complexes show that all of them are electro-active. HL ligand shows one anodic ( $E_a=0.31\text{V}$ ) and one cathodic ( $E_b=-0.52\text{V}$ ) couple. In CV grams of Co(II) and Ni(II) complexes oxidation peaks are observed in  $E_{A1} = 0.59\text{V}$  and  $E_{A1} = 0.69\text{V}$ , respectively, displaying some shifts compared to the ligand. In low potentials regarding to the reduction of oxidized Co(II) and Ni(II) complexes, there are one peak in  $E_B = -0.92\text{V}$  for cobalt complex) and  $E_B = -0.64\text{V}$  for Nickel complex. These oxidation/reduction couples could be related to  $\text{Co}^{\text{III}}/\text{Co}^{\text{II}}$  and  $\text{Ni}^{\text{II}}/\text{Ni}^0$  species, respectively. Similarly, for Mn(II) and Vanadate complexes, there are two anodic peaks in  $E_{A1} = -0.98\text{V}$  and  $E_{A2}=0.59\text{V}$  for Mn(II) complex and  $E_{A3} = 0.22\text{V}$  and  $E_{A4}=0.55\text{V}$  for Vanadate complex. In low range potentials, there are two reduction peaks in  $E_{B1} = -0.64\text{V}$  and  $E_{B2} = -0.88\text{V}$  for Mn(II) complex and two reduction peaks in  $E_{B3} = -0.85\text{V}$  and  $E_{B4} = -0.35\text{V}$  for Vanadate. These reduction peaks could be related to reduction of  $\text{Mn}^{\text{VI}}$  to  $\text{Mn}^{\text{III}}$  and  $\text{Mn}^{\text{III}}$  to  $\text{Mn}^{\text{II}}$ ,  $\text{V}^{\text{V}}$  to  $\text{V}^{\text{IV}}$  and  $\text{V}^{\text{IV}}$  to  $\text{V}^{\text{III}}$ , respectively [4].

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Defining pH-dependent equilibrium reactions as a solution to overcome the correlation between kinetic parameters

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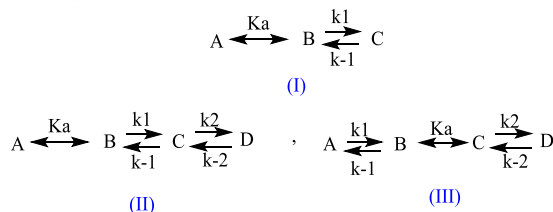
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It is a well-known fact that in first-order reverse reactions ( $A \xrightleftharpoons[k_2]{k_1} B$ ), the rate constants cannot uniquely be determined from incomplete concentration data. This is due to the correlation between the rate constants.

Several well-conducted studies have investigated the theoretical basis and visualization of the correlation for reversible first order reaction schemes [1]. Therefore, breaking this correlation is necessary to determine the rate constants. In this work, coupled equilibrium kinetic processes suggested as a new strategy to overcome this problem. Also, this fact opens the possibility to determine kinetic parameters in multi-step kinetic reactions (scheme.1).



(Scheme.1)

The complete analysis of the complex reaction mechanisms with the possibility of calculating and inserting the equilibrium and kinetic parameters into the fitting algorithm are possible by model-based global analysis. After the fitting process, the optimal equilibrium and kinetic parameters together with an estimate of their standard deviations have been obtained [2-4]. Therefore, in the following, datasets have been simulated for a range of different chemical cases and the pH-dependent keto–enol tautomerization chosen as the experimental case of equilibrium intertwined with kinetic chemical mechanisms ( $E+H \xrightleftharpoons{K_a} EH \rightleftharpoons KH$ ). Herein, the keto–enol tautomerism kinetics of 1-phenyl-1,3-butadione (benzoylacetone, BZA) in aqueous solution has been simulated and investigated in buffered medium in the UV–Vis spectra of BZA at the range of 200-400 nm in 5°C. This system has been monitored for 5 min. Our proposed equilibrium-kinetic model provides rank deficient single data sets which can be broken by matrix augmentation through pH and temperature changes. Different pHs used as an appropriate and convenient augmentation strategy in this study to allow the extracting the equilibrium and kinetic constants.

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## Electrochemical determination of quercetin on sol-gel electrode modified with nanodiamond

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Antioxidants are substances that may protect cells from the damage caused by unstable molecules such as free radicals. Flavonoids are phenolic substances widely found in fruits and vegetables. The previous studies showed that the ingestion of flavonoids reduces the risk of cardiovascular diseases, metabolic disorders, and certain types of cancer. These effects are due to the physiological activity of flavonoids in the reduction of oxidative stress, inhibiting low-density lipoproteins oxidation and platelet aggregation, and acting as vasodilators in blood vessels. Quercetin (QU), a plant pigment is a potent antioxidant flavonoid and more specifically a flavonol, found mostly in onions, grapes, berries, cherries, broccoli, and citrus fruits.

The mechanism of electrochemical oxidation of quercetin on a glassy carbon electrode has been studied using cyclic, differential pulse and square-wave voltammetry at different pH. It proceeds in a cascade mechanism, related with the two catechol hydroxyl groups and the other three hydroxyl groups which all present electroactivity, and the oxidation is pH dependent. <sup>2</sup>

Nanodiamonds or diamond nanoparticles with a size below 1 micrometer. They can be produced by impact events such as an explosion or meteoritic impacts. Because of their inexpensive, large-scale synthesis, potential for surface functionalization, and high biocompatibility, nanodiamonds are widely investigated as a potential material in biological and electronic applications and quantum engineering. There are three main aspects in the structure of diamond nanoparticles to be considered: the overall shape, the core, and the surface. Through multiple diffraction experiments, it has been determined that the overall shape of diamond nanoparticles is either spherical or elliptical. At the core of diamond nanoparticles lies a diamond cage, which is composed mainly of carbons. <sup>3</sup>

Herein, we report the fabrication of ND modified electrode for the sensitive and selective detection of QU. The unique properties of ND modified electrode translate to enhanced electrocatalytic activity and lower overpotential towards the detection of QU. The effect of scan rate and pH on the redox electrochemical QU at ND modified electrode as studied and discussed. By using differential pulse voltammetry as sensitive method the calibration curve was plotted in the concentration range of 0.1  $\mu\text{M}$  to 75  $\mu\text{M}$ . The detection limit was calculated as 0.04  $\mu\text{M}$  based on signal to noise ratio of 3. Lastly, the present method was applied to determine QU in vegetable samples and satisfactory results were obtained with good accuracy.

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Photocatalytic degradation of nitroaromatic derivatives of Redwater in visible light

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In this paper degradation of the PNP and TNT were performed by the catalysts of  $WO_3 \cdot Fe_3O_4$  / $WO_3$  and  $BiVO_4$  under visible light. The catalysts were synthesized by hydrothermal method and the process was performed in a suspension reactor equipped with a metal halid lamp (400 W). The synthesized catalysts were characterized using X-ray diffraction (XRD), Field emission scanning electron microscopy (FE-SEM), and Diffuse reflection spectroscopy (DRS). The effective parameters of pH, reaction temperature, and light intensity have been studied. The results showed that using [Catalyst] =2000 ppm, [PNP] =20 ppm, T=250C, and pH=12 after 240 min, the degradation efficiency for  $WO_3 \cdot Fe_3O_4$  / $WO_3$  and  $BiVO_4$  obtained about 40%, 32%, and 22%, respectively.

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**Development of sensitive impedimetric immunosensor based on Pd-Au@carbon dots nanocomposite for prostate-specific antigen (PSA) detection**

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Cancer is a major public health problem and represents a significant burden of disease in the world. Among cancer concerning men worldwide, prostate cancer (PCa) makes its mark as one of the leading causes of cancer-related morbidity among men over 50 years of age [1]. In the last three decades, serum PSA has been shown to be the most reliable tumor marker for the early detection of PCa at the organ-confined stage and also monitoring the disease recurrence after treatment [2].

In this study, an impedimetric immunosensor based on screen-printed carbon electrode (SPCE) modified with Pd-Au@carbon dots for rapid and sensitive detection of prostate specific antigen (PSA) was developed. To achieve this goal, a zwitterionic polymer brush was fabricated on Pd-Au@carbon dots nanocomposite and then modification with boronic acid was conducted. To preserve the biological activity of antibody and improve the sensitivity, site-specific and self-oriented immobilization of antibodies via interaction of boronic acid and antibody were performed. The fabrication of immunosensor was characterized by using transmission electron microscopy, X-ray diffraction, cyclic voltammetry, and electrochemical impedance spectroscopy. The signaling mechanism of the proposed immunosensor was based on the increase in the  $[\text{Fe}(\text{CN})_6]^{3-/4-}$  charge transfer resistance as an electrochemical probe in the presence of target analyte. The relationship of the impedance changes and the concentration of PSA was well fitted into a simple linear regression in the range of 0.6–280  $\text{pg mL}^{-1}$ . Limit of detection for the immunosensor was determined to be 0.6  $\text{pg mL}^{-1}$ . The developed immunosensor exhibits interesting characteristics such as wide linear range, low detection limit, and excellent specificity.

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**A lateral flow immunoassay for visual detection of prostate-specific antigen (PSA) in food using gold and silver nanocomposite**

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Diagnostics is of great importance in the medical practice, as only timely diagnosis allows choosing an adequate method of treatment. The use of methods of early diagnostics of diseases is one of the main directions of development of preventive medicine. The prostate carcinoma occupies the first rank for prevalence and the second rank for death rate among oncological diseases of men. The disease is characterized by a slow development and asymptomatic course up to the late stages, which complicates its clinical diagnostics [1, 2]. Now the determination of PSA, an oncomarker, in the samples of blood serum is used for an early diagnostics of this disease. The determination of PSA is the obligatory clinical analysis for men after 50 years in the EU countries and the United States. The PSA content in blood serum of healthy men does not exceed 4 ng/ml. Nonmalignant prostate hyperplasia is accompanied by an increase in the PSA level up to 10 ng/ml; at the PSA level above 30 ng/ml, the diagnosis of the prostate carcinoma is confirmed for almost all patients examined. The determination of PSA level is carried out to reveal prostatitis, to monitor the course of the disease, and to control the treatment efficiency. In this study, lateral flow immunoassay (LFA) strip was developed for fast screening of blood samples for prostate-specific antigen (PSA) using the respective monoclonal antibody immobilized on nanoparticles with a silver core and a gold shell (AgAu) as detection reagent. Assay is in sandwich format and uses two specific monoclonal antibodies against PSA, one of which is labeled with AgAu nanoparticles and other is immobilized at test line. The developed biosensor is specific and has a lower detection limit of 0.3 ng/ml. The method may be suitable for testing PSA in blood samples as it is quick, easy to perform and reproducible.

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## Trilinear structure and factor interaction of three-way data structures obtained using two-factor designs

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Experiments performed according to two-way factor designs monitored using multivariate methods produce three-way data structures. The relationship between the presence of factor interaction and the trilinear model structure of the three-way data is investigated.

In this work, this problem is investigated for a lipidomic study of the effects of time and tributyltin TBT dose on multiple samples of *Daphnia Magna* species during their molting and reproduction. Data simulations were performed using previously obtained experimental data [1]. In this simulations, the presence or not of interaction between the two factors, time and TBT dose, were considered, as well as the number of components (sources of data variance), bilinear vs trilinear behavior.

Results show that for one single component systems (one single pattern of variation of the data), no factor interaction implies trilinearity, whereas factor interaction implies the lack of trilinear structure and the data are only bilinear. In the case of multicomponent systems, this relationship is more complex and the presence of interaction was shown in all cases for the global data response. The trilinear model gives individual responses for every separated component without interaction, although the global (all components) response appears to show the interaction between the two factors. In the case of only fulfillment of the bilinear model, the interaction between factors was always present.

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**A novel and facile electrochemical synthesis of WO<sub>3</sub> nanoparticles on the surface of glassy carbon electrode and their enhanced electrocatalytic performance in sensing of isoniazid**

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This work introduces a novel electrochemical approach to synthesize the tungsten oxide nanoparticles (WO<sub>3</sub> NPs) on the GCE surface as an effective electrocatalyst for isoniazid sensor. Stable WO<sub>3</sub> NPs have been prepared by a two-step electrochemical method. At first, the tungsten nanoparticles (W NPs) were electrodeposited on the GCE by potentiostatic method performed in a criterion concentration of tungsten electrolytes (Na<sub>2</sub>WO<sub>4</sub>·2H<sub>2</sub>O, pH=7.0) at -1.3 V (vs. SCE) for 120 s, and then W NPs were oxidized to WO<sub>3</sub> film via repetitive potential cycling between -1.0 V and 1.0 V at a scan rate of 100 mV/s in alkaline solution (0.1 M NaOH). The nanoparticles have been characterized in detail by field emission scanning electron microscopy (FESEM), energy-dispersive X-ray analysis (EDS) and X-ray diffraction (XRD) technique, indicating that the W and WO<sub>3</sub> NPs have been successfully synthesized. The obtained WO<sub>3</sub>/GCE sensor displays a significant enhancement of electrochemical activity towards isoniazid. In addition, the electrochemical response of WO<sub>3</sub>/GCE is not influenced by potential interferents (ascorbic and uric acids, glucose, and various inorganic salts). Therefore, the proposed sensor was successfully used for analysis of isoniazid in biological and pharmaceutical samples. The major important features of this sensor are its low cost, availability, simple and fast fabrication, reversible change of conductivity, increased surface-to-volume ratio, high stability, sensitivity, selectivity and biocompatibility which make it as a promising candidate to design a rapid and low-cost platform for (bio)sensor and catalyst applications.

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## Evaluation of the corrosion resistance of electroless Ni-P and Ni-P-PTFE composite coatings by electrochemical impedance spectroscopy

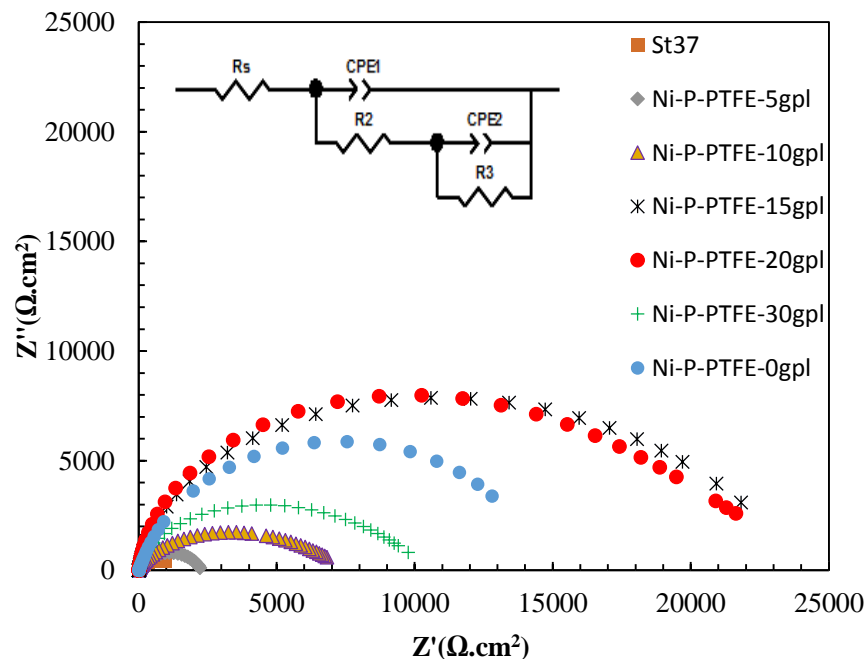
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Electroless Ni-P coatings are widely used for corrosion protection in a variety of environments[1]. In this research different concentrations of PTFE (0-5-10-15-20-30 wt. %) were applied to Ni-P-PTFE composite, in order to enhance lubricant characteristics of the composite. Nickel sulfate, PTFE, NaH<sub>2</sub>PO<sub>2</sub> electroplating bath was used to prepare composites on mild steel. Bath temperature was set to 90±2. Surface morphology and elemental analysis of prepared composites were investigated using scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS), respectively. Among the various techniques for the determination of corrosion resistance, electrochemical impedance spectroscopy (EIS) is considered to be superior as it provides not only an assessment of the corrosion resistance of different deposits but also enables the mechanistic pathway by which the deposits become corroded to be determined. Tafel corrosion test was also used to determine corrosion resistance of composites in order to confirm EIS results. Electrochemical results revealed that PTFE 20 g L<sup>-1</sup> sample had the best corrosion resistance.



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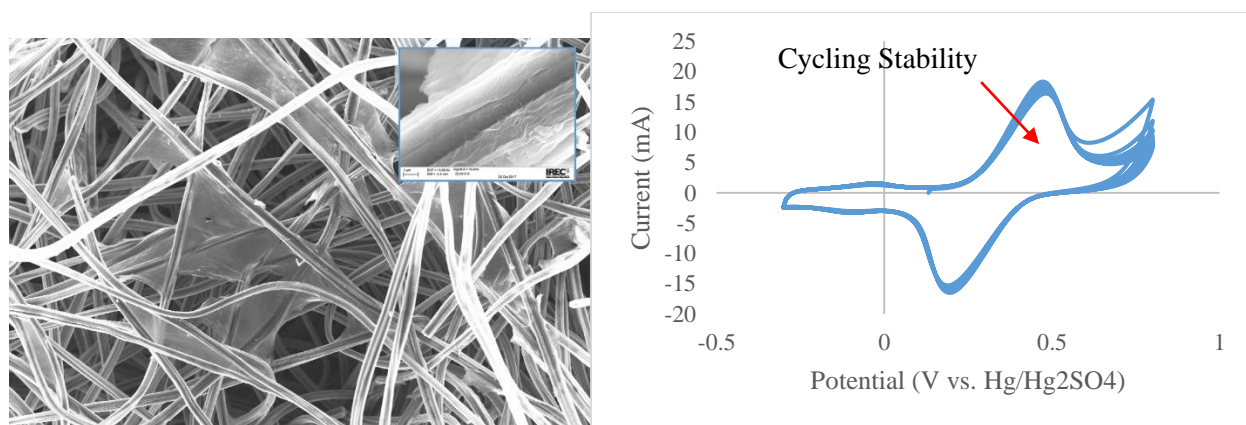
## Graphene Oxide electrospun carbon felt electrode as high performance electrode for Vanadium Redox Flow Batteries

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Vanadium redox flow batteries (VRFBs) have attracted much attention as next-generation large-scale energy storage devices [1]. However, the graphite felt electrodes suffer from a drop in the energy efficiency induced by the large activation polarization during vanadium redox reactions[2]. In this work, we prepared graphene oxide modified carbon felt electrodes. Electrospinning of graphene oxide suspension was used to cover carbon felt fibers with graphene oxide nano-sheet [2]. Morphology of as-prepared electrodes were studied by SEM. XRD patterns were used to investigate the presence of graphene oxide nano sheets.



