Iranian Chemical Society
انجمن شیمی ایران

22nd Iranian Seminar of Analytical Chemistry

26-28 Jan 2016

Chemistry and Chemical Engineering Research Center of Iran

CCERCI

بیست و دومین سمینار شیمی تجزیه ایران

۶-۸ بهمن ۱۳۹۴

تهران، پژوهشگاه شیمی و مهندسی شیمی ایران

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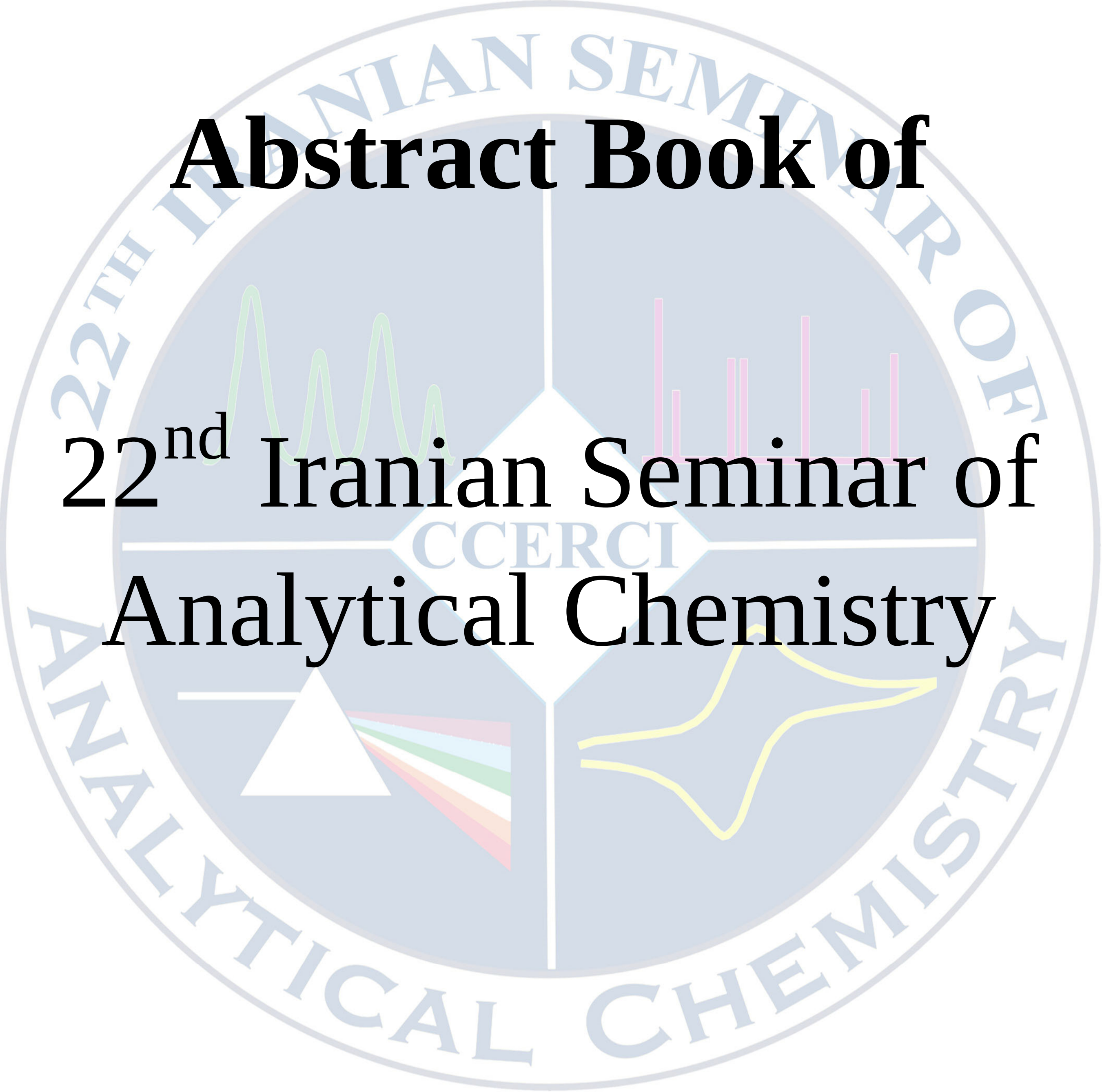

Abstract Book of

22nd Iranian Seminar of Analytical Chemistry

Preface

On behalf of Faculty of Clean Technologies, Chemistry and Chemical Engineering Research Center of Iran (CCERCI), it is my great pleasure to welcome you to the 22nd Iranian Seminar of Analytical Chemistry (ISAC2016) on January26-28, 2016 at Tehran. It is a great honor for us to host ISAC2016, which is a forum for scientists, researchers and scholars to share information, to exchange experiences, to present innovative concepts and researches related to all areas of analytical chemistry for sustainable development and promote the quality of life. This distinguished seminar will be an integral part of our celebration to commemorate the 25th year of Chemistry and Chemical Engineering Research Center of Iran and the 30th year of Iranian Chemical Society (ICS).

Since first meeting in 1990, ISAC has been organized regularly by ICS. With a slightly different format this year, we honored to develop it to a seminar with a new and different outlook to Analytical Chemistry, from research, improvement and education to specific applications. Therefore, most of the time of the seminar is devoted to oral presentation of the latest development in analytical chemistry, especially in Iran by the plenary lecturers. Oral and poster presentations of the participants' papers have also been programed in four sessions. During these three days, about 450 participants will give a total number of 13 plenary lectures, 27 lectures and 471 posters.

My very sincere gratitude to invited speakers and participants for their great contributions, and to all our sponsors, advisory boards, reviewers, colleagues and staffs for putting tremendous efforts into the organizational and administrative arrangements of this important event. The success has encountered is greatly encouraging for the future and we strongly support and promote ISAC to go forward furthermore.

I hope that you will enjoy your visit to ccerci and I sincerely wish you all a successful and productive conference..

Dr. Seyyed Hamid Ahmadi

Chairman of ISAC2016

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Hekmat Main Hall –Morning

Date/ time	9-9:30	9:30-10	10-10:30	10:30-10:40	10:40-11-30	11:30-12	12-12:30	12:30-14
Tuesday 26 Jan.	**Opening Ceremony**			**Sponsor Presentation** **NOVIN EBTEKAR**	**Coffee Break & Exhibition**	**Dr. A. Salimi** *From Clark biosensor to nanomaterial based implantable biofuel cells: Advances and challenges*	**Dr.K.Kargosha** *Analytical chemistry. Past, present and future*	**Pray & Lunch**
Wednsday 27 Jan.	**Dr.F. Faridbod** *Overview of research activities on spectroscopic methods by analytical chemists in Iran*	**Dr.M.R. Khanmohammadi** *An overview on future outlook for detergents*	**Dr.M.Mahmoodi** *Nanobiointerfaces: What the Cells See*	**Sponsor Presentation** **BORDER**	**Coffee Break & Exhibition**	**Dr.P.Nowroozi** *Two decades researches on electrochemical sensors and biosensors in Iran*	**Dr.A. Ghasempour** *Chromatography Used in Industry and Industrial Chromatography*	**Pray & Lunch**
Thursday 28 Jan.	**Ms. N. Zari** *Analytical Chemistry in Geological Survey Projects*	**Dr.A. Mehdinia** *Analytical Chemistry In Marine Sciences*	**Dr.M.Vosough** *Chemometrics Research at the Chemistry & Chemical Engineering Research Center Of Iran*	**Sponsor Presentation** **KARBORD SHIMI TAJHIZ**	**Coffee Break & Exhibition**	**Dr.M.Ayatollahi** *Smartphones as Analytical Devices*	**Closing Ceremony**	**Pray & Lu**

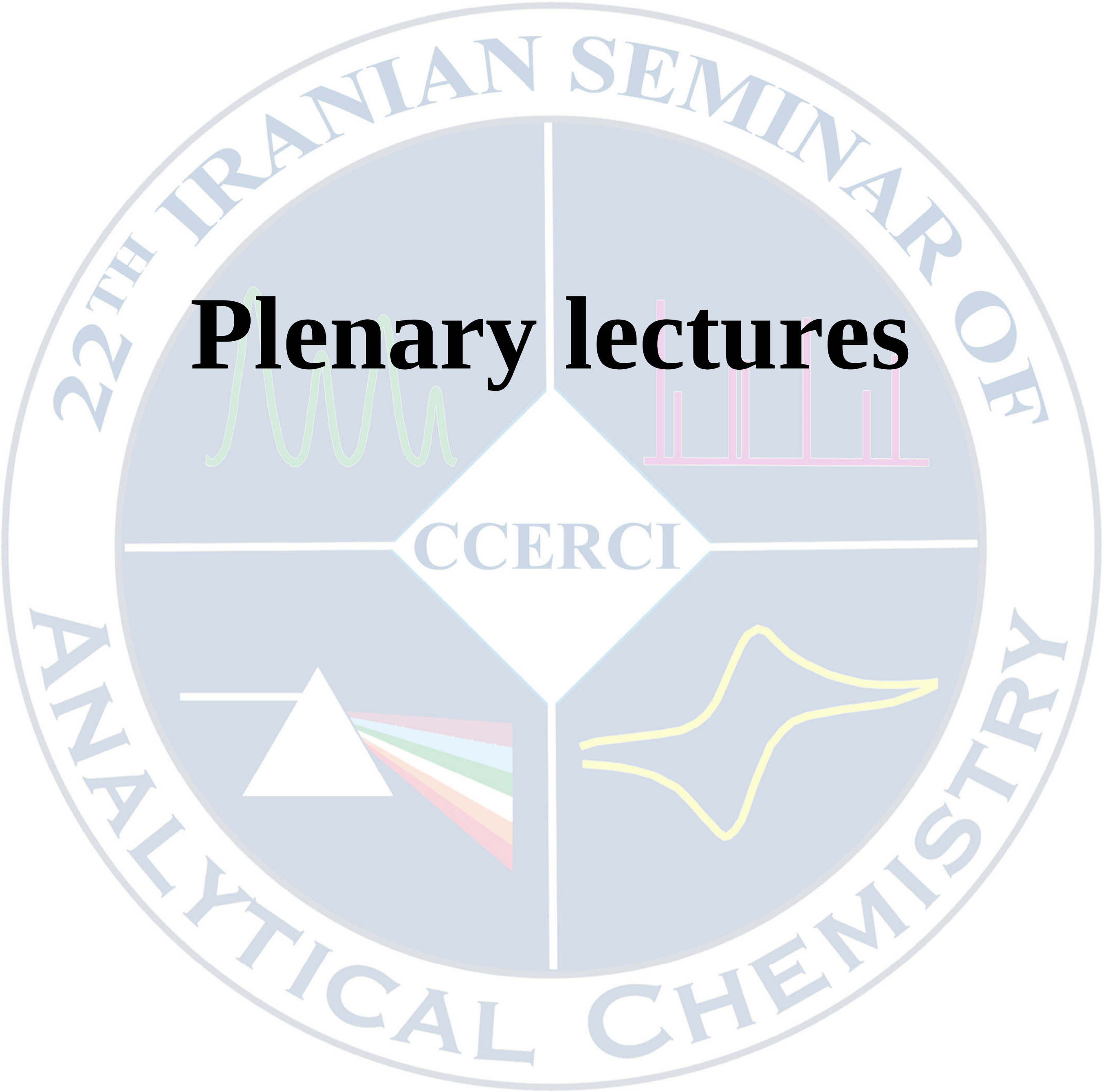
Hekmat Main Hall -Afternoon

Date/ time	14-14:30	14:30-14:40	14:40-15	15-15-20	15:20-15:40	15:40-16:20	16:20-16:40	16:40-17	17-17:20	17:20-17:40
Tuesday 26 Jan.	**Dr.Y.Yamini** *Electromembrane extraction as a powerful technique for extraction trace amounts of drugs from complicated matrices*	**Sponsor Presentation** **SARMAD TEB**	**Dr. A. Manbohi** *Flow-Through Analysis of Antibiotics by Fe3O4 Nanoparticles*	**Dr.F. Momenbeik** *Mesoporous carbon as adsorbent for effervescence-assisted dispersive micro-solid phase extraction of some herbicides*	**Dr.M.Mosadegh** *Carbon nanotubes@silicon dioxide nanohybrids coating for solid-phase microextraction of organophosphorus pesticides followed by gas chromatography–corona discharge ion mobility spectrometric detection*	**Coffee Break, Poster Session& Exhibition**	**F.Yazdankhah** *Comparison of direct, headspace and electrochemically enhanced modes in, in-tube solid phase microextraction with platinized stainless steel needle coated by …*	**M.R.Karimi poor** *A novel solid-state electrochemiluminescence biosensor for detection of cytochrome C based on Ceria Nanoparticles …*	**M.Kamalabadi** *Headspace-solid phase microextraction based on polypyrrole nanowire coupled with ion mobility spectrometry for determination of …*	**Sh.Najafi** *Aptamer based TFME Combined with Flow Injection Analysis using Column-less HPLC for Determination of PSA in Biological Fluid*
Wednsday 27 Jan.	**Dr.B.Hemmatinejad** *The past, Present and the future of chemometrics in Iran*	**Sponsor Presentation** **Arian BERIS**	**Dr.L.Fotoohi** *ndustry oriented analytical chemistry training program*	**A.Abbasi Ahd** *Femtoliter Scale Detection of Salmon Calcitonin by an Invert Thermal Lens Microscope*	**A.Eftekhari** *Development of multivariate analytical figures of merit for quantitative measurements using comprehensive two-dimensional chromatography*	**Coffee Break, Poster Session& Exhibition**	**D.Bigdelifam** *Offering a novel and sensitive method according to restricted access material-molecularly imprinted polymers for selective solid-phase extraction of residual pesticides …*	**E.Haghshenas** *Electrochemically oxidized of multiwalled carbon nanotube/glassy carbon electrode as a probe for simultaneous determination of …*	**Dr. A. Mani** *Untargeted metabolomic profiling of seminal plasma of non-obstructive azoospermia men using gas chromatography- mass spectrometry and advanced chemometric techniques*	

Hekmat Hall A –Afternoon

Date/ time	14:40-15	15-15:20	15:20-15:40	15:40-16:20	16:20-16:40	16:40-17	17-17:20	17:20-17:40
Tuesday 26 Jan.	**M.Ghomi** *A novel dual mode "on and off" fluorescence probe based on embedded label free silver nanoparticles in Poly vinyl alcohol-borax hydrogel for Fe (III) and thiosulfate determination*	**S.Damirchi** *Assessment of a novel and green chemistry colorimetric system for analysis of inorganic arsenic (III) by hydride generation and utilizing a optimized compact digital camera as the sensor with image processing*	**Kh.Dinmohammadi** *Determination of Doxorubicin drug using platinum coated magnetic nano particles: Resonance light scattering studies*	**Coffee Break, Poster Session& Exhibition**	**M.Zarrineh** *Producing and Designing Protein-A affinity Medias for antibody purification*	**Y.Abdossalami** *Development of microfluidic-chip system for liquid–phase microextraction based on two immiscible organic solvents for the extraction and preconcentration of hormonal drugs*	**Sajad Asadi** *Electromembrane extraction combined with cyclodextrin-modified capillary electrophoresis for the quantification of tetrabenazine enantiomers in biological samples*	
Wednsday 27 Jan.	**M.Safari** *Magnetic framework composite as novel adsorbent combined with high performance liquid chromatography for the determination of benzoylurea insecticide in juice fruit*	**V.Babarahimi** *Evaluation of acrylate polymer with monolithic nanostructure for extraction of losartan and valsartan from plasma using HPLC and LC-MS/MS*	**Z.Toorani** *Peanut Agglutinin Lectin: Isolation, Purification and Biological Characterization*	**Coffee Break, Poster Session& Exhibition**	**R.Parchami** *Peak separation property of 18-crown-6 in determination of biogenic amines by head-space solid phase microextraction based on nanostructured polypyrrole fiber coupled to ion mobility spectrometry*	**N.Feizi** *Design and performance of nanostructured supramolecular solvent based on gemini surfactant for microextraction of parabens from cosmetics*	**S.Asadi** *Two Step Voltage Dual Electromembrane Extraction: A New Approach to Simultaneous Extraction of Acidic and Basic Drugs*	

Plenary lectures



From Clark biosensor to nanomaterial based implantable biofuel cells: Advances and challenges

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Since Clark and Lyons first proposed glucose biosensor in 1962, intense efforts focused on the development of various biosensors and reliable biodevices. As in many different technological sections, nanomaterials have demonstrated their appropriateness for sensing, biosensing, and biomedical devices applications. In order to increase sensitivities and to lower detection limits down to even individual molecules, nanomaterials are promising candidates due to the possibility to immobilize an enhanced quantity of bioreceptor units at reduced volumes and even to act itself as transduction element. In beginning 2004, we began the fabrication of novel glucose biosensor, using CNTs for improving of electron transfer and sol-gel as matrix for holding of GOx enzyme, then we continued to work on direct electron transfer involving heme enzymes in nanomaterials films. These bioelectrochemistry efforts eventually led to applications to analysis of important biomolecules. In the first section of this lecture, the application of novel nanomaterials such as metal, metal oxides, quantum dots, carbon nanotubes, silicon, and graphene for design of sensors, biosensors, immunosensors and aptasensors will be surveyed and the effect of light irradiation on improving of signal response will also be evaluated. During the last decade biofuel cells (BFCs) have become an interesting research topic particularly with respect to their sustainability and potential application as power supply for portable, implantable devices in medicine and biosensor systems, because they can generate electrical energy via enzymatic reduction of O_2 with coupling of the enzymatic or enzyme free oxidation of biomass products (alcohols, sugars and organic acid) in mild condition. Stability, generated power and the cell voltage depend to anode and cathode reaction and also on the applied electrode architecture. In the early of 2013, we began the preparation of cathodes and anodes for fuel and biofuel cell design. In the second section of this talk, some recent results from our lab will be presented where we apply different nanomaterials as catalyst for anodic fuels oxidation and O_2 reduction, and the application of novel nanomaterial for immobilization of enzymes in an effort to exploit the high selectivity and reactivity of these interesting systems toward the development of biocathodes or bioanodes will be discussed. Finally, proposed BFC can be optimized as implantable devices to harvest the biochemical energy from glucose in the presence of oxygen in the physiological-like conditions.

Analytical Chemistry: Past, Present, Future

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Analytical chemistry as a science has its Owen history as well as an affecting present and semi-sure future.

The scientific bases of analytical chemistry were developed and established by w.ostwald in his book entitled. (Wissenschafliche grundlagen der analytischen chemie) published in 1894, and because of this he is considered the founder of analytical chemistry as a science [1].

To a large extent (wet) chemical methods, which formed the core part of laboratories of analytical chemistry in past have been superseded by instrumental techniques. Volumetric and gravimetric analysis methods are still taught in many courses. These are considered to be valuable in training students in accurate and precise analytical methodology.

Nowadays metals are determined by one of the various methods available for elemental analysis including ICP-OE, ICP-MS, XRF, EDXA or AAS. The present status of research in analytical chemistry is characterized by the developments of new instruments, methods and applications. Ion chromatography, FT-IR, are new instruments which are developed in middle of the 20th century. Using FT-IR spectroscopy to identify cancerous cell in biological samples is one example of developed application in nowadays. In a cancerous cell the increased rate of replication of DNA produces higher levels of phosphate and hydrogen bonded OH groups. Also the tertiary structure of the proteins and the ratio of CH_3 and CH_2 groups will change. FT-IR can detect these changes and allow us to discriminate cancerous and normal cells [2] A survey of the literature of the five last years show that analytical chemistry will develop and expand in the future based on nano-technology, biological science and electrometric techniques. Clinical analysis, environmental analysis and food analysis will be three prior areas of interest for analytical chemists.

References:

[1] Baiulescu, G.E, Analytical Letters, (2000), 33 (4), 571-577

[2] Almond M, Atkinson S , Marshal L. Royal society of chemistry, Http://www.rsc.org/education/2005 mar.

Electromembrane extraction as a powerful technique for extraction trace amounts of drugs from complicated matrices

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The concept of electromembrane extraction (EME) was initially suggested by Pedersen-Bjergaard and Rasmussen in 2006 [1]. The basis of EME is the migration of charged species in an electric field. The applied voltage in the EME system causes ionizable compounds to be transported from an aqueous sample solution across a supported liquid membrane (SLM) into an acceptor phase [2]. The primary EME setup was exploited for extraction of several classes of analytes, comprising acidic, basic, and zwitterionic compounds, and inorganic cationic/anionic species, and coupled to various analytical instruments, like high performance liquid chromatography (HPLC), capillary electrophoresis (CE), ion chromatograph (IC), and gas chromatograph (GC) with different detectors, for analysis of acceptor phase composition. Since the first application of EME method was reported for extraction of basic drugs, this technique has been wildly used for extraction of this class of analytes. The efficiency of EME has been compared with conventional hollow fiber based on liquid phase microextraction method (HF-LPME) [3] and it was shown that using electrical field impressively improves extraction recovery and reduces extraction time. However, by reversing the direction of electrical field, EME could effectively perform for extraction of acidic compounds and organic anions. EME has been used for extraction of metal ions and inorganic anions as well as peptides and amino acids too. In this presentation, focus is centered on EME. Fundamental of the technique is discussed to present a general vision of the effect of electric fields in carrying out sample treatment. Different modes of EME are introduced. The effect of different parameters on efficiency of EME for extraction of various analytes will be discussed. Finally, the potential of EME for extraction of different drugs from biological fluids is evaluated.

Keywords Electromembrane extraction; Biological samples; Pulsed potential; High performance liquid chromatography; Gas chromatography

References:

[1] S. Pedersen-Bjergaard, K.E. Rasmussen, J. Chromatogr. A 1109 (2006) 183–190.

[2] M. Eskandari, Y. Yamini, L. Fotouhi, S. Seidi, J. Pharm. Biomed. Anal. 54 (2011) 1173–1179.

[3] M. Rezazadeh, Y. Yamini, S. Seidi, A. Esrafili, Anal. Chim. Acta 773 (2013) 52–59.

Overview of research activities on spectroscopic methods by analytical chemists in Iran

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From the past to present, instrumental methods based on spectroscopic techniques are widely used in qualitative and quantitative analysis of different species in various matrices. Diversity in the interaction of electromagnetic radiations with materials creates a wide variety of spectroscopic techniques with numerous applications. Many researchers have been used these techniques qualitatively for identification of the structures. Others have used them as quantitative analysis methods to determine the concentrations. Also, these techniques are applied for interaction studies in physical chemistry and biophysics researches. In this article, we're going to overview the optical spectroscopic studies in Iran from the early reports to 2016 and consider the research activities of the Iranian analytical chemists in this area. Atomic and molecular spectroscopic techniques which have been used in the analysis of different species will be reviewed and at the end we will have a look at the spectro-electrochemical methods. In this regard, the reports are taken form Scopus data bases.

An overview on future outlook for detergents

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Modern detergents contain several chemical ingredients in different proportions and are complex mixtures to reflect the demands of modern day living in the new millennium. As far as it is predictable now, the tendency in detergent product development is leading towards more and more sophisticated detergent formulations.

New ingredients such as bio-surfactants, biopolymers and nano materials may be introduced, that provide additional benefit for the consumer even at low consumption levels [1]. The application of product is going to be made as comfortable as possible by tailored formulation.

The professional cleaning and hygiene market is a stable case. Total market value of the overall detergents and maintenance products industry (for both household and professional cleaning and hygiene products) for 2014 has reached 35 billion euros. The soap, detergent and surfactant industry has seen great change in recent years, responding to the shifts in consumer preferences, environmental pressure, the availability and cost of raw material and energy, demographic and social trends, and the overall economic and political situation worldwide. Currently, detergents product design is examined against the unifying focus of delivering to consumer performance and value, given the constraints of the economy, technological advancement, and environmental imperatives.

Another interacting force will be the further development of analytical science, especially analytical method. In the years to come detergent analysis will of course be influenced by future types and composition of commercial detergent products. Among several spectrometric approaches Fourier transform infrared (FTIR) spectrometry has been introduced as an efficient technique for quantitative determination of ingredients of washing powder samples. Considering the recent advances in on-line control and process analytics technology, IR based methods gained more and more interest. On the other hand, data processing by chemometric techniques would also support the successful development of IR based models for detergent analysis in industrial level.

References:

[1] Khanmohammadi, M.; . Rezaee Rudmianeh, H.; Bagheri Garmarudi, A.;. Ghasemi, K.; " Journal of Surfactants and Detergents 18 (2015), 251-258.

Nanobiointerfaces: What the Cells See

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Nanoparticles are becoming increasingly promising tools for medical diagnostics and therapeutics. Despite this rise, their potential risks to human health, together with environmental issues, have led to increasing concerns regarding their use. As such, a comprehensive understanding of the interactions that occur at the nanobiointerface is required in order to design safe, reliable and efficient nanoparticles for a variety of biomedical applications. To this end, extensive studies have been dedicated to probing the factors that define various properties of the nanobiointerface. However, the literature remains unclear and contains conflicting reports on cytotoxicity and biological fate, even for seemingly identical nanoparticles. To overcome these issues, the main research topic of my laboratory is to look for the overlooked factors at the nanobiointerfaces, in order to determine – unambiguously and reproducibly – the biological fate of nanoparticles both in vitro and in vivo. We also look after other critical applications of nanobiointerfaces in the field of stem cell technology and cardiovascular regenerative medicine, and define how this knowledge can substantially resolve some major issues in those fields. This talk will introduce some of recent fascinating findings in the field of nanobiointerfaces and how these approaches can improve current efforts in clinical translation of nano-based products for medical diagnostics, therapeutics, and regenerative medicines.

New developments in Iranian electrochemical analysis systems

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The combination of new electronic electrochemical EC systems with computer creates new capabilities in electroanalyticals measurements. In this seminar a brief review on the new achievements in developments of manufacturing of the EC instrumentation in Iran. Where, the lab-made EC systems with professional computer program have been offered numerous new advanced voltammetric techniques. The computer program provide on-line data acquisition and processing options based on various application of mathematical procedures, in which the EC signals are decomposed into the complex form for extracting more information. Also, application of FET and CMOS in construction of sensor and biosensor provides new dominations in EC applications in medical device and industrials. The new EC systems could be considered as promising tools for creating new research areas in Iran.