Cyclic voltammetry and electrochemical impedance spectroscopy technics were used to investigate electrochemical behavior of graphene oxide modified electrode towards vanadium redox couples reaction. Graphene oxide modified electrode showed outstanding performance for this purpose and cycling stability was of reliable [3].

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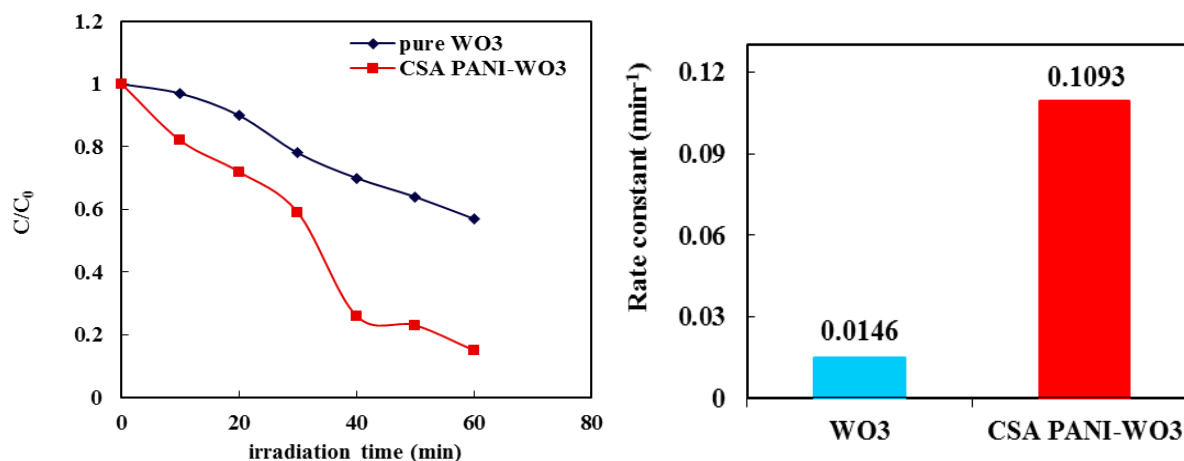
## Evaluating the performance of camphor sulfonic acid doped polyaniline-WO<sub>3</sub> binary nanocomposite as photocatalyst for degradation of methylene blue dye under solar irradiation

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Photocatalytic degradation of organic dyes as toxic pollutants are one of the crucial issues in the environmental fields. Conductive conjugated polymers with inorganic semiconductors have been used extensively as photocatalyst due to their high absorption coefficients, high mobility of charge carriers, and good environmental stability [1, 2]. In this research, camphor sulfonic acid doped polyaniline-WO<sub>3</sub> (CSA doped PANI-WO<sub>3</sub>) nanocomposite was synthesized via in situ emulsion polymerization and used as photocatalyst for degradation of methylene blue (MB) under solar irradiation. The synthesized nanocomposite was characterized with Fourier transform infrared (FTIR) spectroscopy, Raman spectroscopy, Field emission scanning electron microscopy (FESEM) and Energy dispersive X-ray spectroscopy (EDS). In order to photocatalytic studies, 50 mg of pure WO<sub>3</sub> and CSA doped PANI-WO<sub>3</sub> were dispersed in 50 mL aqueous solution containing 10 ppm of MB. The suspensions were stirred in dark conditions for 30 min to establish an adsorption-desorption equilibrium. Then the suspensions were irradiated with 250 W Xenon lamp. At given intervals, samples were taken and centrifuged at 4000 rpm for 15 min. The supernatants were analyzed with T80+ UV/VIS spectrophotometer (PG. Instruments Ltd). The degradation percentage of MB was obtained 43 % and 85 % for pure WO<sub>3</sub> and CSA doped PANI-WO<sub>3</sub>, respectively. Also, the constant rate of CSA doped PANI- WO<sub>3</sub> is 7.49 times higher than pure WO<sub>3</sub>. It is concluded that MB could be degraded more efficiently in the presence of CSA doped PANI- WO<sub>3</sub> nanocomposite.



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## Electrodeposition of Ni-P-PTFE composite coatings and evaluation of their electrochemical behavior

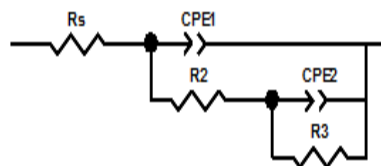
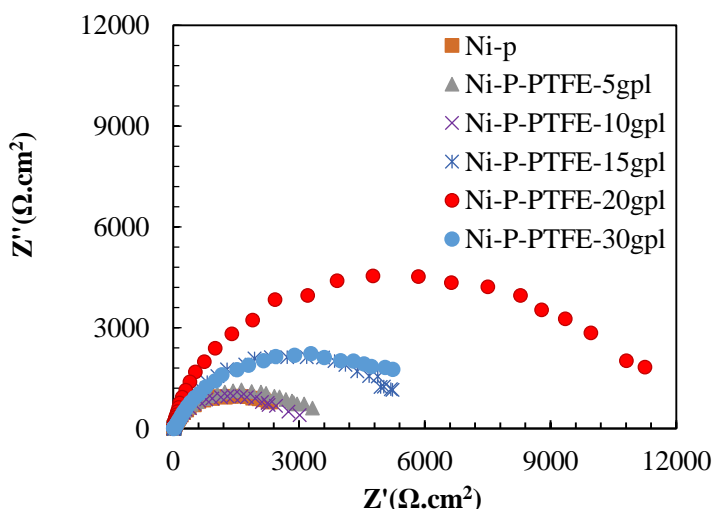
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There are many modern technologies, like medical devices and machines and aerospace need dry coatings with low friction and high wear resistant[1]. Characteristic of Ni-P alloy is that the incorporation of phosphorus, as alloying element, in the nickel lattice affects the structure of the deposit. Thus, depending on the phosphorus content the alloy could be crystalline, amorphous or a mixture of crystalline and amorphous phase. PTFE was added to composite to enhance lubricant characteristics of composite. In this study, the electrochemical performances of electrodeposited nickel-phosphorus (Ni-P) coating containing Polytetrafluoroethylene (PTFE) particles were investigated. Electroplating bath containing six different concentrations of PTFE (0, 5, 10, 15, 20 and 30 g L<sup>-1</sup>) was used to prepare Ni-P-PTFE composites. Ni-P/PTFE composite coatings were produced under direct current conditions from a modified Watts type bath at optimum current of 30 mA cm<sup>-2</sup>. Mild steel and pure nickel plate were used as cathode and anode materials, respectively. Corrosion behavior of the coatings was examined using potentiodynamic polarization and electrochemical impedance spectroscopy (EIS). The results show that there is a significant enhancement in corrosion resistance with the incorporation of PTFE particles into the Ni-P matrix. It was also observed that the addition of PTFE in the Ni-P alloy matrix has resulted in a smoother surface with a low friction coefficient.



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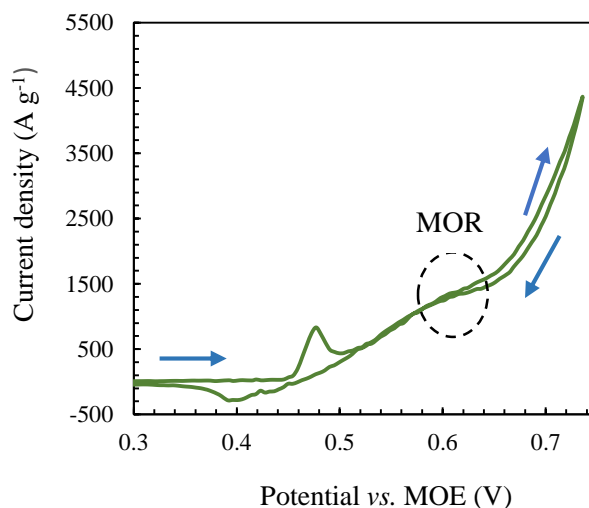
## Electrocatalytic performance of Ni/Pd bimetallic nanoparticles towards methanol electro-oxidation in alkaline medium

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Liquid fuels such as borohydride [1], hydrazine [2] and methanol [3] solutions have been used in the direct liquid-feed fuel cell. The electro-oxidation of these fuels is kinetically slow; thus a catalyst is required to improve the efficiency of the oxidation reaction. In this work, Ni/Pd nanoparticles with a particle size of 10 nm are synthesized successfully using a two-step successive reduction method. The physical characterization of Ni/Pd electrocatalyst is investigated by field emission scanning electron microscopy (FE-SEM), energy-dispersive X-ray spectroscopy (EDX) and transmission electron microscopy (TEM). Electrocatalytic properties of Ni/Pd nanoparticles towards methanol electro-oxidation are studied using cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) methods. The results show that the catalytic activity of the Pd/Ni electrocatalyst toward methanol electro-oxidation is 4.6 times higher than that of Pd because of the synergistic effect between Pd and Ni ( $1450 \text{ A g}^{-1}$  in presence of  $0.5 \text{ mol L}^{-1}$  methanol and scan rate of  $100 \text{ mV s}^{-1}$ ). Additionally, the effects of scan rate, methanol concentration and temperature dependency of methanol oxidation on Ni/Pd electrodes have been explored in this study. The results show that the methanol oxidation reaction on Ni/Pd electrocatalyst is controlled by mass transfer and this reaction has a low activation energy which leads to high catalytic activity. All results show that the Ni/Pd catalyst is a good anode catalyst candidate for the direct methanol fuel cell.



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## Highly Sensitive Detection Method of Dibenzyl Disulfide in Insulating Oil

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Highly sensitive detection method of dibenzyl disulfide (DBDS) in insulation oil was realized using solid phase microextraction (SPME) with, MWCNT/ PANI nanocomposite coating adsorbent followed by gas chromatography equipped with a ECD spectrometry (GC-ECD). An aniline-based polymer was electrochemically prepared and applied as a new fiber coating for solid phase microextraction (SPME) of dibenzyl disulfide (DBDS) in insulation oil. The polyaniline (PANI) film was directly electrodeposited on the platinum wire surface in sulfuric acid solution using cyclic voltammetry (CV) technique<sup>[1]</sup>. The efficiency of new coating was investigated using a laboratory-made SPME device and gas chromatography with electron capture detection for the extraction of dibenzyl disulfide from oil samples. The scanning electron microscopy (SEM) images showed the homogeneity and the porous surface structure of the film. The results obtained proved the ability of this polymer as a suitable SPME fiber coating for trapping the dibenzyl disulfide. The parameters effective On SPME of DBDS (i.e., extraction temperature, extraction time, desorption temperature, desorption time, salt concentration, and stirring rate) were investigated and optimized by one-variable-at-a-time method. Under optimized conditions (extraction temperature,  $55 \pm 1$  °C; extraction time, 35 min; desorption temperature, 260 °C; ; salt concentration, 10% w/v; and stirring rate, 1200 rpm), the limits of detection (LODs) were found in the range of 0.001-0.1  $\mu\text{g L}^{-1}$ , acceptable linear range with correlation coefficients ranging from 0.9878 , the repeatability and fiber-to-fiber reproducibility were in the range 4.7% and 9.4%, respectively.

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**A hard modelling strategy for tuning the apparent equilibrium constants of chemical systems**

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In most equilibrium reactions due to the complexity of complete model of chemical systems, the apparent equilibrium constants are preferable to the thermodynamic constants. Although the thermodynamic constants are changing only by temperature, the apparent constants are altered by environmental changes of chemical systems, e.g. total concentration of reagents, the intensity of light in photo-controlled reactions, types and concentration of solvents or composition of mixed solvents, the ionic strength of the chemical media, etc. Inspiring this, the main goal of this work is to control the conditions governing equilibrium systems in order to tune the apparent constants. Indeed, by extracting the analytic relationship between the parameters of the complete model and apparent model, the exact amount of the apparent constant(s) could be predicted.

At first, a basic strategy for calculating the tunable range of apparent constants of chemical equilibria has been proposed. Next, three case studies for tuning the apparent constants are investigated work. The examples of tuning the apparent constants of different chemical systems include systems with inclusion complexes such as Cyclodextrin complexes, aqueous micellar solutions for investigating the solvent effects and boric acid as a chemical system with a low thermodynamic constant. In all examples tuning the apparent constant is possible by regulating the chemical situation. Also, the Boric acid system selected as a real chemical system to confirm the reliability of the presented theory.

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**Functionalized polyvinyl alcohol/polyethylenimine magnetic iron oxide electrospun fibers as effective chromium (VI) adsorbent for water solution**

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Composite electrospun fibers have been extensively investigated as adsorbents for the waste water treatment. In this study, branched polyethylenimine (b-PEI)/polyvinyl alcohol (PVA) composite electrospun fiber adsorbent was fabricated and followed by cross-linking to render the fibers with good water stability, meanwhile Fe<sub>3</sub>O<sub>4</sub> particles were also immobilized on the fiber surface. The formation of PVA/PEI magnetic nanofibers were characterized via different techniques, with the aim of using them for efficient Cr(VI) removal from aqueous solutions. Various factors, such as solution pH, initial Cr(VI) concentration, contact time and coexisting anions, were analyzed during the adsorption process. The results showed that the Cr(VI) adsorption was highly pH dependent, and the maximum adsorption capacity reached up to 526.4 mg/g at 298 K. Experimental data, obtained from adsorption kinetics and adsorption isotherms studies, could be well fitted by Langmuir adsorption isotherm and first-order model. The desorption efficiencies of Cr(VI)-loaded on PVA/PEI magnetic nanofibers were evaluated using 0.5 mol L<sup>-1</sup> NaOH. The adsorption–desorption process is conducted for 5 cycles and the removal efficiency still keeps 96% after 3 cycles.

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**Synthesis, characterization and implementation of 3D nanoscale epoxy–polyhedral oligomeric silsesquioxanes network for isolation of polycyclic aromatic hydrocarbons in tea and coffee**

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Polyhedral oligomeric silsesquioxanes (POSSs) are 3D nanoscale structures[1] with fascinating potential to be used as extractive phases in solid phase microextraction (SPME). Here, as a case study, the octaglycidyl dimethylsilyl polyhedral oligomeric silsesquioxane (POSS–epoxy) network was fabricated on a stainless steel wire via sol–gel methodology and used as a SPME fiber coating. The uniform pore structure, high surface area, and hydrophobicity of POSS–epoxy[2], make it susceptible toward isolation of non– to semi–polar compounds. Performance of the POSS–epoxy fiber coating was examined considering three classes of typical environmental pollutants including chlorobenzenes (CBs), benzene derivatives (benzene, toluene, ethylbenzene, xylene (BTEX)) and polycyclic aromatic hydrocarbons (PAHs) and acceptable extraction efficiencies were achieved. The effects of various types of sol–gel precursors in the fabrication of fiber coatings were investigated. Also, extraction capability of the POSS–epoxy was compared with some commercial fibers such as polydimethyl siloxane divinyl benzene (PDMS–DVB) were obtained. All the influencing parameters affecting the headspace (HS) analysis and gas chromatography (GC) procedure were investigated and optimized. The POSS–epoxy fiber was applied to develop a HS–SPME–GC–MS method for quantification of PAHs, as model analytes, in tea, coffee and some other environmental water–based real samples. The extractive–phase was found to be very sensitive for determination of PAHs with reliable figures of merit such as acceptable linearity (1–200 ng L<sup>-1</sup>), low limits of detection (LODs), 0.1–0.3 ng L<sup>-1</sup>, suitable intra–day relative standard deviation (RSD% < 10 %) and inter–day (RSD% < 12 %), and long lifespan (number of uses > 200 times).

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**Modification of multi-walled carbon nanotubes surface by urea and its evaluation as electrocatalyst support for palladium in oxygen reduction reaction**

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Fuel cells are considered as a source of green energy of the past two decades. Polymer electrolyte membrane fuel cells (PEMFC) are devices in which, hydrogen and oxygen electrochemically react and produced water, electricity and heat. Basic cell is formed of two cathode and anode electrodes, which separated by an electrolyte. Electrode is made of three-phase of catalyst, ionomer and substrate. catalyst particles should have a good electrical connection with the carbon substrate and are in close contact with the membrane [1].

Insufficient catalytic activity and durability are key barriers to the commercial deployment of PEMFC. Recent observations suggest that carbon-based catalyst support materials can be systematically doped with nitrogen to create strong, beneficial catalyst-support interactions which substantially enhance catalyst activity and stability [2].

To study the effect of the catalyst, the three phase interface and evaluate the oxygen reduction reaction, a homemade half cell test was used. The half cell which made in the lab, has oxygen injection capability from one side and on the other side has proton conductivity from the solution to three phase interface. The part of half cell which is in contact with sulfuric acid, including nafion (for proton transfer of solution) and the other side consists of commercial gas diffusion layer (GDL) to conduct the distribution of oxygen to the interface is threephase. Multi-wall carbon nanotubes(MWCNT) were used to modification with urea. Pd nanoparticles on modified multiwalled carbon nanotubes (Pd-urea /MWCNT) catalysts have been prepared by an intermittent microwave heating (IMH) technique[3]. From the synthesized material, the catalyst ink was made and placed on the GDL by dropping. The electrode hot-pressed to the Nafion and placed in the half-cell. Electrochemical Measurements such as Cyclic voltammetry (CV), Electrochemical Impedance Spectroscopy(EIS) and Linear sweep voltammetry (LSV) use for evaluation. The electrochemical data of Pd-urea/MWCNT obtained were compared with Pd/MWCNT and commercial Pd/C for efficiency and stability, and the results indicate that improvement has been achieved.

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**A photoluminescent nanopaper integrated with molecularly imprinted polymer with a smartphone readout towards selective diagnosis of phenylketonuria**

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Phenylketonuria (PKU) is an inherited disorder of metabolism that causes an increase in the blood of a chemical known as phenylalanine. Phenylalanine comes from a person's diet and is used by the body to make proteins. Women who have high levels of phenylalanine during pregnancy are at high risk for having babies born with mental retardation, heart problems, small head size (microcephaly) and developmental delay. PKU is usually diagnosed through newborn screening testing that is done shortly after birth on a blood sample (heel stick).

Since the phenylketonuria disease is directly related to the amount of L-phenylalanine in blood, it can be controlled by changing the amount of this enzyme. Conventional methods for detection of L-phenylalanine have good performance; however they are not suitable to be utilized as user-friendly methods because the most of them are time-consuming and require sophisticated and expensive instruments and trained operators that limit their applications. Herein, we present a cost-effective, selective, fast and easy-to-use sensing bioplatform integrated with molecularly imprinted polymer (MIP) with a smartphone readout for selective determination of L-phenylalanine level in blood. The developed sensing platform consists of two parts: separation and sensing. During the preliminary experiments it was found that the fluorescence (FL) intensity of graphene quantum dots (GQDs) embedded in bacterial cellulose (BC) nanopaper could be dramatically quenched by  $\text{Cu}^{2+}$  due to binding the  $\text{Cu}^{2+}$  as a FL quencher to the surface of GQDs. But, in the presence of L-phenylalanine,  $\text{Cu}^{2+}$  ions prefer to bind to L-phenylalanine and subsequently are released from the surface of GQDs owing to their high affinity toward L-phenylalanine. Hence, upon addition of L-phenylalanine the FL of GQDs/BC- $\text{Cu}^{2+}$  is recovered ("turn-off-on" FL strategy). The recovered FL intensity of GQD/BC- $\text{Cu}^{2+}$ , which can be monitored visually using a smartphone or spectroscopically using a spectrofluorimeter, was linearly proportional to the concentration of L-phenylalanine in the range of 10-1000  $\mu\text{g mL}^{-1}$  and was utilized as an analytical signal for L-phenylalanine sensing. Building upon the fascinating features of BC nanopaper as a very promising bioplatform in optical (bio)sensing applications we are confident our developed sensing bioplatform could be potentially used as a selective, cost-effective, portable, rapid and easy-to-use diagnostic device for accurate detection of L-phenylalanine and PKU diagnosis at the point-of-care and clinical laboratories as well.

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## Discrimination of Biothiols Using Ratiometric Fluorescence Sensor Array on Nanopaper Platform

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Considering the crucial role of biothiols in many biological processes, which turns them into highly valuable biomarkers for early diagnosis of various diseases, the development of an affordable, sensitive and portable probe for identification and discrimination of these compounds is of great importance [1]. Here we developed ratiometric fluorescence (RF) sensor array [2] with a wide color emissive variation, on a bacterial cellulose (BC) nanopaper substrate for visual discrimination of biothiols. To this aim, RF sensing elements including N-Acetyl L-Cysteine capped green CdTe QDs -Rhodamin B (GQDs-RhB) and red CdTe QDs- Carbon dots (RQDs-CDs) at two different NaOH concentrations (0 and 5 mM) were utilized as sensor elements for the discrimination of biothiols. Owing to the high affinity of thiols group (SH) to the surface of CdTe QDs, the fluorescence (FL) emission of QDs changed while the emission of CDs and rhodamine B were remained almost unchanged upon the addition of biothiols. Accordingly, characteristic rainbow-like FL fingerprint patterns were created for each biothiols which were then distinguished both visually and spectroscopically. Hierarchical cluster analysis (HCA) and linear discriminant analysis (LDA) pattern recognition techniques were employed for the identification and discrimination of biothiols. Bacterial cellulose nanopaper (BC) was chosen as a flexible and transparent substrate for developing convenient, rapid, sensitive and portable probe [3]. Therefore, based on the designed RF sensor array, convenient test strips. were fabricated on BC nanopaper for visual discrimination of biothiols. It has been shown that this probe can successfully identify biothiols in human plasma as well. Altogether, the developed nanopaper-based sensor array offers an efficient biothiols discrimination tool that can be potentially exploited in near future in theranostic and point-of-care applications.

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## Folate decorated Gold nanoparticles for differentiation of cancer and normal cells

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Cancer is one of the main causes of death worldwide. WHO reports was revealed that about 8.8 million persons passed away by cancer in 2015 where Lung, liver colorectal, stomach and breast were most prevalent cancers [1]. Specific detection of cancer cell has the great importance for developing diagnosis methods [2]. Folate receptor (FR) is a target specific biomarker of various cancer which is over-expressed on the membrane of various carcinoma cells [3]. However, FR is also expressed in some normal cells of apical membrane which are not exposed to the blood stream [4]. The FRs binds to the folate (FA) with high affinity (K<sub>d</sub> of 0.1-1 nM) where serves the specific attaching to the FRs overexpressed cancer cells. Therefore, FRs have regarded as a favorable biomarker for distinguishing, imaging and counting of cancer cells. The folate decorated gold nanoparticles (AuNPs/FA) were utilized as selective targeting of the HT 29 cells. Fluorescent microscopy imaging investigations revealed that the produced FA conjugated AuNPs could specifically attach to the target FR-positive tumor cells. The fabricated electrochemical-based cytosensor possesses a dynamic range from 250 to 5000 cell.mL<sup>-1</sup> with high selectivity. *In vitro* toxicity tests has shown low toxicity of the synthesized AuNPs where the minimum viability is about 60 %. The proposed AuNPs/FA based cytosensor provides a novel platform for detection of HT 29 cells of colon cancer which could be developed as a point of care cancer diagnosis biodevice in clinics.

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**Coupling homogeneous liquid–liquid extraction and dispersive liquid–liquid microextraction as an efficient extraction and preconcentration approach**

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Phenols are aromatic components which contain one or more hydroxyl groups that are attached to an aromatic ring. The chemical properties of phenols are unique and are used widely in industry [1]. Owing to the increasing production and application of these compounds, they are found in ground waters, rivers, and drinking waters [2]. Due to their toxicity, carcinogenicity and persistence, some of them have been included in the lists of priority pollutants of several countries and are required to be determined [3]. Homogeneous liquid–liquid extraction (HLLE) that extracts the desired solutes existing in a homogeneous aqueous solution into a water–immiscible solvent formed by each kind of phase separation phenomenon [4]. In 2006, Assadi and coworkers developed a novel LPME technique termed dispersive liquid–liquid microextraction (DLLME) [5], which is based on a ternary component solvent system. Some advantages of DLLME are simplicity of operation, rapidity, low sample volume, low cost, and relatively high enrichment factors. In this study, an efficient, simple, and fast method has been introduced for the derivatization, extraction, and preconcentration of some phenolic compounds (phenol, *o*-, *m*- and *p*-cresol, 4-chlorophenol, and 2-nitrophenol) from wastewater samples and their determination by gas chromatography–flame ionization detection. In this method, initially the phenolic compounds are derivatized with acetic anhydride in an alkaline pH. In the following, the derivatized analytes are extracted into mL–volume of acetonitrile during homogeneous liquid–liquid extraction and further enrichment of the target analytes are accomplished by their extraction into  $\mu\text{L}$ –volume of 1,1,2-trichloroethane through dispersive liquid–liquid microextraction step. Effective parameters controlling the performance of the proposed method such as type and volume of derivatization agent and catalyst, derivatization reaction time, type and volume of extraction/disperser solvent in homogeneous liquid–liquid extraction, and type and volume of extraction solvent and salt addition in dispersive liquid–liquid microextraction are optimized. Under optimum extraction conditions linear range of the proposed method was obtained in the range of 0.7–4000  $\mu\text{g L}^{-1}$ . Limits of detection and quantification were in the ranges of 0.07–0.20 and 0.23–0.70  $\mu\text{g L}^{-1}$ , respectively. Enrichment factors and extraction recoveries were ranged from 220 to 440 and 44 to 88%, respectively.

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**Nickel-cobalt layered double hydroxide ultrathin nanosheets coated on CoMoO<sub>4</sub>/nickel foam as electrode material for high capacitance supercapacitor**

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Renewable alternative energy sources are required to decrease or eliminate the use of environmentally unfriendly fossil fuels. Hydrogen produced by electrolysis has been identified as one such renewable energy carrier. In this work, the hierarchical CoMoO<sub>4</sub>/Ni-Co layered double hydroxide (LDH) core-shell nanosheets arrays have been synthesized, which are grown directly on Ni foam (NF) as an integrated electrode for supercapacitors. Nanosheets arrays of cobalt-molybdenum precursors are synthesized first by a hydrothermal reaction and used as the "core" [1]. Then the Ni-Co LDH nanosheets were electrochemically deposited on CoMoO<sub>4</sub>/NF by applying an external voltage for 10 min [2,3]. This core-shell heterostructure exhibits desirable electrochemical properties. It shows a high specific capacitance of 1667 F g<sup>-1</sup> at 1 A g<sup>-1</sup> and an energy density of 67.51 Wh kg<sup>-1</sup> and a power density of 270.05 W kg<sup>-1</sup>. In conclusion, the CoMoO<sub>4</sub>/Ni-Co LDH composites could be used as promising electrode material for electrochemical energy storage due to their remarkable electrochemical properties.

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**Modified glassy carbon Electrode as a sensitive voltammetric sensor Based on Chromium metal-organic framework for codeine detection**

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In the past decade, the important role of metal-organic frameworks in implementing various applications such as sensing has been considerable. Hence, in this study, by introducing a metal-organic framework, we tried to improve and modify electrode to determine and increase their performance and efficiency in detection codeine compound. Cr (III) based metal-organic framework (MIL-101) were prepared via hydrothermal pathway without any surfactants The nano structure and morphology of the synthesized MOF were characterized by Field Emission Scanning Electron Microscopy (FE-SEM), powder X-ray diffraction, thermo gravimetric analysis (TGA), elemental analysis and FTIR spectroscopy. Moreover, Voltammetric determination of nano particle has been studied. Chromium MOF shows high selectivity for sensing of alkaloid compound such as codeine. In this investigation, a glassy carbon electrode (GCE) was used to determination of analgesic effect of codeine [2,3], using a MOF-MIL101 (Cr)-NH<sub>2</sub> nano tube as a sensor and one-step electrochemical synthesis in a sodium acetate environment. Therefore, Codeine showed an anodic peak in terms of optimum conditions using GCE at pH 8. The oxidation process was irreversible and controlled by the diffusion process in the applied pH range. The calibration curve performed using a differential pulse voltammetry technique for measuring codeine was linear in the concentration range of 30  $\mu$ M to 600  $\mu$ M. Hence, we design a simple and boosted detection strategy for sensing Codeine with limit of detection 10  $\mu$ M.

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**Aptamer based fluorometric acetamiprid assay using three kinds of nanoparticles for powerful signal amplification**

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Acetamiprid is an insecticide with a widespread usage. So that, determination of acetamiprid in human serum and water is highly desirable. Here, a novel fluorescent analytical assay was designed for specific and ultrasensitive detection of acetamiprid, based on target-induced release of FAM-labeled complementary strand of aptamer (CS) from aptamer (Apt)/CS conjugate (dsDNA) and three kinds of nanoparticles with opposite effects on the fluorophore (FAM). These nanomaterials are gold nanoparticles (AuNPs), single-walled carbon nanotubes (SWNTs) and silica nanoparticles coated with streptavidin (SiNP-Streptavidin). In the presence of acetamiprid, FAM-labeled CS was released from dsDNA-modified SiNP-Streptavidin complex and accumulated in the supernatant (Phase I) after centrifugation of sample. The fluorescence intensity significantly decreased when the supernatant was added to the environment of SWNTs and AuNPs which are strong fluorescence quenchers (Phase II). So, in this situation the relative fluorescence intensity (Phase I – Phase II) was too much. In the absence of target, dsDNA-modified SiNP-Streptavidin complex remained intact and no FAM-labeled CS was in the supernatant, and consequently, in the environment of AuNPs and SWNTs. So, the relative fluorescence intensity was too low. The designed assay showed high selectivity toward acetamiprid with a limit of detection (LOD) as low as 127 pM. In addition, the analytical method was successfully utilized to detect acetamiprid in serum and water with LODs of 198 and 130 pM, respectively.





**A conductometric study on the effect of Solvent upon complex formation between kryptofix22DD with Ho<sup>3+</sup> metal cation in organic solvents**

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Lanthanide complexes are of interest due to their importance in optical imaging of cells, as luminescent chemosensors for medical diagnostics, contrast reagents for medical magnetic resonance imaging, shift reagents for NMR spectrometry [1, 2], as well as, their potential applications in fundamental and applied science [3–5] such as organic synthesis, bioorganic chemistry and homogeneous catalysis. The complexation reaction between Ho<sup>3+</sup> cation with macrocyclic ligand kryptofix22DD, was studied in ethylacetate (EtOAc), methanol (MeOH), propylenecarbonate(PC), tetrahydrofuran (THF) at different temperatures using conductometric method. Kryptofix22DD forms a 1:1 complex with Ho<sup>3+</sup> cation. The stability order of (kryptofix22DD.Ho)<sup>3+</sup> complex changes with the type of the organic solvents and also with temperature. The stability constant of the complex in the non aqueous solutions varies in order: EtOAc > THF > PC > MeOH. The values of standard thermodynamic parameters ( $\Delta S^\circ$ ,  $\Delta H^\circ$ ) for formation of (kryptofix22DD.Ho)<sup>3+</sup> complex were obtained from temperature dependence of the formation constant of the complex using the van't Hoff plots. The obtained results show that the entropy and enthalpy complexation reaction between kryptofix22DD with this metal cation depend on the nature of the solvents.

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**Application of a new cobalt oxide modified nano-zeolite for removal of methylene blue, methyl green and methyl red dyes**

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Dyes even in low concentration, not only affect on the visual view of water, but also on the absorption and reflection of sun light and have a negative effect on the bacterial growth and also photosynthesis [1-2]. Therefore it is essential to manage them with an effective and economic method [3]. In this work cobalt oxide modified nano-zeolite was synthesized and characterized by X-ray diffraction (XRD), Fourier transform infrared (FTIR), Field emission scanning electron microscopy (FESEM) and Energy-dispersive X-ray spectroscopy (EDX) techniques. The prepared nanocomposite was successfully applied for removing some color compounds such as methylene blue, methyl green, and methyl red and also binary dye mixtures.

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**Development of an efficient extraction method by combining of QuEChERS–microwave-assisted dispersive liquid liquid microextraction using deep eutectic solvent; Application in extraction of some widely used pesticides from tomato samples**

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Pesticides such as insecticides, herbicides, fungicides, and acaricides are widely used during cultivation and post-harvest storage of crops. It is intended that their use to prevent the destruction of crops by controlling agricultural pests or unwanted plants and thereby improve food production [1, 2]. Although the use of pesticides in agricultural applications provides a wide range of beneficial effects, their misuse can result in unacceptable high levels of them in the products and also pollutes soil, air, and surface water. So, it is significant to develop a detection method with high sensitivity for evaluating food, water, and other environmental samples safety and possible risks to human health. In order to determine trace level of pesticide residues, an extraction and preconcentration step is necessary. Dispersive liquid–liquid extraction (DLLME) [3] is an important sample preparation method because of its simplicity, efficiency, and wide acceptance in many standard methods.

In the present study, combination of QuEChERS-microwave-assisted DLLME/gas chromatography-flame ionization detection was investigated for the extraction, pre-concentration and determination of ten widely used pesticide residues in tomato samples. A mixture of a deep eutectic solvent (extraction solvent) and acetonitrile (disperser solvent) obtained from QuEChERS method was rapidly injected into the sample solution heated for 20s in microwave. Analytical parameters including enrichment factors (2150–2900), linearity ( $r > 0.997$ ), limits of detection ( $0.62\text{--}2.9 \text{ ng mL}^{-1}$ ) and quantification ( $2.2\text{--}7.5 \text{ ng.mL}^{-1}$ ), relative standard deviations ( $<7\%$ ) and extraction recoveries (43–58%) showed the high efficiency of the developed method for analysis of the target analytes. The proposed procedure was used effectively to analyze analytes in tomato samples, and metalaxyl and penconazole were found in tomato samples.

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## Removal of Free Fatty Acids in edible oils by an efficient functionalized magnetic nanoparticles

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A fast, sensitive, and simple method using magnetic nanoparticles (MNPs) coated by tetraethyl ortho silicate (TEOS) and modified with 1,1-dimethylbiguanide (Metformin), as an adsorbent has been successfully developed for removal of free fatty acids from oils [1]. The effect of contact time and concentration on the adsorption of oleic acid (OA) from ethanol–hexane solutions was investigated at room temperature using equilibrium batch experiments. The results showed that the adsorption is rapid (<10 min). The maximum adsorption capacity of oleic acid was determined to be 286 mg g<sup>-1</sup>. Size, structure and magnetic property of the prepared modified magnetic nanoparticles (MNPs) were studied by scanning electron microscopy (SEM), X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR) and vibrating-sample magnetometer (VSM). Adsorption of FFA by metformin functionalized was proved by acid-base interactions between N and NH group and carboxylic acid groups. Desorption of fatty acids was readily achieved upon basic treatment and the regenerated magnetite nanoparticles were found to be recyclable for repeated use. The separation of fatty acids from olive and sunflower oils (as real sample) was investigated without added solvent [2]. MNPs were found to remove up to 96% of the fatty acids in the oil within 10 min with a 1 wt% load at room temperature, without alteration of composition and other conditions. Excellent adsorption capacity of the modified nanoadsorbent with other advantages such as reusability, easy separation by an external magnetic field, make it suitable adsorbent for removal of fatty acids [3].

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## The 25<sup>th</sup> Iranian Seminar of Analytical Chemistry

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### Graphene oxide nanosheet: characterization, modification, and dye removal

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Among various methods that have been developed for removal of heavy metal ions and dyes from wastewater including ions exchange, electro-dialysis, biodegradation, and coagulation, adsorption becomes most popular due to its high efficiency and simplicity [1]. The adsorption process is mainly dependent on different parameters such as pH, temperature, the type and concentration of adsorbent [2]. nano GO flakes [3] have numerous hydrophilic functional groups on its surface that make it dispersible in aqueous media [4]; indeed GO high surface area provide an ideal platform for immobilization of different molecules. However, GO nano flakes tend to become aggregated in the presence of different ions. In order to overcome such screen effect the surface chemistry should be considered wisely. Galactose as a common carbohydrate with multiple hydrophilic functional groups could not only enhance GO dispersibility but also could provide more active sites for interaction with heavy metal ions and dyes [5].