Chromatography Used in Industry and Industrial Chromatography

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What aspects of liquid chromatography (LC) are used in industrial and clinical applications? What advances and developments have been attained in LC and related technologies to suit industrial and clinical requirements? What is the technique to inspect petrochemical industries, pesticide and herbicide monitoring, quality assurance of cosmetic products, food safety, etc? What single process or the combination of orthogonal methods could be performed for quality control, assay determination, validation of the obtained data, and calibration of the measuring instruments for these samples? What kinds of industrial methods should be operated for purification of active compounds ranging from small molecules (drugs and supplement compounds) to biomolecules (proteins, genes, viruses and vaccines)? What kinds of isolation methods should be applied in order to obtain highly purified products of active pharmaceutical ingredients, biotechnological compounds (microbial and plant based), as well as analytical-specific samples (blood byproducts such as heparin)? In clinical studies, what method does exist for "*Omics-"* technologies (metabolomics, genomics and proteomics)? And how this relationship plays a key role in biological and clinical applications? How the biomarkers for medical disorders such as newborn screening PKU test, different types of cancer, autoimmune diseases, etc are monitored? From the perspective of industrial chromatography, packing materials of LC columns have been revolutionized in response to clinical and industrial applications. Different stationary phases based on silica, gel and synthetic polymers are now being developed for analysis and purification of various specimens of natural and synthetic compounds. What are the roles of silica gel based chiral and preparative chromatography in clinical and industrial studies, and what are the latest advancements in column specifications? What are the reasons behind the development of affinity chromatography columns, especially multiple affinity removal system columns? What part of the market is devoted to agarose based and affinity chromatography? What industrial applications could be covered by monolithic columns (synthetic polymers)? What are employment opportunities for the LC experts and how is the employment rate? What are the drawbacks of conventional LC techniques and what additional systems can be suggested to cover these weaknesses? The focus of this study is to introduce "LC techniques used in industry" and "industrial chromatography" as well as having responses to some of the mentioned questions.

The past, Present and the future of chemometrics in Iran

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Chemometrics research was started in the late of 1970 decade by the collaborative works of two chemists from United States and Sweden; B.R. Kowalski and S. Wold, respectively. About two decades later, chemometrics research was begun in Iran. The first published Iranian article in the subject of chemometrics has appeared in the literature in 1998 [1]. From this time to 2005, in spite of a long delay in start of chemometrics in Iran, it grew rapidly; a sum of 200 articles were published and many chemometrics research groups were established in different Iranian Universities and research institutes [1]. Also, teaching of chemometrics in workshops and university courses was started and many master and PhD students different fields of chemometrics as topic of their thesis. The large interests of Iranian Chemists on chemometrics caused a dramatic increase in the number of published papers from 2005 to 2012 such that the number of publications passed the record of 1500. Still we are observing continued interests on chemometrics in Iran. Up to date of writing this abstract, more than 2250 articles from Iranian Chemometrecians are cited in the web of knowledge core collection data bank.

In this presentation, I will give some statistical data regarding the different fields of chemometrics that have been paid attention by Iranian Chemometrecians. To show the evolution and grows of different fields of chemometrics in Iran, these fields will be analyzed chronologically. The presentation will be concluded by explaining some new fields in chemometrics that are active in my research group.

Keywords: Chemometrics; multivariate calibration; multivariate curve resolution; experimental design; QSAR; QSPR

References

[1] B. Hemmateenejad, *Chemom. Intell. Lab. Syst.* 2006, **81**, 202-208.

[2] A. Naseri, MN. Bahram, *J. Chemometr.* 2013, **27**, 263-277.

Analytical Chemistry in Geological Survey Projects

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Many projects within the Geological Survey use chemical analyses as a tool in the study of various earth, ecological, and biological processes and features. Often, the success of these projects is dependent upon the availability of modern, rapid, multi-element analytical instruments and techniques that are beyond the scope and capability of most individual projects. These projects should be provided by accessibility to state-of-the-art chemical analysis instrumentation and software, as well as the expertise of highly experienced research scientists to help solve unusually difficult problems in the field of analytical geochemistry that cannot be addressed by the routine methods of even the best commercial laboratories. As needs are identified for which routine methods currently do not exist, scientists from analytical chemistry conceptualize, develop, test, and validate new analytical techniques to provide high quality analytical data to Geological Survey researchers in the programmatic areas. For existing in-house methodologies, analytical chemists provide the expertise necessary for continuous improvement, ensuring high-quality data. Analytical chemists have expertise in the areas of chemical species analysis using a variety of techniques, including Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES), Inductively Coupled Plasma Mass Spectrometry (ICP-MS), Atomic Absorption Spectrometry (AAS), Xray Fluorescence Spectrometry (XRF), Ion Chromatography (IC), Gas Chromatography (GC), High Performance Liquid Chromatography (HPLC) specific element instrumentation such as Hg, C, and S analyzers, preparation of various types of environmental and geochemical samples, including water, rocks, minerals, and soils, sequential extractions and direct analysis of solids using techniques such as Laser Ablation , X-ray Fluorescence, Scanning Electron Microscope and X-ray Diffraction. As a whole the objectives of the analytical chemists in Geological Survey Projects are:

[1] Develop new and emerging geoanalytical techniques needed to support Geological Survey science goals and projects.

[2] Develop new geochemical standard reference materials that are used by Geological Survey and other scientists to calibrate analytical instruments, validate models, and monitor laboratory performance.

[3] Development and validation of analytical protocols for difficult-to-analyze samples that are beyond the routine capabilities of commercial laboratories.

Analytical Chemistry in Marine Sciences

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Analytical chemistry plays a key role in the exploitation of marine resources, not only because of the central significance of chemical analysis and instrumentation in this field, but because of the analytical chemists' expertise in sampling, measurement, separation of chemical species, concentration techniques, processing and assimilating data, and their broad scientific knowledge and interests.

The science of marine chemistry has advanced to the point where it is concerned not only with concentrations and compositions, but also with the routes and mechanisms of reactions which occur in the oceanic environment. Further new knowledge must be based, in part, upon measurements of actual ionic species, activities, and activity coefficients. The development of ion selective electrodes is particularly significant.

The major electrolytes dramatically affect the rates and equilibriums of the chemical reactions in the sea. The development and applications of analytical techniques for accurate determination and speciation in seawater, and on the effect of pollution on the marine environment, since small quantities of other elements may have a significant influence on global chemical cycling, is one of the applications of analytical chemistry in marine science. In order to understand these interactions, it is necessary to have a detailed knowledge of the major, minor and trace chemical components. The improvements are needed in the development of equipment for rapid and automated analyses in marine environment, and it is one the roles of analytical chemistry in marine sciences. Marine radioactivity measurements, marine pollution monitoring and assessment, climate change studies using isotopic records in the marine environment and also development of analytical methods for characterization of dissolved organic matter (DOM) in marine environment with Ultrahigh-resolution Fourier transform ion cyclotron resonance mass spectrometry (FT-ICRMS) are another examples of analytical chemistry applications in marine sciences.

Keywords Dissolved organic matter; Pollutants; Isotopic analysis; Ocean acidification

Chemometrics Research at the Chemistry and Chemical Engineering Research Center of Iran

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Due to rapid development of modern analytical instruments capable of producing multidimensional arrays, various chemometric data analysis methods have gained widespread acceptance over the past decades, responding to the need to study increasingly complex samples through improving traditional analytical protocols [1-3]. There is intensive research devoted to the development and the testing of multivariate algorithms applied to progressively more difficult chemical scenarios.

During recent years, our research group working in Chemometics Laboratory of *Chemistry and Chemical Engineering Research Center of Iran* has carried out different research projects in the fields of design of experiment and optimization, two way and three way multivariate data analysis and calibration, signal preprocessing and classification. In all studies, real samples with different complexities have been considered for analysis and internal and/or external validation parameters have been evaluated. The current presentation covers relevant analytical problems found in the analysis of food, drugs, environmental samples, biological fluids, and cosmetics, highlighting some significant examples, employed chemometric methods and the corresponding challenges in each case based on hyphenated chromatographic systems (HPLC-DAD, GC-MS) and fluorescence spectroscopy. Finally, advantages and the limitations of the different applied algorithms, are demonstrated.

Keywords: Chemometrics, Complex samples, Internal validation, External validation

References:

[1] M. Vosough, N. J. Iravani, Talanta 148 (2016) 454.

[2] M. Vosough, M. Rashvand, H. M. Esfahani, K. Kargosha, A. Salemi, Talanta 135 (2015) 7.

[3] G.M. Escandar, H.C. Goicoechea, A.M. de la Peña, A.C. Olivieri, Anal. Chim. Acta 806 (2014) 8-26.

Smartphones as Analytical Devices

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Smartphones combine cell-phone technologies with handheld personal computer that revolutionize our daily lives. While they became unseparated part of our new modern lifestyle, their many features are still unknown for us. These incredible little machines consist of various sensors including: accelerometer, gyroscope, magnetometer, proximity, barometer, thermometer, CCD camera, light sensor and…. Moreover, modern smartphones are turning to super-powerful computational devices. The vast availability of smartphones and their broad capacity for the application in the scientific researches are making them as new promising, simple, portable, cheap candidates for opening new horizons in the research, especially as diagnosis, detection, transduction and computational tools. In this seminar, an overview on the current outgoing researches on the application of smartphones in computational chemistry[1], colorimetry and spectroscopy[2], image analysis[3], electrochemistry[4], sensors and biosensors[5], cancer and genetic disease diagnosis[6] and … will be presented.

Keywords: Smartphones, Sensors, Biosensors, Diagnostic tool, Image Analysis

References:

[1] H. Parastar, H. Shaye, Chemometr. Intell. Lab. 147 (2015) 105.
[2] H. Yu, Y. Tan, B. T. Cunningham, Anal. Chem. 86 (2014) 8805.
[3] V. Oncescu, D. O'Dell, D. Erickson, Lab Chip 13 (2013) 3232.
[4] V. Velusamy, K. Arshak, O. Korostynska, A. Shamma, Key Eng. Mat. 543 (2013) 47.
[5] P. Liang, T. S. Park, J. Yoon, Sci. Rep. 4(2014) 5953.
[6] S. M. Khoshfetrat, M. Ranjbari, M. Shayan, M. A. Mehrgardi, A. Kiani, Anal. Chem. 87 (2015) 8123.

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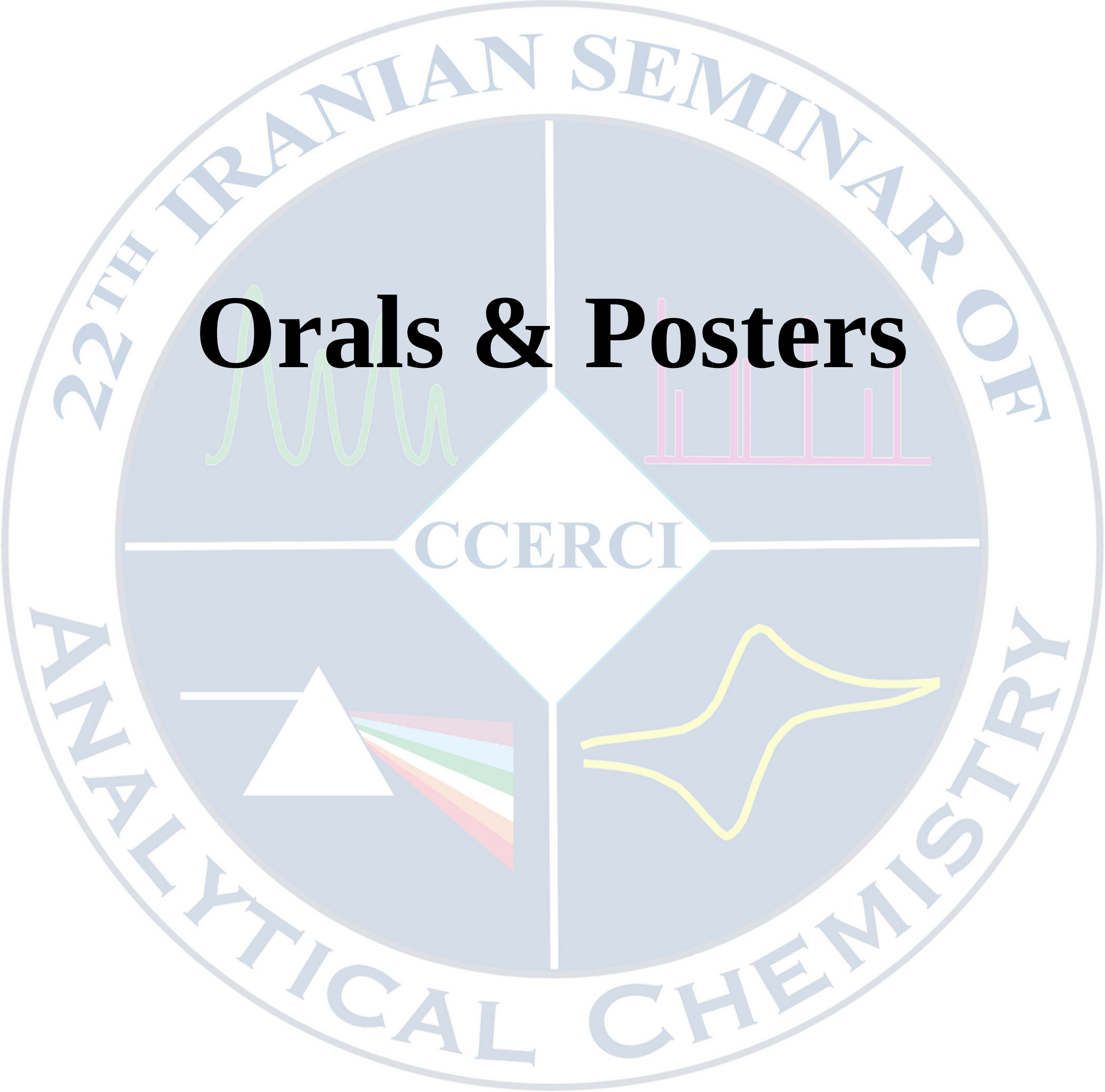

Fabrication of dye sensitized solar cells with two kinds of TiO_2 nanocrystals and effect of them on the efficiency of as prepared cells

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In this research, two kinds of as prepared TiO_2 and commercial TiO_2-P25 nanocrystals with sizes around 20 nm and 30 nm respectively, were used for fabrication of the dye sensitized solar cells (DSSC). TiO_2 nanocrystallines with diameters of 20-23 nm were prepared by using hydrothermally method with using titanium tetraisopropoxide (TTIP) as the TiO_2 precursor. TiO_2 nanocrystallines could be used as two semi-transparent TiO_2 layers to form the photoanode of the dye sensitized solar cells. TiO_2-P25 nanocrystallines (30-35 nm) and hydrothermally TiO_2 nanocrystallines were used to prepare a paste in ethanol based solvent using ethylcellulose and terpineol. The TiO_2 pastes were finally used to make the photoanode of the DSSC with different thicknesses. The results represented that the dye adsorption and cells efficiency are enhanced by using of the photoanode with hydrothermally TiO_2 nanocrystallines in the specific thickness. Different thicknesses of hydrothermally TiO_2 nanocrystallines and TiO_2-P25 nanocrystallines layers were applied in the experiments. The best fabricated dye sensitized solar cells was obtained in photoanode thickness of 12 µm, hydrothermally TiO_2 nanocrystallines and demonstrated the photovoltaic characteristics of J_{sc}=15.15 mA/cm^2, V_{oc}=655 mV and η=6.75%, the result represented 18% increase in efficiency compared with the DSSC made of the photoanode including TiO_2-P25 nanocrystallines. It's shows that type of TiO_2 nanocrystallines and diameter of them have effect on efficiency.

Keywords: Dye sensitized solar cells, Efficiency, Photoanode, TiO_2 nanocrystallines

4-Aminohippuric acid-functionalized carbon nanotubes for stripping voltammetric determination of copper(II) ions

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In this study, we have demonstrated that 4-Aminohippuric acid (AHA) can be coupled to acid-treated multiwalled carbon nanotubes (MWNTs) in the presence of 1-Ethyl-3-(3-dimethylaminopropyl)-carbodiimide (EDC) and N-Hydroxysuccinimide (NHS) and assembled as AHA-MWNT composites. These functionalized MWNTs can be used for modification of glassy carbon electrode and applied for determination of copper(II) ions. The electrochemical method was based on preconcentration of copper ions onto an electrode surface and then their anodic stripping voltammetric determination. The analytical curve for Cu(II) ions covered the linear range varying from 1.0 up to 230.0 µg L^{-1}. The limit of detection was found to be 0.4 µg L^{-1}, while the relative standard deviation at 5.0 and 200.0 µg L^{-1} were 1.5 and 1.1%, respectively. Most of the coexisting ions had little or no effect on the determination of copper(II). The obtained results suggest that the proposed method can be applied as a simple and efficient alternative way for the determination of copper ions which have good accuracy in real samples such as human hair and natural waters.

Keywords: 4-Aminohippuric acid, Copper(II), Multiwalled carbon nanotube, Stripping voltammetry

References:

[1] A. Mohadesi, Z. Motallebi, *Analyst*, 135(2010)1686.
[2] T.A. Ali, G.G. Mohamed, *Sens. Actuator. B-Chem.*, 202(2014)699.

Electrochemical sensor based on multi-walled carbon nanotube - cetyltrimethylammonium bromide / serine for Simultaneous determination of epinephrine and ascorbic acid

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A promising electrochemical sensor was developed based on a layer process by electropolymerization of serine on the surface of the multi-walled carbon nanotubes - cetyltrimethylammonium bromide pre-coated glassy carbon electrode (GCE). The effects of pH, scan rate and interference on the response of AA and EP were studied. The rate constants and anodic transfer coefficient (α) and exchange current density (j_0) of the electro-oxidation reactions are reported. The surface morphology and property of the modified electrode were characterized by scanning electron. Individual and simultaneous determination of AA, EP were carried out by differential pulse voltammetry. Under the optimum experimental conditions, the detection limits of 7.66 µM for AA and 0.23µM for EP were achieved by using DPV method. The modified electrode was applied successfully to the simultaneous determination of AA and EP in human blood serum by DPV method. Good stability and durability in the determination of AA and EP were observed for the sensor.

Keywords Ascorbic acid; Epinephrine; Cetyltrimethylammonium bromide; MWCNTs

References:

[1] C.C.Kocak, Z. Dursun, Journal of electroanalytical chemistry, **2013**, 694, 94- 103.
[2] S.Shahrokhian, R.S.Saberi, Electrochimica Acta, **2011**, 57, 132 –138.
[3] W. Ren, H.Q.Luo, N.B.Li, Bisensors and Bioelectronics, **2008**, 21, 1086- 1092.

Fabrication of Strontium selective electrode based on 1,13-bis(8-quinolyl)-1,4,7,10,13-pentaoxatridecane (kryptofix5) as a macromolecule ionophore and investigation of its behavioral characteristics

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Strontium is an important alkaline earth metal using in production of glasses for coloured television sets and ferrite magnets, in refining of zinc and added to tin and lead alloys for increasing hardness and durability. It has also been used as fireworks, signal flares and nuclear wastes [1,2]. Therefore, the determination of strontium is important due to its effects on living creatures and ecosystems. Among different techniques that are used for measuring metal cations, potentiometric technique using ion selective electrodes is a simple, rapid, inexpensive and selective method [3]. In this study, a strontium selective coated graphite electrode based on kryptofix5 as a neutral ionophore incorporated in polyvinyl choloride (PVC) membrane in tetrahydrofuran (THF) was fabricated. The electrode exhibits significantly enhanced response toward strontium ions over the concentration range 1.0×10^{-6} to 1.0×10^{-1} M with slope of 29.2±0.3 mV/decade of concentration and a detection limit of 4.54×10^{-7} M. The electrode has a good reproducibility with fast response time of 5s and could be used for at least 2 Weeks without any divergence in potential. The electrode operates in the wide pH range of 2.0–10.0. The proposed electrode showed a good discriminating ability towards strontium(II) ion over a wide variety of other metal ions including alkali, alkaline earth, transition, and heavy metal ions.

Keywords; Ion selective electrode; Strontium cation; Kryptofix 5; Potentiometry

References:

[1] M. Shamsipur, S. Rouhani, H. Sharghi, M. R. Ganjali and H. Eshghi, Analytical Chemistry, 1999, 71, 4938.
[2] P. K. Mohapatra, P. N. Pathak, A. Kelkar and V. K. Manchanda, New Journal of Chemistry, 2004, 28, 1004.
[3] G. H. Rounaghi, R. Mohammad Zadeh Kakhki and H. Sadeghian, Electrochimica Acta, 2011, 56, 9756.

Electrodeposition of Cu-based metal-organic framework and its electrocatalytic activity

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Metal–organic frameworks (MOFs) are a new member in the vast field of porous materials. MOFs are attracting considerable attention because of their unique structural properties, such as high surface areas, tunable pore sizes, and open metal sites, which enable them to have potential applications in gas storage, catalysis, sensors, drug release, and separation. Several preparation methods for the formation of MOFs have been developed throughout the years such as hydro- and solvothermal, ionothermal, microwave assisted, sonochemical, electrochemical, and mechanochemical syntheses.

In the present work, we electrodeposited a Cu-based MOF on the surface of graphite electrode for the first time by applying a constant voltage in the solution of ligand, metal ions and $NaNO_3$. The experimental parameters such as applied voltage, the ratio of metal cation:ligand and reaction time were optimized in order to get high purity and lowest metal plating. Cu-based MOF electrosynthesized was characterized by XRD, SEM and FT-IR. The electronic conductivity of Cu-based MOF electrosynthesized was analyzed by electrochemical impedance spectroscopy and the results showed that it can form excellent electron pathways between the electrode and electrolyte. The electrocatalytic activity of Cu-based MOF for oxidation of methanol was investigated. Before adding methanol, an irreversible wave with E_P = 1.16 V were observed, which was assigned to the metal-based oxidation of Cu-MOF. Upon adding methanol to the electrolyte, a considerable enhancement in the oxidative current density (~1.3mAcm^{-2}) and a negative shift in potential (~76mV) were observed during the positive scan. The methanol electrooxidation on this MOF material is dependent on the methanol concentration. With an increasing methanol concentration, the current density increased continuously.

Keywords: electrodeposition, metal-organic framework, methanol

Comparison of direct, headspace and electrochemically enhanced modes in, in-tube solid phase microextraction with platinized stainless steel needle coated by MWCNT/PANI nanocomposite for extraction of nicotine from biological fluids

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A multiwalled carbon nanotube-polyaniline (MWCNT/PANI) nanocomposite was electrochemically prepared on inner surface of a platinized stainless steel needle and applied for in-tube solid-phase microextraction (IT-SPME) of nicotine followed by gas chromatography-flame ionization detection (GC-FID). Three modes of direct immersion (DI), headspace (HS), and electrochemically enhanced (EE) were investigated and compared through IT-SPME-GC-FID analysis. Different affecting experimental variables in each mode, including extraction temperature and time, pH of sample solution, ionic strength, sampling flow rate, and voltage were studied. Comparison of the results showed that coupling of DI and EE methods (i.e., EE-DI-IT-SPME) provided the most efficient strategy for the extraction of nicotine from biological samples. Under the optimized conditions of the proposed EE-DI-IT-SPME-GC-FID method good linearity of the calibration curve (R^2=0.996) was obtained in the concentration range of 0.1-30 µg mL^{-1}. The limit of detection (LOD) was found to be 0.1 ng mL^{-1}. The relative standard deviation (RSD %) for 1 µg mL^{-1} of nicotine was obtained 2.5%, for six replicated analysis. The proposed EE-DI-IT-SPME-GC-FID setup was successfully applied for the extraction and determination of nicotine contents in human plasma. The results obtained by the proposed method showed good agreements with a standard official method.

Keywords: In-tube solid-phase microextraction; Direct Immersion; Head space; Electrochemically enhanced; Nicotine; Multiwalled carbon nanotube-polyaniline nanocomposite.

Direct electropolymerized coatings of polypyrrole-CNT on stainless steel 310 and their corrosion protection performance

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Stainless steel 310 (SS 310) is widely used in many fields due to its good corrosion resistance as well as its mechanical properties. The resistance to corrosion in aqueous media is attributed to the presence of a thin protective chromium-enriched oxide film. Several strategies have been used to generate more protective interfaces on stainless steels, including the use of conducting polymers [1, 2]. In this work, homogeneous, uniform and adherent polypyrrole-carbon nanotube (Ppy-CNT) nanocomposite coatings were electrosynthesized on SS 310 by using the current density fixed in the under galvanostatic conditions method. The synthesized coatings were characterized by Fourier transform infrared spectroscopy (FT-IR), SEM and UV-Vis spectroscopy. The corrosion performances of coatings were investigated in 5000 ppm NaCl solution used by the potentiodynamic polarization technique and electrochemical impedance spectroscopy (EIS).The current corrosion decreases significantly from 150 μA cm^{-2} for blank electrode SS 310 to 0.3 $\mu A cm^{-2}$ for Ppy-CNT nanocomposite coatings, under optimal conditions. Also, the potential corrosion increases from -380 mV versus Ag/AgCl for blank electrode SS 310 to -42 mV versus Ag/AgCl for Ppy-CNT nanocomposite coated stainless steel electrodes under optimal conditions. The results of this study clearly ascertain that the Ppy-CNT has outstanding potential to protect the SS 310 against corrosion in a chloride environment.

Keywords: Nanocomposite, Electrochemical synthesis, Corrosion, Stainless steel 310

Reference

[1] Ghoreishi, S.M.; Shabani-Nooshabadi, M.; Behpour, M.; Jafari, Y.; Prog. Org. Coat. 74 (2012) 502.

[2] Shabani-Nooshabadi, M.; Ghoreishi, S.M.; Behpour, M.; Corr. Sci. 52 (2011) 3035.