Graphene-based hybrid materials were fabricated through chemical modification of graphene oxide surface by Galactose and it has been characterized by Fourier transform infrared spectroscopy (FT-IR), X-ray powder diffraction (XRD), Ultraviolet-visible spectroscopy (UV-Vis) and Scanning electron microscope (SEM). 5 mg/L of Synthesized composite has been used for the treatment of methylene blue (15 mg/L) at pH 6. The results indicate 49% degradation efficiency in first 10 min compared to the 19% of the pure GO, verifying the modification of the GO has a positive effect on removal efficiency.

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**Evaluation of the potential dye removal using adsorption by amino acid modified graphene oxide nanoflakes**

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Lately, the introduction of different toxic pollutant to environment become a serious hazard to wellbeing [1]. The presence of extra pollutants in water over the standard criteria cause serious health hazard for local dwellers and endanger ecosystem. Plating, battery, electronic industries are the most producers of heavy metal ions based pollutants [2]. There are different established methods for removal of pollutants such as sedimentation, coagulation, ion exchanges and reverse osmosis [3]. However adsorption process as an inexpensive and green method attracted great attentions. Lysine with three-functional group was mainly used as nitrogen supplement for feeding livestock [4].

Graphene oxide (GO) surface functionalized by nontoxic aliphatic amino acid (lysine) via the nucleophilic substitution and condensation reactions through the epoxy and carboxylic acid functional group presented on GO surface, and it has been characterized by X-Ray Powder Diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR), Ultraviolet-Visible spectroscopy (UV-Vis) Scanning Electron Microscope (SEM). The results indicates that the synthesized composites remove 53% of the pollutant in the first 10 minutes, while GO remove 21% of the pollutant at the same time, approving the high absorbance capacity of the modified GO.

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**Anodic stripping voltammetric determination of trace Zinc(II) using**

**A mercury film electrode**

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In the present research, to use the advantages of mercury electrode and to avoid exposure to metallic mercury, Mercury film electrode was prepared by chemical deposition of mercury from mercury salt solution on a palladized aluminum electrode [1]. Cyclic voltammetry studies of the Hg/Pd-Al electrode, showed the simultaneous appearance of oxidation and reduction peaks of mercury, indicating the reversibility of the reaction.

The effect of concentration and deposition time of palladium and mercury, as well as the pH, type and concentration of the background electrolyte were investigated to provide optimum conditions for zinc(II) measurement in its standard solution using differential pulse anodic stripping voltammetry. The anodic peak currents of  $Zn^{2+}$  was increase linearly with increasing its concentration in the range of 0.1 to 50  $\mu M$  in acetate buffer with pH=5. Calibration curve with a correlation coefficient of 0.998 and a detection limit of  $8 \times 10^{-8}$  M was obtained. The present method was successfully applied to determination of zinc(II) in a zinc plus tablet.

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فارغ التحصیلان مقطع دکتری شیمی تجزیه دانشگاه تبریز



فرم مشخصات فارغ التحصیلان دکتری شیمی تجزیه دانشگاه تبریز

	<p>نام: فرزانه  نام خانوادگی: شمیرانی  استاد راهنما: دکتر منظوری لشگر  سال ورود به مقطع دکتری: ۱۳۷۰  سال فارغ التحصیلی از مقطع دکترا: ۱۳۷۴  آدرس الکترونیکی: shemirani@khayam.ut.ac.ir  محل دانشگاه فعلی: دانشگاه تهران</p>
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سوابق آموزشی و پژوهشی

ایشان هم اکنون با درجه‌ی استاد تمام در دانشگاه تهران مشغول فعالیت هستند و طبق آمار ایشان (ESI (Essential Science Indicators، در جمع یک درصد دانشمندان و نخبگان علمی جهان قرار دارند. دکتر شمیرانی سابقه‌ی تدریس دروس شیمی عمومی ۱ و ۲، آزمایشگاه شیمی عمومی ۱ و ۲، تجزیه‌ی دستگاهی، آزمایشگاه شیمی تجزیه‌ی ۱ و ۲، آزمایشگاه تجزیه دستگاهی، روش‌های فیزیکی و شیمیایی جداسازی، شیمی تجزیه‌ی پیشرفته، اسپکتروسکوپی تجزیه‌ای، تجزیه دستگاهی (بیوتکنولوژی) و اسپکتروسکوپی تجزیه‌ای را در این دانشگاه دارند. ایشان همچنین تخصص کار با دستگاه‌ها و تجهیزات مختلف آزمایشگاهی اعم از اسپکتروسکوپی، جداسازی و را دارند. ، ۱۶۲ مقاله در مجلات معتبر بین المللی به چاپ رسانیده و ۱۹ عنوان مقاله در کنفرانس‌های ملی و بین‌المللی ارائه نموده‌اند. دکتر شمیرانی سه کتاب با عناوین زیر به چاپ رسانیده اند.

عنوان کتاب	ترجمه	تألیف	ناشر	تاریخ چاپ
Atomic Absorbtion and Emission Spectrscopy	√		دانشگاه تهران	۲۰۰۲
cold induced aggregation microextraction based on ionic liquid		√	Intech	۲۰۱۰
Principles of Fluorescence and phosphoresence Spectroscopy	√		دانشگاه تهران	۲۰۰۴

فرم مشخصات فارغ التحصیلان دکتری شیمی تجزیه دانشگاه تبریز



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سوابق علمی-آموزشی-فناوری

زمینه‌ی تحقیقاتی دکتر رئوف "الکتروود های اصلاح شده شیمیایی"، "حسگرها و زیست حسگرهای الکتروشیمیایی" و "پیل های سوختی و نانو الکتروشیمیایی" می‌باشد. از افتخارات ایشان می‌توان به کسب عناوین استاد نمونه‌ی دانشگاه مازندران، پژوهشگر نمونه‌ی دانشگاه مازندران، پژوهشگر نمونه استان مازندران، چهره‌ی ماندگار استان مازندران، برگزیده از طرف ستاد مشاهیر و فرزندان مازندران، نخبه بسیجی استان مازندران در هفته بسیج، استاد نمونه‌ی بسیجی کشور، استاد برگزیده دومین جشنواره جهادگران علم و فناوری کشور، استاد نمونه کشور در سال ۱۳۹۱ را اشاره کرد. ایشان همچنین در زمره‌ی ۱٪ دانشمند ایرانی پراستناد از طرف مؤسسه تامسون - روتترز از ۲۰۱۲ میلادی قرار دارند و لوح زرین سپاس به منظور قدردانی و تجلیل از خدمات و فعالیت‌های علمی در رشته شیمی تجزیه از ریاست محترم جمهوری اسلامی ایران در جلسه‌ی هیات محترم دولت در استانداری مازندران در ۱۳۹۲/۰۲/۱۸ دریافت نمودند. دکتر رئوف همچنین معاونت اداری و مالی دانشکده علوم پایه، معاونت اداری و مالی دانشگاه مازندران، ریاست دانشکده علوم پایه و معاونت پژوهشی دانشگاه مازندران را برعهده داشتند و مؤلف بیش از ۲۸۰ مقاله منتشره در مجلات معتبر بین المللی، ۴۴ عنوان مقالات ارائه شده در کنفرانس‌های علمی خارجی، ۳۰۰ عنوان مقالات ارائه شده در کنفرانس‌های علمی داخلی از تاکنون ۲۰۰۲، هستند. در اجرای ۸ مورد پروژه‌ی تحقیقاتی مشارکت داشته و راهنمایی ۶۰ دانشجوی کارشناسی ارشد و ۱۲ نفر دانشجوی دکتری را بر عهده داشته‌اند. دکتر رئوف همچنین عضو هیئت تحریریه چندین نشریه‌ی علمی هستند. ایشان، ۳ کتاب ترجمه و ۲ کتاب ویرایش نموده‌اند و سه مورد اختراع داخلی با عنوان "ساخت زیست حسگر DNA خودکار و قابل حمل برای تشخیص نقص‌های ژنتیکی با استفاده از سیستم پیل سوختی میکروبی"، "آپتا حسگر ایمپدیمتری بسیار حساس بر مبنای طرح ساندویچی برای تشخیص بدون نشانگر انتخابی سلول های سرطانی روده بزرگ" و "تهیه‌ی آپتاسگر الکتروشیمیایی برای تشخیص اپیروبیسین، با استفاده از سنجش اتصال رقابتی، در حضور شناساگر ضد سرطان کورکومین" به ثبت رساندند.

فرم مشخصات فارغ التحصیلان دکتری شیمی تجزیه دانشگاه تبریز



نام و نام خانوادگی: داود نعمت الهی

استاد/ اساتید راهنما: دکتر گلابی

سال ورود به مقطع دکتری: ۱۳۷۰

سال فارغ التحصیلی از مقطع دکترا: ۱۳۷۵

آدرس الکترونیکی: [nemat@basu.ac.ir](mailto:nemat@basu.ac.ir)

محل فعالیت/ محل دانشگاه فعلی: دانشگاه بوعلی سینا همدان

سوابق آموزشی و پژوهشی

ایشان مقطع کارشناسی را در دانشگاه کاشان به اتمام رساندند. سپس دو مقطع کارشناسی ارشد و دکترا را در دانشگاه تبریز سپری نمودند و هم اکنون در زمینه الکتروشیمی مشغول فعالیت آموزشی و پژوهشی هستند. ایشان همچنین مولف ۳۱۳ مقاله‌ی منتشره در مجلات معتبر بین المللی می‌باشند و در انجام ۱۵ طرح تحقیقاتی مشارکت داشته‌اند.

فرم مشخصات فارغ التحصیلان دکتری شیمی تجزیه دانشگاه تبریز



نام و نام خانوادگی: رضا اوجانی

استاد/اساتید راهنما: جناب آقای دکتر محمد حسین پورنقی آذر

سال ورود به مقطع دکتری: ۱۳۷۰

سال فارغ التحصیلی از مقطع دکترا: ۱۳۷۵

آدرس الکترونیکی: fer-o@umz.ac.ir

محل فعالیت/محل دانشگاه فعلی: دانشگاه مازندران

سوابق علمی-آموزشی-فناوری

ایشان عضو هیئت علمی دانشگاه مازندران هستند و در سال ۱۳۸۶ به مرتبه استادی ارتقاء یافته‌اند. دکتر اوجانی در سال ۲۰۱۲ بر مبنای گزارش ISI به عنوان پژوهشگری با ارجاع بالا معرفی شدند. ایشان سابقه‌ی تدریس دروس شیمی عمومی ۱ و ۲، آزمایشگاه شیمی عمومی ۱ و ۲، شیمی تجزیه‌ی ۱ و ۲، آزمایشگاه شیمی تجزیه‌ی ۱ و ۲، شیمی حلال‌های نآبی، مباحث نوین در شیمی تجزیه، کمپلکس‌ها در شیمی تجزیه، الکتروشیمی تجزیه‌ای، الکتروشیمی در حلال‌های نآبی، روش‌های رادیوشیمیایی، مباحث نوین در الکتروشیمی تجزیه‌ای را در این دانشگاه دارند. ایشان در زمینه‌های "مطالعه‌ی رفتار الکتروشیمیایی برخی ترکیبات در آب و کلروفرم"، "الکتروکاتالیزهای همگن و ناهمگن"، "الکتروپلیمریزاسیون و مطالعه‌ی الکتروشیمی پلیمرها"، "ساخت الکترودهای اصلاح‌شده و کاربردهای آنها در الکتروشیمی تجزیه‌ای"، "سیستم‌های نوسانگر شیمیایی" و "الکتروسنتز" به فعالیت‌های پژوهشی مشغول بوده‌اند. همچنین ایشان سمت‌های مدیریتی "ریاست کتابخانه مرکزی دانشگاه مازندران"، "مدیریت گروه شیمی تجزیه"، "معاون آموزشی دانشکده شیمی"، "ریاست دانشکده شیمی" را در دانشگاه مازندران بر عهده داشته‌اند.

فرم مشخصات فارغ التحصیلان دکتری شیمی تجزیه دانشگاه تبریز



نام و نام خانوادگی: میرعلی فرج زاده

استاد/اساتید راهنما: آقای دکتر جوانشیر جوزن

سال ورود به مقطع دکتری: ۱۳۷۰

سال فارغ التحصیلی از مقطع دکترا: ۱۳۷۴

آدرس الکترونیکی: mafarajzadeh@tabrizu.ac.ir

محل فعالیت/ محل دانشگاه فعلی: دانشگاه تبریز

سوابق علمی-آموزشی-فناوری

ایشان در سال‌های ۱۳۸۵-۱۳۶۹ عضو هیأت علمی دانشگاه ارومیه بوده‌اند. از سال ۱۳۸۶ عضو هیأت علمی گروه شیمی تجزیه دانشکده‌ی شیمی دانشگاه تبریز می‌باشند و هم‌اکنون با مرتبه‌ی استادی مشغول فعالیت و پژوهش هستند. دکتر فرج‌زاده در زمینه‌ی توسعه‌ی روش‌های آماده‌سازی نمونه و تکنیک‌های مختلف کروماتوگرافی مشغول فعالیت و پژوهش هستند. ایشان موفق به چاپ ۱۶۰ عنوان مقاله‌ی ISI در مجلات معتبر علمی و بین‌المللی، اجرای ۱۲ طرح تحقیقاتی، شرکت در ۷۵ سمینار داخلی و خارجی و تألیف ۴ جلد کتاب در زمینه‌ی علم شیمی شده‌اند. ایشان همچنین کسب عناوین پژوهشگر برتر دانشگاه ارومیه در سال ۱۳۸۲-۱۳۸۱، پژوهشگر برتر استان در سال ۱۳۸۳ و کسب عنوان پژوهشگر برتر کشوری علوم پایه در سال ۱۳۹۶ را در کارنامه‌ی خود دارند.

فرم مشخصات فارغ التحصیلان دکتری شیمی تجزیه دانشگاه تبریز

	<p>نام: ودود نام خانوادگی: حسن زاده نیری استاد/ اساتید راهنما: دکتر میرمحسنی نمین و دکتر میلانی سال ورود به مقطع دکتری: ۱۳۷۳ سال فارغ التحصیلی از مقطع دکترا: ۱۳۷۸ آدرس الکترونیکی: - محل فعالیت/ محل دانشگاه فعلی: -</p>
<p>سوابق آموزشی و پژوهشی</p>	

فرم مشخصات فارغ التحصیلان دکتری شیمی تجزیه دانشگاه تبریز



نام: یعقوب

نام خانوادگی: اسدی قشلاق سفلی

استاد/ اساتید راهنما: دکتر جوزن

سال ورود به مقطع دکتری: ۱۳۷۳

سال فارغ التحصیلی از مقطع دکترا: ۱۳۷۸

آدرس الکترونیکی: [yassadi2003@yahoo.com](mailto:yassadi2003@yahoo.com), [yassadi2018@gmail.com](mailto:yassadi2018@gmail.com)

محل فعالیت/ محل دانشگاه فعلی: داروسازی دانا

سوابق آموزشی و پژوهشی

ایشان تمام مقاطع تحصیلات دانشگاهی خود را اعم از کارشناسی، کارشناسی ارشد و دکتری در دانشگاه تبریز به اتمام رسانده‌اند. حوزه‌ی پژوهشی دکتر اسدی روش‌های جداسازی می‌باشد و در سال ۲۰۰۶ روش استخراج مایع-مایع پخشی را برای اولین بار معرفی کردند که روشی کارآمد برای آنالیز آنالیت‌های مختلف می‌باشد و مقاله‌ی چاپ شده در این زمینه از پراستنادترین مقالات در زمینه‌ی جداسازی می‌باشد. ایشان همچنین مؤلف ۴۴ مقاله در مجلات مختلف بین‌المللی می‌باشند.





فرم مشخصات فارغ التحصیلان دکتری شیمی تجزیه دانشگاه تبریز



نام: حبیب

نام خانوادگی: رزمی

استاد راهنما: محمدحسین پورنقی آذر

سال ورود به مقطع دکتری: ۱۳۷۴

سال فارغ التحصیلی از مقطع دکترا: ۱۳۷۹

آدرس الکترونیکی: h.razmi@azaruniv.edu

محل دانشگاه فعلی: دانشگاه شهید مدنی آذربایجان

سوابق آموزشی و پژوهشی

ایشان هم اکنون به عنوان مدیر کل تحصیلات تکمیلی دانشگاه شهید مدنی آذربایجان و همچنین عضو کارگروه تخصصی نظارت و ارزیابی بر دانشگاه های جامع علمی-کاربردی استان مشغول به فعالیت هستند. دکتر رزمی همچنین سمت های عضویت در هیات ممیزه دانشگاه شهید مدنی آذربایجان، ریاست کمیسیون تخصصی گروه شیمی - زیست شناسی و نیز معاونت آموزشی - پژوهشی دانشکده علوم پایه دانشگاه شهید مدنی آذربایجان را در کارنامه مسئولیت ها و سمت های اجرایی خود دارند. از سوابق تدریس ایشان می توان به تدریس دروس الکتروشیمی در محلول های ناآبی در مقطع دکترای تخصصی، شیمی تجزیه پیشرفته، الکتروشیمی تجزیه ای پیشرفته، کمپلکس ها در شیمی تجزیه، روش های فیزیکی و شیمیایی جداسازی در مقطع کارشناسی ارشد و همچنین دروس شیمی تجزیه (۱)، شیمی تجزیه (۲)، شیمی عمومی (۲) و آزمایشگاه های مربوطه در مقطع کارشناسی اشاره کرد. از جوایز و افتخارات ایشان عناوین پژوهشگر برتر دانشگاه ده مورد، پژوهشگر برتر استانی یک مورد، کسب تقدیرنامه از مقام وزارت علوم و در نهایت یک مورد چاپ مقاله ی داغ می باشد. ایشان همچنین بیش از ۸۰ عنوان مقاله در کنفرانس های ملی و ۱۲ مقاله در کنفرانس های بین المللی ارائه نموده اند.

زمینه های تحقیقاتی مورد علاقه ی دکتر رزمی به شرح زیر می باشد:

- طراحی و ساخت حسگرهای الکتروشیمیایی مبتنی بر نانو مواد
- تهیه الکترودهای اصلاح شده برای اهداف تجزیه ای
- طراحی و ساخت جاذب های کم بها مبتنی مواد طبیعی برای پیش تغلیظ و اندازه گیری برخی آلاینده های زیست محیطی
- ساخت نانو کامپزیت های مبتنی مواد طبیعی کم بها با نانو مواد کربنی

فرم مشخصات فارغ التحصیلان دکتری شیمی تجزیه دانشگاه تبریز



نام: احد

نام خانوادگی: باویلی تبریزی

استاد/ اساتید راهنما: دکتر منظوری لشگر

سال ورود به مقطع دکتری: ۷۶

سال فارغ التحصیلی از مقطع دکترا: ۸۱

آدرس الکترونیکی: abavilitabrizia@gmail.com, a.bavili@tbzmed.ac.ir

محل فعالیت/ محل دانشگاه فعلی: دانشگاه علوم پزشکی تبریز

سوابق آموزشی و پژوهشی

ایشان تمام مقاطع تحصیلات عالی خود را اعم از کارشناسی، کارشناسی ارشد و دکتری در دانشگاه تبریز به اتمام رسانده‌اند. دکتر باویلی هم اکنون با درجه‌ی استادی در دانشکده داروسازی دانشگاه تبریز مشغول فعالیت می‌باشند و زمینه‌ی پژوهشی ایشان "توسعه‌ی روش‌های استخراج در آنالیز مواد دارویی، فلزات و آلودگی‌های محیط زیستی" است. دکتر باویلی چاپ حدود ۲۷ مقاله در مجلات بین‌المللی و اجرای ۱۰ طرح پژوهشی را در کارنامه‌ی پژوهشی خود دارند.

فرم مشخصات فارغ التحصیلان دکتری شیمی تجزیه دانشگاه تبریز

نام: احمد

نام خانوادگی نوزاد گلی کند

استاد/ اساتید راهنما: دکتر گلابی

سال ورود به مقطع دکتری: ۱۳۷۶

سال فارغ التحصیلی از مقطع دکترا: ۱۳۸۱

آدرس الکترونیکی:-

محل فعالیت/ محل دانشگاه فعلی: پژوهشگاه علوم هسته‌ای تهران

سوابق آموزشی و پژوهشی

ایشان هر سه مقطع کارشناسی، کارشناسی ارشد و دکترا را در دانشگاه تبریز به پایان رساندند و هم اکنون با مرتبه‌ی استادی مشغول فعالیت هستند. دکتر نوزاد همچنین مولف ۳ و مترجم ۵ کتاب و ۱۲۰ مقاله‌ی منتشره در مجلات معتبر بین المللی می‌باشند. ایشان همچنین در انجام ۱۸ طرح پژوهشی مشارکت داشته‌اند.

فرم مشخصات فارغ التحصیلان دکتری شیمی تجزیه دانشگاه تبریز



نام: ملیحه

نام خانوادگی: امیرذهنی

استاد/ اساتید راهنما: دکتر جوانشیر جوزن

سال ورود به مقطع دکتری: ۷۶

سال فارغ التحصیلی از مقطع دکترا: ۸۲

آدرس الکترونیکی: maliheamirzehni@iaut.ac.ir

محل فعالیت/ محل دانشگاه فعلی: دانشگاه آزاد واحد تبریز

سوابق آموزشی و پژوهشی

ایشان هم اکنون هیأت علمی گروه شیمی دانشگاه آزاد واحد تبریز می باشند و راهنمایی حدود ۲۵ دانشجوی کارشناسی ارشد و سه دانشجوی دکتری شیمی تجزیه را بر عهده داشتند. دکتر امیرذهنی ۸ مقاله در مجلات معتبر بین المللی به چاپ رسانیده و بیش از ۳۰ عنوان مقاله در کنفرانس های ملی و بین المللی ارائه نموده اند.

فرم مشخصات فارغ التحصیلان دکتری شیمی تجزیه دانشگاه تبریز



نام و نام خانوادگی: رضا امامعلی سبزی

استاد/اساتید راهنما: دکتر پورنقی آذر-دکتر گلابی

سال ورود به مقطع دکتری: بهمن ماه ۱۳۷۷

سال فارغ التحصیلی از مقطع دکترا: دی ماه ۱۳۸۲

آدرس الکترونیکی: r.emamalisabzi@urmia.ac.ir

محل فعالیت/ محل دانشگاه فعلی: دانشگاه ارومیه

سوابق علمی - آموزشی - فناوری

ایشان دوره کارشناسی خود را در سال ۱۳۶۸ در دانشگاه شیراز در رشته شیمی محض اخذ نمودند. در نیم سال دوم همان سال در دانشگاه تربیت مدرس در دوره کارشناسی ارشد به تحصیل مشغول شدند. در دی ماه ۱۳۷۱ از این دانشگاه فارغ التحصل شده و در دانشگاه ارومیه به عنوان مربی مشغول به تدریس شدند. مدت ۵ سال به تدریس مشغول بودند تا در کنکور اعزام به خارج قبول شدند و به علت مشکلات کشوری قبولی خود را از طریق وزارت به داخل تبدیل و در دانشگاه تبریز مشغول به تحصیل شدند. ایشان پایان نامه‌ی خود را زیر نظر دکتر پورنقی آذر و دکتر گلابی به اتمام رساندند. بعد از فارغ التحصیلی در سال ۱۳۸۲ به تدریس و آموزش دانشجویان کارشناسی ارشد در دانشگاه ارومیه مشغول شدند. دی ماه ۱۳۸۸ برای انجام یک فرصت مطالعاتی ۹ ماهه به کشور استرالیا رفته و با دکتر Dusan Losic در دانشگاه استرالیای جنوبی مشغول همکاری در کارهای تحقیقاتی شدند که حاصل این فرصت مطالعاتی چاپ ۲ مقاله بود. ایشان تا کنون در پایان نامه های ۵ دانشجوی دکتری و بیش از ۶۰ دانشجوی کارشناسی ارشد مشارکت نموده اند و حاصل این تحقیقات انتشار بیش از ۴۶ مقاله در مجلات مختلف بوده است. زمینه کاری ایشان تهیه حسگرها و بیوحسگرهای الکتروشیمیایی می باشد.

فرم مشخصات فارغ التحصیلان دکتری شیمی تجزیه دانشگاه تبریز



نام و نام خانوادگی: سلیمان بهار

استاد/اساتید راهنما: دکتر جوزن

سال ورود به مقطع دکتری: ۱۳۷۷

سال فارغ التحصیلی از مقطع دکترا: ۱۳۸۳

آدرس الکترونیکی: s.bahar@uok.ac.ir

محل فعالیت/ محل دانشگاه فعلی: دانشگاه کردستان

سوابق علمی - آموزشی - فناوری

دکتر بهار هم اکنون عضو هیئت علمی دانشگاه کردستان هستند و سابقه‌ی تدریس دروس شیمی عمومی، تجزیه‌ی دستگاهی، شیمی تجزیه‌ی ۱ و ۲، شیمی تجزیه‌ی پیشرفته را دارند. ایشان ۲۰ مقاله در مجلات معتبر بین المللی به چاپ رسانیده و ۹ عنوان مقاله در کنفرانس‌های ملی و بین‌المللی ارائه نموده‌اند. زمینه‌ی تحقیقاتی و مورد علاقه‌ی دکتر بهار ارائه‌ی روش‌هایی جدید برای جداسازی و پیش‌تغلیظ ترکیبات آلی و معدنی و آنالیز آنها در نمونه‌های حقیقی با سیستم‌های کروماتوگرافی است.

فرم مشخصات فارغ التحصیلان دکتری شیمی تجزیه دانشگاه تبریز



نام: محمد

نام خانوادگی: امجدی

استاد/ اساتید راهنما: جمشید منظوری

سال ورود به مقطع دکتری: ۱۳۷۷

سال فارغ التحصیلی از مقطع دکترا: ۱۳۸۳

آدرس الکترونیکی: amjadi@tabrizu.ac.ir

محل فعالیت/ محل دانشگاه فعلی: دانشگاه تبریز

سوابق آموزشی و پژوهشی

دکتر محمد امجدی عضو هیئت علمی دانشگاه تبریز می‌باشند. ایشان تدریس دروس شیمی عمومی ۱، شیمی عمومی ۲، شیمی تجزیه کیفی، تجزیه دستگاهی و اسپکتروسکوپی تجزیه‌ای در مقطع کارشناسی، شیمی تجزیه‌ای پیشرفته و اسپکتروسکوپی تجزیه‌ای ۲ در مقطع کارشناسی ارشد و مباحث نوین در مقطع دکتری را برعهده داشته‌اند. زمینه‌ی فعالیت‌های پژوهشی دکتر امجدی اسپکتروسکوپی لومینسانس، نانومواد پلاسمونی و نقاط کوانتومی کاربردهای تجزیه‌ای محیط‌های سازمان یافته و مایعات یونی، آنالیز مواد دارویی و زیست محیطی می‌باشد. ایشان بر اساس اعلام پایگاه استنادی طلایه داران علم تامسون رویترز در جمع پژوهشگران یک درصد برتر دنیا قرار گرفتند.

فرم مشخصات فارغ التحصیلان دکتری شیمی تجزیه دانشگاه تبریز



نام و نام خانوادگی: حسین داستانگو

استاد/اساتید راهنما: دکتر پورنقی آذر

سال ورود به مقطع دکتری: -

سال فارغ التحصیلی از مقطع دکترا: ۱۳۸۴

آدرس الکترونیکی: dastango@yahoo.com

محل فعالیت/ محل دانشگاه فعلی: دانشگاه تبریز

سوابق آموزشی و پژوهشی

ایشان به عنوان هیئت علمی دانشگاه تبریز در زمینه‌ی الکتروشیمی مشغول فعالیت آموزشی و پژوهشی هستند.



فرم مشخصات فارغ التحصیلان دکتری شیمی تجزیه دانشگاه تبریز

نام: کریم

نام خانوادگی: اسدپور زینالی

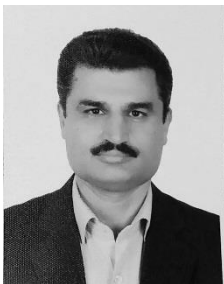
استاد/ اساتید راهنما: دکتر میررضا کریمی – دکتر ابوالقاسم جویبان

سال ورود به مقطع دکتری: ۱۳۷۸

سال فارغ التحصیلی از مقطع دکتری: ۱۳۸۴

آدرس الکترونیکی: asadpour@tabrizu.ac.ir

محل فعالیت/ محل دانشگاه فعلی: دانشگاه تبریز



سوابق آموزشی و پژوهشی

دکتر کریم اسدپور زینالی از سال ۱۳۸۴ عضو هیئت علمی دانشگاه تبریز می‌باشند. ایشان از سال ۱۳۸۶ تا ۱۳۹۰ مدیریت گروه شیمی تجزیه دانشکده شیمی دانشگاه تبریز را بر عهده داشتند و از سال ۱۳۹۲ تاکنون به عنوان معاون آموزشی دانشکده شیمی دانشگاه تبریز مشغول به فعالیت هستند. از سوابق تدریس ایشان می‌توان به تدریس دروس شیمی تجزیه‌ی کیفی، شیمی تجزیه کشاورزی، شیمی تجزیه مهندسی، شیمی تجزیه نمونه‌های حقیقی، آزمایشگاه شیمی تجزیه ۲ و آزمایشگاه شیمی تجزیه دستگاهی در مقطع کارشناسی و همچنین تدریس کمومتری کس در مقطع دکتری اشاره کرد. دکتر اسدپور در سال ۱۳۸۶ به عنوان پژوهشگر برتر جوان دانشگاه تبریز برگزیده شدند و تاکنون بیش از ۸۰ مقاله علمی ISI به چاپ رسانده و بیش از ۱۰۰ مقاله در همایش‌ها و کنفرانس‌های ملی و بین‌المللی ارائه نموده‌اند. ایشان راهنمایی ۳۶ پایان‌نامه کارشناسی ارشد و ۳ رساله دکتری را بر عهده داشتند. هم‌اکنون نیز راهنمایی ۳ پایان‌نامه کارشناسی ارشد و ۴ رساله دکتری را عهده‌دار می‌باشند.

فرم مشخصات فارغ التحصیلان دکتری شیمی تجزیه دانشگاه تبریز



نام و نام خانوادگی: ابراهیم قربانی کلهر

استاد/اساتید راهنما: دکتر محمد حسین سرورالدین، دکتر محمدرضا رشیدی

سال ورود به مقطع دکتری: ۱۳۷۸

سال فارغ التحصیلی از مقطع دکترا: ۱۳۸۴

آدرس الکترونیکی: ekalhor@iaut.ac.ir

محل فعالیت/ محل دانشگاه فعلی: دانشگاه آزاد اسلامی تبریز

سوابق آموزشی و پژوهشی

ایشان هم اکنون به عنوان عضو هیئت علمی دانشگاه آزاد اسلامی تبریز مشغول فعالیت هستند و دانشیار پایه‌ی ۱۱ گروه شیمی، عضو شورای آموزشی گروه شیمی و شورای پژوهشی دانشکده علوم پایه و گروه شیمی و عضو شورای این دانشگاه می‌باشند.

ایشان ۳۱ مقاله در نشریات و مجلات ISI و ۵ مقاله در نشریات و مجلات ISC به چاپ رسانیده و ۳۴ عنوان مقاله در سمینارها و کنفرانس‌های ملی و بین‌المللی ارائه نموده‌اند. ایشان همچنین ویراستار علمی یک کتاب می‌باشند. دکتر کلهر راهنمایی ۳۲ دانشجوی کارشناسی ارشد، ۳ دانشجوی دکتری، راهنمایی و مدیریت ۱۳ پروژه‌ی کارشناسی، ارزیابی، داوری و نظارت بر ۳ مورد فعالیت‌های پژوهشی، فناوری و نوآوری، مشاوره‌ی یک پایان‌نامه‌ی دکتری و بیش از ۱۵ پایان‌نامه‌ی دوره کارشناسی ارشد و همچنین داوری ۲۵ مقاله‌ی علمی ISI خارجی و علمی پژوهشی را در کارنامه‌ی آموزشی و پژوهشی خود دارند و در سال ۱۳۹۴ به عنوان پژوهشگر برتر واحد تبریز برگزیده شدند.



نام: حسین

نام خانوادگی: نهال پروری

استاد راهنما: دکتر محمدحسین پورنقی آذر

سال ورود به مقطع دکتری: ۱۳۷۸

سال فارغ التحصیلی از مقطع دکترا: ۱۳۸۵

آدرس الکترونیکی: [hmoshaver@yahoo.com](mailto:hmoshaver@yahoo.com), [azmoonmt@yahoo.com](mailto:azmoonmt@yahoo.com)

محل دانشگاه فعلی: مؤسس و مدیر آزمایشگاه‌های آکرودیته آزمون مرجع/پژوهش آزما

تبریز-دانشگاه هنر اسلامی تبریز

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#### سوابق آموزشی و پژوهشی

تدریس دروس شیمی تجزیه، شیمی تجزیه دستگاهی و شیمی عمومی در دانشکده مهندسی معدن، متالورژی و مهندسی شیمی در دانشگاه صنعتی سهند تبریز، شیمی رنگ و شیمی عمومی در دانشگاه هنر اسلامی تبریز از سوابق علمی ایشان می‌باشد. دکتر نهال پروری تدوین، عضویت در کمیته‌ی تدوین و نیز ویراستاری رسمی بیش از سیصد استاندارد ملی ایران را برعهده داشته‌اند. ایشان همچنین کارشناس رسمی استاندارد در زمینه‌ی فرآورده‌های شیمیایی، پلیمری و رنگ و مواد نفتی می‌باشند.

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فرم مشخصات فارغ التحصیلان دکتری شیمی تجزیه دانشگاه تبریز

نام: قاسم

نام خانوادگی: کریم نژاد

استاد/ اساتید راهنما: دکتر جمشید منظوری لشکر

سال ورود به مقطع دکتری: ۱۳۷۸

سال فارغ التحصیلی از مقطع دکترا: ۱۳۸۴

آدرس الکترونیکی: g.knezhad@gmail.com


محل فعالیت/ محل دانشگاه فعلی: دانشگاه پیام نور تبریز



سوابق آموزشی و پژوهشی

عضو هیئت علمی دانشگاه پیام نور تبریز هستند و در زمینه‌های الکتروشیمی و اسپکتروسکوپی مشغول فعالیت آموزشی و پژوهشی بودند. ایشان مولف ۵۵ مقاله‌ی منتشره در مجلات معتبر بین المللی و همچنین یک کتاب برای دانشجویان کارشناسی ارشد می‌باشند. دکتر کریم‌نژاد راهنمایی حدود ۴۵ دانشجوی کارشناسی ارشد و ارائه‌ی ۴۵ مقاله در کنفرانس‌های داخلی و خارجی و اجرای ۱۵ طرح پژوهشی در کارنامه آموزشی و پژوهشی خود دارند.

فرم مشخصات فارغ التحصیلان دکتری شیمی تجزیه دانشگاه تبریز

	<p>نام: بیوک نام خانوادگی: حبیبی استاد راهنما: دکتر محمد حسین پورنقی آذر سال ورود به مقطع دکتری: ۱۳۸۱ سال فارغ التحصیلی از مقطع دکترا: ۱۳۸۵ آدرس الکترونیکی: B.Habibi@azaruniv.edu محل دانشگاه فعلی: دانشگاه شهید مدنی آذربایجان</p>
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سوابق آموزشی و پژوهشی

ایشان از سال ۱۳۸۵ با درجه‌ی استادیار فعالیت‌های خود را در دانشگاه شهید مدنی آذربایجان آغاز کردند و در سال ۱۳۸۹ به مرتبه‌ی دانشیاری و در سال ۱۳۹۴ به مرتبه استادی ارتقاء یافته‌اند. دکتر حبیبی سابقه‌ی تدریس دروس شیمی عمومی ۱ و ۲، آزمایشگاه شیمی عمومی و آزمایشگاه شیمی تجزیه، شیمی تجزیه‌ی ۱ و ۲، شیمی هسته‌ای، شیمی تجزیه پیشرفته، روش‌های فیزیکی و شیمیایی جداسازی، مباحث نوین در شیمی تجزیه، الکتروشیمی در حلال‌های ناآبی، روش‌های جدید در شیمی تجزیه‌ای را در این دانشگاه دارند. ایشان همچنین فعالیت‌های تحقیقاتی در زمینه‌های کامپوزیت‌های سه بعدی نانوذرات پلاتینیوم دوپه شده با پلیمرهای آلی، نانوکاتالیست‌های آلیاژهای پلاتین در کامپوزیت‌های سه بعدی، الکردهای اصلاح شده و ... داشته‌اند. همچنین در سال‌های ۱۳۸۰-۱۳۷۵ و ۱۳۹۶-۱۳۹۲ ریاست دانشگاه شهید مدنی آذربایجان را بر عهده داشته‌اند و به عنوان استاد راهنما در پایان نامه‌های ۲۸ دانشجوی کارشناسی ارشد و ۴ دانشجوی دکتری مشارکت داشته‌اند. دکتر حبیبی سه کتاب با عنوان "مسائل شیمی عمومی" و "اصول شیمی تجزیه" منتشر نموده‌اند. ایشان ۵۳ مقاله در مجلات معتبر بین المللی به چاپ رسانیده و در ۹۶ کنفرانس‌های ملی و شرکت نموده‌اند.