Surface functionalization of silica-coated magnetic nanoparticles for covalent attachment of lipase

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The potential of the modified magnetic nanoparticles for covalent immobilization of lipase has been investigated for the first time. The synthesis and immobilization processes were simple and fast. The co-precipitation method was used for synthesis of magnetic iron oxide (Fe3O4) nanoparticles (NPs) which were subsequently coated with silica through a sol-gel reaction. The amino-functionalized NPs were prepared by treating silica-coated NPs with 3-aminopropyltriethoxysilane followed by covalently immobilization of lipase. With glutaraldehyde as the coupling agent, the lipase from Serratia marcescens was successfully immobilized onto the amino-functionalized magnetic nanoparticles. The synthesized materials were characterized by transmission electron microscopy (TEM), Fourier transform infrared spectroscopy (FTIR) and X-ray diffraction (XRD). The results showed that the immobilized protein load could reach as high as 70 mg protein per gram support and the activity recovery was up to 60.0%. The optimum enzyme concentration and incubation time for immobilization reaction were 100 mg and 3 h, respectively. The optimum pH for maximal catalytic activity of the immobilized enzyme was 8 at 50 °C. The kinetic studies on the immobilized enzyme and its free counterpart revealed an acceptable change of Km and Vmax. The Km values were found as 0.66 and 0.57 mM for free and immobilized enzymes, respectively. The Vmax values for the free and immobilized enzymes were calculated as 0.14 and 0.47 µmol/mg min, in turn, when paranitrophenyl butyrate (PNPB) was used as the substrate. In comparison to the free enzyme, the immobilized enzyme was thermally stable and was reusable for 10 cycles while retaining 64 % of its initial activity.

Keywords: Enzyme activity, Enzyme satability, Immobilization, lipase, Magnetic nanoparticles.

Reference:

[1] Lu AH, Salabas EL, Schuth F.. Angew Chem Int Ed 2007;46:1222–44.
[2] Zhao LL, Xu JH, Zhao J, Pan J, Wang ZL. ECU1010. Process Biochem 2008;43:626–33.
[3] V. Swarnalatha, R., Journal of Molecular Catalysis B: Enzymatic 96 (2013) 6– 13.

Application of a Sensitive Nanocomposite-based Electrochemical Sensor for Voltammetric Simultaneous Determination of Tyrosine and Dicyclomine in Real Samples

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Electrochemical techniques with excellent merits of rapid response and simple operation have attracted a lot of interest in the detection of biomolecules. Tyrosine (Ty) is a kind of essential amino acids in human and herbivores bodies**.** Dicyclomine (DI) is an antispasmodic and anticholinergic drug, a medication that reduces the effect of acetylcholine on smooth muscles. Altering the concentration of these species is cause to several diseases, so their determination in much essential.

In the present study a glassy carbon electrode, modified with nanocomposite of gold nanoparticles/multiwalled carbon nanotubes (GNPs/MWCNTs/GCE) was used for the simultaneous determination of Ty and DI. The results showed that synergetic effects of GNPs and MWCNTs highly improved electrochemical response and sensitivity of the sensor. The electrochemical oxidation of Ty and DI was investigated by cyclic voltammetry (CV) and differential pulse voltammetry (DPV). Also, scanning electron microscopy (SEM) was used to evaluate microstructure of electrochemical sensor. The effect of various experimental parameters including pH and scan rate on the voltammetric response of Ty and DI were investigated. Under the optimal conditions linear response was observed in range of 4.0–130.0 µmol L^{-1} and 5.0–120.0 µmol L^{-1} for Ty and DI, respectively. The lower detection limits were found to be 0.9 µmol L^{-1} and 0.55 µmol L^{-1} for Ty and DI, respectively. The investigated method showed good stability, reproducibility and repeatability. The proposed sensor was successfully applied to the simultaneous determination of Ty and DI in real samples.

Keywords: Dicyclomine; Electrochemical sensor; Gold nanoparticle; Multiwalled carbon nanotubes; Tyrosine

Metal free and highly fluorescent nitrogen-doped graphene quantum dots as a Biosensor for determination of sunitinib

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Anti-angiogenic (AA) drugs are proposed as novel agents for targeted therapies in hepatocellular carcinoma (HCC)[1]. One of these drugs is, Z-Sunitinib malate, a multi-targeted tyrosine kinase inhibitor (TKI) that is registered for the treatment of advanced clear cell renal cell carcinoma (RCC). Various methods have been used to determined sunitinib, including LC-MS/MS method, RP-HPLC method, UPLC-MS/MS, paper spray–MS method [2], Herein, we developed a sensitive, selective, rapid, facile, and especially green method based on the fluorescence quenching of N-GQDs as a highly fluorescent nitrogen-doped graphene quantum dots, a free metal quantum dot and facile biosensor, that obtained using a one-step pyrolysis of citric acid (CA) as a carbon source, and tris (hydroxymethyl) aminomethane (Tris-HMA) as a surface passivation agent, for determination of sunitinib malate in real samples . Prepared quantum dots were characterized by TEM , XRD and IR measurements.

The influences initial pH, volume of N-GQDs and contact time have been researched in order to find the optimum quenching conditions. the calibration equation is A= 0.1909 C +0.4837 with a correlation coefficient of 0.999 (n=9).

Keywords: nitrogen doped graphene quantum dots, sunitinib, fluorescence, biosensor.

References:

[1] L.Bedouet, V.Verret, S.Louguet, Pharmaceutics (**2015**) 218-227.

[2] F.Ramazani, C.Hiemstra, R.Steendam, Pharmaceutics and Biopharmaceutics (2015) 1-10.

Design and construction of a label-free aptasensor for electrochemical detection of digoxin

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In the present manuscript, a label-free electrochemical aptasensor for the detection of digoxin has been described. The aim of this study was to introduce a sensitive digoxin assay method for clinical applications. For the construction of the sensor the surface of the gold working electrode was modified by self-assembling monolayer of 3-mercaptopropionic acid (MPA), following by covalent binding of amino-functionalized digoxin specific aptamer to MPA via carbodiimide chemistry. Electrochemical impedance spectroscopy (EIS) experiments in the presence of $[Fe(CN)_6]^{3-/4-}$ as negative redox probes demonstrated that the electrode surface was more blocked in the presence of digoxin because of the specific interaction between digoxin molecules and the aptamer and caused significant increasing of interfacial electron transfer resistance (R_{ct}). Furthermore, in-line with EIS observations, a remarkable drop in the square wave voltammetric (SWV) signal of the redox probe was observed. This concentration dependent drop in the current followed by SWV, was used to construct a calibration curve for real sample assay. Under optimal conditions, the detection limit of the constructed aptasensor was found 0.1 nM and delivered a linear dynamic range over 1-50 nM of digoxin. The applicability of the aptasensor for clinical applications was successfully evaluated by detection of digoxin in blood serum samples without any interference from the serum matrix.

Keywords: electrochemical detection; digoxin; aptasensor; self-assembled monolayer

Multi-walled carbon nanotube/ionic liquid modified carbon paste electrode for the potentiometric determination of atorvastatin in biological fluids and pharmaceuticals

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For the first time a novel derivatized multi-walled carbon nanotubes/ionic liquid-based on atorvastatin carbon paste electrodes is reported. At optimum values of variable conditions, the proposed electrodes responded toward atorvastatin linearly in the range of 1.0×10^{-9} - 1.0×10^{-3} mol L^{-1} with slope of 59.57±0.2 $mVdecade^{-1}$ of atorvastatin concentration and detection limit of 1.0×10^{-9} $molL^{-1}$ for ATOR/MWCNTs/I.L-CPE(electrode(17). The electrode response is independent of pH in the range of 3–8, with a fast response time (6 s) at 25 ◦C for electrode (17). Moreover, the electrodes also showed high selectivity and long life time (more than 13 and 15 weeks) for electrode (17). The electrodes showed good selectivity for atorvastatin toward wide variety of species. The proposed sensors were successfully applied for the determination of atorvastatin in pharmaceutical and biological fluids and as indicator electrodes.

Keywords: Atorvastatin determination, carbon paste electrode, Ionic liquid, multi-walled Carbon nanotube, Potentiometry,

Reference:

[1] Bertolini, S., Bittolo Bon, Atherosclerosis, 1997. **130**((1-2)): p. 191-197.
[2] M. Sacks, F., Am, Cardiol, 2001. **88**: p. 14-18.
[3] Organization, W.H., *The world health report 2002: reducing risks, promoting healthy life*. World Health Organization, 200.

A high sensitive method for electrochemical determination of omeprazole in real samples with $Ni_{0.5}Zn_{0.5}Fe_2O_4$ nanocomposite modified multi-walled carbon nanotubes - glassy carbon electrode

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In this study, a simple and highly sensitive sensor for the determination of omeprazole based on magnetic nickel zinc ferrite nanocomposite ($Ni_{0.5}Zn_{0.5}Fe_2O_4$), as the modifier, on multi-walled carbon nanotubes (MWCNTs) modified glassy carbon electrode ($Ni_{0.5}Zn_{0.5}Fe_2O_4$/MWCNTs-GCE) is reported. Omeprazole (OMZ), is a benzimidazole derivative which acts as proton pump inhibitor (PPI). It is a drug used for the effective treatment of gastric and duodenal (peptic) ulcers, reflux esophagitis, Zollinger-Allison syndrome, and other gastrointestinal conditions where gastric acid reduction is beneficial, and has found worldwide popularity over the past decade. Electrochemical methods have confirmed to be highly sensitive for the analysis of drugs in pharmaceutical formulations and also in human body fluids. These methods are simple and versatile due to their advantages such as cheap instrumentation, quick response time, high sensitivity and wide linearity. Scanning electron microscopy (SEM) along with energy dispersive X-ray spectroscopy (EDS), cyclic voltammetry (CV) and differential pulse voltammetry (DPV) were used to characterize the nanostructure and performance of the sensor and the results were compared with those obtained at the multi-walled carbon nanotube modified glassy carbon electrode (MWCNTs/GCE). Under the optimized experimental conditions omeprazole gave linear response over the range of 0.03-100 $\mu mol\ L^{-1}$. The detection limit was found to be 0.017 $\mu mol\ L^{-1}$. The effect of common interferences on the current response of omeprazole was investigated. The practical application of the modified electrode was demonstrated by measuring the concentration of omeprazole in plasma and pharmaceutical samples. This revealed that the $Ni_{0.5}Zn_{0.5}Fe_2O_4$/MWCNTs-GCE shows excellent analytical performance for the determination of omeprazole in terms of a very low detection limit, high sensitivity, very good accuracy, repeatability and reproducibility.

Keywords: Differential pulse voltammetry, Electrochemical sensor, Magnetic nickel zinc ferrite nanocomposite, Multi-walled carbon nanotube, Omeprazole determination

Glassy Carbon Electrodes Modified with Carbon Nanostructures: Application to Sensitive Voltammetric Determination of Furazolidone

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Furazolidone, 3-{[(5-nitro-2-furyl)methylene]amino}-1,3-oxazolidin-2-one, FZD, is a nitrofuran antibacterial drug. It is **administered** for human and veterinary medicine in case of bacteria or protozoan and Myxobolus cerebralis infections, respectively. In the recent years, carbon–based nanomaterials have attracted enormous interests due to their excellent electrical, chemical and mechanical properties, which make them suitable for developing nano-electronics and electrochemical sensors [1,2]. In this work, various modified electrodes were prepared by the GCE surface pre-coated with different carbon nanomaterials, including, carbon nanotubes (CNTs), carbon nanoparticles (CNPs), nanodiamond/graphite nanomixture (NDG), graphene oxide (GO), reduced graphene oxide (RGO) and RGO-CNT mixtures (with various ratios). Linear sweep voltammetry (LSV) was used to study the electrochemical behavior of FZD on the surface of the prepared modified electrodes. The best modified electrode was selected based on higher improvement of electrochemical response of FZD in comparison to the bare GCE. Using selected modified electrode, RGO/GCE, the reduction mechanism of FZD was discussed in details. The surface morphology and nature of the RGO film was thoroughly characterized by scanning electron microscopy (SEM), atomic force microscopy (AFM), electrochemical impedance spectroscopy (EIS) and cyclic voltammetry (CV) techniques. Under the optimal experimental conditions, the reduction peak current was proportional to FZD concentration in the range of 0.001 – 10 µM. The detection limit was 0.3 nM. This sensor was used successfully for FZD determination in pharmaceutical and clinical preparations.

Keywords: Carbon nanotubes, Electrochemical, Furazolidone, Graphene, Linear sweep

References:

[1] J. Wang, M. Li, Z. Shi, N. Li, Z. Gu, *Electrochim. Acta*, 47 (2001) 651.
[2] I. Streeter, G.G. Wildgoose, L. Shao, R.G. Compton, *Sens. Actuators B*, 133 (2008) 462.

Electrochemically oxidized of multiwalled carbon nanotube/glassy carbon electrode as a probe for simultaneous determination of dopamine and doxorubicin in biological samples

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A facile and effective approach of fabricating oxidized multiwalled carbon nanotube/glassy carbon electrode (OMWCNT/GCE) is herein reported. The OMWCNT/GCE was prepared by electrochemical oxidation method in basic media (0.5 mol L^{-1} NaOH solution) and used as a sensor for simultaneous determination of dopamine (DA) and doxorubicin (DOX). Scanning electron microscopy, energy dispersive X-ray spectroscopy and cyclic voltammetry were used for characterization and performance study of the OMWCNT/GCE. The modified electrode exhibited good electrocatalytic properties toward the oxidation of DA and DOX. Peaks potential difference of 240 mV between DA and DOX was large enough to determine DA and DOX individually and simultaneously. Square wave voltammetry (SWV) was used for the simultaneous determination of DA and DOX in their binary mixture. Under the optimum conditions, the linear concentration dependences of SW peak current responses were observed for DA and DOX in the concentration ranges of 0.03-55 μmol L^{-1} and 0.04-90 μmol L^{-1}, respectively. The detection limits (S/N = 3) were 8.5×10^{-3} μmol L^{-1}, and 9.4×10^{-3} μmol L^{-1} for DA and DOX, respectively. The analytical utility of OMWCNT/GCE was also successfully demonstrated for the simultaneous determination of DA and DOX in human blood serum and urine samples.

Keywords: Dopamine; Doxorubicin; Multiwalled carbon nanotube; Square wave voltammetry; Simultaneous determination.

References:

[1] Z. Temoçin, Sens Actuators, B176 (2013) 796–802.
[2] Z. Jemelková, J. Zima, J. Barek, Collect Czech Chem Commun 74 (2009)1503–1515.
[3] T. Madrakian, E. Haghshenas, A. Afkhami Sens Actuators, B 193 (2014) 451–460.

A new electrochemical sensor based on nanoparticles of molecularly imprinted polymer (MIP) for determination of chlordiazepoxide drug

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The determination of drugs in biological samples, mainly in patients' plasma, has been extensively applied to pharmacokinetic studies, in forensic toxicology, to evaluate intoxications by illicit drugs, to assure the therapeutic effectiveness (therapeutically drug monitoring), and to minimize the adverse effects (toxicity symptoms) of prescribed drugs.

In this study, a new sensitive voltammetric sensor based on carbon paste electrode modified with chlordiazepoxide(CPZ) imprinted polymer nanoparticles as a recognition element for determination of chlordiazepoxide is described.

The determination of chlordiazepoxide after its extraction onto the electrode surface was carried out by square wave voltammetry (SWV) method. The chlordiazepoxide binding experiments indicated that the sensor modified by Nano−MIP have much higher adsorption ability than the non−imprinted polymer (NIP) nanoparticles based sensor. Under the optimized extraction and analysis conditions, the peak current obtained at the Nano-MIP modified carbon paste electrode was proportional to the chlordiazepoxide concentration within the range of 6.0×10^{-10} to 8.0×10^{-8} mol L^{-1} ($R^2 = 0.9981$) with a detection limit of 2.65×10^{-10} mol L^{-1}. The reproducibility of the developed sensor in terms of relative standard deviation was 3.2%. This sensor was successfully applied for determination of chlordiazepoxide in pharmaceutical formulation and human serum samples.

Keywords: Carbon paste electrode; imprinted polymer; nanoparticles; chlordiazepoxide.

Reference:

[1] M.R.Milani Hosseini, A. Motaharian, *RSC Advances* 5 (2015) 81650.
[2] S. Sadeghi, A. Motaharian, A. Z. Moghaddam, Sens.Actuators, B, 168 (2012) 336.

Molecularly imprinted polymer (MIP) nanoparticles based electrochemical sensor for selective determination of diazinon pesticide

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The use of artificial host materials in chemical/biological detections has become increasingly attractive, because the synthetic recognition systems such as molecularly imprinted polymers (MIPs) usually have lower costs, higher physical/chemical stability ,easier preparation and better engineering possibility than biological receptors.

In this research a new molecularly imprinted electrochemical sensor is prepared for selective and sensitive determination of diazinon (DZN) pesticide. A diazinon selective MIP and a non-imprinted polymer (NIP) nanoparticles were synthesized and then incorporated in the carbon paste to prepare the modified carbon paste electrodes.

Cyclic voltammetry (CV) and square wave voltammetry (SWV) methods were applied to electrochemical measurements. The results showed that the Nano-MIP modified carbon paste electrode (MIP-CPE) have much higher adsorption ability to DZN than the CPE based non-imprinted polymer nanoparticles (NIP-CPE). Different parameters including the ratio of materials in the electrode composition, extraction pH, extraction time and pH of supporting electrolyte were evaluated. Under optimized conditions, the proposed electrode showed two linear ranges include 2.5×10^{-9} to 1.0×10^{-7} mol L^{-1} ($R^2 = 0.9971$) and 1.0×10^{-7} to 2.0×10^{-6} mol L^{-1} ($R^2 = 0.9832$) with a detection limit of 7.9×10^{-10} mol.L^{-1}. This sensor was successfully used for determination of DZN in a water sample.

Keywords: Electrochemical sensor; Molecularly imprinted polymer; nanoparticles; Diazinon.

Reference:

[1] G. Guan, B. Liu, Z. Wang, Z. Zhang, *Sensors* 8 (2008) 829.

Electrodeposition of polydiphenylamine nano-sheets on activated carbon fibers and its application in supercapacitors

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Conducting polymers (CPs) are a special class of materials with high electronic and ionic conductivity. These polymers have wide range of applications in optic and electronic industries and in energy storage systems specially supercapacitors. Diphenylamine (DPA) is an N-substituted aniline derivative which can be polymerized and used as an active material in supercapacitors electrode. In this study, electro-polymerization of DPA was accomplished through different electrochemical techniques in different acidic mediums on the carbon fibers substrate. Electrodeposited polymers were characterized by SEM and ATR. At first Carbon fibers substrate was activated by applying constant potential in acidic medium. PDPA nano-sheet was obtained through pulse amprometry technique in 0.5 M H_2SO_4 solution containing 1 mM of DPA. The mass of electrodeposited polymer was calculated by UV-Vis technique. The electrochemical performance of deposited PDPA was investigated by cyclic voltammetry, charge/discharge and electrochemical impedance spectroscopy techniques. PDPA nano-sheets exhibited maximum specific capacitance of 530 F/g and specific energy and power of 121 Wh/kg and 65 kW/kg, respectively.

Keywords: Supercapacitors; Conducting polymers; Polydiphenylamine; Nono-sheet; Electrochemical synthesis

References:

[1] S. P. Palaniappan, P. Manisankar, Electrochim. Acta 56 (2011) 6123.
[2] M. Baibarac, I. Baltog, S. Frunza, A. Magrez, D. Schur, Mater 32 (2013) 72.
[3] V. Rajendran, A. Gopalan, T. Vasudevan, C. T. Wen, J. Electrochem. Soc 147 (2000) 3014.

Poly-eriochrome black T modified glassy carbon electrode for the electrocatalytic determination of hydrazine

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In this work the fabrication of an electrochemical sensor was reported for the electrocatalytic determination of hydrazine (HZ) based on a polymerized film of eriochrome black T (EBT) on the surface of a glassy carbon (GC) electrode in alkaline solution. The poly (EBT)-modified glassy carbon electrode is shown to be very effective for the detection of hydrazine. Using the proposed electrode, the catalytic oxidation peak current of hydrazine was high and the over potential of its oxidation decreased. Based on the obtained results, a mechanism for electrooxidation of hydrazine at poly (EBT)-modified glassy carbon electrode demonstrated a four-electron transfer involved in the overall reaction. It has been shown that using the poly (EBT)-modified electrode, HZ can be determined by differential pulse voltammetry (DPV) and amperometry with limit of detection 11.5 and 6.7μM, respectively. The results of the analysis suggest that the proposed method promises accurate results and could be employed for the routine determination of HZ.

Keywords: Poly (eriochrome black T) modified electrode; Hydrazine; Electrocatalytic determination

References:

[1] M. Yang, H. L. Li, Talanta, 55 (2011) 479.
[2] M.R. Majidi, A. Jouyban, K. Asadpour-Zeynali, Electrochim. Acta, 52 (2007) 6248.
[3] X. Liu, L. Luo, Y. Ding, Z. Kang, D. Ye, Bioelectrochem., 86 (2012) 38.

Electrocatalytic determination of isoniazid by a glassy carbon electrode modified with Poly (eriochrome black T)

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A film of poly-eriochrome black T (EBT) as modifier was prepared on the surface of a glassy carbon (GC) electrode in alkaline solution by cyclic voltammetry (CV). Voltammetric behavior of isoniazid (INH) was studied at this modified electrode. The poly (EBT)-modified glassy carbon electrode exhibited catalytic activity toward the electro-oxidation of INH, which appeared as a reduced overpotential in a wide operational pH range of 2–13. It has been found that the catalytic current depends on the concentration of isoniazid and solution pH. The overall number of electrons involved in the catalytic oxidation of isoniazid and the number of electrons involved in the rate determining step were found to be 4 and 1, respectively. The diffusion coefficient of isoniazid was also estimated using chronoamperometry. The experimental results showed that the mediated oxidation peak current of isoniazid is linearly dependent on the concentration of isoniazid in the ranges of 8.0×10^{-6}M – 1.38×10^{-3}M and 2.9×10^{-5} M – 6.98×10^{-4} M with differential pulse voltammetry (DPV) and amperometry methods, respectively. The detection limits (S/N = 3) were found to be 10.3 μM and 16.4 μM by DPV and amperometry methods, respectively. This developed method had been applied to the determination of isoniazid in tablet samples with satisfactory results.

Keywords: Isoniazid; Poly (eriochrome black T) modified electrode; Voltammetric behavior

References:

[1] M.R. Majidi, A. Jouyban, K. Asadpour-Zeynali, Electroanal., 17 (2005) 915.
[2] M.A.A. Lomillo, O.D. Renedo, M.J.A. Martínez, Anal. Chim. Acta 449 (2001) 167.
[3] H.Y. Xia, X.Y. Hu, Anal. Lett. 38 (2005) 1405.

Transition metal –polymer nanocomposite for electrochemical analysis of pharmaceuticals

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Poly (3-methylthiophene) (P3MT) is an electroconductive polymer, which is easily deposited onto electrodes by electro-oxidation of its monomer. P3MT modified electrodes have shown excellent electrocatalytic effect on some compounds which have conjugated double bond in molecular structure [1]. Silver nanoparticles (AgNPs) are one of the well-developed materials and have been used to modify the surface of working electrodes because they are inexpensive, possess good chemical and physical properties, providing excellent electron transfer rates, and greatly decrease the overpotential of oxidizing or reducing agents [2]. Galantamine (Gal) is used to moderate and delay the manifestation of Alzheimer's disease symptoms. Standard analytical methods for Gal that combine, HPLC, on-line coupled UV, MS, and biochemical detection has been published. Electrochemical technique is an attractive method due to simplicity, rapidity, low expense, high sensitivity and possibility of miniaturization. The modification of the P3MT films with metal nanoparticles might hopefully promote its electrocatalytic properties. In the present work, hybrid nanocomposite containing AgNPs and P3MT at glassy carbon electrode surface was used for the selective determination of Gal. This modified electrode has been successfully prepared by use of an in situ cyclic voltammetry method. The proposed sensor has a linear response in the 10^{-6} - 7×10^{-4} mol L^{-1} concentration range and a low detection limit of 5.7×10^{-7} mol L^{-1} of galantamine. The reative standard deviation (RSD) obtained was 0.42% for 1.0×10^{-4} mol L^{-1}.

Keywords: Ag nanoparticles, Galantamine, Nanocomposite, Poly (3-methylthiophene)

References:

[1] A.S. Widge, M. Jeffries-El, X.Y. Cui, C.F. Lagenaur, Y. Matsuoka, *Biosens. Bioelectron.* 22 (2007) 1723.

[2] X. Li, Y. Liu, L. Zheng, M. Dong, Z. Xue, X. Lu, et al., *Electrochim. Acta* 113 (2013) 170.

Study of Complexation Process between Kryptofix 5 with UO_2^{2+} and ZrO^{2+} Cations in Some Binary Mixed Solvents

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The coplexation reactions between Kryptofix 5 with $UO_2^{2+}$and ZrO^{2+} *cations* were studied in tetrahydrofuran-methanol (THF-MeOH), tetrahydrofuran-acetonitrile (THF-AN) and tetrahydrofuran-dimethylformamide (THF-DMF) binary solvent solutions at different temperatures using conductometric method. The obtained results show that in most cases, the stoichiometry of the complexes formed between the ligand and the cations is 1:1 [M:L], but in some of the solvent systems, in addition of formation of [ML] complexes, 1:2 [M:L_2] complexes are formed in solutions. The stability order of (Kryptofix 5.UO_2)$^{2+}$ complex in the binary mixed solvents with 50 mol % of THF was found to be: (THF-AN) > (THF-MeOH) > (THF-DMF) ,but the sequence of the stability of complexes changes with the composition of the mixed solvents and also with temperatures. The values of thermodynamic quantities for the complexation reactions,were determined from temperature dependence of the stability constants of the 1:1 [ML] complexes and it was found that the complexation processes depending on the solvent system are athermic or exothermic and in most cases, positive values characterized the formation of the complexes .