فرم مشخصات فارغ التحصیلان دکتری شیمی تجزیه دانشگاه تبریز



نام و نام خانوادگی: حسین عبدالمحمدزاده

استاد راهنما: دکتر جمشید منظوری لشکر

سال ورود به مقطع دکتری: ۱۳۸۰

سال فارغ التحصیلی از مقطع دکترا ۱۳۸۵

آدرس الکترونیکی: h.abdol@azaruniv.ac.ir

محل دانشگاه فعلی: دانشگاه شهید مدنی آذربایجان

سوابق آموزشی و پژوهشی

دکتر حسین عبدالمحمدزاده دانش آموخته دانشگاه تبریز می باشد که تمام مقاطع تحصیلات عالی خود را اعم از کارشناسی، کارشناسی ارشد و دکتری در همین دانشگاه به اتمام رسانده اند. استاد راهنمای ایشان در مقطع کارشناسی ارشد دکتر محمد حسین پورنقی آذر و در مقطع دکتری، دکتر جمشید منظوری لشکر بودند. ایشان فارغ التحصیل دکترای سال ۱۳۸۵ و بورسیه‌ی دانشگاه شهید مدنی آذربایجان بودند که بلافاصله پس از دفاع از رساله‌ی دکترای خود به عنوان استادیار گروه شیمی فعالیت‌های آموزشی و پژوهشی خود را در دانشگاه شهید مدنی آذربایجان شروع کردند. تدریس دروس مختلف تخصصی در مقاطع کارشناسی، کارشناسی ارشد و دکترا و همچنین پذیرش دانشجوی کارشناسی ارشد در سال‌های اول ورود به دانشگاه شروع و چند سال بعد، پذیرش دانشجوی دکتری صورت گرفت. حوزه‌ی پژوهشی مورد علاقه دکتر عبدالمحمدزاده "به کارگیری نانومواد در آماده سازی نمونه‌های حقیقی و اندازه‌گیری مقادیر جزئی گونه‌های مختلف آلی و معدنی در نمونه‌های زیست محیطی، غذایی و کلینیکی" می باشد. ایشان در سال ۱۳۸۹ به مرتبه دانشیاری و در سال ۱۳۹۴ به مرتبه استادی ارتقاء یافته‌اند. دکتر عبدالمحمدزاده راهنمایی حدود ۳۵ دانشجوی کارشناسی ارشد و دکتری، چاپ حدود ۵۰ مقاله ISI، ارائه ۶۰ مقاله در کنفرانس‌های داخلی و خارجی و داوری بیش از ۹۰ مقاله ISI منتشر شده در مجلات مختلف بین المللی را در کارنامه آموزشی و پژوهشی خود دارند. ایشان عضو انجمن شیمی ایران، عضو انجمن نانوفناوری ایران، عضو هیئت تحریریه سه مجله بین المللی و یک مجله داخلی بوده و سه بار به عنوان پژوهشگر برتر دانشگاه شهید مدنی آذربایجان معرفی شده‌اند.

فرم مشخصات فارغ التحصیلان دکتری شیمی تجزیه دانشگاه تبریز



نام و نام خانوادگی: عبدالحسین ناصری

استاد/اساتید راهنما: دکتر محمدحسین سرورالدین/ دکتر حمید عبدالهی

سال ورود به مقطع دکتری: ۱۳۸۰

سال فارغ التحصیلی از مقطع دکترا: ۱۳۸۵

آدرس الکترونیکی: ab.nasari@gmail.com

محل فعالیت/ محل دانشگاه فعلی: دانشگاه تبریز

سوابق آموزشی و پژوهشی

ایشان ورودی سال ۱۳۷۴ در مقطع کارشناسی دانشگاه بوعلی سینای همدان می باشند و دو مقطع کارشناسی ارشد و دکترا را در سال های ۸۰ و ۸۵ در دانشگاه تبریز به پایان رسانیدند. از سال ۱۳۸۴ تا ۱۳۸۸ در دانشگاه آزاد اسلامی واحد تبریز مشغول فعالیت آموزشی و پژوهشی بودند و از بهمن ماه سال ۱۳۸۸ در دانشگاه تبریز مشغول به فعالیت می باشند. هم اکنون دانشیار این دانشگاه هستند که مولف بیش از شصت مقاله منتشره در مجلات معتبر بین المللی و همچنین دو کتاب می باشند. کتاب "کاربرد کامپیوتر در شیمی" را توسط انتشارات دانشگاه تبریز منتشر نموده اند. دکتر ناصری عضو پیوسته انجمن شیمی ایران و رئیس کمیته ی کمومتریکس آن انجمن به مدت دو سال (۱۳۹۵ تا ۱۳۹۷) بوده است. دبیر علمی سومین سمینار دو سالانه کمومتریکس ایران (سال ۱۳۹۰- دانشگاه تبریز) و دبیر بیست و پنجمین سمینار شیمی تجزیه انجمن شیمی ایران (۱۳۹۷- دانشگاه تبریز) بوده است.

فرم مشخصات فارغ التحصیلان دکتری شیمی تجزیه دانشگاه تبریز



نام و نام خانوادگی: اسماعیل علی پور  
استاد راهنما: دکتر محمدحسین پورنقی آذر - دکتر محمدسعید حجازی  
سال ورود به مقطع دکتری: ۱۳۸۲  
سال فارغ التحصیلی از مقطع دکترا ۱۳۸۷  
آدرس الکترونیکی: i-alipour@tabrizu.ac.ir  
محل دانشگاه فعلی: دانشگاه تبریز

سوابق آموزشی و پژوهشی

دکتر اسماعیل علی پور دانش آموخته دانشگاه تبریز می باشند که تمام مقاطع تحصیلات عالی خود را اعم از کارشناسی، کارشناسی ارشد و دکتری در همین دانشگاه به اتمام رسانده اند. استاد راهنمای ایشان در مقطع حجازی بودند. ایشان فارغ التحصیل دکتری سال ۱۳۸۷ با رساله ای تحت عنوان "تهیه بیوسنسور الکتروشیمیایی DNA بر پایه ی ژن اینترلوکین- ۲ انسانی و به کارگیری آن برای تشخیص پلاسمیدهای نو ترکیب" می باشند. ایشان از فروردین سال ۱۳۸۸ به عنوان استادیار گروه شیمی تجزیه فعالیت های آموزشی و پژوهشی خود را در دانشگاه تبریز شروع کردند. تدریس دروس مختلف تخصصی در مقاطع کارشناسی، کارشناسی ارشد و دکترا و همچنین پذیرش دانشجوی کارشناسی ارشد از سال ۱۳۹۰ پذیرش دانشجوی دکتری از سال ۱۳۹۲ صورت گرفت. ایشان جزو اولین الکتروشیمیست هایی هستند که در ایران در زمینه ساخت بیوسنسورهای الکتروشیمیایی DNA شروع به پژوهش کرده اند و حاصل کار ایشان در این زمینه در قالب مقاله های پژوهشی متعددی در معتبرترین مجلات الکتروشیمی تجزیه ای دنیا به چاپ رسیده اند. ایشان هم اکنون با مرتبه دانشجویی به همراه تیم تحقیقاتی خود، در تشخیص زودهنگام بیماری های ژنتیکی به ویژه سرطان ها در زمینه بکارگیری بیوسنسورهای الکتروشیمیایی DNA فعالیت می کنند. از افتخارات ایشان می توان به کسب عنوان استاد نمونه دانشگاه تبریز اشاره کرد. دکتر علیپور هم اکنون استاد مشاور استعدادهای درخشان دانشکده شیمی، و مسئول کمیته علمی المپیاد شیمی قطب ۴ کشوری می باشند.



فرم مشخصات فارغ التحصیلان دکتری شیمی تجزیه دانشگاه تبریز

	<p>نام: معصومه</p> <p>نام خانوادگی: شقاقی سراسکاندرود</p> <p>استاد راهنما: دکتر منظوری لشگر</p> <p>سال ورود به مقطع دکتری: ۱۳۸۲</p> <p>سال فارغ التحصیلی از مقطع دکترا: ۱۳۸۷</p> <p>آدرس الکترونیکی: m.shag2003d@yahoo.com</p> <p>محل دانشگاه فعلی: دانشگاه پیام نور تبریز</p>
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سوابق آموزشی و پژوهشی

ایشان هر سه مقطع کارشناسی، کارشناسی ارشد و دکترا را در دانشگاه تبریز در به پایان رساندند و در زمینه‌ی برهمکنش دارو با پروتئین و DNA مشغول فعالیت آموزشی و پژوهشی بودند. ایشان همچنین مولف ۱۵ مقاله‌ی منتشره در مجلات معتبر بین المللی می‌باشند و در انجام ۳ طرح پژوهشی مشارکت داشته‌اند.

فرم مشخصات فارغ التحصیلان دکتری شیمی تجزیه دانشگاه تبریز

نام: تهمینه

نام خانوادگی: باهری اسلامی

استاد/ اساتید راهنما: دکتر جوزن

سال ورود به مقطع دکتری: ۱۳۸۲

سال فارغ التحصیلی از مقطع دکترا: ۱۳۸۷

آدرس الکترونیکی:-



محل فعالیت/ محل دانشگاه فعلی: دانشگاه علوم انتظامی امین

سوابق آموزشی و پژوهشی

ایشان هر سه مقطع کارشناسی، کارشناسی ارشد و دکترا را در دانشگاه تبریز به پایان رساندند و در زمینه‌ی کروماتوگرافی و جداسازی مشغول فعالیت بودند. دکتر باهری همچنین مولف ۲۰ مقاله‌ی منتشره در مجلات معتبر بین المللی می‌باشند. ایشان همچنین در انجام ۳ طرح پژوهشی مشارکت داشته‌اند.

فرم مشخصات فارغ التحصیلان دکتری شیمی تجزیه دانشگاه تبریز

	<p>نام: بهرام نام خانوادگی: ابراهیمی استاد/ اساتید راهنما: دکتر جوزن و دکتر فرج زاده سال ورود به مقطع دکتری: ۱۳۸۳ سال فارغ التحصیلی از مقطع دکترا: ۱۳۸۸ آدرس الکترونیکی: bahram302.ebrahimi@gmail.com محل فعالیت/ محل دانشگاه فعلی: دانشگاه آزاد سنندج</p>
<p>سوابق آموزشی و پژوهشی</p>	
<p>ایشان مقطع کارشناسی را در دانشگاه رازی کرمانشاه و مقاطع کارشناسی ارشد و دکترا را در دانشگاه تبریز به پایان رساندند و هم اکنون با مرتبه‌ی استادیاری مشغول فعالیت در دانشگاه سنندج هستند. دکتر ابراهیمی همچنین مولف ۱۸ مقاله‌ی منتشره در مجلات معتبر بین المللی می‌باشند و در انجام ۴ طرح پژوهشی مشارکت داشته‌اند.</p>	

فرم مشخصات فارغ التحصیلان دکتری شیمی تجزیه دانشگاه تبریز

نام: سیما

نام خانوادگی: قلیزاده

استاد/ اساتید راهنما: دکتر مجیدی، دکتر حجازی

سال ورود به مقطع دکتری: ۱۳۸۳

سال فارغ التحصیلی از مقطع دکترا: ۱۳۸۸


آدرس الکترونیکی: -

محل فعالیت/ محل دانشگاه فعلی: -

سوابق آموزشی و پژوهشی

ایشان هر سه مقطع کارشناسی، کارشناسی ارشد و دکترا را در دانشگاه تبریز در به پایان رساندند و در زمینه الکتروشیمی (سنسور و بیو سنسور) مشغول فعالیت آموزشی و پژوهشی بودند. دکتر قلیزاده مولف ۵ مقاله‌ی منتشره در مجلات معتبر بین المللی می‌باشند.

فرم مشخصات فارغ التحصیلان دکتری شیمی تجزیه دانشگاه تبریز

	<p>نام: بهنام نام خانوادگی: حافظی استاد/ اساتید راهنما: دکتر مجیدی سال ورود به مقطع دکتری: ۱۳۸۴ سال فارغ التحصیلی از مقطع دکترا: ۱۳۸۹ آدرس الکترونیکی:- محل فعالیت/ محل دانشگاه فعلی: داروسازی توفیق دارو</p>
<p>سوابق آموزشی و پژوهشی</p>	
<p>ایشان ورودی سال ۱۳۷۳ در مقطع کارشناسی و ۱۳۷۷ مقطع کارشناسی ارشد دانشگاه تبریز می باشند و در حال حاضر مدیریت کنترل کیفیت داروسازی توفیق دارو را بر عهده دارند.</p>	

فرم مشخصات فارغ التحصیلان دکتری شیمی تجزیه دانشگاه تبریز



نام: مرتضی

نام خانوادگی: ایرانی فام

استاد/ اساتید راهنما: دکتر محمد حسین سرورالدین

سال ورود به مقطع دکتری: ۱۳۸۴

سال فارغ التحصیلی از مقطع دکترا: ۱۳۸۹

آدرس الکترونیکی: MortezaIranifam@yahoo.com

محل فعالیت/ محل دانشگاه فعلی: دانشگاه مراغه

سوابق آموزشی و پژوهشی

ایشان هر سه مقطع کارشناسی، کارشناسی ارشد و دکترا را در دانشگاه تبریز به پایان رساندند. دکتر ایرانی فام هم‌اکنون با عنوان دانشیار در زمینه‌ی اسپکتروسکوپی و کمی لومینسانس مشغول فعالیت‌های آموزشی و پژوهشی دانشگاه مراغه هستند و راهنمایی ۱۶ پایان‌نامه‌ی کارشناسی ارشد را بر عهده داشته‌اند. ایشان همچنین مولف بیش از چهل مقاله‌ی منتشره در مجلات معتبر بین‌المللی می‌باشند.

فرم مشخصات فارغ التحصیلان دکتری شیمی تجزیه دانشگاه تبریز



نام: جعفر

نام خانوادگی: ابوالحسنی

استاد/اساتید راهنما: دکتر منظوری لشگر

سال ورود به مقطع دکتری: ۱۳۸۵

سال فارغ التحصیلی از مقطع دکترا: ۱۳۸۹

آدرس الکترونیکی: Abolhasani@iaut.ac.ir

محل فعالیت فعلی: دانشگاه آزاد تبریز

سوابق آموزشی و پژوهشی

ایشان هر سه مقطع کارشناسی، کارشناسی ارشد و دکترا را در دانشگاه تبریز به پایان رساندند. هم اکنون دانشیار دانشگاه آزاد تبریز هستند و مولف بیش از پنجاه مقاله منتشره در مجلات معتبر بین المللی و همچنین دوازده طرح پژوهشی می باشند. دکتر ابوالحسنی در زمینه ی آنالیز مواد غذایی و دارویی، استفاده از نانوساختارها و شیمی سبز مشغول فعالیت و پژوهش هستند.

فرم مشخصات فارغ التحصیلان دکتری شیمی تجزیه دانشگاه تبریز



نام: جمال

نام خانوادگی: نوروزی

استاد/اساتید راهنما: دکتر جوانشیر جوزن و دکتر میرعلی فرج زاده

سال ورود به مقطع دکتری: ۱۳۸۵

سال فارغ التحصیلی از مقطع دکترا: ۱۳۹۱

آدرس الکترونیکی: j.norouzi@yahoo.com

محل فعالیت/محل دانشگاه فعلی: دانشگاه آزاد واحد شبستر

سوابق آموزشی و پژوهشی

ایشان به عنوان ریاست باشگاه پژوهشگران جوان و نخبگان دانشگاه آزاد اسلامی واحد شبستر، مسئول دفتر ارتباط با صنعت و جامعه‌ی دانشگاه آزاد اسلامی واحد شبستر و مسئول انجمن‌های ادبی و علمی دانشگاه آزاد اسلامی واحد شبستر مشغول به فعالیت بوده‌اند. همچنین سابقه‌ی تدریس دروس شیمی تجزیه دستگاهی، شیمی تجزیه ۱ و ۲، آزمایشگاه‌های روش‌های نوین آزمایشگاهی، شیمی عمومی ۱ و ۲ و شیمی تجزیه پیشرفته را دارند. از سوابق پژوهشی ایشان، می‌توان به طرح پژوهشی با عنوان "توسعه‌ی روش میکرواستخراج با فاز جامد کوپل شده با کروماتوگرافی گازی (GC-SPME) در حضور امواج ریز (میکروویو) جهت استخراج ترکیبات آلی فرار از نمونه‌های خاک و کاربرد آن در آنالیز آفت‌کش دیازینون موجود در خاک‌های کشاورزی" اشاره کرد. ایشان سه مقاله در کنفرانس‌های بین‌المللی و داخلی ارائه نموده‌اند و چهار مقاله در مجلات بین‌المللی به چاپ رساندند.



فرم مشخصات فارغ التحصیلان دکتری شیمی تجزیه دانشگاه تبریز



نام: فاطمه

نام خانوادگی: آهور

استاد/ اساتید راهنما: دکتر محمد حسین پور نقی آذر، دکتر محمد سعید حجازی

سال ورود به مقطع دکتری: ۱۳۸۵

سال فارغ التحصیلی از مقطع دکتری: ۱۳۹۰

آدرس الکترونیکی: Fatemeh.ahour@gmail.com

محل فعالیت/ محل دانشگاه فعلی: دانشگاه ارومیه

سوابق آموزشی و پژوهشی

دکتر فاطمه آهور تمام مقاطع تحصیلات خود را اعم از کارشناسی، کارشناسی ارشد و دکتری در دانشگاه تبریز به اتمام رسانده‌اند. ایشان هم‌اکنون با عنوان استادیار در زمینه الکتروشیمی مشغول فعالیت‌های آموزشی و پژوهشی هستند و راهنمایی سه پایان‌نامه‌ی کارشناسی ارشد را بر عهده داشته‌اند. ایشان همچنین در انجام ۳ طرح پژوهشی با عناوین "کاربرد الکتروود مغز مداد اصلاح شده با گرافن اکساید و نانو ذرات پالادیم پوشیده شده با آبی پروس برای اندازه‌گیری انتخابی و حساس هیدروژن پراکسید" با دانشگاه ارومیه، "استفاده از الکتروود آلومینیوم اصلاح شده با آبی پروس به عنوان سنسور آمپرومتری برای اندازه‌گیری تیول‌ها نظیر گلوکاتینون و  $N$ -استیل سیستئین" و "اندازه‌گیری آمپرومتری هیدروژن پراکسید در محیط زیست و نمونه‌های بیولوژیکی با بهره‌گیری از احیای آن بر روی الکتروود آلومینیوم اصلاح شده با آبی پروس" با قطب علمی شیمی پاک دانشگاه تبریز مشارکت داشته‌اند. دکتر آهور همچنین مولف ۱۶ مقاله‌ی منتشره در مجلات معتبر بین‌المللی و ۵ مقاله‌ی ارائه شده در سمینارهای داخلی می‌باشند.