Keywords: Complaxation; Conductometric; Kryptofix 5; UO_2^{2+} and ZrO^{2+} cations

Fabrication of an Impedimetric Aptasensor for the Detection of Cocaine Based on a Host-guest Recognition of Ferrocene-labeled Aptamer with β-Cyclodextrin, Immobilized on a Nanostructured Polymer Film

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Cocaine, a powerful addictive stimulant drug, has a variety of adverse effects on the body, thus its sensitive detection is very important. Here, we report on a simple, label-free and sensitive impedimetric sensor for determination of cocaine. First, we prepared nanostructured poly N-acetylaniline film via electropolymerization of its monomer on a glassy carbon electrode (PNAANI/GC), subsequently overoxidized it and conjugated β-CD to the polymer backbone. The designed and synthesized nanostructured PNAANI film serves a dual function in the sensor: on one hand it maintains a high effective surface area on a geometrically small electrode that significantly enhances the number of β-CD molecules immobilized on the electrode, on the other hand it provides an upright-oriented β-CD conjugation to the polymer backbone, thus all the β-CD receptors are actively involved in responding to the target. Then, ferrocene-labeled cocaine aptamer is attached onto the β-CD/PNAANI/GCE through host–guest recognition between ferrocene and β-CD in order to obtain the sensing interface. After immersing the sensing interface into the target solution, the aptamer can recognize the target. We attributed the changes in the interfacial charge transfer resistance (R_{ct}) of the electrode to cocaine concentration. Under optimized condition, the sensor responded to cocaine concentration in the range of 50 nM to 100 µM with a detection limit of 2 nM. Selectivity of the sensor for cocaine relative to some potential inferring compounds was also investigated and the results were promising. The proposed approach exhibited an extended dynamic range, a low detection limit, a good sensitivity and a high selectivity, which provides an efficient application prospect for on-field cocaine sensing.

Keywords: Aptasensor; Cocaine; Cyclodextrin; Electrochemical nanosensor; Nanostructured polymer film

A new colloidal synthesis of CdSe quantum dots/metal nanoparticles and its application in sensitive electroanalysis of rifampin

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A new method for the colloidal synthesis of CdSe quantum dots was introduced and characterized by X-ray diffraction (XRD), Scanning electron microscopy (SEM) with energy dispersive X-ray (EDX) analysis and UV-vis spectrophotometer. To our best knowledge, it is the first time to synthesis of CdSe quantum dots/metal nanoparticles and modify the surface of glassy carbon electrode with its suspension to fabricate an electrochemical sensor. It was found that the combination of quantum dots and metal nanoparticles in a single motif causes the dual behavior of core shell nanoparticle, which shows enhanced fluorescence as well as electrochemical properties. Voltammetric experiments showed a shift of the peak potential of rifampin oxidation to less positive value with the high peak current as compared with that of a bare GC electrode. The proposed sensor has remarkable advantages such as: high sensitivity, easy preparation of the modified electrode, low cost, long time stability, reproducibility. Finally, the sensor was effectively applied for the determination of rifampin in some real samples using differential pulse voltammetry without any interference.

Keywords: CdSe quantum dots/metal nanoparticles; Differential pulse voltammetry (DPV); Electrochemical sensor; Rifampin

References:

[1] S. Patra, E. Roy, R. Madhuri, P.K. Sharma, Biosens. Bioelectron. 63(2015) 301.
[2] Y.D. Liang, J.F. Songa, M. Xu, Spectrochim. Acta A 67 (2007) 430.

Hydrogen Bubble Dynamic Template Synthesis of Porous Copper Film Supported by Graphene Nanosheets for Sensitive Electrochemical Determination of Nitrite

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Nitrite is well known as carcinogenic substance, which is commonly used in chemical industry and food processing. So an accurate determination of nitrite is important to protect environmental and human health. In this work, the three-dimensional (3D) porous copper film was fabricated on the graphene nanosheets (GNs) modified glassy carbon electrode (GCE) as a novel sensor for sensitive determination of nitrite. Preparation, characterization and application of this sensor were systematically investigated. The porous Cu structure was synthesized by a one-step strategy of potentiostatic utilizing hydrogen bubble dynamic template without using any surfactants or stabilizers. The surface morphology of this electrode was characterized by scanning electron microscopy (SEM), energy dispersive X-ray (EDX) analysis and X-ray diffraction (XRD) technique. The 3D porous structure of Cu film with a greatly enhanced surface area is an attractive structure for fabrication of effective electrocatalysts. Also, the synergistic effect of GNs and porous Cu significantly improves electrochemical responses. The cyclic voltammetric experiments exhibited the porous Cu/GNs/GCE has a remarkable catalytic activity toward the nitrite oxidation. In more detailed analysis, the effect of pH and scan rate on nitrite oxidation was investigated. Also, this sensor showed a stable and repeatable electrochemical behavior, thus it can be considered as a suitable sensor in the determination of nitrite.

Key words: Porous copper film, Hydrogen bubbles template, Electrodeposition, Nitrite oxidation

References:

[1] R. Ojani, E. Hasheminejad, J.B. Raoof, Int. J. Hydrogen Energy, **2014**, 39, 8194-8203.
[2] Y. Li, Y.Y. Song, C. Yang, X.H. Xia, Electrochem. Commun., **2007**, 9, 981–988.
[3] S. Cherevko, X. Xing, C.H. Chung, Appl. Surf. Sci., **2011**, 257, 8054–8061.

GDH enzyme molecules integrated to nano-biomolecular architecture by changing the surface chemistry: Fabrication of an efficient bioanode for a glucose/oxygen membrane-less enzymatic biofuel cell

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Hybrid of Au NPs and Guanine-Ionic Liquid derived Ordered Mesoporous Carbon (GIOMC) was used to integrate the GDH (glucose dehydrogenase) enzyme molecules at the electrode surface and construct an efficient bioanode for the first time. The special morphology of (GIOMC) used for reduction of NAD coenzyme regeneration overpotential and elimination of required mediator for GDH enzyme bioactivity. By electrochemical deposition of gold nanoparticles (Au NP) on this surface, not only the electrocatalytic current of NADH coenzyme oxidation increased considerably but also biocompability of the surface increased and GDH enzyme molecules could retained their activity after covalent attachment on the electrode surface. This integrated modified electrode could catalyze the glucose oxidation with considerable current density in suitable potentials. Thus, it can be used as bioanode versus BOD enzyme immobilized at Au NPs modified IOMC-$PhSO_3H$ (Ionic Liquid derived Ordered Mesoporous Carbon modified by Ph-SO3H) electrode in the membrane-less glucose/oxygen biofuel cell. The constructed membrane-less enzymatic biofuel cell produces maximum power density output equal to 33 (□W.cm^{-2}) at 257 mV. The open circuit voltage of this biofuel cell and maximum produced current density are 508 mV and 0.252(mA.cm^{-2}) respectively.

Keywords: carbon porouse, enzymatic biofuel cell, membrane less

Simultaneous Determination of Hydrazine and Hydroxylamine Based on an Iron Oxide Nanoparticles / Nafion Composite Modified Glassy Carbon Electrode

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This paper descries the electrocatalytic properties of magnetic iron oxide nanoparticles (Fe_2O_3 and Fe_3O_4) as highly sensitive sensors for the simultaneous determination of hydrazine and hydroxylamine using a glassy carbon electrode. The experimental results indicate that modified electrode with magnetite nanoparticles has better performance than modified electrode with hematite nanoparticles towards oxidation of hydrazine. High sensitivity, selectivity and good reproducibility of the voltammetric responses, and detection limit (0.65 μM) are the advantages of modified electrode by magnetite nanoparticle. The electrocatalytic behavior of hydrazine and hydroxylamine was investigated using cyclic voltammetry and differential pulse voltammetry techniques. The results show that, at the modified electrode surface by magnetite nanoparticles, the peaks of hydrazine and hydroxylamine oxidation were well resolved. These features will facilitate the determination of hydrazine and hydroxylamine in samples at a magnetic iron oxide modified electrode.

Keywords Electrocatalysis, Hydrazine, Hydroxylamine, Magnetic nanoparticles, Modified electrodes

High performance electrochemical sensor based on electrodeposited iron oxide nanoparticle: catecholamine as analytical probe

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In this paper we report synthesis and electrocatalytic activity of electrodeposited Fe_2O_3 nanoparticles modified on a glassy carbon electrode as highly sensitive sensors for determination of catecholamines. Results showed that the Fe_2O_3 nanoparticles on a glassy carbon electrode exhibits excellent electrocatalytic activity towards catecholamines oxidation, including levodopa, dopamine, and epinephrine, resulting in a marked lowering in the peak potential and considerable improvement of the peak current as compared to the electrochemical activity at the bare glassy carbon electrode. The electrochemical characterizations of catecholamines were performed using cyclic voltammetry, chronoamperometry and differential pulse voltammetry techniques. The electrocatalytic currents increase linearly with the levodopa, dopamine, and epinephrine concentrations in the ranges of 0.0625–1000, 0.25–1500, and 0.125–1000 µM, respectively and the detection limits (3σ) were 24 ±2, 14 ±2, and 12 ±2 nM respectively.

Keywords: Magnetic nanoparticles, Levodopa, Dopamine, Epinephrine, Electrocatalysis, Modified electrodes

Application of electromembrane extraction with three electrodes combined with capillary electrophoresis for simultaneous determination of salmeterol and salbutamol in water and wastewater samples

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Salmeterol and salbutamol are a selective, beta 2-agonist that has been studied in the treatment of allergen-induced asthma. Salmeterol and salbutamol major advantage over other inhaled beta-agonists is its long duration of action, making it an excellent choice for treatment of nocturnal asthma.

In the current work, a new setup including two cathodes and one anode was designed and employed for EME of salmeterol and salbutamol from water and wastewater samples. Because these analytes have different lipophilicities, the composition of supported liquid membrane (SLM) should be optimized for each drug and it is impossible to extract of two drugs simultaneously using common electromembrane setups. The SLMs employed for the simultaneous extraction of two drugs were pure 2-nitrophenyl octyl ether (NPOE) and a mixture of 90% NPOE and 10% di-(2- ethylhexyl) phosphate (DEHP), respectively, which were immobilized in the pores of two different hollow fibers. An electric field of 125 V was applied to transfer the analytes from the sample solution across the SLMs into acidic acceptor solutions with pH 1.0 that were located inside the lumens of hollow fibers. Under the optimum experimental conditions, the proposed technique provided for Salmeterol and salbutamol good linearity (R^2> 0.9963-0.9978), repeatability (RSD < 4.5), low limits of detection (7.25–10.6 ngmL^{-1}), respectively.. Finally, this method was successfully applied to determine the concentration of two drugs in water and wastewater samples.

Keywords: Capillary electrophoresis; Cyclodextrin; Electromembrane extraction; Salmeterol, Salbutamol; water and wastewater samples

References:

[1] S. Pedersen-Bjergaard, K. E. Rasmussen, J. Chromatogr. A 1109 (2006) 183.

[2] L. Arjomandi-Behzad, Y. Yamini, M. Rezazadeh, Anal. Biochem. 438 (2013) 136.

[3] S. Nojavan, A. R. Fakhari, J. Sep. Sci. 33 (2010) 3231.

Electromembrane extraction combined with cyclodextrin-modified capillary electrophoresis for the quantification of tetrabenazine enantiomers in biological samples

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Recently electromembrane extraction (EME) was presented in order to decrease the extraction time. In this concept, charged analytes are extracted across the SLM based on electrokinetic migration. In this work, EME method was developed for preconcentration and determination of tetrabenazine enantiomers in urine samples using electromembrane extraction combined with cyclodextrin-modified capillary electrophoresis (CE). During the extraction, tetrabenazine enantiomers migrated from a 4 mL sample solution through a thin layer of 2-nitrophenyl octyl ether (NPOE) immobilized in the pores of a hollow fiber, and into a 20 µL acidic aqueous acceptor phase presented inside the lumen of the fiber. Optimized extraction conditions were: NPOE as supported liquid membrane, 125 V potential difference, 25 min as the extraction time, acceptor phase pH 2.0, donor phase pH 4 and stirring rate of 1000 rpm. Then, the extract was analyzed using optimized cyclodextrin (CD)-modified CE method for the separation of tetrabenazine enantiomers. The extraction method was very reproducible. Under the optimum experimental conditions, the proposed technique provided good linearity (R^2> 0.9974-0.9983), repeatability (RSD < 4.7%), low limits of detection (3.03– 4.54 ngmL^{-1}) for tetrabenazine enantiomers Finally, this method was successfully applied to determine the concentration of tetrabenazine enantiomers in plasma and urine samples without any pretreatment.

Keywords: Capillary electrophoresis; Cyclodextrin; Electromembrane extraction; Tetrabenazine; Biological samples

References:

[1] S. Pedersen-Bjergaard, K. E. Rasmussen, J. Chromatogr. A 1109 (2006) 183–190.

[2] M. Rezazadeh, Y. Yamini, S. Seidi, J. Chromatogr. B 879 (2011) 1143–1148.

[3] S. Nojavan, A. R. Fakhari, J. Sep. Sci. 33 (2010) 3231–3238.

Fabrication of LightScribe Graphene (LSG) and its application as a supercapacitor

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By increasing demands for microscale energy storage systems using a method which is scalable and not cumbersome is really needed. In this work we have prepared an interdigitated micro-supercapacitor using the Laser in LightScribe DVD writers. We used this LightScribe system for direct writing on graphite oxide (GO) films. FE-SEM is used to show differences between GO and LSG structures. After preparing the interdigitated pattern by using a current collector and H2SO4 1 M as the electrolyte electrochemical experiments such as cyclic voltammetry and charge/discharge was performed.

The color changes from yellow brownish of GO to black which indicates LightScribed-graphene is synthesized. The SEM of GO shows stacked sheets which are not completely accessible for electrolyte ions while after writing with Laser, it forms a three-dimensional structure with open pores which is crucial to achieve high powers. It's cyclic Voltammograms show rectangular shape even at higher scan rates (10 and 20 V/s) which demonstrates high rate capability of device. And it's charge/discharge curves shows triangular shape with low IR drop.

Keywords: graphene, light-scribed graphene, supercapacitor

Two Step Voltage Dual Electromembrane Extraction: A New Approach to Simultaneous Extraction of Acidic and Basic Drugs

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The simultaneous extraction of acidic and basic analytes is a challenging task. A novel and efficient method named two step voltage dual electro membrane extraction (TSV-DEME) was applied for the simultaneous extraction of acidic and basic drugs in a single step. Thus, Codeine and Ketamin was chosen as basic drugs and Naproxen as acidic drug. Simultaneous extraction of acidic and basic drugs is done by applying the potential of 150 V as first step for 6 min and 400 V as second step for 19 min, model compounds were extracted from a 4 mL of sample solution (pH=6), into 20 µL of each acceptor solution (32 mM NaOH for acidic drug and 32 mM HCL for basic drugs). 1-octanol was immobilized in the pores of a porous hollow fiber of polypropylene as SLM for acidic drug and 2-ethyle hexanol as SLM for basic drugs. The proposed method was compared with DEME. The proposed TSV-DEME technique provided good linearity with correlation coefficients from 0.993 to 0.998 over a concentration range of 1-1000 ng mL^{-1}. The detection limits of the drugs was 0.3-1.5 ng mL^{-1}, while reproducibility ranged from 7.5 to 15.5% (n = 5). Finally, the application of the new method to wastewater and urine samples was demonstrated.

Keywords: Two step voltage, Electromembrane extraction, Simultaneous extraction, Acidic and basic drugs, Wastewater

References:

[1] S. Seidi, Y. Yamini, M. Rezazadeh, A. Esrafili, J. Chromatogr. A 1243 (2012) 6.
[2] M.H. Koruni, H. Tabani, H. Gharari, A.R. Fakhari, J. Chromatogr. A 1361 (2014) 95.

GDH enzyme molecules integrated to nano-biomolecular architecture by changing the surface chemistry: Fabrication of an efficient bioanode for a glucose/oxygen membrane-less enzymatic biofuel cell

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Hybrid of Au NPs and Guanine-Ionic Liquid derived Ordered Mesoporous Carbon (GIOMC) was used to integrate the GDH (glucose dehydrogenase) enzyme molecules at the electrode surface and construct an efficient bioanode for the first time. The special morphology of (GIOMC) used for reduction of NAD coenzyme regeneration overpotential and elimination of required mediator for GDH enzyme bioactivity. By electrochemical deposition of gold nanoparticles (Au NP) on this surface, not only the electrocatalytic current of NADH coenzyme oxidation increased considerably but also biocompability of the surface increased and GDH enzyme molecules could retained their activity after covalent attachment on the electrode surface. This integrated modified electrode could catalyze the glucose oxidation with considerable current density in suitable potentials. Thus, it can be used as bioanode versus BOD enzyme immobilized at Au NPs modified IOMC-$PhSO_3H$ (Ionic Liquid derived Ordered Mesoporous Carbon modified by Ph-SO3H) electrode in the membrane-less glucose/oxygen biofuel cell. The constructed membrane-less enzymatic biofuel cell produces maximum power density output equal to 33 (□W.cm^{-2}) at 257 mV. The open circuit voltage of this biofuel cell and maximum produced current density are 508 mV and 0.252(mA.cm^{-2}) respectively.

Keywords: carbon porous, enzymatic biofuel cell, membrane less

Facile synthesis of Cu@Porous silicon nanostructure for non-enzymatic glucose sensing

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Cu@PSi (copper@porous silicon) nanocomposite powder was prepared by chemical etching of silicon (Si) powder in a HF/HNO_3 solution, followed by electroless plating of copper nanoparticles on the etched PSi powder in a solution containing $CuSO_4$ as a metal precursor [1]. The resulting nanocomposite was characterized by X–ray diffraction (XRD), scanning electron microscopy (SEM), cyclic voltammetry (CV) and FT–IR spectroscopy. The copper nanoparticles in PSi support show the good chemical and electrochemical stability as well as electrocatalytic effect on Glc oxidation, hence the Cu@PSi nanocomposite was used to modify carbon paste electrode (CPE) to fabricate non-enzymatic Glc sensor. The electrocatalytic activity of Cu@PSi nanocomposite was investigated for Glc oxidation in alkaline and neutral solutions using cyclic voltammetry and chronoamperometry. The novel developed sensor displayed a fast amperometric response time of less than 4 s, long time stability, good signal reproducibility and two linear ranges from 1.0 µmol L^{-1} to 2.3 mmol L^{-1} of Glc with a detection limit of 0.2 µmol L^{-1}. The sensor exhibited no interference from common interferences. The good analytical performance, low cost and easy preparation method made this novel electrode material promising for the development of effective

Keywords: Porous silicon; Copper nanoparticles; Glucose sensing; Non-enzymatic sensor

References:

[1] A.A. Ensafi, M.M. Abarghoui, B. Rezaei, Sens. Actuators B 196 (2014) 398.

Study on electrical current variations in electromembrane extraction process: Relation between extraction recovery and magnitude of electrical current

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This contribution presents an experimental approach to improve analytical performance of electromembrane extraction (EME) procedure, which is based on studying the current pattern within EME systems under different extraction conditions, such as using different organic solvents as supported liquid membrane, electrical potentials, pH values of donor and acceptor phases, variable extraction times, temperatures, stirring rates, different hollow fiber lengths and the addition of salts or organic solvents to the sample matrix, and discussing the relationship between the extraction recovery and current level.

In this study, four basic drugs (codeine, verapamil, trimipramine and clomipramine) with different polarities (log P 1.34-5.04) were extracted under different conditions with the corresponding electrical current patterns compared against extraction recoveries.

The extraction process was demonstrated in terms of EME-HPLC analyses of selected basic drugs. In most cases, a sharp decrease in the electrical current was observed within about the first 2 minutes of the extraction experiment which could be attributed to the formation of electrical double layer. Also, the observations showed that, in most cases (not all of them, however), larger current magnitudes (> 400 µA) resulted in lower extraction recoveries.

Also, the current patterns of extractions from wastewater, plasma and urine samples were demonstrated. When extracting from real samples, although clearly similar results were found in terms of extraction recover, but the current patterns and magnitudes were completely different. This can show that, sample composition dramatically effects current pattern. Finally, the results revealed that, different extraction conditions produce completely different results in terms of electrical current; i.e. electrical current pattern is influenced by all parameters including applied voltage, donor and acceptor pH values, stirring rate, composition of SLM, hollow fiber length and sample composition.

Keywords: Electromembrane extraction, basic drugs, electrical current variations, current Pattern

Fabrication of an electrochemical sensor based on a mesoporous carbon & Ionic liquid for determination of eugenol in clove extract

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A novel defective mesoporous carbon (DMC) was synthesized and its structural properties were investigated by N2-adsorption/desorption, XRD, SEM and Raman spectroscopy methods. The Synthesized mesoporous carbon was used for fabrication of carbon ionic liquid electrode. The modified renewable paste electrode was prepared by mixing of graphite powder (35%), DMC (10%), BMIM.BF6 (7.5%) and mineral oil (47.5%). The obtained electrode (DMC-IL) was successfully applied for simple and rapid determination of eugenol in standard solutions and clove extract by using differential pulse voltammetry (DPV) method. The modified electrode displayed an obvious increase in the peak current compared with the bare carbon paste and DMC electrodes. The study of experimental parameters showed that the oxidation reaction is quasi reversible and maximum current response was obtained at pH=2.75 in 0.05 Britton-Robinson buffer. Under the optimum experimental conditions, eugenol could be linearly detected in the wide concentration range of 0.8 µM- 45 µM. The detection limit was down to around 0.3 µM (S/N=3). Since the prepared modified electrode exhibits a very good resolution between the DPV peaks of ascorbic acid, dopamine, anatole and carvacrol, it can be applied for detection of eugenol in the presence of these compounds in herbal extracts.

Keywords: BMIM.BF6; clove extract; differential pulse voltammetry; eugenol; Mesoporous carbon;

Electromembrane extraction through a virtually rotating supported liquid membrane

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Electromembrane extraction (EME) of model analytes was carried out using a virtually rotating supported liquid membrane (SLM). The virtual (nonmechanical) rotating of the SLM was achieved using a novel electrode assembly including a central electrode immersed inside the lumen of the SLM and five counter electrodes surrounding the SLM. A particular electronic circuit was designed to distribute the potential among five counter electrodes in a rotating pattern. The effect of the experimental parameters on the recovery of the extraction was investigated for verapamil (VPL), trimipramine (TRP), and clomipramine (CLP) as the model analytes and 2-ethyl hexanol as the SLM solvent. The results showed that the recovery of the extraction is a function of the angular velocity of the virtual rotation. The best results were obtained at an angular velocity of 1.83 RadS^{-1} (or a rotation frequency of 0.29 Hz).

The optimization of the parameters gave higher recoveries up to 50% greater than those of a conventional EME method. The rotating also allowed the extraction to be carried out at shorter time (15 min) and lower voltage (200 V) with respect to the conventional extraction. The model analytes were successfully extracted from wastewater and human urine samples with recoveries ranging from 38 to 85%. The RSD of the determinations was in the range of 12.6 to 14.8%.

Keywords: Electromembrane extraction; Human plasma; Rotating supported liquid membrane; Tricyclic anti-depressant; Wastewater

Silica Nanoparticles Modified Carbon Paste Electrode as a voltammetric sensor for determination of diclofenac

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In this work, the use of a new carbon paste electrode modified using Silica nanoparticles prepared by a simple and rapid method for the determination of diclofenac sodium (DCF) was described. Diclofenac, namely 2-[(2,6-dichlorophenyl)amino]benzene acetic acid, is a non-steroidal anti-inflammatory drug used for the treatment of different diseases such as rheumatoid arthritis, ankylosing spondylitis, osteoarthritis, and treatment of different diseases such as rheumatoid arthritis, ankylosing spondylitis, osteoarthritis. The morphology of Silica Nano Particles Carbon paste electrode was investigated by scanning electron microscopy (SEM). The electrochemical behavior of diclofenac sodium was investigated at the surface of Silica nanoparticles modified carbon paste electrode (SilicaNPs-CPE) using cyclic voltammetry (CV) and differential pulse voltammetry (DPV). The influence of some experimental variables such as carbon paste composition, working solution pH, scan rate and possible interferences were studied. The catalytic oxidation peak currents show a linear dependence on the diclofenac Linear analytical curves were obtained in the ranges of 0.1 µM -500.0 µM and detection limit 0.046 µM. Furthermore, the proposed modified electrode exhibited a high sensitivity, an excellent reproducibility, good selectivity and was successfully also the construction process is too simple. The interferences of foreign substances were investigated. The method was applied for the determination of diclofenac sodium present in pharmaceutical.

Keywords: Cyclic Voltammetry; Diclofenac Sodium; Differential Pulse voltammetry; modified carbon paste electrode; Silica nanoparticles.

Electroanalytical study of tamoxifen as breast anticancer drug using differential pulse anodic adsorptive striping voltammetry at glassy carbon electrode and different supporting electrolytes and it’s extraction from tablets

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In this work, the electrochemical behavior of tamoxifen as an anti cancer drug were investigated at a glassy carbon electrode (GCE) in Britton-Robinson (BR) buffer at different pH as well as in H_2SO_4. H_2SO_4 was the best supporting electrolyte in this work. Cyclic voltammetry (CV) and chronoamperometry were used to understand the electrochemical characteristics of tamoxifen (Tam). Based on the results of the recorded CV, the electrodeposition and anodic striping behavior of the Tam were investigated at the surface of GCE. To find the best conditions for taking a sharp analytical peak concerning the electro-oxidation of Tam, differential pulse anodic adsorptive striping voltammetry (DPAASV) was studied. The primary experiments demonstrated that the DPAASV presents a sufficient oxidation peak current at approximately 1.1 V vs Ag/AgCl. Therefore, the effects of different parameters such as deposition potential, deposition time and concentration of H_2SO_4 have been studied and optimized. The obtained results shown that the -1.4 V, 30s and H_2SO_4 0.5 M are the optimal values, respectively. Then the calibration curve was plotted in the range of 1 to 10 µM and the limits of detection (LOD) and quantitation (LOQ) were calculated to be 0.621 and 2.07 µM, respectively. The mean, standard error and relative standard deviation (RSD) for five replicates of 4.0 µM were found to be 4.1 µM, 2.65 % and 3.62 %, respectively. To estimate the application potential of the proposed method, the extraction of Tam from tablets containing 20 mg Tam were investigated and optimized. Finally, the proposed method was successfully employed for determination of Tam in spiked physiological samples.

Keywords: Tamoxifen; DPAASV; Striping voltammetry; deposition

Electrochemical and surface study of modified glassy carbon electrode by MWCNTs/Ag NPs-TSC

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This work describes the synthesis of silver nanoparticles with thiosemicarbazide ligand and modification of electrode with the new synthesized nanoparticle and carbon nanotube for Electrochemical and surface study. The surface characteristics of modified electrode investigated by electrochemical impedance spectroscopy (EIS) and cyclic voltammograms (CV) in $K_3Fe(CN)_6/K_4Fe(CN)_6$ solution. The records illustrated that MWCNTs-COOH and AgNPs-TSC grafted on GCE efficiently decreased the charge transfer resistance value of electrode and improved the electron transfer kinetic between analyte and electrode [1]. For the more electrochemical study a surface of modified glassy carbon electrode checked by Fe-SEM images. The GC electrode modified by MWCNTs-COOH and AgNPs-TSC called AgNPs-TSC/MWCNTs-COOH/GCE. The electrode area calculated by Randles–Sevcik equation [2], 0.0712, 0.1350 and 0.1711 cm^2 obtained for GCE, MWCNTs/GCE and AgNPs-TSC/MWCNTs/GCE, respectively. These calculated values confirm larger effective surface area and high electron transfer rate for AgNPs-TSC/MWCNTs/GCE.

Keywords: Impedance spectroscopy; Ag nanoparticles; MWCNTs; Modified glassy carbon.

References:

[1] A.A. Rafati, A.Afraz, Materials Science and Engineering C, 39 (2014) 105.
[2] J. Wang, Analytical Electrochemistry, Wiley, (2004).

ZnO nanoparticles modified carbon paste electrode for determination of Diazepam using square wave voltammetric

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The presented study investigates synthesis and application of ZnO nanoparrticle(ZnO/NPs) and room-temperature ionic liquid, n-hexyl-3-methylimidazolium hexafluoro phosphate as a fast and high sensitive sensors for voltammetric determination of diazepam using carbon past electrode (CPE) in biological samples. ZnO/NPs were characterized with different methods such as UV-vis absorption spectroscopy, Fourier transform infrared spectroscopy (FT-IR), X-ray diffraction (XRD) and scanning electron microscopy (SEM). The study was carried out by using cyclic voltammetry (CV) and square wave voltammetry (SWV) techniques. The cyclic voltammogram showed an irreversible oxidation peak at -0.88 V (vs. Ag/AgClsat), which corresponded to the oxidation of diazepam. Under the optimized conditions, diazepam was detected a wide linear detection range from of 7.0×10^{-9} to 1.0×10^{-6} mol L^{-1} with a detection limit of 5.3×10^{-9} mol.L^{-1} (3σ), using square wave voltammetry. Relative standard deviation(RSD) was 6.61%. Finally, Experimental results showed that the proposed electrode could be used as an effective and sensitive sensor for Direct detection of diazepam in biological samples with recovery values in the range of 92–103%.

Keywords: Diazepam; Ionic liquid; Carbon past electrode; ZnO nanoparrticle

Using Impedance and Potentiometry Techniques for Study Effect of Multiwalled carbon nanotube carbon on Ion-Selective Response

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In this work, a chemically modified carbon paste electrode with multiwalled carbon nanotube (MWCNT) was prepared and used as a sensor for salicylate ion. Response surface methodology (RSM) in conjunction with central composite design (CCD) for modeling and optimization of the influence of some process variables (ionophor (F1), MWCNT (F2) and additive (F3)); on the performance of carbon paste electrodes salicylate is discussed. Potentiometric with ISEs is one of the most successful methods for detecting ionic species in complex samples. Ion-selective electrodes (ISEs), as an important class of chemical sensors with properties such as simplicity, fast response, wide linearity range, and low cost are able to detect a particular species of cationic or anionic components in samples. Nowadays, electrochemical impedance spectroscopy (EIS) has played an essential role in the characterization of many types of sensors. EIS has been used to provide information on various fundamental processes that occur at the electrode electrolyte interface. This method is a non-destructive steady-state technique that involves the application of signals of very low amplitude (either of potential or current) around a stationary reference state and the linear response of the system is measured over a range of frequencies. The linear frequency response analysis makes EIS very useful for studying electrochemical systems exhibiting complex non-linear behavior. The result of the potentiometric method using modified carbon paste electrode showed, the constructed electrode at optimum condition (ionophor (0.002 g), MWCNT (0.004 g) and additive (0.003 g)) displayed the Nernstian slope of 59.2 ± 0.2 mV at linear concentration range of 1.0×10^{-7} mol L^{-1} to 1.0×10^{-1} mol L^{-1}over a wide pH range (3.0-9.0). Detection limit obtained in the optimal conditions was 6.9×10^{-8}mol $L^{-1.}$ Importantly, the effect of the MWCNT on the performance of electrode was investigated by impedance technique, that showed the MWCNT helps the transduction of the signal in carbon paste electrode and the charged transfer resistance (R_{ct}) was reduced. The impedimetric results indicated that the linear concentrations range 1.0×10^{-9} mol L^{-1} to 1.0×10^{-1} mol L^{-1} and in comparison with potentiometry, the pH range increased to 4.0–10.0. In this work the ion-selective electrode was made in the presence or absence of MWCNT. The results showed that MWCNT cause increased sensitivity, lower detection limit at wide range of pH and increasing the concentration range.

Keywords: Impedance; Potentiometry; MWCNT

Investigation of Response of Salicylate Anion- Selective Electrode By Impedimetric and Potentiometric Techniques

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Salicylic acid is one of the common metabolites of acetylsalicylic acid (aspirin), which is widely used as an analgesic and inflammatory agent as well as to prevent heart attacks. The free acid is widely used as an antiseptic and preservative for foods. Salicylic acid is also employed in analytical practice and in synthesis of days. Potentiometric methods based on ion selective electrodes (ISEs) offer great advantages such as: speed, wide dynamic ranges, and no requirement for the sample pretreatment. They have been widely used for analysis of ions in biological environmental and industrial samples. Electrochemical impedance spectroscopy (EIS) is another technique used for evaluating interactions within the membrane. In this technique, using an alternating small magnitude signal creates a perturbation at a steady state in the system. In this work, a PVC membrane electrode based on dichloro (N-(2-pyridinylmethylene) benzoylhydrazone) copper(II), $Cu(HL)Cl_2$ as ionophor was prepared. The operational feature of the modified electrode was investigated by potentiometric and EIS methods. The ion selective electrode was tested by different anions and showed a good selectivity for salicylate ion. The electrode exhibits a Nernstian response for salicylate ions over a wide concentration range (1.0×10^{-7} - 1.0×10^{-1} M) with a slope of 59.5 ± 0 .3 mV per decade. It shows a short response time (20 s) for whole concentration range and can be used for 1 month with good reproducibility. Detection limit obtained in the optimal conditions was 9.6×10^{-8} mol L^{-1}. The selective coefficients were determined by the fixed interference method and could be used in the pH range of 4.0 to 9.0. On the other hand, while using the EIS technique, the linear concentrations range was 1.0×10^{-8} - 1.0×10^{-1} M and the pH range increased to 4.0−10.0. In comparison, the impedance method has high sensitivity and lower detection limit at wide range of pH.

Keywords: Impedance; Potentiometry; Salicylate - selective electrode

Simultaneous determination of isoproterenol, acetaminophen and tyrosine using a modified glassy carbon electrode

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Isoproterenol (IP) is a drug which used for the treatment of primary pulmonary hypertension and allergic emergencies, bronchitis, cardiac chock and heart attack [1].

L-tyrosine is a kind of essential aromatic amino acids and a vital constituent of proteins [2]. Acetaminophen is a commonly used pain killer and antipyretic [1]. Hematoxylin is widely used as a biological stain in biomedical research laboratories and diagnostic procedures. Graphene as a two-dimensional sp^2 connected carbon sheet is an excellent material that has exceptional properties such as superior surface-to-volume fraction, little electrical noise, and outstanding transport properties [3]. In this paper, glassy carbon electrode modified with graphene/hematoxylin was fabricated for the simultaneous determination of IP, AC and Tyr, which is very important in the clinical diagnosis. The experiment results showed good linear response range for detection of IP, AC and Tyr and the detection limits were 0.25µM-1000.0µM and 0.09M respectively. Moreover, the modified electrode exhibited excellent stability and reproducibility.

Keywords: Isoproterenol; Acetaminophen; Tyrosine; Graphene; Hematoxylin.

References:

[1] S. Tajik, M. A. Taher, H. Beitollahi, Sens. Actuators B 197(2014) 228
[2] M. Taei, G. Ramazani, Colloids Surf. B 123 (2014) 23.
[3] P. Damlin, M. Suominen, M. Heinonen, C. Kvarnström, Carbon, 93 (2015) 533.

Ionic liquids/nanocomposite modified carbon paste electrode as voltammetric sensor for the simultaneous determination of ascorbic acid and cysteine

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Ascorbic acid (AA) is very popular for its antioxidant property, and present in the human diet as a vital vitamin[1]. L-cysteine (Cys), a non-essential amino acid,plays important physiological role in living cells such as detoxification of harmful substances in the body and protein synthesis . AA and Cys show high activity for electrocatalytic oxidation at the surface of the most reported modified electrodes .Thus, the simultaneous determination of AA and Cys for quality control analysis and for medical control is very important. Electrochemical methods appear to be very promising since they ensure reasonably good analytical performance characteristics with essentially no need for expensive and complicated instrumentation. In recent days the nanostructure base ionic liquid modified carbon paste electrodes very well as an electrochemical sensor for biological and pharmaceutical compound analysis[2]. In this paper, $Fe_3O_4@SiO_2/Go$ based electrochemical sensor was fabricated for the simultaneous determination of ascorbic acid (AA) and Cysteine (Cys), which is very important in the clinical diagnosis. Electrochemical studies were carried out by using cyclic voltammetry (CV), differential pulse voltammetry (DPV) and chronoamperometry (CHA). The experiment results showed good linear response range for detection of AA and Cys and the detection limits were1.0µM-1000.0µM and 0.5µM respectively. Moreover, the modified electrode exhibited excellent stability and reproducibility. The analytical performance of this sensor was also would be valuable for the clinical assay of ascorbic acid and cysteine.

Keywords: Ascorbic acid; Carbon Paste Electrode; Cysteine; $Fe_3O_4@SiO_2/Go$

References:

[1] M. Kumar, and B. E. Kumara Swamy, Mater. Sci. Engin. C 58 (2016) 142.

[2] A. Taherkhani, T. Jamali, H. Hadadzadeh, H. Karimi-Maleh, H. Beitollahi, M. Taghavi, and F. Karimi, Ionics 20 (2014) 421.

Using of functionalized nanoporous silica gel in fabrication of modified carbon paste electrode for determination of samarium ions

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In this study the use of functionalized nanoporous silica gel in fabrication of modified carbon paste electrode for determination of samarium ions is studied. A new ion selective electrode based on potentiometric method was developed for the determination of samarium ions. The carbon paste electrode was modified with a new functionalized nanoporous silica gel with NH^{2+} (PZ18) in order to improve the electrochemical behaviour of proposed carbon paste electrode. The carbon paste electrode incorporates with graphite powder, paraffin oil and PZ18. The best performance was obtained with the electrode having a composition (w/w) of PZ18 (10.0%), graphite powder (67.5%) and paraffin oil (22.5%). The sensor display stable and linear response with a slope of +19.3 mV decade^{-1} at pH 5.0 for the samarium concentration in the range of 1.0×10^{-7} to 1.0×10^{-2} mol L^{-1} and with a detection limit of 8.13×10^{-8} mol L^{-1} of samarium ions. The proposed sensor displays good selectivity over a variety of alkali, earth alkalis and heavy metal ions because selectivity coefficient data for some common cations and heavy metal ions investigation show negligible interference. The potentiometric response in the pH range 2 – 5.5 is independent of the pH of the measured solution. The electrode show easy construction, low cost, fast response (within 40.0 sec) and can be used for a period of 4.0 months without significant change in its performance characteristics. Application of this potentiometric sensor for samarium determination in sample mineral water is investigated without especial pretreatment.

Keywords: Functionalized nanoporous silica gel; Modified carbon paste; Potentiometric sensor; Samarium ions.

References:

[1] M.R. Ganjali, F. Faridbod, B. Larijani , and Norouzi, P., Mater Sci & Engineering, 30 (2010) 555.
[2] A.K.Singh, A.K.Jain, and S. Mehtab, , Anal. Chim. Acta, 597 (2013) 322.

Electrocatalytic measurement of H_2O_2 concentration using modified carbon past electrod with copper complex nanoparticles

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The electrochemical behavior of a copper complex mixed in a carbon paste electrode (CPE) and its electrocatalytic reduction of H_2O_2 were examined using cyclic voltammetry, chronoamperometry, and differential pulse voltammetry. Cyclic voltammetry was used to study the redox properties of copper complex-CPE at various potential scan rates. Copper complex had excellent electrocatalytic activity for H_2O_2 reduction in 0.1 mol/L phosphate buffer solution (pH 5.0), and it decreased the overpotential by 650 mV as compared to CPE alone. The diffusion coefficient and kinetic parameters such as the heterogeneous catalytic electron transfer rate constant and electron transfer coefficient for the reduction of H_2O_2 at the copper complex-CPE surface were also determined using electrochemical methods. Differential pulse voltammetry showed linear dynamic ranges of 10.0-200.0 μmol/L and a detection limit of 3.2 μmol/L H_2O_2. The copper complex-CPE has excellent reproducibility and long term stability, and it was successfully applied for the determination of H_2O_2 in buffer solution (pH 5.0).

Keywords: Copper complex; Electrochemical behavior; Hydrogen peroxides; Phosphate buffer.

References:

[1] H. Cheng, H.T. Chen, K.C. Hsien, P.Y. Chen, *Electrochem. Commu 40 (***2014)** 38.
[2] M. Zhang, Q. Sheng, F. Nie, J. Zheng, *J. Electroanal. Chem.*730 (**2014)** 10.
[3] Y.K. Hsu, Y.C. Chen, Y.G. Lin, *Appl. Surf. Scien.* 354 (**2015)** 85.

A sensing platform based on gold nanorodes–graphene oxide–carbon nanotube nanocomposite for sensitive detection of pharmaceuticals

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Over the past two decades, the design of multifunctional nanostructures modified electrodes has attracted the efforts of many researchers. Noble metal nanorodes, such as gold nanorodes (Au NRs), is of interest because of their high catalytic activity, high surface area, special electronic properties and excellent biocompatibility. The hybrid structures in electrochemical sensing have attracted a widespread interest of scientists [1]. The graphene-oxide (GO), usually exfoliated from graphite oxide by ultrasonic treatment, has been proved to possess over whelming physical/chemical properties. Its properties such as large surface area, excellent conductivity and good chemical stability make GO as apromising candidate for sensors and electrocatalysis [2]. Amlodipine (AML) is currently the most frequently used drug for hypertensive patients. It inhibits calcium ions to be transported into vascular smooth muscle and cardiac muscle to protect the target organs. Therefore, pharmaceuticals containing AML have to undergo a strict quality control, which requires the development of simple and reliable analytical methods for the detection. Electrochemical techniques have the inherent advantages of high sensitivity, low cost and simple instrumentation. Due to excellent characteristics of Au NRs–GO and carbon nanotube (CNT) nanocomposite, we selected this nanocomposite as a sensing platform for the electrochemical detection of AML. Compared with bare electrode, the Au NRs–GO–CNT nanocomposite greatly improved the surface area of the electrode, reduced the peak potential and amplified the electrochemical signal. All the measurements were done by voltammetric methods in phosphate buffer solution 0.1 M (pH 7.0) and the oxidation peak was observed at 0.849 V. The oxidation peak currents at GCE, GO/GCE, GNRs–GO/GCE and GNRs–GO–CNT/GCE were obtained 0.6, 6.79, 50.47 and 82.12 µA respectively.

Keywords: Amlodipine; Carbon nanotube; Gold nanorodes; Graphene oxide

References:

[1] M. Arvand, T.M. Gholizadeh, *Sens. Actuators B* 186 (2013) 622.
[2] X. Han, X. Fang, A. Shi, J. Wang, Y. Zhang, *Anal. Biochem.* 443 (2013) 117.

Construction of a novel electrochemical sensor based on nanocomposite ZnO-CS/C MWCNTs with Synergistic effects for determination of acyclovir in real samples

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The electrochemical oxidation of an antiviral drug, acyclovir (ACV) at a new sensitive and simple base on Zinc oxide-Chitosan/carboxylated multi-walled carbon nanotubes nanocomposite was studied by voltammetric techniques. The electrooxidation of ACV was studied on modified glassy carbone electrode using cyclic voltammetry as diagnostic techniques. The oxidation peak potential of ACV on the Zno-Cs/cMWCNT/GCE appeared at 0.89V which was accompanied with smaller over potential and increase in oxidation peak current compared to that obtained on the bare glassy carboe electrode (GCE). Under optimum conditions the sensor provides two linear responses in the range of 9–90 nM and 90- 1000 nM for ACV with a detection limit of 6 nM through differential pulse stripping voltammetry (DPSV) measurements were carried out in phosphate buffer solution (pH 7.0, 0.1 M). The surface of the Zno-CS/cMWCNT/GCE was characterized by X-ray diffractometry (XRD) , scanning electron microscopy (SEM) and ectrochemical impedance spectroscopy (EIS) and analysis. The influence of the effective parameters such as:pH, scan rate on the electrochemical behavior of ACV was investigated. Under optimized conditions, the proposed sensor was applied for low level ACV determination. The modified electrode exhibited a good sensitivity, stability and pleasant reproducibility, and it was applied for the determination of ACV in real sample, with satisfactory results.

Keywords*:* Acyclovir; Zinc oxid nanoparticles; Chitosan; multi-walled carbone nanotubes; Cyclic voltammetry.

References:

[1] N.P.Shetti, S.J.Malode,S.T.Nandibewoor,Electrochemical behavior of antiviral drug acyclovire at fullerene-C60-modifide electrode, Bio electrochemistry, 88(2012) 76-83.

[4] F. Mirrahimi, M.A. Taher, H. Beitollahi, R. Hosseinzadeh, Appl. Organometal. Chem.,26(2012) 194-198.

[3] S. Alwarappan, S. Prabhulkar, ADurygin, C.Z. Li, Journal of nanoscience and nanotechnology,9(2009), 2991-2996.

Electrochemical behavior of CdS/Ag/CPE and its application for sensitive determination of isoprenaline

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In present paper, the CdS Quantum Dots/Ag nanopartical carbon paste electrode (CdS/Ag/CPE) was firstly prepared with the mixed of CdS/Ag into the carbon paste mixture. Compared with conventional CPE, an improved electrochemical response of CdS/Ag/CPE toward the redox couple of $Fe(CN)_6^{3-/4-}$ was demonstrated owing to the excellent electrical conductivity. The CdS/Ag/CPE was further used for the successful determination of isoprenaline, and it showed an excellent electrocatalytic oxidation activity toward isoprenaline with a lower overvoltage, pronounced current response, and good sensitivity. Under the optimized experimental conditions, the proposed electrochemical isoprenaline sensor exhibited a rapid response to isoprenaline within 10 s and a linear calibration plot ranged from 1.0×10^{-7} to $1. \times10^{-3}$M was obtained with a detection limit of 3.1×10^{-8} M.

Keywords CdS Quantum Dots; Isoprenaline; CdS Quantum Dots/Ag nanopartical; carbon paste electrode

References:

[1] L. Chee shan, H. Katerina, A. Adriano, P. Martin, *Electrochem. Commum.* **52 (2015**) 75.
[2] P.Thakur, S. Joshi, S. Kapoor, T. Mukherjee, *Longmuir 25* (**2009)** 6377.

Supramolecular β-Cyclodextrin/Multi-walled Carbon Nanotube Paste Electrode for amperometric detection of Naproxen

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The electrochemical behavior of Naproxen at a novel β-Cyclodextrin/Multi-walled carbon nanotube paste electrode (β-CD/CNTPE) was investigated. The study was carried out by using cyclic voltammetry (CV) and chronoamperometry (CA) techniques. The overall analysis involved an accumulation step, in which the Naproxen was adsorbed onto β-cyclodextrin, followed by amperometric quantification of Naproxen. Various parameters such as amount of β-CD, accumulation time, pH and scan rate were optimized. The proposed electrode showed a good response for amperometric detection of Naproxen based on its complexation with β-CD. The calibration plot for Naproxen determination is linear in the range of 0.4 to 23 μg mL^{-1} under optimum experimental conditions. The limit of detection based on 3sb/b was found to be 0.37 μg mL^{-1}. The proposed electrode (β-CD/CNTPE) presented good repeatability, evaluated in term of relative standard deviation (2.7%) for five replicate measurements. The modified electrode shows good selectivity toward naproxen in the presence of some organic and inorganic species. Also, the analytical applicability of the proposed electrode was tested through the analysis of several pharmaceutical preparations. The recovery values were achieved to be between 97.9% and 103.6%. It is evident that the proposed electrode can be used successfully for quantification of Naproxen in pharmaceutical samples.

Keywords: Amperometry, β-cyclodextrin, Multi-walled carbon nanotube paste electrode, Naproxen,

Gold digital versatile disc platform modified with nano-porous mercury/gold amalgam as a solid-state disposable electrochemical sensor for detection of para-nitrophenol

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Solid amalgam electrodes were found to be suitable electrode materials to investigate the electrochemical reduction of para-nitrophenol (PNP) and can be used as potential electrochemical sensor for determination of nitrophenols in various real samples. Herein, a novel solid-state disposable electrochemical sensor based on gold digital versatile disc (GDVD) platform modified with nano-porous Hg/Au amalgam is constructed for detection of PNP. The modification of GDVD mini-chip is accomplished via a two step procedure. First, the gold nanoparticles were electrodeposited onto the GDVD surface which is then followed by an electro-amalgamation step. The formation of nano-porous Hg/Au amalgam was characterized using scanning electron microscopy. Linear sweep voltammetry and square wave voltammetry were used to study the electrochemical behavior of PNP. The influence of several relevant operating parameters was investigated and optimized. The calibration curve was linear within the concentration ranges of 1 µM to 500 µM of PNP. A corresponding detection limit was achieved to be 0.94 µM (based 3sb/m criterion). Also, the RSDs were found to be 5% for 4 parallel detections with the same and separate electrodes and 3% for 10 successive measurements with one electrode. The proposed sensor was successfully applied for the direct determination of PNP in water samples.

Keywords: Disposable sensor, Gold digital versatile disc, Gold nanoparticles, Mercury/gold amalgam, para-Nitrophenol

Electromembrane Extraction Using a Round Headed Platinum Wire as the Inner Electrode: A Simple and Practical Way to Enhance the Performance of Extraction

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In this work, Electromembrane extraction (EME) was carried out using a round headed platinum wire as the inner electrode. The round headed platinum wire was prepared by a simple electrothermal process based on discharging the electrical energy stored in a capacitor bank. The advantages of a round headed inner electrode over a conventional extraction were studied using Amlodipine (AM), Verapamil (VPL) and Clomipramine (CLP)as the model analytes. High performance liquid chromatography (HPLC) equipped with UV detection was applied for the determination of model compounds in order to evaluate the performance of the extraction in both systems .The calibration curves gave R^2 values ranging from 0.997 to 0.998.The enrichment factor of 15 was achieved and limits of detection based on S/N = 3 for AM, VPL and CLP were found to be 6.67, 3.3 and 3.3μg L^{-1}, respectively. The limit of quantification (S/N = 10) for VPL, TRP and CLP were calculated to be 20, 10 and 10 μg L^{-1}, respectively. The RSD values for 5 replicated measurements at a concentration of 1mg L^{-1}were in the range of 6.7−9.93%. The method was successfully applied to determine AM, VPL and CLP in water and satisfactory recoveries were obtained within the range of 35−49%. Recoveries up to 15.6% greater than those of a conventional method were obtained after the optimization of the experimental parameters.

Keywords: Electromembrane extraction, Round headed electrode, Calcium channel blocker, Tricyclic anti-depressant

Electrosynthesis of the Ni-Co Binary Hydroxide Nanosheets as High Performance Supercapacitor by Controlled Current Density

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Supercapacitors, also known as electrochemical capacitors, have been attracting much attention in recent years due to their significant potential for energy storage and electric vehicles. Transition metal hydroxides, nickel and cobalt hydroxides in particular, have drawn great interest in the world of electrochemical energy storage due to their desirable electrochemical activity, relatively low cost, and environmentally friendly nature. In this work, Ni-Co Binary Hydroxide nanostructures have been prepared by cathodic electrodeposition of mixed Ni/Co solution. The electrodeposition step has been carried out galvanostatically at different current densities ranging from 0.15 mA cm^{-2} to 0.55 mA cm^{-2} from a nitrate bath containing Ni and Co at an initial Ni/Co ratio of 0.5. The whole process has been monitored by a variety of characterization methods including X-Ray diffraction (XRD), Scanning electron microscopy (SEM) and Energy dispersive X-Ray spectrometry (EDS). The SEM micrographs revealed that the obtained nanocrystals are composed of interlocked nanosheets. The storage ability of the samples was investigated by cyclic voltammetry in 1M KOH aqueous solution at different scan rates ranging from 1 to 50 mVs^{-1}. The results showed that the storage ability is a complex function of various structural parameters including morphology, stoichiometry and Ni/Co ratio of the obtained nanosheets. High capacitance of 1268 F g^{-1} for the sample prepared can be achieved at a current density of 0.15 mA cm^{-2}. The proposed method provides a facile, cost effective and high performance strategy for the synthesis of Ni-Co Binary Hydroxide for supercapacitor applications.

Key words: Electrosynthesis, Nanosheets, Ni-Co Binary Hydroxide, Supercapacitor

References:

[1] X. Sun, G. Wang, H. Sun, F. Lu, M. Yu, J. Lian, *J. Power Sources*, **2013**, 238, 150-156.
[2] Y. Song, X. Cai, X. Xu, X. X. Liu, *J. Mater. Chem. A*, **2015**, 3, 14712-14720.

Application of electromembrane extraction followed by corona discharge ion mobility spectrometry analysis as a fast and sensitive technique for determination of tricyclic antidepressants in urine samples

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This paper aims to introduce a new analytical strategy based on electromembrane extraction (EME) method coupled with corona discharge ion mobility spectrometry (CD-IMS) for determination of antidepressant drugs (desipramine, sertraline, clomipramine, citalopram) in urine samples. IMS is a well-known, comparatively inexpensive, robust and easy to operate analytical instrumentation. This combination would provide a selective and sensitive determination. In order to achieve the best extraction efficiency, optimization of the variables affecting these methods was carried out. Optimal extractions were accomplished with 2-nitrophenyl octyl ether as the supported liquid membrane, with 190 V as the driving force, and with pH 4 in donor and pH 1 in acceptor solutions. Equilibrium extraction conditions were obtained after 30 min of operation with the whole assembly agitated at 1000 rpm.