فرم مشخصات فارغ التحصیلان دکتری شیمی تجزیه دانشگاه تبریز



نام و نام خانوادگی: مسعود سعادت

استاد/اساتید راهنما: دکتر محمدحسین سرورالدین

سال ورود به مقطع دکتری: ۱۳۸۵

سال فارغ التحصیلی از مقطع دکترا: ۱۳۸۹

آدرس الکترونیکی: m.saadati@cfu.ac.ir

محل فعالیت فعلی: دانشگاه فرهنگیان

سوابق آموزشی و پژوهشی

ایشان هر سه مقطع کارشناسی، کارشناسی ارشد و دکترا را در دانشگاه تبریز به پایان رساندند. دکتر مسعود سعادت بیش از بیست سال سابقه تدریس دروس مختلف شیمی از سطح متوسطه تا دانشگاه دارند و هم اکنون استادیار دانشگاه فرهنگیان هستند. مولف ۹ مقاله علمی-پژوهشی (ISI) در مجلات بین المللی تخصصی شیمی و ۶ مقاله علمی-ترویجی در مجلات تخصصی شیمی داخلی، می باشند. دکتر سعادت دو کتاب ترجمه نموده اند و در ۱۸ کنفرانس مختلف علمی ملی و بین المللی شرکت نموده اند و ۷ مقاله بصورت سخنرانی و ۱۱ مقاله علمی بصورت پوستر ارائه نموده اند.

فرم مشخصات فارغ التحصیلان دکتری شیمی تجزیه دانشگاه تبریز



نام: سعید محمد

نام خانوادگی: سرورالدین

استاد/ اساتید راهنما: دکتر جوانشیر جوزن و دکتر میرعلی فرج زاده

سال ورود به مقطع دکتری: ۸۶

سال فارغ التحصیلی از مقطع دکترا: ۹۱

آدرس الکترونیکی: [ssoreddin@tabrizu.ac.ir](mailto:ssoreddin@tabrizu.ac.ir)

محل فعالیت/ محل دانشگاه فعلی: دانشگاه تبریز

سوابق آموزشی و پژوهشی

دکتر سعیدمحمد سرورالدین عضو هیئت علمی دانشگاه تبریز هم اکنون به عنوان استادیار دانشکده شیمی دانشگاه تبریز مشغول به فعالیت می‌باشند. ایشان به مدت ۶ سال در دوره‌های کارشناسی و تحصیلات تکمیلی سابقه تدریس دارند. زمینه‌ی پژوهشی دکتر سرورالدین روش‌های میکرواستخراج و آنالیز مواد دارویی و زیست محیطی می‌باشد. ایشان تاکنون ۱۸ مقاله‌ی ISI و ISC در این زمینه به چاپ رسانده و ۱۵ عنوان مقاله نیز در کنفرانس‌های ملی ارائه نموده‌اند.

فرم مشخصات فارغ التحصیلان دکتری شیمی تجزیه دانشگاه تبریز



نام: امین

نام خانوادگی: ایمانی نبیی

استاد/ اساتید راهنما: آقای دکتر محمدحسین سرورالدین

سال ورود به مقطع دکتری: ۱۳۸۷

سال فارغ التحصیلی از مقطع دکترا: ۱۳۹۳

آدرس الکترونیکی: aamin\_imani@yahoo.com

محل فعالیت/ محل دانشگاه فعلی: شغل آزاد

سوابق آموزشی و پژوهشی

ایشان تمام مقاطع تحصیلی کارشناسی، کارشناسی ارشد و دکترای تخصصی را در دانشگاه تبریز سپری کرده و به مدت ۴ سال عضو هیئت علمی گروه شیمی دانشگاه پیام نور و به مدت ۲ سال مسئول امور جاری و سرپرست دانشگاه پیام نور مرکز میانه بوده‌اند.

فرم مشخصات فارغ التحصیلان دکتری شیمی تجزیه دانشگاه تبریز

	<p>نام: جواد نام خانوادگی: حسن زاده استاد/ اساتید راهنما: دکتر امجدی، دکتر منظوری لشکر سال ورود به مقطع دکتری: ۱۳۸۷ سال فارغ التحصیلی از مقطع دکترا: ۱۳۹۲ آدرس الکترونیکی: - محل فعالیت/ محل دانشگاه فعلی: -</p>
<p>سوابق آموزشی و پژوهشی</p>	
<p>ایشان در زمینه‌ی اسپکتروسکوپی مشغول فعالیت آموزشی و پژوهشی بودند و مولف ۳۲ مقاله‌ی منتشره در مجلات معتبر بین المللی می‌باشند.</p>	

فرم مشخصات فارغ التحصیلان دکتری شیمی تجزیه دانشگاه تبریز

	<p>نام: لیلا</p> <p>نام خانوادگی: قوشجوئی</p> <p>استاد / اساتید راهنما: دکتر میرعلی فرج زاده</p> <p>سال ورود به مقطع دکتری: ۱۳۸۷</p> <p>سال فارغ التحصیلی از مقطع دکترا: ۱۳۹۲</p> <p>آدرس الکترونیکی: Goushju.leila@gmail.com</p> <p>محل فعالیت / محل دانشگاه فعلی: ستاد فناوری نانو / شرکت کیمیا شینگرز پارس</p>
<p>سوابق آموزشی و پژوهشی</p>	
<p>ایشان دو مقطع کارشناسی و کارشناسی ارشد را در دانشگاه ارومیه به پایان رساندند و هم اکنون در زمینه‌ی اسانس‌ها و مواد غذایی و روش‌های کروماتوگرافی مشغول فعالیت آموزشی و پژوهشی هستند. ایشان همچنین مولف ۶ مقاله‌ی منتشره در مجلات معتبر بین المللی می‌باشند و در انجام یک طرح پژوهشی مشارکت داشته‌اند.</p>	

فرم مشخصات فارغ التحصیلان دکتری شیمی تجزیه دانشگاه تبریز



نام: افسانه

نام خانوادگی: سعادت‌ی راد

استاد/ اساتید راهنما: دکتر میررضا مجیدی

سال ورود به مقطع دکتری: ۱۳۸۸

سال فارغ التحصیلی از مقطع دکترا: ۱۳۹۳


آدرس الکترونیکی: afsaadatyrad@gmail.com

محل فعالیت/ محل دانشگاه فعلی: -

سوابق آموزشی و پژوهشی

ایشان تمام مقاطع تحصیلات عالی خود را اعم از کارشناسی، کارشناسی ارشد و دکتری در دانشگاه تبریز به ترتیب در سال‌های ۸۴، ۸۶ و ۹۳ به اتمام رسانده‌اند. دکتر سعادت‌ی چاپ حدود ۱۰ مقاله‌ی ISI، ارائه‌ی ۷ مقاله در کنفرانس‌های داخلی و خارجی و یک طرح پژوهشی با عنوان "اندازه‌گیری همزمان پاراستامول (آستامینوفن)، اسید آسکوربیک (ویتامین C) و کدئین در حد آثار به روش پالس ولتامتری افتراقی با استفاده از الکتروود اصلاح شده آلومینیوم" را در کارنامه آموزشی و پژوهشی خود دارند.

فرم مشخصات فارغ التحصیلان دکتری شیمی تجزیه دانشگاه تبریز

	<p>نام و نام خانوادگی: طوبی حلاج</p> <p>استاد/اساتید راهنما: جناب آقای دکتر امجدی و جناب آقای دکتر منظوری</p> <p>سال ورود به مقطع دکتری: ۱۳۸۸</p> <p>سال فارغ التحصیلی از مقطع دکتری: ۱۳۹۳</p> <p>آدرس الکترونیکی: t.hallaj@tabrizu.ac.ir</p> <p>محل فعالیت/محل دانشگاه فعلی: دانشگاه تبریز</p>
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سوابق آموزشی و پژوهشی

ایشان هم اکنون در حال گذراندن دومین دوره ی پسادکتری خود تحت حمایت صندوق حمایت از فناوران و پژوهشگران و تحت راهنمایی جناب آقای دکتر امجدی در دانشگاه تبریز هستند. دکتر حلاج در دوره اول پسادکتری به راهنمایی آقای دکتر امجدی از حمایت فدراسیون سرآمدان علمی ایران استفاده کرده اند. حاصل کارهای تحقیقاتی ایشان، به صورت ۲۲ مقاله ISI و ۲۰ مقاله به صورت سخنرانی و پوستر در سمینارهای داخلی و بین المللی منتشر شده است. همچنین، در انجام ۳ طرح تحقیقاتی داخلی و بین المللی در دانشگاه تبریز مشارکت داشته اند و مشاوره ی ۹ پایانامه ی کارشناسی ارشد در دانشگاه تبریز را برعهده داشته اند. دکتر حلاج همچنین سابقه ی تدریس دروس مختلف شیمی تجزیه در مقطع کارشناسی و کارشناسی ارشد در دانشگاههای آزاد و پیام نور و دروس شیمی عمومی را در دانشگاه تبریز را دارند.



فرم مشخصات فارغ التحصیلان دکتری شیمی تجزیه دانشگاه تبریز



نام و نام خانوادگی: لیلا خوشمرام

استاد/اساتید راهنما: دکتر میرعلی فرجزاده

سال ورود به مقطع دکتری: ۱۳۸۸

سال فارغ التحصیلی از مقطع دکترا: ۱۳۹۲

آدرس الکترونیکی: l.khoshmaram@gmail.com

محل فعالیت/ محل دانشگاه فعلی: دانشگاه شهید مدنی آذربایجان

سوابق آموزشی و پژوهشی

حوزه‌ی پژوهشی دکتر خوشمرام " توسعه‌ی روش‌های آماده‌سازی نمونه و تکنیک‌های کروماتوگرافی " می‌باشد. ایشان مولف ۱۴ مقاله منتشره در مجلات بین‌المللی می‌باشند و هم‌اکنون عضو هیئت علمی دانشگاه شهید مدنی آذربایجان هستند.

فرم مشخصات فارغ التحصیلان دکتری شیمی تجزیه دانشگاه تبریز

نام: لیلا

نام خانوادگی: فرزادپور

استاد/ اساتید راهنما: دکتر امجدی

سال ورود به مقطع دکتری: ۱۳۸۸

سال فارغ التحصیلی از مقطع دکترا: ۱۳۹۳

آدرس الکترونیکی: -

محل فعالیت/ محل دانشگاه فعلی: -

سوابق آموزشی و پژوهشی

ایشان هر سه مقطع کارشناسی، کارشناسی ارشد و دکترا را در دانشگاه تبریز در به پایان رساندند و در زمینه‌ی اسپکتروسکوپی مشغول فعالیت آموزشی و پژوهشی بودند. ایشان همچنین مولف ۴ مقاله‌ی منتشره در مجلات معتبر بین المللی می‌باشند.

فرم مشخصات فارغ التحصیلان دکتری شیمی تجزیه دانشگاه تبریز

نام: رعنا

نام خانوادگی: فاضلی بختیاری

استاد/اساتید راهنما: دکتر محمد حسین سرورالدین - دکتر ابوالقاسم جویبان

سال ورود به مقطع دکتری: ۱۳۸۸

سال فارغ التحصیلی از مقطع دکترا: ۱۳۹۴

آدرس الکترونیکی: rana\_fazeli@yahoo.com

محل فعالیت/محل دانشگاه فعلی: دانشگاه علوم پزشکی مشهد



سوابق آموزشی و پژوهشی

ایشان مقطع کارشناسی ارشد و دکتری را در دانشگاه تبریز گذراندند و در هر دو مقطع عضو استعدادهای درخشان دانشگاه تبریز بوده‌اند. دکتر فاضلی دوره فرصت مطالعاتی داخل را در زمینه سم شناسی تجزیه ای در دانشگاه علوم پزشکی مشهد و دوره ی پسا دکترا را در زمینه ی آنالیز بیومدیکال در دانشگاه علوم پزشکی تبریز به پایان رساندند. ایشان همچنین به تدریس در دانشگاه آزاد و پیام نور پرداخته‌اند و داوری مقالات مجلات علمی را بر عهده داشته‌اند. ایشان همچنین ۱۰ مقاله در مجلات ISI به چاپ رساندند و ۸ مقاله در همایش‌ها و سمینارهای تخصصی شیمی تجزیه ارائه داده‌اند و در انجام طرح‌های پژوهشی همکاری داشته‌اند.

فرم مشخصات فارغ التحصیلان دکتری شیمی تجزیه دانشگاه تبریز



نام: رضا

نام خانوادگی: فداکار باجه باج

استاد راهنما: دکتر میررضا مجیدی

سال ورود به مقطع دکتری: ۱۳۸۹

سال فارغ التحصیلی از مقطع دکترا: ۱۳۹۳


آدرس الکترونیکی: rezafadakar89@gmail.com

محل دانشگاه فعلی: دانشگاه تبریز

سوابق آموزشی و پژوهشی

ایشان مقاطع تحصیلی کاشناسی، کارشناسی ارشد و دکتری را در دانشگاه تبریز سپری کرده و هم اکنون در دوره‌ی پست دکتری در این دانشگاه مشغول فعالیت می‌باشند. زمینه‌ی فعالیت‌های پژوهشی ایشان اصلاح سطوح انواع الکتروود و به کارگیری آنها در اندازه‌گیری الکتروشیمیایی ترکیبات آلی است. دکتر فداکار ۱۱ عنوان مقاله در مجلات معتبر علمی به چاپ رسانده و ۶ عنوان مقاله در کنفرانس‌های ملی و بین‌المللی ارائه نموده‌اند.

فرم مشخصات فارغ التحصیلان دکتری شیمی تجزیه دانشگاه تبریز

	<p>نام: اعظم نام خانوادگی: صمدی استاد راهنما: دکتر محمد امجدی سال ورود به مقطع دکتری: ۱۳۸۹ سال فارغ التحصیلی از مقطع دکترا: ۱۳۹۴ آدرس الکترونیکی: samadi_azam@yahoo.com محل دانشگاه فعلی: دانشگاه علوم پزشکی تبریز</p>
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سوابق آموزشی و پژوهشی

ایشان مقطع کارشناسی و کارشناسی ارشد را در دانشگاه تبریز گذراندند. سپس، مقطع دکترا را در همین دانشگاه با موضوع توسعه‌ی جادب‌های نوینی بر پایه‌ی اکسیدهای فلزی نانوساختار برای جداسازی و پیش‌تغلیظ برخی یون‌های فلزی و اندازه‌گیری آنها با روش‌های اسپکتروفوتومتری به پایان رساندند. از سال ۱۳۹۵ در دوره‌ی پست دکترا مشغول به تحصیل در دانشگاه علوم پزشکی تبریز می‌باشند. دکتر صمدی همچنین به تحقیق بر روی سنسورهایی بر پایه‌ی نقاط کوانتومی برای اندازه‌گیری داروهای ضد صرع می‌پردازند، مشاوره‌ی پایان‌نامه‌های دانشجویان ارشد را بر عهده دارند و مشغول تدریس در دانشگاه آزاد اسلامی واحد تبریز هستند. ایشان همچنین به عنوان مسئول دستگاه جذب اتمی مشغول فعالیت هستند و تخصص کار با دستگاه‌ها و تجهیزات اسپکتروسکوپی از جمله فلوریمتر، اسپکتروفوتومتر، طیف‌سنج جذب اتمی و طیف‌سنج مادون قرمز تبدیل فوریه را دارند. همچنین ۱۰ بیش از مقاله در مجلات بین‌المللی به چاپ رساندند و در انجام پروژه‌های تحقیقاتی همکاری دارند.

فرم مشخصات فارغ التحصیلان دکتری شیمی تجزیه دانشگاه تبریز

نام: فاطمه

نام خانوادگی: طاهرزاده

استاد راهنما: دکتر اسدپور زینالی

سال ورود به مقطع دکتری: ۱۳۸۹

سال فارغ التحصیلی از مقطع دکترا: ۱۳۹۴

آدرس الکترونیکی: fatemeh\_taherzadeh@yahoo.com

محل دانشگاه فعلی: مرکز پژوهشگاه فضایی

سوابق آموزشی و پژوهشی

ایشان مقطع کارشناسی را در دانشگاه رازی کرمانشاه گذراندند و سپس دو مقطع کارشناسی ارشد و دکترا را در دانشگاه تبریز در به پایان رساندند. دکتر طاهرزاده در زمینه‌ی کمومتریکس مشغول فعالیت آموزشی و پژوهشی بودند. ایشان مولف ۸ مقاله‌ی منتشره و ۳ طرح پژوهشی در مجلات معتبر بین المللی می‌باشند.