Under the optimized conditions, the proposed technique provided good linearity ($R^2 > 0.9974$), repeatability (RSD < 4.5), low limits of detection (0.9-1.5 ng mL^{-1}), excellent preconcentration factor (PF = 158-190) and high recoveries (79 - 95%). Finally, developed method was applied to quantification of antidepressant drugs in urine samples.

Keywords: Antidepressant drugs, Electromembrane extraction, Ion mobility spectrometry, Urine samples

References:

[1] M.T. Jafari, B. Rezaei, B. Zaker, Anal. Chem. 81 (2009) 3585.
[2] S. Pedersen-Bjergaard, K.E. Rasmussen, J. Chromatogr. A 1109 (2006) 183.
[3] M. Tabrizchi, V. Ilbeigi, J. Hazard. Mater. 176 (2010) 692.

Carrier assisted electromembrane extraction based on nonionic lipophilicsurfactant as carrier for determination of basic drugs in urine samples

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Herein, a new strategy for highly efficient carrier assisted electromembrane extraction coupled to capillary electrophoresis has been proposed for quantitation of basic drugs (i.e. pseudoephedrine and tramadol) in urine samples. The presence of nonionic lipophilic surfactant in supported liquid membrane acts as carrier and promotes ionic analytes efficient migration through the organic liquid membrane. All variables affecting the extraction efficiency were investigated for the proposed method. Optimal extractions were accomplished with 2-nitrophenyl octyl ether containe 0.25mM Span 80 as the supported liquid membrane, with 200 V as the driving force and with pH 5.0 in donor and pH 1 in acceptor solutions. Equilibrium extraction conditions were obtained after 30 min of operation where the whole assembly agitated at 1000 rpm.

Under the optimum experimental conditions, the linear range was 10–2000 and 5–2000 ng/mL for pseudoephedrine and tramadol, respectively ($R^2 \geq 0.9975$). The limits of detection were calculated to be 3.03 and 1.51ng/mL. The relative standard deviation was lower than 4.1%. The enrichment factors were between 178 and 188. The method was successfully applied for the analysis of these drugs in urine samples.

Keywords: Basic drugs, Capillary electrophoresis, Electromembrane extraction, Nonionic surfactant, Span 80

References:

[1] A. SarafrazYazdi, Z. Es'haghi, J. Chromatogr. A 1094 (2005) 1.
[2] S. Pedersen-Bjergaard, K.E. Rasmussen, Anal. Bioanal. Chem. 388 (2007) 521.
[3] K.S. Hasheminasab, A.R. Fakhari, A. Shahsavani, H. Ahmar, J. Chromatogr. A 1285 (2013) 1.

A new electrochemical sensor for the simultaneous determination of acetaminophen and codeine based on porous silicon/palladium nanostructure

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The large scale therapeutic uses of acetaminophen (ACT) and codeine (COD) require fast, simple and sensitive methods to be developed for their determination. In this work, a new nanostructure is synthesized by galvanic loading of palladium (Pd) nanoparticles on porous silicon (PSi) particles via a simple redox reaction between Pd ions and PSi in an aqueous solution of hydrofluoric acid (HF). The nanocomposite combines the unique properties of porous silicon and the electrocatalytic activity of palladium nanoparticles. The novel nanostructure was then characterized by different spectroscopic and electrochemical techniques including field emission scanning electronmicroscopy (FE-SEM), X-ray diffraction (XRD), energy dispersive X-ray spectroscopy (EDX), fourier transform infrared spectroscopy (FT-IR) and 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 COD at the surface of the proposed sensor. Simultaneous determination of ACT and COD was explored using differential pulse voltammetry. A linear range of 1.0–700.0 mmol L^{-1} was achieved for ACT and COD with detection limits of 0.4 and 0.3 mmol L^{-1} , respectively. Finally, the proposed method was used for the determination of ACT and COD in blood serum, urine and pharmaceutical compounds.

Keywords: Porous silicon/palladium nanostructure, Acetaminophen, Codeine, Differential pulse voltammetry, Simultaneous determination

References:

[1] A.A. Ensafi, M.M. Abarghoui, B. Rezaei, Sens. Actuators B, **2014**,196, 398–405.
[2] J.M. Westra, V. Vavrunkova, P. Sutta, R.A.C.M.M. van Swaaij, M. Zeman, Energy Procedia, **2010**, 2, 235–241.
[3] Y.F.Li,K.J.Li,G.Song,J.Liu,K.Zhang,B.X.Ye,Sens.ActuatorsB, **2013**,182, 401–407.

Poly(5-sulfosalicylic acid)/Cu(OH)$_2$-graphite nanocomposite modified glassy carbon electrode for sensitive detection of tartrazine

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Tartrazine (TT) is a synthetic organic food dye that can be found in common food products such as beverages, candies and dairy products. However, the content of TT must be controlled due to its potential harmfulness to human beings such as allergies, migraines, eczema, and even cancer. Thus, accurate methods for the determination of TT are required. The assay of TT in foods can be carried out using many techniques, such as spectrophotometry, high performance liquid chromatography–mass spectrometry and capillary electrophoresis. However, these mentioned methods have some disadvantages. Electrochemical methods provide a convenient, sensitive, cheap and fast way to detect of TT [1]. In the past few years, polymer-modified electrodes have attracted enormous interest due to their reproducibility, more active sites, and strong adherence to electrode surface [2]. Nanostructured transition metal hydroxides/oxides have excellent properties such as high surface area and enhanced chemical/electrochemical activities, as well [3]. Herein, we have fabricated a Poly(5-sulfosalicylic acid) (PSA)/Cu(OH)$_2$-graphite modified GCE for the analysis of TT. All the measurements were done in phosphate buffer solution 0.1 M (pH 2.0) and the oxidation peak was observed at 990 mV. The modified electrode showed excellent electrocatalytic properties with obvious reduction of overpotential and enhancement of oxidation current, making it suitable for the analytical purpose. This electrode exhibited electrocatalytic activity for oxidation of TT and showed good linear relationship over the concentration range of 0.5–20 μM with detection limit of ۰.۰۷۳5 μM (S/N=3).

Keywords: Cu(OH)$_2$ nanoparticles; Electropolymerization; 5-solfusalicylic acid; Tartrazine

References

[1] L. Zhao, B. Zeng, F. Zhao, *Electrochim. Acta* 146 (2014) 611–617.
[2] X. Ba, L. Luo, Y. Ding, X. Liu, *Sens. Actuators B* 187 (2013) 27– 32
[3] M. Arvand, T.M. Gholizadeh, M. Zanjanchi, *Mater. Sci. Eng. C* 32 (2012) 1682–1689.

Preparation of an electrochemical sensor using zinc oxide nanoparticles and its application for study and determination of riboflavin

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Riboflavin commonly called vitamin B2 is a water soluble vitamin. It is very stable during thermal processing, storage, and food preparation but is susceptible to degradation on exposure to light [1]. Vitamins are necessary for the normal functioning of organic metabolism. Their absence in humans can lead to different diseases. Almost all vitamins require to be obtained from dietary sources since they are not produced by the human body [2]. Therefore, developing a sensitive and selective sensor for riboflavin detection is very important. In the research a carbon paste electrode in corporate with zinc oxide nanoparticles was prepared and used for electrochemical study and determination of riboflavin. Characterization of the modified nanosensor was carried out by different techniques such as scanning electron microscopy, electrochemical impedance spectroscopy and cyclic voltammetry. Various electrochemical techniques such as linear sweep voltammetry, chronocoulometry and chronoamperometry were performed for study of riboflavin. Also, after optimizing of experimental conditions, the dynamic range for riboflavin was from 0.01μM to 30.00 μM and the detection limit was found to be 2.83 nM using differential pulse voltammetry at the surface of zinc oxide nanosensor. Also, for the measurements, excellent selectivity, stability and repeatability were achieved. The prepared electrode was successfully applied for determination of riboflavin in the real and pharmaceutical samples.

Keywords: Riboflavin; Zinc oxide nanoparticles; Surface studies; Electrochemical techniques

References

[1] A. Safari, N. Maleki , H. Ershadifar, F. Tajabadi , Anal. Chim. Acta, **2010**, 674, 176-181.
[2] É.S. Sá, P.S. da Silva, C.L. Jost, A. Spinelli, Sens. Actuators B, **2015**, 209, 423-430.

Investigation of Fentanyl Electrochemical Behavior in Aqueous Solution

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Fentanyl is a member of the class of drugs known as fentanyls, rapid-acting opioid drugs that alleviate pain without causing loss of consciousness. In this research, we have investigated the electrochemical oxidation of fentanyl using cyclic voltammetry and differential pulse voltammetry. The electrochemical behavior of fentanyl is studied on surface of different electrodes. The glassy carbon electrode is selected as the best electrode due to its sensitivity. Cyclic voltammetry studies indicated that the process was irreversible. In phosphate buffer solution (pH 7), fentanyl had a sensitive oxidative peak at 0.845 V. The peak current was linear with the fentanyl concentration in the range of 4×10^{-6} to 1×10^{-4} mol L^{-1} and the detection limit was found to be 1×10^{-6} mol L^{-1}. The relative standard deviations for the determination of fentanyl at different concentration levels were less than 7.1% (n=3).

Keywords: Cyclic voltammetry; Differential pulse voltammetry; Electrochemical behavior; Fentanyl

Electrochemical reduction of metronidazole at glassy carbon electrode modified with gold nanoparticles

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Due to the critical roles of metronidazole (MTZ) in the pharmaceutical industry, its determination is important in biological fluids and drug formulations. Among different methods for MTZ determination, electrochemical techniques have some advantages including simplicity, cost-effectiveness, rapidity, high selectivity and sensitivity. Gold nanoparticles (AuNPs) have attracted considerable attention in electrochemical and biological sensor applications due to their unique optical, electrical, and catalytic properties.

In this work AuNPs modified glassy carbon electrode was prepared. The surface morphology of the AuNPs modified electrode was characterized by scanning electron microscopy (SEM) and energy dispersive X-ray (EDX) techniques. Voltammetric behavior of MTZ on the prepared modified GCE was investigated. The cyclic voltammetric results indicate that AuNP/GCE can remarkably enhance electrocatalytic activity towards the reduction of MTZ in neutral solutions. This allows the development of a highly sensitive voltammetric sensor for determination of MTZ in pharmaceutical samples. The electrochemical response characteristics toward metronidazole were investigated by cyclic and differential pulse voltammetry. A well-defined catodic peak was obtained at -0.42 V (vs. SCE) in phosphate buffer solution pH=7. The calibration curve indicated a good linearity with linear dynamic range of 6.3×10^{-6} to 4.3×10^{-3} mol L^{-1}. The limit of detection of the differential pulse voltammetry method was 6.3×10^{-6} mol L^{-1}.

Keywords: Eelectrochemical reduction; Gold nanoparticle; Metronidazole; Modified electrode

An impedimetric study of a graphene oxide/ds-DNA/gold nanorods sandwich modified glassy carbon electrode

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Electrochemical methods compared other analytical techniques such as chromatography or spectroscopy, are generally simpler, faster and more economical, and have comparative sensitivity. Various chemically modified electrodes have been reported for detection of a variety of compounds such as foods, toxins, metals, drugs and so on. The interaction of gold nanorods (GNRs) with double-strand DNA (ds-DNA), which was immobilized onto graphene oxide (GO) modified glassy carbon electrode (GCE) was employed for constructing a sensitive biosensor. GNRs/ds-DNA/GO/GCE was used to detection and determination of carcinogenic, mutagenic, teratogenic and immunosuppressive toxins and pesticides such as aflatoxin, diazinon, malathion and other compounds. Scanning electron microscopy (SEM) was used to showing the specific structure of synthesized graphene oxide. Electrochemical impedance spectroscopy (EIS) and cyclic voltammetry (CV) were used to demonstrating the establishment of modifier layers on sandwich ds-DNA biosensor. Voltammetric behavior of toxin compounds on the modified electrode was studied. To find optimum conditions in sample analysis, some important parameters such as pH (6.0) and scan rate (0.1 V s^{-1}) were examined and finally a mechanism was proposed for the analyte oxidation. The work was completed by calculation of electrode dynamic range and detection limit. Finally the proposed modified ds-DNA biosensor was used to measuring the analyte in real sample.

Keywords: Impedance spectroscopy; ds-DNA; Gold nanorods; Graphene oxide

Design of a new electrochemical method for detection and determination of Aflatoxin B1 in food industry

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Electrochemical sensors have aroused interest for detection of vast variety of compounds such as proteins, drugs, foods, pesticides, toxins and so on [1]. Aflatoxins are known carcinogenic, mutagenic, teratogenic and immunosuppressive [2]. In this work, a new design of electrochemical sensor was introduced for determination of aflatoxin B1.

According to structure of aflatoxin B1, the modifiers were selected. Multiwalled carbon nanotubes-gold nanoparticle composite was spiked first, to accelerate conductivity, and then the electrode was immersed in cysteamine solution to functionalization for capturing the aflatoxin B1 molecules.

The optimum pH and scan rate for determination of aflatoxin B1, were 6 and 0.5 mV.s^{-1}, respectively, by cyclic voltammetry. Diffusion coefficient of aflatoxin B1, RedOx mechanism, calibration curve and real sample analysis are other figure of merits that are calculated and will be expressed.

Keywords: MWCNTs; Gold nanoparticles; Aflatoxin B1; Modified electrode

References:

[1] A. Ansari, A. Kaushik, P.R. Solanki, B.D. Malhotra, Bioelechtrochem, 77 (2010) 75.
[2] N. H.S. Ammida, L. Micheli, G. Palleschi, AnalChimActa, 520 (2004) 159.

Electrochemical study 0f 1,5-diaminonaphthalene

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The electro chemical methods are widely applied to the study of organic species, since they can be used to obtain both thermodynamic and kinetic information cyclic voltammetry is one of the most useful techniques for studying the electrode reactions that involve an unstable intermediate or product.

The electrochemical oxidation of 1,5-diaminonaphthalene have been studied in detailed.We are currently concerned with the cyclic voltammetric study of (1,5-DAN) with two functional groups. It wasdemonstrated that a reaction such as polymerization or synthesis by different nucleophile occurred selectivity via the -NH2groups.

The electrochemical behaviors of this compound were assessed at various pHs by cyclic voltammetry and present related mechanisms. We have done the electro oxidation of (1,5-DAN) in ethanol solution and buffer solution as a supporting electrode from pH=1 to pH=10. The working electrode used was a glassy carbon disk (1.8 mm diameter) and a platinum wire was used as the counter electrode and a saturated calomel electrode (SCE) as reference electrode was used.

Cyclic voltammogramsof 1.0 mMsolution of (1,5-DAN) in ethanol-water solution (30:70) at various pHs are shown that1,5-DAN electro-oxidize quasi-reversibly and the oxidation of the monomers appear as the broad peaks in the potential region of ca.0.1-0.6, probably corresponds to the oxidation of the parent NH2 groups to thecationradicals and further to the dications.

Keywords: 1,5-diaminonaphthalene; Cyclic voltammetry; Quasi-reversible

Simultaneous Electrochemical Determination of Dopamine and Serotonin at a Nano-Scale Nickel Hydroxide Modified Carbon Ionic Liquid Electrode

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A nano-scale nickel hydroxide modified carbon ionic liquid electrode ($Ni(OH)_2$/CILE) was used for direct simultaneous determination of Dopamine (DA) and Serotonin (5-HT) by adsorptive differential pulse voltammetry (ADPV).

Parameters affecting the current efficiency for dopamine and serotonin, including the electrode composition (ratio of nickel hydroxide, graphite powder and ionic liquid), the electrolyte features (type of buffer, concentration and pH) and electrochemical parameters (amplitude, step potential and adsorption time) were examined. Large peak separations between DA and 5-HT allows their simultaneous determination at $Ni(OH)_2$/CILE by using ADPV. Two oxidation peaks for DA (0.055V) and 5-HT (0.250V) (vs. Ag/AgCl, KCl, 3.0M) were observed with a significant peak separation of ~250mV on $Ni(OH)_2$/CILE as a high performance electrode in phosphate buffer solution (pH 8.5). The linear ranges were obtained as $1.0\text{-}2.5\times10^{3}$ μM and 0.5-300 μM and detection limits were estimated to be 0.6 μM and 0.4 μM for DA and 5-HT, respectively.

Keywords Nano scale Nickel hydroxide; Simultaneous determination; Dopamine; Serotonin

References:

[1] A. Safavi, N. Maleki, E. Farjami, Biosens. Bioelectron. 24 (2009) 1655–1660.
[2] A. Babaei, A.R. Taheri, Sensors Actuators B Chem. 176 (2013) 543–551.
[3] Luo, P.; Prabhu, S. V; Baldwin, R. P. *Anal. Chem. 62* (1990) 752–755.

Zinc Oxide Nano Particles–Ionic Liquid NanocompositeModified Carbon Ceramic Electrode for Sensitive Determination of Sunset Yellow in Food Samples

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Synthetic dyes are usually added to foodstuffs and soft drinks not only to improve appearance, color and texture but also to maintain the natural color during process or storage. Sunset yellow (SY) is a synthetic organic dye that can be found in common food products [1]. The presence and content of this dye must be controlled due to its potential harmfulness to human beings; therefore, sensitive and selective determination of SY is necessary. As we know, electrochemical methods are quick, convenient, sensitive, low-cost and environmentally friendly in comparison with other methods. Carbon-ceramic electrodes (CCEs) are comprised of a dispersion of carbon powder that is held together by sol-gel derived ceramic binder. However, bare carbon-ceramic electrodes have some drawbacks such as low detection sensitivity and poor resolution to specific analytes; therefore, their modification is necessary.Zinc oxide nanoparticles are an important semiconductor material and, recently, have attracted considerable attentions in optoelectronic materials, nanosensors, ultraviolet lasers and field emission devices [2]. Thus, we modified CCE with zinc oxide nanoparticles and ionic liquid (IL) to determine SY in food samples. On the modified CCE a pair of well-defined redox peaks appeared at about80 (E_{pa}) and 73 (E_{pc})mV, indicating the electrochemical reaction of SY take place on this sensor.Operational parameters, such as the amount of ZnO NPs, IL volume and solution pH were optimized.The redox peak intensity varied with the pH value of citrate buffer solution and obtained results showed that at pH 4.8 we have maximum current value (I_{pa}=151 and I_{pc}= –141 μA).

Keywords: Carbon ceramic electrode;Food sample; Ionic liquid; SunsetYellow;Zinc oxide nanoparticles

References:

[1] M. Majidi,R. FadakarBajehBaj, A. Naseri, *Food Anal. Methods*,6 (2013) 1388.
[2] M. Arvand, S. Tajyani, N. Ghodsi,*Mater.Sci.Eng.C*, 46 (2015) 325.

Hydrothermal Synthesis of a Novel Spinel Sulfide/Polypyrrole Nanocomposite for High-Performance Supercapacitors

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Of the many available energy storage and conversion technologies, supercapacitors have received intense attentions due to high power density, fast dynamics of charge propagation and long life stability. Electrode materials for supercapacitors are categorized to three types: carbon materials, metal oxides and electronically conducting polymers. Unfortunately, most of metal oxides, carbon materials and conducting polymers suffer from the problems of poor electronic conductivity, low specific capacitance and cycling stability. In order to overcome these problems, the combination of conducting polymer with transition metal sulfide or metal oxide can be used. In this study, nanocomposite of polypyrrole and spinel-nickel-cobalt sulfide was synthesized by hydrothermal method as electrode material for supercapacitors. This nanocomposite demonstrates prominent electrochemical performance with a high specific capacitance (almost 1700 F g^{-1}) and a good cycling stability (maintaining 85% of the initial capacitance after 2000 cycles). Our results suggest this electrode as promising material for designing future supercapacitor.

Keywords: Hydrothermal; Conducting polymers; Nanocomposite; Supercapacitor

References:

[1] Safavi, A.; Kazemi, S. H.; Kazemi, H. Electrochim. Acta 2011, 56, (25), 9191.
[2] Zhou, C.; Zhang, Y.; Li, Y.; Liu, J. Nano Lett. 2013, 13, (5), 2078.
[3] Peng, H.; Ma, G.; Sun, K.; Mu, et al. J. Mater. Chem. *A* 2014**,** 2, (10), 3303.
[4] Kazemi, S. H.; Karimi, B.; Aghdam, S. A.; Behzadnia, H.; Kiani, M. A. RSC Advances 2015, 5, (84), 69032-69041.

Synthesis and Characterization of Hierarchical 3D Nanosheets of $NiMoO_4$@graphene for Supercapacitor Applications

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Fabrication of new electrode materials with controllable morphology and size is a challenging subject in energy storage studies. An effective strategy to make the suitable electrode materials for supercapacitors is constructing hybrid nanocomposites of graphene nanosheets and metal oxide with hierarchical 3D porous structures. We introduce herein, for the first time, a facile and low cost hydrothermal method to synthesis the $NiMoO_4$@graphene nanosheets with robust adhesion to substrate as a binder-free electrode for supercapacitor. The well-ordered mesoporous morphology offered remarkable electrochemical behavior and excellent supercapacitive performance. A maximum specific capacitance of 2800 F g^{-1} was estimated, also this electrode almost maintained 67% of its initial capacitance when the scan rate increased from 5 to 50 mV s^{-1}; indicating an excellent rate capability. Notably, this electrode showed exceptional operational cycling stability. Such an excellent capacitive performance is related to positive synergistic effect between $NiMoO_4$ and graphene. Our findings suggest the potential application of $NiMoO_4$@graphene electrode for building high performance supercapacitors.

Keywords Hydrothermal; Binder-free; Graphene; Nanosheets; Supercapacitor

References:

[1] S. Habib Kazemi, A. Asghari, Materials Letters, 142 (2015) 156-159.
[2] D. Cai, S. Xiao, D. Wang, B. Liu, L. Wang, Y. Liu, H. Li, Y. Wang, Q. Li, T. Wang, Electrochimica Acta, 142 (2014) 118-124.
[3] Cai, B. Liu, D. Wang, Y. Liu, L. Wang, H. Li, Y. Wang, C. Wang, Q. Li, T. Wang, Electrochimica Acta, 115 (2014) 358-363.

Simultaneous Voltammetric Determination of Captopril and Hydrochlorothiazide on a Copper Hydroxide Nanoparticles Composite Carbon Ionic Liquid Electrode

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The angiotensin converting enzyme inhibitor, captopril, has been used in the treatment of essential hypertension and to reduce mortality in patients with acute myocardial infraction. Hydrochlorothiazide is indicated for the treatment of edemas associated with the heart, liver and kidneys and has been used in monotherapy or in combination with other drugs such as captopril and losartan. A carbon ionic liquid electrode (CILE) modified with $Cu(OH)_2$ nanoparticles has been employed for simultaneous determination of captopril (CPT) and hydrochlorothiazide (HCT) by square wave voltammetry. Electrocatalytic oxidations of both CPT and HCT were investigated with this electrode in phosphate buffer solution at pH 8.0. After optimizing the operational conditions, linear concentration ranges of 0.7-10 µM and 10-70 µM for CPT, plus 3-100 µM and 100-600 µM for HCT were obtained. Detection limits of 12.5 nM and 59.7 nM were obtained for CPT and HCT, respectively. The method was successfully applied for analysis of CPT and HCT in pharmaceutical preparations. The electrode showed good reproducibility, repeatability and storage stability.

Keywords Captopril; Hydrochlorothiazide; Carbon Ionic Liquid Electrode; $Cu(OH)_2$ nanoparticle; Square wave voltammetry.

References:

[1] A. Safavi, N. Maleki, E. Farjami, F. A. Mahyari, Anal. Chem. 81 (2009), 7538–7543. [2] M. B. Gholivand, M. Khodadadian, Electroanalysis, 5 (2013),1263–1270.

Determination of Melamine on a Copper Hydroxide Nanoparticles Composite Carbon Ionic Liquid Electrode By Differential Pulse Anodic Stripping Voltammetry

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Melamine (MEL) is a nitrogen-containing compound used in the production of plastics, glues, and thermoset polymers. It forms insoluble complexes with cyanuric acid, depending on urine pH, which could lead to crystallization and subsequent tissue injury, such as urolithiasis and bladder cancer. Unfortunately, some unethical manufacturers illegally add melamine to food products to artificially elevate the protein content values. A carbon ionic liquid electrode (CILE) modified with $Cu(OH)_2$ nanoparticles was employed for anodic stripping voltammetric determination of MEL by differential pulse voltammetry. Electrocatalytic oxidation of MEL was investigated by using this electrode in borate buffer solution at pH 10.0. After optimizing the operational conditions, linear concentration ranges of 6-30 μM and 30-200 μM with a detection limit of 0.63 μM were obtained for MEL. The method was successfully applied for analysis of MEL in cow milk. This electrode showed good reproducibility, repeatability and storage stability.

Keywords Melamine; $Cu(OH)_2$ nanoparticles; Ionic liquid; Carbon ionic liquid electrode; Anodic stripping voltammetry.

References:

[1] Q. Cao, H. Zhao, L. Zeng, J. Wang, R. Wang, X. Qiu, Y. He, Talanta, 80 (2009), 484.
[2] W. R. Araujo, T. R.L.C. Paixão, Electrochim. Acta, 117 (2014), 379.

Nanoarchitectured Metal-Hexacyanoferrates Reduced Graphene Oxide Nanosheets for Electrochemical Supercapacitors

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Supercapacitors are superior energy storage devices in term of high power density, fast charge/discharge rate, long lifespan and low maintenance cost. Graphene has received great attentions as an ideal electrode material for supercapacitors due to its extremely high theoretical surface area and excellent theoretical capacitance. Recently, transition metal hexacyanoferrates have been extensively considered in energy storage devices such as supercapacitor, due to 3D network and tunnel structure, low cost and low environmental toxicity. Herein, we electrodeposited nanostructured of cobalt hexacyanoferrate/graphene on Ni substrate (CoHCF@rGO/NF). The CoHCF@rGO/NF electrode displayed high areal and mass capacitances compared to pure graphene or CoHCF/NF electrodes. The CoHCF@rGO electrode shows remarkable stability cycles. These results suggest the CoHCF@rGO composite as electrode material for high performance supercapacitor devices. A maximum specific capacitance of almost 580 F/g at 1 A/g current density was achieved. Also, long life cycle stability test was performed in which more than 90% of initial capacitance was retained after 1500 successive charge/discharge cycles.

Keywords: Hexacyanoferrates; Electrodeposition; Graphene; Supercapacitor

References:

[1] Y. Yang, Y. Hao, J. yuan, L. Niu, F. Xia, Carbon, 84 (2015) 174-184.
[2] J. Chen, K. Huang, S. Liu, Electrochemistry Communications, 10 (2008) 1851-1855.
[3] A. Safavi, S.H. Kazemi, H. Kazemi, Electrochimica Acta, 56 (2011) 9191-9196.
[4] S.H. Kazemi, B. Karimi, S.A. Aghdam, H. Behzadnia, M.A. Kiani, RSC Advances, 5 (2015) 69032-69041.

Facile synthesis of TGA-capped CdSe@Ag_2Se core-shell quantum dot nanoparticles as modifier of glassy carbon electrode for methyldopa sensing in the presence of uric acid in pharmaceutical and biological samples

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In this work, we introduce a new approach to prepare the CdSe@Ag_2Se core–shell fluorescent quantum dots as a novel and sensitive electrochemical sensor for methyldopa by dropping of an aliquot of TGA-capped CdSe@Ag_2Se on a glassy carbon electrode surface. Characterizing the CdSe@Ag_2Se was investigated by cyclic voltammetry, UV–vis, photoluminescence spectroscopy, X-ray diffraction (XRD), FT-IR spectroscopy, and scanning electron microscopy (SEM) techniques. Under the optimal experimental conditions (pH=2), the current response of the electrochemical sensor obtained with differential pulse voltammetry was increased linearly with methyldopa concentrations in the wide range from 0.09 to 60 µmolL^{-1}, with the detection limit of 0.04 µmolL^{-1}. The developed sensor was successfully applied to the analysis of methyldopa in biological and pharmaceutical samples without interferences from uric acid and ascorbic acid due to its high sensitivity and selectivity, very good repeatability and reproducibility, and low detection limit.

Keywords: Electrochemical sensor; Differential pulse voltammetry (DPV); Methyldopa; TGA-capped CdSe@Ag_2Se core-shell; Thioglycolic acid (TGA).

References:

[1] R.J. Zheng, Y.M. Fang, S.F. Qin, J. Song, A.H. Wu, J.J. Sun, Sens. Actuator B-Chem. 157 (2011) 488.

[2] X.Z. Ai, L. Niu, Y.Y. Li, F.P. Yang, X.G. Su, Talanta 99 (2012) 409.

Effect of PH on the Properties and electrochemical performance of $LiFePO_4$ Composite for using in Lithium-Ion Batteries

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In recent years, the ordered olivine lithium iron phosphate ($LiFePO_4$) has been extensively and intensively investigated as a cathode material for Lithium-ion batteries in electric vehicles (EVs) because of its low cost, nontoxic, high theoretical capacity and perfect flat voltage profile at 3.45 V vs Li^+/Li compared with other cathode materials [1-3]. In this work Lithium iron phosphate (LFP) particles LFP-1, LFP-2, and LFP-3 in different PH, are synthesized by a solvothermal reaction followed by heat treatment calcination process. Citric acid and ascorbic acid as inhibitors for prevention of conversion of Fe^{+2} to Fe^{+3}, water and ethylene glycol were used as solvent. The effect of PH on the physical and electrochemical properties of the LFP electrodes was investigated by XRD analysis, SEM, TEM, CV, EIS and charge/discharge test. SEM and TEM observations revealed that the particle size of $LiFePO_4$ was significantly affected by the process parameters and the $LiFePO_4$ nanoparticles with a geometric mean diameter of 60nm by the present method. According to the data obtained in this study, increasing PH, enhance the electrochemical performance of $LiFePO_4$ samples. When these materials used as the cathode materials in the lithium-ion batteries with an electrochemical cell of $Li|1MLiClO_4$ in PC $|LiFePO_4$, the resultant of LFP-3 nanoparticles shows high capacity and good cycle stability about 141 $mAhg^{-1}$ at 0.1 C first discharge capacity, with 14% capacity fading after 40 cycles while LFP-2 about 125 and LFP-1 about 110 $mAhg^{-1}$. The desirable electrochemical performance can be attributed to Nano sized structure. Also, the cells with LFP-3 cathode material exhibited excellent reversibility in cyclic voltammetry and the EIS results showed that the conductivity is enhanced.

Keywords: Solvothermal synthesis; Lithium iron phosphate; LFP; PH effect; Lithium ion batter.

Electrochemical sensor for paracetamol based on nano-structured Hexacyanoferrate(III) intercalated Ni/Al layered double hydroxide modified glassy carbon electrode

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Paracetamol also known as acetaminophen (PC) is widely used as an analgesic and antipyretic drug. Since paracetamol is an electroactive compound and, electrochemical methods have some merits such as sensitivity, time-saving, low cost and simple operation, therefore electrochemical methods can be applied as a suitable technique for the determination of paracetamol [1]. Until now, many kinds of nano-sized material modified electrodes have been used for this purpose owing to their unique structure and properties [2].

In this work, nano-structured hexacyanoferrrate(III) intercalated Ni–Al layered double hydroxide (Ni–Al–HCF LDH) was synthesized using co-precipitation method. The as–prepared LDH structurally and morphologically was characterized by scanning electron microscopy, X–ray diffraction, Fourier transform IR, and cyclic voltammetry. The Ni–Al–HCF LDH modified glassy carbon electrode exhibited excellent electrocatalytic activity toward the oxidation of paracetamol. The electrochemical behavior of paracetamol on the Ni–Al–HCF film was investigated in detail. The electrocatalytic response of the modified GC electrode was linear in the PC concentration range 3×10^{-6}–1.5×10^{-3} mol L^{-1}, with a correlation coefficient of 0.999, using hydrodynamic amperometry. The diffusion coefficient of PC (D) was found to be 7.8×10^{-6} $cm^2\ s^{-1}$. The fabricated electrode was applied to determination of paracetamol in various pharmaceutical preparations and human serum samples with satisfactory results.

Keywords: Electrocatalysis; Layered double hydroxide; Modified electrode; Paracetamol

References:

[1] D. Lu, Y. Zhang, L. Wang, S. Lin, C. Wang, X. Chen, Talanta 88 (2012) 181– 186.
[2] J. Luo, C. Fan, X. Wang, R. Liu, X. Liu, Sens. Actuators, B 188 (2013) 909– 916.

Electrochemical determination of carbamazepin in the presence of paracetamol using a carbon ionic liquid paste electrode modified with a three-dimensional graphene/MWCNTs hybrid composite film

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In this research work, a carbon ionic liquid paste electrode (CILPE) based on butyl-3-metylimidazolium bis (trifluorometylsulfonyl) imide ([bmim] NTF2) was fabricated and further modified with graphene/ multiwall carbon nanotubes (GR/ MWCNTs) hybrid composite .The modified electrode (GR/ MWCNTs /CILPE) was used for measurement of carbamazepine (CBZ) in the presence of paracetamol (PA) with an excellent electrochemical catalytic behavior. The application of the electrode was investigated by cyclic voltammetry and differential pulse voltammetry. The oxidation peak currents of CBZ and PA were linear at the ranges of 1-60 µM and 2-80 µM, respectively. Also, the detection limits for CBZ and PA were 0.233 µM and 0.262 µM, respectively. The proposed sensor was successfully applied for the determination of CBZ and PA in tablet and urine samples.

Keywords: Carbon ionic liquid electrode; Graphene; Multiwall carbon nanotubes; Carbamazepine; Paracetamol; Voltammetry

References:

[1] A. Veiga, A. Dordio, A.J. Palace Carvalhoa, D. M. Teixeira, J. G.Teixeiraa, Analytica Chimica Acta 674 (2010) 182–189.
[2] S. S. Kalanur, S. Jaldappagari, S.Balakrishnan, Electrochimica Acta 56 (2011) 5295–5301.
[3] N. Thapliyal, R. V. Karpoormath, R. N. Goyal. Analytica Chimica Acta 853(2015) 59-76.

Designing a sensitive nanostructured sensor based on Fe_3O_4 nanoparticles for simultaneous determination of gallic acid and tryptophan

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Gallic acid (GA) is a strong antioxidant, and their biological properties include anti-inflammatory antihistaminic and antitumor activities, scavenging of free radicals and protection against cardiovascular diseases (1). Therefore, developing a sensitive and selective sensor for GA detection is very important. Tryptophan (Trp) is an important amino acid owing to its crucial roles in biological systems. It is a vital constituent of proteins and indispensable in human nutrition for establishing and maintaining a positive nitrogen balance (2). Trp is also an essential amino acid for brain functions and neuronal regulatory mechanisms. In the present study, a new sensor based on Fe_3O_4 nanoparticles mixed by chitosan (Ch) was prepared and used for simultaneous determination of GA and Trp. Characterization of the modified nanosensor was carried out by different techniques such as scanning electron microscopy (SEM), electrochemical impedance spectroscopy (EIS) and cyclic voltammetry (CV). The prepared nanosensor showed voltammetric responses for the two analytes with high sensitivity. After optimizing the chemical and instrumental conditions, the peak currents of the two components showed a linear correlation to their concentrations with broad linear dynamic ranges and low detection limits. Finally, the proposed method was successfully applied for simultaneous detection of GA and Trp in real samples.

Keywords: Gallic acid, Tryptophan, Chitosan, Fe_3O_4 nanoparticles, Simultaneous detection

References:

[1] I. Mudnic, D. Modun, V. Rastija, J. Vukovic, I. Brizic, V. Katalinic, B. Kozina, M. Medic-Saric, M. Boban, Food Chem. 119 (2010) 1205–1210.
[2] Ensafi A.A., Hajian R. Determination of tryptophan and histidine by adsorptive cathodic stripping voltammetry using H-point standard addition method. Anal. Chim. Acta. 2006;580:236–243.

Poly(3,4-ethylendioxythiophene)/Zirconia Nanocomposite as a Sensing Platform for Electrochemical Detection of Progesterone

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Progesterone (P4) belongs to a group of steroid hormones derived from cholesterol and plays an important role in the stabilization and maintenance of pregnancy in mammals, acting in the synthetic route of various biologically active steroids. Various analytical methods have been reported for P4 determination in commercial formulations, serum, human and bovine milk and rat plasma. Recently, some attempts have also been made to include voltammetric methods as alternative for the detection and electrochemical study of several hormones [1]. In recent years, metal oxide nanoparticles have been the focus of much current research in designing and constructing of chemical and electrochemical sensors owing to their special properties. Among the metal oxide nanomaterials, ZrO_2 nanoparticles (NPs) have gained considerable attention as alternative electrode materials due to their chemical inertness and lack of toxicity [2]. In the present work, poly(3,4-ethylendioxythiophene)/zirconia nanocomposite modified sensor was used for the determination of P4 in different matrices. The proposed sensor showed large specific area, high conductivity and rapid redox properties, which makes it an excellent sensing platform for sensitive determination of P4. The differential pulse voltammetric response of the modified electrode exhibits linear relationship against the concentration of P4 in the ranges of 0.5–100 and 100–1000 µM. The limit of detection was found to be 0.2 µM.

Keywords: Modified electrode; Poly(3,4-ethylendioxythiophene); Progesterone; ZrO_2 nanoparticles

References:

[1] C.A. de Lima, A. Spinelli, *Electrochim. Acta*, 107 (2013) 542.
[2] T. Nie, K. Zhang, J. Xu, L. Lu, L. Bai, *J. Electroanal. Chem.*, 717 (2014) 1.

Comparative Study of Carbon Nanostructures and Metal Nanoparticles-Based Electrochemical Sensor for the Sensitive Determination of Ceftizoxime

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Carbon nanostructures offer unique advantages in several areas, like high surface-volume ratio, high electrical conductivity, chemical stability and strong mechanical strength and are thus frequently being incorporated into sensing elements [1]. On the other hands entrance of metal nanoparticles into carbon nanostructures showed enhancement in electronic, magnetic and catalytic properties. In the field of electrochemical sensors and biosensors, due to their good biocompatibility, low toxicity, easy preparation, high adsorption ability, high surface area and low mass transfer resistance, metal nanoparticles are more helpful in promoting the redox process [2]. In this study The surface of the glassy carbon electrode was coated with thin films of five carbon nanostructures, including carbon nanotubes (CNTs), carbon nanoparticles (CNPs), Nano diamond-graphite (NDG), graphene oxide (GO) and carbon nanotube-graphene oxide hybrid nanocomposites (CNT-GO) to comparison of sensitivity, stability and repeatability in response to Ceftizoxime (CFX). MWCNTs selected as the best carbon nanostructure that created these parameters perfectly. In the second step and according to functional groups in the chemical structure of the CFX, five metal nanoparticles including Au, Pt, Ag, Ni (OH)2 and CuO deposited on the surface of the MWCNTs/GCE electrochemically for enhancement of results. Finally AuNPs/MWCNTs/GCE chose as a promising candidate for the trace analysis of CFX in pharmaceutical and clinical preparations. Scanning electron microscopy (SEM), atomic force microscopy (AFM), cyclic voltammetry (CV) and linear sweep voltammetry (LSV) were employed for the surface analysis of the modified electrodes. Experimentally parameters and electro deposition condition of Au nanoparticles were optimized and under this condition, linear response of the CFX in the range of 0.02-8 μM with detection limit of 6nM was obtained. Also in the presence of some potentially interference, this modified electrode was tasted and suitable results was achieved.

Keywords: Carbon nanostructures; Metal nanoparticles; Electrochemical deposition; Ceftizoxime; Voltammetry

References:

[1] R. Cui, X. Wang, G. Zhang, C. Wang, *Sens. Actuators B* 161 (2012) 1139.
[2] M. Moyo, L. R. Florence, J. O. Okonkwo, *Sens. Actuators B* 209 (2015) 898.

Novel Spinel Nickel-Cobalt oxide/Polypyrrol Nanocomposite for High Performance Supercapacitors

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Among energy storage devices, supercapacitors can maintain the capability to store higher energy density compared to the conventional capacitors, also deliver higher power density compared with batteries fuel cells. Carbon materials, conducting polymers and metal oxides are the most important types of electrode materials for supercapacitors. Among all the pseudocapacitive materials, conducting polymers have been the most studied, due to their due to their excellent chemical, electrical and optical properties. Unfortunately, they display low-rate capabilities and cycling performance. This problem mitigated by the combination of metal oxide and conducting polymers. In the present work we introduce a hydrothermal method to synthesize nikcel cobalt oxide@polypyrrole nanocomposite. The as-synthesized electrode exhibits an ultrahigh specific capacitance of 1600 F/g, excellent rate performance and outstanding cycling stability (95% capacity retention over 2000 cycles). Thus, we suggest the application of this electrode for making the high performance supercapacitor.

Keywords Hydrotermal; Conducting polymer; Nanocomposite; Supercapacitor

References:

[1] C. Zhu, J. Zhai, D. Wen, S. Dong, Journal of Materials Chemistry 22 (2012) 6300.
[2] Z. H. Dong, Y. L. Wei, W. Shi, G. A. Zhang, Mater. Chem. Phys131 (2011) 529.

Graphene quantum dots/ magnetic nanoparticles/ carbon nanotube nanocomposite as a sensing platform for sensitive electrochemical detection of progesterone

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In recent years, with the highly developed nanotechnology, numerous sensitive biosensors have been reported by using various nanomaterials. Graphene quantum dots (GQDs) are a kind of 0D material which can be regarded as small pieces of graphene. As compared to other carbon nanomaterials, GQDs possess high surface area, biocompatibility, and good electrical conductivity, which make them ideal materials for the application in electrochemical sensors [1]. Moreover great improvement of the electrochemical response was observed on magnetic nanoparticles (MNPs) (such as magnetite (Fe_3O_4)) and carbon nanotubes (CNTs) modified electrode, due to their excellent properties [2]. Progesterone is a steroid hormone and used as a drug in hormone replacement therapies and plays an important role in human body. Thus, it is very important to determine progesterone levels in body by high sensitive, simple, cheap and fast electrochemical method [3]. In the present work, electrochemical measurements were performed at a glassy carbon electrode modified with MNPs, GQDs and functionalized CNTs (Fe_3O_4-GQD/f-CNT/GCE). Fe_3O_4 nanoparticles were synthesized by co-precipitation method in the presence of GQDs. TEM, SEM, XRD and FT–IR were used to characterize the Fe_3O_4-GQD nanocomposite. All the measurements were done in phosphate buffer solution 0.1 M (pH 7.0) and the oxidation peak was observed at 0.75 V. Voltammetric peak currents showed a linear response for progesterone concentration in the range of 10 to 500 nM and the detection limit of 3.107 nM (S/N=3). The proposed electrode provides wide potential applications to determine progesterone in clinical and pharmaceutical analysis.

Keywords: Carbon nanotubes; Graphene quantum dots; Magnetic nanoparticles.

References:

[1] F.H. Cincotto, F.C. Moraes, S.A.S. Machado, *Chem. Eur. J.* 20 (2014) 4746–4753.
[2] M. Arvand, M. Hassannezhad, *Mater. Sci. Eng. C* 36 (2014) 160–167.
[3] J. Hou, F. Bei, M. Wang, S. Ai, *J. Appl. Electrochem.* 43 (2013) 689–696.

High sensitive voltammetric sensor based on graphene modified carbon paste electrode for determination of cefotaxime

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Cefotaxime belongs to semisynthetic cephalosporin antibiotics and is widely used to treat bacterial infections, mostly respiratory and urinary infections, because it is active against many bacteria [1]. In this work, a simple and sensitive sensor based on carbon paste electrode (CPE) modified by graphene was developed for the electrochemical determination of cefotaxime. Graphite oxide was synthesized from graphite by the Hummers method [2]. Graphene was prepared according to the literature [3]. The proposed sensor was characterized with scanning electron microscopy (SEM) and electrochemical impedance spectroscopy (EIS). The electrooxidation of cefotaxime was studied on graphene modified carbon paste electrode using cyclic voltammetry, chronoamperometry and differential pulse voltammetry as diagnostic techniques. The oxidation peak current of cefotaxime increased significantly at grapheme modified carbon paste electrode compared with bare carbon paste electrode, indicating that graphene possessed electrocatalytic activity towards cefotaxime. Under optimized conditions, the modified electrode exhibited a linear response over the concentration range of 0.001-10 µM cefotaxime, with a detection limit of 0.3 nM. Also, the applicability of the method to the direct assays of the pharmaceutical and biological fluid real samples was investigated.

Keywords: cefotaxime; graphene; Differential pulse voltammetry (DPV); Modified carbon paste electrode

References:

[1] P. Gehanno, I. Boucot, D. Chiche, P. Berche, Med. Mal. Infect 21 (1991) 61.
[2] N. Kovtyukhova, P. Ollivier, B. Martin, T. Mallouk, S. Chizhik, E. Buzaneva, A. Gorchinskiy, Chemistry of Materials 11(1999) 771.
[3] C. Shan, H. Yang, J. Song, D. Han, A. Iyaska, L. Niu, Analytical chemistry 81 (2009) 2378.

Development of ultrasound assisted mixed hemimicelles magnetic solid phase extraction followed by high performance liquid chromatography-UV-Vis detection for quantification of atorvastatin in biological samples

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A new method based on the combination of ultrasound assisted magnetic solid phase extraction (UAMSPE) [1] and high performance liquid chromatography-UV-Vis (HPLC-UV-Vis) was developed for isolation and preconcentration of atorvastatin (AT) [2] form urine, plasma and water samples using dodecyl sulfate coated Fe_3O_4 nanoparticles (NPs) as a sorbent [3]. The unique properties of Fe_3O_4 NPs including high surface area and strong magnetism were utilized effectively in the MSPE process. The prepared magnetic nanaoparticles was characterized by scanning electron microscopy and X-ray diffraction. Effect of different parameters influencing the extraction efficiency including pH, the amount of Fe_3O_4 nanoparticles, the amount of SDS, extraction time, desorption solvent, desorption time and solvent volume were optimized. Additionally, the effect of sample volume on percent recovery of AT were studied. Under optimized condition, the method was successfully applied to the extraction of atorvastatine from water samples and absolute recovery of 99.8 %, detection limit of 0.1 ng L^{-1} and a relative standard deviation of 6.8% were obtained. The method linear response was over a range of 0.5–60 μg L^{-1} with $R^2 = 0.9961$. The relative recoveries in different biological matrices were investigated and values of 89.3 to 109.5 % were obtained.

Keywords: Magnetic solid phase extraction; mixed hemimicelles; magnetite nanoparticles; atorvastatin.

References:

[1] K. Aguilar-Arteaga, J. A. Rodriguez, E. Barrado, Anal. Chim. Acta 674 (2010) 157.

[2] L. Sun, L. Chen, X. Sun, X. Du, Y. Yue, D. He, H. Xu, Q. Zeng, H. Wang, L. Ding Chemosphere 77 (2009) 1306.

[3] D.M. Black, R.G. Bakker-Arkema, J.W. Nawrocki, Arch. Intern. Med. 158 (1998) 577.

A high sensitive method for electrochemical determination of ultra-trace levels of molybdenum in food samples using $Ni_{0.5}Zn_{0.5}Fe_2O_4$ nanocomposite modified carbon paste electrode

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A new chemically modified carbon paste electrode (CPE) was constructed and used for rapid, simple, accurate, highly sensitive, and selective determination of Mo (VI) using differential pulse voltammetry. Molybdenum is an essential trace element for both animals and plants. It has an important role in enzymatic redox reactions. . Because of the low concentration of these metals in food and biological samples, the development of new methods for quantifying trace metals is required and challenged. In some common procedures for the determination of low concentrations of heavy metals a pre-concentration step is needed before performing determination. nanoparticles due to high surface to valume ratio have many sites that used for preconcentration of analytes. In this study nanoparticle of $Ni_{0.5}Zn_{0.5}Fe_2O_4$ for The modified electrode was used. nanoparticle of $Ni_{0.5}Zn_{0.5}Fe_2O_4$ prepared according to the chemical co-precipitation route. The SEM image, XRD pattern and EDS spectrum showed that the $Ni_{0.5}Zn_{0.5}Fe_2O_4$ nanocomposites, synthesized. The synthesized nanocomposite contain Fe, Ni, Zn and O elements and The crystallite size was obtained around 3.5 nm .The electrode was prepared using magnetic nickel zinc ferrite nanocomposite ($Ni_{0.5}Zn_{0.5}Fe_2O_4$), as the modifier, in CPE. The cation Mo (VI) was determined after preconcentration at the surface of the modified electrode at -0.7 V vs. Ag/AgCl. Under the optimal conditions, the linear dynamic range and limit of detection was 0.005-1.00 and 0.003 µg/mL, respectively. The effects of different cations and anions on the determination of Mo (VI) was investigated. The results indicated that the electrode is highly selective. Furthermore, the present method was applied to the determination of Mo (VI) in several plant foodstuff samples with satisfactory results.

Keywords: Carbon paste modified electrode, Magnetic nickel zinc ferrite nanocomposite, determination of Mo (VI) ion, Electrochemical, Food Samples

High sensitive voltammetric sensor based on multiwalled carbon nanotubes modified carbon paste electrode for determination of anticancer drug idarubicin

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Anthracyclines were originally isolated from a pigment producing Streptomyces and are among the most widely used anticancer agents. Idarubicin is an anthracycline, which exerts antitumour activity in several solid tumours and hematological malignancies [1]. Idarubicin, a synthetic analogue of daunorubicin, acts by intercalating between DNA base pairs and inhibiting topoisomerase II. Additionally, it induces free oxygen radicals leading to destruction of DNA and cell membrane [2, 3]. In this research, a carbon paste electrode modified with Multiwalled Carbon Nanotubes (MWCNTs) was prepared and used for study and low level determination of idarubicin using cyclic voltammetry (CV) and differential pulse voltammetry (DPV). Compared with the unmodified carbon paste electrode, the modified electrode facilitated the electron transfer of idarubicin, since it notably increased the oxidation peak current of drug. Also, the oxidation peak potential shifts towards less positive value when the bare electrode is modified with MWCNTs as a modifier. The electronic transfer property of the MWCNTs carbon paste electrode was characterized by electrochemical impedance spectroscopy (EIS). Also, morphology of the electrode was characterized by scanning electron microscopy (SEM). Under optimized conditions, the modified electrode exhibited a linear response over the concentration range of 0.005-1 µM idarubicin, with a detection limit of 1.5 nM. Also, the applicability of the method to the direct assays of the pharmaceutical and biological fluid real samples was investigated.

Keywords: Multiwalled Carbon Nanotubes (MWCNTs); Differential pulse voltammetry (DPV); Modified carbon paste electrode; Idarubicin

References:

[1] D. J. Booser, G. N. Hortobagy, Drugs 47 (1994) 223.

[2] G. Minotti, P. Menna, E. Salvatorelli, G. Cairo, L. Gianni, Pharmacol. Rev 56 (2004) 185.

A DNA biosensor based on chitosan-TiO_2 nano composite for the electrochemical determination of paracetamol in biological samples

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Paracetamol, with the chemical name of N-acetyl-p-aminophenol, is a widely used analgesic pain reliever and fever reducer [1]. It is considered to be safe when administered at recommended dosages; however, it can cause hepatotoxicity at higher doses [2]. For the determination of paracetamol, we used a carbon paste electrode modified with chitosan-TiO_2 nano composite covered with DNA (working electrode). DNA immobilization was carried out in 0.50 M acetate buffer with pH=4.8 containing 10 mg/L DNA under 0.50 V potential for 400 s. The working electrode was rinsed and then immersed in 0.30 M phosphate buffer (pH 3.0) containing paracetamol. Differential pulse voltammogram was recorded using pulse amplitude of 0.05 V and scan rate of 25 mV/s. A peak current related to the concentration of paracetamol at about 550 mV was taken as analytical signal.

The effects of different experimental parameters on the oxidation current of paracetamol were studied and optimized. The electrochemical signal was found to be linear in the concentration range of 0.50-35.0 µM and 35.0-300.0 µM with a detection limit of 0.14 µM. In addition, the values of RSD% for the determination of paracetamol at 18 µM and 150 µM were calculated to be 2.2% and 1.3%, respectively (n=5). Accuracy of the proposed technique was evaluated by the determination of paracetamol in a 325-mg paracetamol tablet. The resulted recoveries were satisfactory. A serum sample was also analyzed before and after spiking. The obtained results indicated the applicability of the method for real samples.

Keywords: Paracetamol; DNA biosensor; nano composite; Voltammetry

References:

[1] R.V. Aghababian, *Essentials of Emergency Medicine*, Jones and Bartlett Publishers, Massachusetts, 2010.