فرم مشخصات فارغ التحصیلان دکتری شیمی تجزیه دانشگاه تبریز



نام: نینا

نام خانوادگی: نوری

استاد راهنما: دکتر میر علی فرج زاده

سال ورود به مقطع دکتری: ۱۳۸۹

سال فارغ التحصیلی از مقطع دکترا: ۱۳۹۲

آدرس الکترونیکی: n\_nouribaki@yahoo.com

محل دانشگاه فعلی: پژوهشگاه استاندارد

سوابق آموزشی و پژوهشی

ایشان مقطع کارشناسی و کارشناسی ارشد را در دانشگاه تبریز گذراندند. سپس، مقطع دکترا را در همین دانشگاه با موضوع توسعه‌ی جادب‌های نوینی بر پایه‌ی اکسیدهای فلزی نانوساختار برای جداسازی و پیش‌تغلیظ برخی یون‌های فلزی و اندازه‌گیری آنها با روش‌های اسپکتروفوتومتری به پایان رساندند. از سال ۱۳۹۵ در دوره‌ی پست دکترا مشغول به تحصیل در دانشگاه علوم پزشکی تبریز می‌باشند. دکتر صمدی همچنین به تحقیق بر روی سنسورهایی بر پایه‌ی نقاط کوانتومی برای اندازه‌گیری داروهای ضد صرع می‌پردازند، مشاوره‌ی پایان‌نامه‌های دانشجویان ارشد را بر عهده دارند و مشغول تدریس در دانشگاه آزاد اسلامی واحد تبریز هستند. ایشان همچنین به عنوان مسئول دستگاه جذب اتمی مشغول فعالیت هستند و تخصص کار با دستگاه‌ها و تجهیزات اسپکتروسکوپی از جمله فلوریمتر، اسپکتروفوتومتر، طیف‌سنج جذب اتمی و طیف‌سنج مادون قرمز تبدیل فوریه را دارند. همچنین ۱۰ بیش از مقاله در مجلات بین‌المللی به چاپ رساندند و در انجام پروژه‌های تحقیقاتی همکاری دارند.

فرم مشخصات فارغ التحصیلان دکتری شیمی تجزیه دانشگاه تبریز



نام: سهیران

نام خانوادگی: قادری

استاد راهنما: دکتر مجیدی

سال ورود به مقطع دکتری: ۱۳۹۰

سال فارغ التحصیلی از مقطع دکترا: ۱۳۹۵

آدرس الکترونیکی: seyranghaderi@gmail.com

محل دانشگاه فعلی: دانشگاه پیام نور مهاباد

سوابق آموزشی و پژوهشی

سهیران قادری سه مقطع کارشناسی، کارشناسی ارشد و دکترا را به ترتیب در دانشگاه‌های ارومیه، اصفهان و تبریز به اتمام رساندند و هم اکنون در دانشگاه پیام نور مشغول فعالیت می‌باشند. ایشان بیش از ۱۰ مقاله در مجلات معتبر علمی به چاپ رسانده و بیش از ۶ مقاله نیز در کنفرانس‌های ملی ارائه نموده‌اند. ایشان همچنین عضوی دفتر استعدادهای درخشان دانشگاه تبریز بوده‌اند.



فرم مشخصات فارغ التحصیلان دکتری شیمی تجزیه دانشگاه تبریز



نام: پری

نام خانوادگی: کرمی

اساتید راهنما: دکتر مجیدی- دکتر امیدی - دکتر علیپور

سال ورود به مقطع دکتری: ۹۱

سال فارغ التحصیلی از مقطع دکترا: ۹۵

آدرس الکترونیکی: p\_karami@yahoo.com

محل دانشگاه فعلی: آزمایشگاه جامع علوم پزشکی تهران

سوابق آموزشی و پژوهشی

دکتر پری کرمی در سال ۱۳۸۵ وارد دانشگاه تبریز شدند و در رشته شیمی کاربردی به تحصیل پرداختند. در سال ۱۳۸۹ در المپیاد بین المللی شیمی شرکت کرده و رتبه ی ۳۱ را کسب نمودند. در همین سال در کنکور ارشد رتبه ی یک را در نانوشیمی، رتبه ی دو را در رشته های شیمی کاربردی و پیشرانه و رتبه ۱۲ را در شیمی تجزیه کسب نمودند و بلافاصله پس از اتمام دوره کارشناسی، به دلیل علاقه زیادی که به شیمی تجزیه و آنالیز داشتند و به ادامه تحصیل در رشته شیمی تجزیه در دانشگاه صنعتی شریف پرداختند. با راهنمایی های جناب آقای دکتر هرمزی نژاد تجارب زیادی در زمینه اسپکتروسکوپی، سنتز نانو مواد و اندازه گیری مواد به وسیله نانو ذرات کسب نمودند. در سال ۱۳۹۱ از رساله ی کارشناسی ارشد خود با دفاع کردند و بلافاصله در همین سال با کسب رتبه ۲۹ در کنکور دکتری به ادامه تحصیل در همین رشته در دانشگاه تبریز پرداختند. با راهنمایی های جناب آقایان پرفسور مجیدی، پرفسور امیدی و دکتر علیپور تجارب زیادی در زمینه های الکتروشیمی و بیوسنسورها و اندازه گیری مارکرهای سرطانی کسب نمودند و در سال ۱۳۹۵ از رساله دکتری خود دفاع کردند. قابل ذکر است که حاصل تجارب علمی ایشان به صورت ۶ مقاله ی ISI چاپ شده است. در حال حاضر هم با آزمایشگاه جامع علوم پزشکی تهران همکاری دارند و در طرح هایی در زمینه های ساخت کیت های تشخیص اعتیاد و بارداری، ساخت دستگاه های پرتابل تشخیصی و طراحی بیوسنسور برای تشخیص مارکر های سرطانی مثل EGFR، VEGF و PSA و ... فعالیت دارند.

فرم مشخصات فارغ التحصیلان دکتری شیمی تجزیه دانشگاه تبریز

	<p>نام: پریسا نام خانوادگی: خرم استاد راهنما: دکتر میرعلی فرج زاده سال ورود به مقطع دکتری: ۱۳۹۱ سال فارغ التحصیلی از مقطع دکترا: ۱۳۹۵ آدرس الکترونیکی: khorram_parisa@yahoo.com محل دانشگاه فعلی: پژوهشگاه استاندارد</p>
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سوابق آموزشی و پژوهشی

ایشان مقاطع کارشناسی ارشد و دکترا را در دانشگاه تبریز در به پایان رساندند و در زمینه‌های استخراج و کروماتوگرافی مشغول فعالیت آموزشی و پژوهشی بودند. دکتر خرم مولف ۱۹ مقاله‌ی منتشره در مجلات معتبر بین المللی می‌باشند.

فرم مشخصات فارغ التحصیلان دکتری شیمی تجزیه دانشگاه تبریز

	<p>نام: رقیه نام خانوادگی: جلیلی کهنه شهری اساتید راهنما: دکتر محمد امجدی - دکتر جمشید منظوری سال ورود به مقطع دکتری: ۹۱ سال فارغ التحصیلی از مقطع دکترا: ۹۶ آدرس الکترونیکی: R.jalili@tabrizu.ac.ir محل دانشگاه فعلی: دانشگاه علوم پزشکی تبریز</p>
<p>سوابق آموزشی و پژوهشی</p>	
<p>دکتر جلیلی مولف ۶ مقاله در مجلات بین المللی به چاپ رساندند و به تحقیق در زمینه‌های پلیمرهای قالب مولکولی، نانو تکنولوژی، استخراج فاز جامد و... پرداخته‌اند.</p>	

فرم مشخصات فارغ التحصیلان دکتری شیمی تجزیه دانشگاه تبریز



نام: محمدرضا

نام خانوادگی: افشار مقدم

استاد راهنما: دکتر میر علی فرج زاده

سال ورود به مقطع دکتری: ۱۳۹۱

سال فارغ التحصیلی از مقطع دکترا: ۱۳۹۵

آدرس الکترونیکی: mr.afsharmogaddam@yahoo.com

محل دانشگاه فعلی: دانشگاه علوم پزشکی تبریز

سوابق آموزشی و پژوهشی

ایشان دو مقطع کارشناسی ارشد و دکترا را در دانشگاه تبریز به پایان رساندند و از مقطع کارشناسی تا دکتری عضو استعداد های درخشان دانشگاه تبریز بوده‌اند. دکتر افشار مقدم همچنین عضو بنیاد ملی نخبگان و برنده ی جایزه تحصیلی این بنیاد، دانشجوی نمونه دانشگاه تبریز در سال ۱۳۹۴ و برنده ی جایزه پویایی و خلاقیت دانشگاه تبریز در سال ۱۳۹۴ بوده‌اند و تدریس در مقاطع کارشناسی، کارشناسی ارشد و همچنین راهنمایی بیش از ده عنوان پایان نامه ی کارشناسی ارشد و مشاوره ی بیش از ۱۲ دانشجوی کارشناسی ارشد را بر عهده داشته‌اند. هم اکنون مولف بیش از پنجاه مقاله ی منتشره در مجلات معتبر بین المللی و همچنین ۱۵ مقاله ی ارائه شده در سمینار های داخلی می‌باشند. ایشان همچنین در انجام ۱۰ طرح پژوهشی در زمینه های استخراج و مشتق سازی همزمان برخی از آلاینده های آمینی و فنولی در نمونه های آبی و زیست محیطی و اندازه گیری آن ها با روش کروماتوگرافی گازی- مجهز به دتکتور اسپکترومتر جرمی، بررسی مقادیر تعدادی از آفتکش های پرکاربرد) در تخم مرغ های عرضه شده در استان آذربایجان شرقی، تعیین باقی مانده ی حشره کش های کارباماتی از نمونه های آب میوه و سبزیجات به روش میکرواستخراج مایع-مایع پخشی کوپل شده با استخراج فاز مایع کنترل شده با دما و اندازه گیری آنها با HPLC و... مشارکت داشته‌اند.

فرم مشخصات فارغ التحصیلان دکتری شیمی تجزیه دانشگاه تبریز



نام: بهروز

نام خانوادگی: فریدونی

استاد راهنما: دکتر میر علی فرج زاده

سال ورود به مقطع دکتری: ۱۳۹۲

سال فارغ التحصیلی از مقطع دکترا: ۱۳۹۶

آدرس الکترونیکی: behruzferiduni@yahoo.com

محل دانشگاه فعلی: دبیر شیمی (تبریز)

سوابق آموزشی و پژوهشی

دکتر فریدونی دانشجوی ممتاز جشنواره پویایی و خلاقیت دکتر پولاد در گروه عمده‌ی علوم پایه در دانشگاه تبریز و عضو استعداد های درخشان این دانشگاه بوده‌اند. ایشان مولف سیزده مقاله‌ی منتشره در مجلات معتبر بین المللی و همچنین ۵ مقاله‌ی ارائه شده در سمینار های داخلی می‌باشند.

فرم مشخصات فارغ التحصیلان دکتری شیمی تجزیه دانشگاه تبریز



نام و نام خانوادگی: فریبا ملارسولی

استاد/اساتید راهنما: جناب آقای دکتر کریم اسدپورزینالی

سال ورود به مقطع دکتری: ۱۳۹۲

سال فارغ التحصیلی از مقطع دکترا: ۱۳۹۶

عنوان رساله دکتری: توسعه روش‌های جدید سنتز نقاط کوانتومی هسته-پوسته و ساختارهای نانوکروی، نانومیله‌ای و نانولوله: استفاده آن‌ها در ساخت حسگرها برای کاربردهای الکتروشیمی تجزیه‌ای

آدرس الکترونیکی: [faribamo@ucm.es](mailto:faribamo@ucm.es) و [f.mollarasouli@gmail.com](mailto:f.mollarasouli@gmail.com)

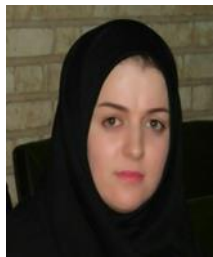
آدرس گوگل اسکولار:

<https://scholar.google.com/citations?user=r-q5rNMAAAAJ&hl=en>

سوابق آموزشی و پژوهشی

ورودی سال ۱۳۸۶ در مقطع روزانه کارشناسی رشته شیمی محض دانشگاه تبریز می‌باشند. پس از پایان دوره کارشناسی در سال ۱۳۹۰، بلافاصله تحصیلات دانشگاهی خود را در گرایش شیمی تجزیه در دانشگاه تبریز ادامه دادند و در سال‌های ۱۳۹۲ و ۱۳۹۶ مقاطع کارشناسی ارشد و دکتری خود را به پایان رساندند. در بهمن ماه ۱۳۹۵ به عنوان Visiting Researcher و در قالب فرصت مطالعاتی خارج از کشور با حمایت وزارت علوم ایران، به تیم پژوهشی بیوسنسور (gebe) به سرپرستی پروفسور خوزه مانوئل پینگرون در دانشگاه کامپلوتنسه مادرید (UCM) پیوست. حاصل این همکاری، طراحی و ساخت کیت تشخیصی و آنالیز بیومارکر AXL می‌باشد که گزارش آن در سایت خبری ستاد نانو آمده است. زمینه‌ی پژوهشی دکتر ملارسولی، سنتز نقاط کوانتومی و کاربرد آن‌ها در ساخت بیوسنسورها و ایمونوسنسورها جهت آنالیزهای دارویی، زیست-محیطی و بیومارکر است. ایشان به عنوان استاد مدعو، سابقه‌ی تدریس دروس شیمی عمومی ۱ و ۲ و آزمایشگاه شیمی تجزیه‌ی ۱ و ۲، را در دانشگاه تبریز و پیام نور واحد تبریز دارند. همچنین، تاکنون ۶ مقاله از کارهای ایشان در مجلات ISI با مجموع ایمپکت فاکتور ۳۰ به چاپ رسیده و ۸ مقاله در کنفرانس‌های ملی و یک مقاله در کنفرانس‌های بین-المللی ارائه نموده‌اند. عضو انجمن شیمی، باشگاه پژوهشگران جوان و استعدادهای درخشان دانشگاه تبریز هستند. دکتر ملارسولی در جایگاه نخست استعدادهای درخشان دانشجویان دکتری در سال ۲۰۱۳ قرار داشته-اند و جایزه‌ی بهترین پوستر را در کنگره‌ی شهر Sitges اسپانیا کسب نمودند.

فرم مشخصات فارغ التحصیلان دکتری شیمی تجزیه دانشگاه تبریز



نام: ساحله

نام خانوادگی: شیخی زاده میزان

استاد/ اساتید راهنما: دکتر عبدالحسین ناصری

سال ورود به مقطع دکتری: ۹۲

سال فارغ التحصیلی از مقطع دکترا: ۹۷

آدرس الکترونیکی: Sheykhizadehsaheleh@yahoo.com

محل فعالیت/ محل دانشگاه فعلی: دانشگاه تبریز- آزمایشگاه رادین

سوابق آموزشی و پژوهشی

ایشان دانش آموخته دانشگاه تبریز میباشند که تمام مقاطع تحصیلات عالی خود را اعم از کارشناسی، کارشناسی ارشد و دکتری در همین دانشگاه تحت نظر راهنمایی دکتر میر علی فرج زاده در مقطع کارشناسی ارشد و دکتر عبدالحسین ناصری در مقطع به اتمام رسانده اند. در دوره کارشناسی ارشد عضو دفتر استعداد درخشان دانشگاه بوده اند.

حوزه پژوهشی ایشان در زمینه کمومتریکس اعم از روشهای تشخیص الگو و برازش مدل و همچنین در زمینه استخراج در نمونه های زیست محیطی و غذایی، با استفاده از روش های آنالیز کروماتوگرافی مایع و گازی میباشد. چاپ حدود ۹ مقاله ISI و تدوین یک کتاب آموزشی را در کارنامه آموزشی و پژوهشی خود دارند.

فرم مشخصات فارغ التحصیلان دکتری شیمی تجزیه دانشگاه تبریز



نام: رقیه

نام خانوادگی: امینی

استاد/اساتید راهنما: دکتر کریم اسدپور زینالی

سال ورود به مقطع دکتری: ۹۲

سال فارغ التحصیلی از مقطع دکترا: ۹۷

آدرس الکترونیکی: r.amini\_chem@yahoo.com

سوابق علمی-آموزشی-فناوری

ایشان دو مقطع کارشناسی و دکترا را در دانشگاه تبریز به پایان رساندند. حوزه‌ی پژوهشی دکتر امینی در مقطع کارشناسی ارشد در زمینه‌ی "پیش تغلیظ برخی از یون‌های فلزی با استفاده از نانو ذرات هیدروکسیدهای دوگانه لایه‌ای قبل از اندازه‌گیری به روش اسپکترومتری جذب اتمی" و در مقطع دکترا در زمینه‌ی "تهیه‌ی الکترودهای اصلاح شده بر پایه نانوذرات هیدروکسیدهای دوگانه لایه‌ای و کاربرد الکتروتجزیه‌ای آن‌ها" می‌باشد. دکتر امینی همچنین مولف پنج مقاله‌ی منتشره در مجلات معتبر بین المللی می‌باشند.



## فرم مشخصات فارغ التحصیلان دکتری شیمی تجزیه دانشگاه تبریز



نام: عادلہ

نام خانوادگی: یادگاری

استاد راهنما: دکتر میرعلی فرج‌زاده

سال ورود به مقطع دکتری: ۱۳۹۳

سال فارغ التحصیلی از مقطع دکترا ۱۳۹۷

آدرس الکترونیکی: [Adi\\_yadegari@yahoo.com](mailto:Adi_yadegari@yahoo.com)

محل فعالیت/محل دانشگاه فعلی: آزمایشگاه رادین

### سوابق علمی-آموزشی-فناوری

عادلہ یادگاری دانش آموخته دانشگاه تبریز می‌باشند که تمام مقاطع تحصیلات عالی خود را اعم از کارشناسی، کارشناسی ارشد و دکتری در همین دانشگاه به اتمام رسانده‌اند. استاد راهنمای ایشان در مقاطع کارشناسی ارشد و دکتری دکتر میرعلی فرج‌زاده بودند. ایشان فارغ التحصیل کارشناسی شیمی کاربردی در سال ۱۳۹۱، کارشناسی ارشد در سال ۱۳۹۳ و دکترای سال ۱۳۹۷ هستند. حوزه‌ی پژوهشی مورد علاقه‌ی دکتر یادگاری زمینه‌ی استخراج، میکرواستخراج، مشتق‌سازی و همچنین به کارگیری نانومواد در آماده‌سازی نمونه‌های حقیقی و اندازه‌گیری مقادیر جزئی گونه‌های مختلف آلی و معدنی در نمونه‌های زیست محیطی، غذایی و بیولوژیکی با استفاده از روش‌های آنالیز کروماتوگرافی مایع و گازی می‌باشد. خانم یادگاری چاپ حدود ۱۳ مقاله ISI را در کارنامه‌ی آموزشی و پژوهشی خود دارند و هم‌اکنون به عنوان مسئول فنی آزمایشگاه رادین فعالیت می‌کنند.



مركز مستنداتي العالم راسالي علوم و فنون



انجمن شیمی تجزیه ایران  
25th  
ISAC  
3-5 Sep. 2018  
دانشگاه شیمی تبریز

# 25th Iraninan Semminar of Analytical Chemistry

## Booklet of Articles

3-5 Sep 2018

Iran - Tabriz