[2] L.P. James, P.R. Mayeux, J.A. Hinson, Drug Metab. Dispos 31 (2003) 1499.

Construction of an electrochemical sensor for determination of anticancer drug dacarbazine using multiwalled carbon nanotubes modified carbon paste electrode and its application in pharmaceutical samples

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Dacarbazine (DTIC, 5-(3,3-dimethyl-l-triazeno)-imidazole-4-carboxamide) has for a long time been used as an antitumor agent. The single-agent DTIC remains the standard chemotherapy [1]. No multiagent chemotherapy has yet proved superior to single-agent DTIC chemotherapy in phase III clinical trials [1–3]. In this work, a carbon paste electrode modified with Multiwalled Carbon Nanotubes (MWCNTs) was prepared and used for study and low level determination of dacarbazine using cyclic voltammetry (CV) and differential pulse voltammetry (DPV). Compared with the unmodified carbon paste electrode, the modified electrode facilitated the electron transfer of dacarbazine, since it notably increased the oxidation peak current of drug. The electronic transfer property of the MWCNTs carbon paste electrode was characterized by electrochemical impedance spectroscopy (EIS). Also, morphology of the electrode was characterized by scanning electron microscopy (SEM). Under optimized conditions, the modified electrode exhibited a linear response over the concentration range of 0.01-5.1 µM dacarbazine, with a detection limit of 3 nM. Also, the applicability of the method to the direct assay of the pharmaceutical real sample was investigated.

Keywords Dacarbazine; Multiwalled Carbon Nanotubes (MWCNTs); Differential pulse voltammetry (DPV); Modified carbon paste electrode

References:

[1] L. Serrone, M. Zeuli, F. Sega, F. Cognetti, J. Exp. Clin. Cancer Res.: CR 19 (2000) 21–34.

[2] M.R. Middleton, P. Lorigan, J. Owen, L. Ashcroft, S. Lee, P. Harper, N. Thatcher, Br. J. Cancer 82 (2000) 1158–1162.

[3] U. Keilholz, C.J. Punt, M. Gore, W. Kruit, P. Patel, D. Lienard, J. Thomas, T.M. Proebstle, A. Schmittel, D. Schadendorf, J. Clin. Oncol. 23 (2005) 6747–6755.

electro-oxidation mechanism of buspirone and its sensitive voltammetric determination in blood serum and urine samples using a boehmite nanoparticles modified carbon paste electrode

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The electrochemical behavior of buspirone at a new boehmite nanoparticles modified carbon paste electrode in aqueous solution was studied in details by applying the cyclic voltammetric method. Two probable mechanisms of buspirone oxidation depending on pH are suggested in the pH range of 5.0 to 8.0 and pH > 8.0. In the pH range of 5.0 to 8.0, the nitrogen present nearby the heteroaromatic ring underwent a one-electron oxidation to form a free radical cation and in pH > 8.0 the oxidation of buspirone takes place in the nitrogen present nearby the aliphatic chain. The modified electrode exhibited excellent stability, reproducibility, validation and robustness for the electrochemical detection of buspirone. Under optimized experimental conditions, the peak current showed a linear dependence to buspirone concentration in the range of 0.126 – 27.80 μg mL^{-1} (0.3 – 66 μM) with a detection limit of 0.06 μg mL^{-1} by differential pulse Voltammetric method. The effect of interfering compounds usually found in pharmaceuticals and biological samples was examined at the modified carbon paste electrode. Finally, this method was used for determination of buspirone in human serum and urine samples with satisfactory results.

Keywords Boehmite; Buspirone; Carbon paste electrode; Voltammetry

References:

[1] G. Pavlaković, J. Tigges, T.A. Crozier, BMC Pharmacology and Toxicology, 9 (2009) 12.

Partial Least Squares-assisted simultaneous voltammetric determination of Rosuvastatin, Simvastatin, Atorvastatin and Clopidogrel

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For the first time, the partial least squares (PLS) modeling was constructed for the multivariate calibration of the linear sweep voltammetric (LSV) data for the simultaneous determination of Rosuvastatin, Simvastatin, Atorvastatin and Clopidogrel at a glassy carbon electrode. All factors affecting on the sensitivity were optimized and the linear dynamic range for determination of Rosuvastatin, Simvastatin, Atorvastatin and Clopidogrel were found. The simultaneous determination of mixtures of these drugs by using LSV method is a difficult problem, due to their interferences. The compositions of the calibration mixtures were selected according to a simplex lattice design (SLD) and validated with an external set of analytes' mixtures. The effects of pre-processing techniques such as genetic algorithm (GA) and orthogonal signal correction (OSC) on the predictive ability of the mentioned multivariate calibration model (PLS) were examined. The proposed method was recommended to simultaneously assay the concentrations of Rosuvastatin, Simvastatin, Atorvastatin and Clopidogrel in human serum sample.

Keywords Atorvastatin; Clopidogrel; Rosuvastatin; Simvastatin; Simultaneous determination; PLS

High sensitive insulin sensor based on CHN modified carbon-ceramic electrode

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Because of the central role of insulin in diabetes, development of efficient analytical methodologies for direct detection of it in blood is one of the clinical exigencies for diagnosis of diabetes [1]. In this context, in the present study we describe the preparation and electrocatalytic activity of cobalt hydroxide nano-particles (CHN) electro-deposited on the surface of highly porous carbon-ceramic electrode (CCE) for insulin detection. CHN were prepared onto a carbon-ceramic electrode (CHN|CCE) using cyclic voltammetry (CV) technique. The modified electrode was characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM). The results showed that CHN with a single-layer structure were uniformly electrodeposited on the surface of CCE. The electrocatalytic activity of the modified electrode toward the oxidation of insulin was studied by CV. CHN|CCE was also used in a homemade flow injection analysis (FIA) system for insulin determination. The limit of detection (S/N= 3) and sensitivity were found to be 0.11 nM and 11.8 nA/nM, respectively. Moreover, the sensor was used to detection of insulin in human serum samples. This sensor showed attractive properties such as high stability, reproducibility and high selectivity.

Keywords Flow-injection analysis; Insulin sensor; Cobalt hydroxide

Reference

[1] C. Guo, C. Chen, Z. Luo, L. Chen, Anal. Methods, 4 (2012) 1377-1382.

Increased photoresponsive efficiency of graphene-modified ZnCdS nanocomposite under solar irradiation

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Photoelectrochemical (PEC) hydrogen production from photo-induced water splitting based on nanostructured materials has received increasing attention because of its potential in simultaneously solving energy and environmental problems. In this research, photoresponsive behavior of pure $Zn_{0.8}Cd_{0.2}S$ and graphene-modified $Zn_{0.8}Cd_{0.2}S$ nanocomposites have been reported under simulated solar irradiation. At first, for the study of PEC activity of RGO/$Zn_{0.8}Cd_{0.2}S$ nanocomposite, the electrophoretic method was applied to deposit graphene oxide (GRO) nanosheets on a titanium sheet (Ti) as a suitable substrate. Then, Ti/RGO/$Zn_{0.8}Cd_{0.2}S$ and Ti/$Zn_{0.8}Cd_{0.2}S$ photoanodes prepared by a facile co-precipitation hydrothermal strategy using thiourea as the S source. Structural and morphological properties of the samples have been investigated by XRD and SEM techniques. PEC measurements including choronoamperometry, choronopotentiometry and linear-sweep-voltametry (LSV) were carried out using a three-electrode electrochemical cell with Ti/RGO/$Zn_{0.8}Cd_{0.2}S$ or Ti/$Zn_{0.8}Cd_{0.2}S$ photoanode as a working electrode, a Pt plate as a counter electrode, and a Ag/AgCl (KCl 3.0 M) as a reference electrode. A high-intensity Xe lamp with UV filter was used as the source of the visible light irradiation. During all measurements, 0.1 M Na_2S was used as electrolyte. The transient photoresponse of the photoanodes were recorded under the applied bias potential of 0V with switching-on and -off model. The results showed the photocurrent density of Ti/RGO/$Zn_{0.8}Cd_{0.2}S$ is much higher (7 times) than Ti/$Zn_{0.8}Cd_{0.2}S$. This work creates a green and simple way for using RGO as a support to enhance the PEC H_2-production activity of $Zn_{0.8}Cd_{0.2}S$.

Keywords: Hydrogen production, Photoelectrochemical, RGO/$Zn_{0.8}Cd_{0.2}S$

References:

[1] Q. Li, H.Meng, P. Zhou, Y. Zheng, J. Wang, J. Yu, J.R. Gong, *ACS Catal.*3 (2013) 882.
[2] J. Zhang , W. Zhao, Y. Xu , H. Xu , B. Zhang, *Hydrogen Energy* 39(2014)702.

A voltammetric sensor based on $Fe_3O_4@SiO_2$/Go ionic liquid carbon past electrode for determination of L-Tyrosine

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L-Tyrosine (Tyr) is an important amino acid which is considered nonessential because the human body can make it from another amino acid called phenylalanine. It is a vital precursor for neurotransmitters and hormone in mammalian animals such as dopamine and norepinephrine.The absence of Tyr could cause albinism and alkaptonuria, while a high Tyr concentration in culture medium results in increased sister chromatid exchange[1]. Therefore, detecting and determining of Tyr in samples are of great importance for pharmaceutical, clinical, and food industries . Various methods have been developed to analysis of Tyr including chromatography, flow-injection chemiluminescence and electrolysis. Among the methods mentioned above, electrochemical method presents distinctive advantages, such as quick response, low detection limit, low cost, simple operation and the absence of pretreatment. In recent days the nanostructure base ionic liquid modified carbon paste electrodes very well as an electrochemical sensor for biological and pharmaceutical compound analysis. In this paper we describe the modification of a carbon paste electrode (CPE) with a new type of nanocomposite based on graphene oxide decorated with magnetic core–shell $Fe_3O_4@SiO_2$ nanoparticles ($Fe_3O_4@SiO_2$ /Go) and an ionic liquid (IL) for the determination of L-tyrosine. cyclic voltammetry, differential pulse voltammetry and chronoamperometry analysis demonstrated that the modified electrode is responsive towards the target molecule. The detection of L-Tyrosine in the range of 5.0μMto 1000.oμM at ionic liquids/nanocomposite carbon paste electrode was monitored by DPV with a limit of detection of 2.0μM. the modified electrode was used as a selective, simple and precise new electrochemical sensor for the determination of L-Tyrosine in the real samples, such as pharmaceutical and biological fluids.

Keywords: carbon paste electrode; Ionic liquids; L-Tyrosine;nanocomposite

Reference:

[1] M. Taei, F. Hasanpour, H. Salavati, S.H. Banitaba, andF. Kazemi, Mater. Sci. Engin. C 59 (2016) 120.

Determination trace level of trazodone with electrochemical sensore base on nanocomposite Tio2-CMWCNTs/GC

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Electrochemical sensor for the detection of trazodone was proposed base on Titanium oxide(Tio2)-Multiwall carbon nanotube (MWCNT) nanocomposite on glassy carbon (GC) electrode for the TRZ. X-ray diffractometry (XRD), Scaning electron microscopy(SEM) and electrochemical impedance Spectroscopy (EIS) were Used to confirm the successful stepwise assembly procedure of the sensore. The elecctrochemicaly behaviors of the sensore were also investigated cyclic voltammetry (CV) and differential pulse voltammetry (DPSV). The result showed that Tio2-MWCNT nanocomposite exibite a remarkable electrochemicaly activity for the oxidation in Epa= 0.71V. Under optimal conditions, the sensor provides two linear responses in the range of 6–100 nM and 100- 1000 nM for TRZ with a detection limit of 5 nM through differential pulse stripping voltammetry (DPSV) measurements were carried out in phosphate buffer solution (pH 7.0, 0.1). Furthermore, the selectivity of the proposed sensor in the presence of interferences the response of the sensor was exhibited a good sensitivity, stability and pleasant reproducibility, and it was applied for the determination of ACV in real sample, with satisfactory results.

Keywords: Trazodone ; Titanium oxide nanoparticles; multi-walled carbone nanotubes; Differential pulse stripping voltammetry.

References:

[1] F. Arduini, Electrochem. Commun. 12 (2010) 346.
[2] M.Gholivand, M, Shamsipur, N.Amini, ElectrochemicalActa 123(2014) 569.
[3] M. Mazloum-Ardakani, H. Rajabi, H. Beitollahi, B.F.Mirjalili, A akbari, N.Taghvinia, Electrochem. Sci., 5 (2010) 147.

Electrical impedance measurementsof electromembrane extraction systems using voltage pulse excitation

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In the present work, for the first time electrical impedance wascalculated for electromembrane extraction systems (EME).To electricalimpedance measurement, EME system have considered asa Randles cell. Parameters of Randles cell impedanceincluding Solution resistance (Rs), membrane resistance (Rm) and Double-layer Capacitance (Cp) were evaluated during the extraction using sodium diclofenac as the model analyte. The obtained results were plotted *vs.* time in the different experimental conditions including applied potentials, pH of the acceptor and donor phases, and agitationspeeds. According to the diagrams,the balance point can be obtained. In the optimum condition,the balance point wasapproximately at the time of 20 minute. The results showed that beforethe balanced system, Rm, and Cp were decreased while Rs is increased. After the balance point, all three parameters were nearly constant along with fluctuation. This result contrasts relatively with the previous researches.

Keywords: electrical impedance measurement; Randles cell; Electromembrane extraction; pulse excitation;

Speciation and simultaneous electrochemical determination of Catechol, Hydroquinone and Resorcinol by polymer film of 5-amino-1,3,4-thiadiazole-2-thiolmodifiedelectrode

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Hydroquinone (HQ), Catechol (CT) and resorcinol (RS) are three most important isomers of phenolic materials which are announced as environmental contaminant by the European Union and the US Environmental Protection Agency. CT in cigarette smoke is also found and researches demonstrate that it induces damage to DNA, so it can cause cancer [1].Hence simultaneous determination of HQ, CT and RS is very important for environmental analysis. A highly sensitive sensor for speciation and simultaneous determination of HQ, CT and RS with polymer film of 5-amino-1,3,4-thiadiazole-2-thiol(ATT) modified Glassy Carbon (GC) electrode is reported.Ultrathin film of ATT electropolymerizedon GC electrode by 15 successive potential sweeps between −0.2 and 1.7V at a scan rate of 50mVs^{-1} in 1mM of ATT containing0.1M H_2SO_4 [2]. Due to the excellent catalytic activity of ATT the simultaneous determination of HQ, CT and RS with three well-defined peaks were achieved at the p-ATT modified electrode. Comparing with those achieved at the bare GC, the oxidation currents of HQ, CT and RS increased remarkably. The catalytic peak current obtained, was linearly dependent on the HQ, CT and RS concentrations in the range of 0.66 – 266.6 µM. The detection limits for HQ, CT and RS were 0.08µM. The diffusion coefficient for the oxidation of HQ, CT and RS at the modified electrode was calculated as 4.4×10^{-5}, 4.42×10^{-5} and 3.06×10^{-5} cm^2 s^{-1}, respectively.The presented sensor was successfully applied for the simultaneous determination of HQ, CT and RS in water samples.

Keywords: Electrochemical sensor; Speciation and simultaneous determination; polymer

References:

[1] H.Yina, Q. Zhang, Y.Zhoud,Q. Ma,*ElectrochimicaActa*,**2011,**56, 2748–2753.
[2] P. Kalimuthu, S.A. John, Electrochem. Commun.**2009**, 11, 367.

Different Polymer content in preparing thin film based dopamine sensor

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Dopamine (DA), as one of the important neurotransmitters, plays a significant role in the function of human metabolism, cardiovascular, central nervous, renal, and hormonal systems. Deficiency of DA may cause several diseases and neurological disorders such as Schizophrenia, Huntington's disease, and Parkinson's disease [1]. It is known that the oxidation peaks of DA and ascorbic acid (AA) at a bare electrode are at nearly the same potential, which results in overlapped voltammetric responses making their discrimination greatly difficult. In this study, zinc oxide/polyvinyl alcohol nanostructured hybrid films which are different in polymer content were prepared by electrochemical deposition method on the F-doped SnO_2 conductive glass (FTO/ZnO/PVA). PVA as a polymeric organic additive can interact with ZnO upon the electrodeposition process and strongly influence on the ZnO growth to form a mixed film made of ZnO crystals embedded in a polymer matrix. In addition, PVA incorporates other advantageous to the sensing transducer surface by affording electrical conductivity to the ZnO-Polymer hybrid film [2, 3]. Electrochemical studies using cyclic voltammetry (CV) and differential pulse voltammetry (DPV) were done to determine dopamine. The prepared films at 8.0 gL^{-1} PVA concentration showed desired results in omitting AA oxidation peak and also improving DA peak current.

Keywords: Differential pulse voltammetry; Dopamine sensor; Electrodeposition; Thin film

References:

[1] Michael L. A. V. Heien, Amina S. Khan, Jennifer L. Ariansen, Joseph F. Cheer, Paul E. M. Phillips, Kate M. Wassum, and R. Mark Wightman, Proc. Natl. Acad. Sci. USA 102 (2005) 10023.
[2] Massafera MP, Torresi S. I. C. d. Sens. Actuators B.137 (2009) 476.
[3] R. Rahmanian, S.A. Mozaffari, Sens. Actuators B.207 (2015) 772.

Using indium tin oxide thin film electrode for voltammetric detection of dopamine in the presence of ascorbic acid

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Dopamine (DA), as one of the important neurotransmitter, plays a significant role in the function of the central nervous, renal and hormonal systems. The abnormal levels of DA may result in several diseases and neurological disorders such as schizophrenia, Parkinson’s and Alzheimer’s diseases. Because of its electrochemical activity, dopamine detection attracts tremendous interest in electroanalysis [1-3]. However, there exist some challenges to measure DA under physiological conditions. The primary challenges are the very low levels of DA and the interference of coexisting ascorbic acid (AA) in organisms, which sharing a similar oxidation potential in electrochemical detection. Thus, it is desirable for diagnostic applications to develop a simple and rapid method for the determination of DA with high selectivity and sensitivity [2]. In this study, electrochemical measurements were performed at thin film of In-doped SnO_2 conductive glass (ITO). The electrochemical experiments were carried out using a potentiostat/galvanostat instrument with a conventional three electrode cell system at room temperature. Modified ITO electrode was used as working electrode. A saturated calomel electrode (SCE) and a platinum wire were used as the references and auxiliary electrodes, respectively. Detection of dopamine in the presence of ascorbic acid was done with cyclic voltammetry (CV) and differential pulse voltammetry (DPV). The calibration curve was obtained over the range of 10.0-100.0 µmol/L DA and the detection limit of 1 µmol/L DA was obtained at pH 7.4.

Keywords: Differential pulse voltammetry; Dopamine sensor; Indium thin oxide; Thin film

References

[1] J.-L.Chang, G.-T. Wei, J.-M. Zen, Electrochem. Commun *13 (* 2011) 174.
[2] M. Chen et al., Mater. Sci. Eng., C 31 (2011) 1271.
[3] Q. Liu , X. Zhu, Z. Huo, X. H., Yong Liang, M. Xu, Talanta 97 (2012) 557.

Electrochemical reduction of graphene oxide for sensory application in sensitive voltammetric determination of tinidazole

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Tinidazole is a prominent member of the nitroimidazole antibiotics that is an anti-parasitic drug used against protozoan infections. The electrochemical methodes have attracted an increasing interest for investigation drugs and pharmaceutical samples. The reduced graphene oxide (RGO) acts as a sensing material to modify glassy carbon electrode for the determination of Tinidazole (TNZ). Electrochemical behavior of tinidazole on the modified electrode was investigated by using cyclic voltammetry (CV), linear sweep voltammetry (LSV) and electrochemical impedance spectroscopy (EIS). The surface morphology of the modified electrode was characterized by scanning electron and atomic force microscopy techniques. The RGO electrode exhibited a distinctly higher activity for the electro-oxidation of tinidazole than GO.electrode. The effect of experimental parameters such as the amount of casted graphene oxide, the accumulation time and the pH on the electrochemical oxidation of TNZ were examined. Under optimal conditions, the modified electrode showed a wide linear range toward the oxidation of TNZ in the range of 0.08–100 μM with a detection limit of 24nM. Finally, the prepared electrode was successfully applied for the determination of TNZ in pharmaceutical and clinical samples.

Keywords: Cyclic voltammetry, Graphene oxide, Modified Electrode , Reduced Graphene oxide ,Tinidazole

Photoelectrocatalytic degradation of organic dye pollutant under visible light irradiation

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Advanced oxidation techniques based on photocatalysts have proven to be highly effective for the photodegradation of a wide spectrum of organics [1-3]. Wide studies have been focused on TiO_2 photoanodes for the treatment of water samples [1]. However, TiO_2 generates electron-hole pair under UV irradiation because of its wide band gap. In this work, photoelectrocatalytic (PEC) and photocatalytic (PC) degradation of organic dye has been studied by the fabrication of hematite-based photoanode. The PEC and PC activities of hydrothermally deposited α-Fe_2O_3 (hematite) on Ti sheet were evaluated by the photodegradation of methylene blue (MB) as a model compound. The cleaned Ti foil was vertically placed in an autoclave containing $Fe(NO_3)_3$ and $NaNO_3$ which were then put into an oven at 100 ˚C for 6 h. After the hydrothermal reaction, the resulting photoanode (Ti/Hem) was rinsed with deionized water and dried in air. Finally, Ti/Hem was annealed in a furnace at 500˚C. PEC experiments were carried out using a three-electrode system with Ag/AgCl as reference electrode, a platinum foil as auxiliary electrode, and Ti/Hem as working electrode. The PEC degradation of MB was conducted under visible irradiation, vigorous stirring with a positive 0.5 V bias potential. At a regular time intervals, specified volume of the reaction solution was withdrawn and analyzed using a spectrophotometer. Ti/Hem showed high photodegradation efficiency in PEC degradation of MB under visible light irradiation. This study provides a useful insight into the design and preparation of α-Fe_2O_3 for cost-effective and high efficient PEC applications.

Keywords: Photoelectrocatalysis; Photoanode; Hematite; Methylene blue

References:

[1] Y. Liu, H. Wang, Y. Wang, H. Xu, M. Li, H. Shen, Chem. Commun. 47 (2011) 3790.
[2] W. Liu, X. Quan, Q. Cui, M. Ma, S. Chen, Z.J. Wang, Ecotox. Env. Saf. 71 (2008) 267.
[3] M.N. Chong, B. Jin, C.W.K. Chow, C. Saint, Water Res 44 (2010) 2997.

A Novel Hydrogel-Potato Powder Modified Carbon Paste Electrode as a Biosensor for Determination of Paracetamol

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An electrochemical biosensor based on paraffin/graphite modified with potato powder as a source of polyphenol oxidase and hydrogel as a matrix for immobilization of enzyme was developed and it was used for determination of paracetamol. This enzyme, catalyses the oxidation of paracetamol to n-acetyl-p-benzoquinoneimine. The electrochemical behavior of paracetamol was studied by hydrogel-potato powder carbon paste electrode using cyclic voltammetry (CV). For construction of the electrode, the tissue of potato was fragmented, exposed to air, washed with distilled water to remove the oxidation products from the tissue, and then it was vacuum dried and pulverized to a fine powder. The acrylic based hydrogel was synthesized; afterwards, a novel, simple modified carbon paste electrode with hydrogel was prepared. The chemical and electrical parameters affecting the voltammetric response of the biosensor like potato and hydrogel composition, pH, scan rate, temperature, were optimized. The results obtained by cyclic voltammetry revealed that the hydrogel-potato powder carbon paste electrode shows a higher current response about 4 folds compared to a potato powder carbon paste electrode and about 20 folds compared to a bare carbon paste electrode. The linear calibration range of the biosensor was 25μM to 1.25 mM (R2= 0.995) with a detection limit of 4.0 μM paracetamol. The proposed electrode exhibits a long life time (2 months) and was successfully applied to paracetamol determination in urine samples.

Keywords: Tissue biosensor, Carbon paste, Polyphenol oxidase, Hydrogel

Platinum-Tetramethyl benzidine/Carbon Ionic Liquid Electrode as an Effective Electrocatalyst for Hydrogen Evolution

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Greenhouse gas emission in the atmosphere is one of the major concerns of human society. The renewable energy sources such as solar, wind, hydroelectric power, tidal power, nuclear energy and hydrogen production technologies are good replacements to reduce gas originated pollutions [1]. Hydrogen as a fuel with the highest gravimetric energy density and great compatibility with electrochemical processes could be used in CO_2-free energy conversion processes .There are several ways to produce hydrogen including water electrolysis, photolysis and reforming of gas from biomass and natural gas or any other fossil fuel . Production of hydrogen by water electrolysis is one of the sustainable and greenhouse gas free processes[1].

In this study Platinum-Tetramethyl benzidine/Carbon Ionic Liquid Electrode (Pt-TMB/CILE) was used as a new and efficient electrocatalyst for hydrogen evolution reaction (HER). The Pt-TMB nanohybrid structure is synthesized by a wet chemical route [2]. The nanostructures are characterized by scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS). The electrode is prepared by hand mixing Pt-TMB with graphite as the conducting phase and ionic liquid (IL) as the binder. The activity of electrocatalyst is explored toward HER in acidic solution. The efficiency of the electrode for HER is retained successfully in high concentration of sulfuric acid. Tafel slope of 22.8 $mV.dec^{-1}$ is measured in the acidic solution which shows that the HER follows the Volmer-Tafel mechanism.

Keywords: Pt-TMB, Inorganic-organic nanohybrid, Electrocatalysis, Hydrogen evolution reaction, Carbon ionic liquid electrode.

References:

[1] S. Baranton, C. Coutanceau, Appl. Catal. B Environ. 136-137 (2013) 1.
[2] J. Yang, H. Wang, L. Lu, Y. Wang, W. Shi, H. Zhang, Synth. Met. 158 (2008) 572.

Effect of Carboxymethyl cellulose on the corrosion of Aluminum in aqueous solutions

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Recently Great attention has been paid to the use of polymers as corrosion inhibitors. Polymers form complexes with metal ions through their functional groups and these complexes by blanketing the metal surface occupy a large surface area and protect the metal from corrosive agents present in the solution. Carboxymethyl cellulose (CMC) is an anionic water-soluble polymer which is one of the most widely used cellulose derivatives.

In this work the corrosion behavior of aluminum in solutions containing of CMC at different pH has been studied by using potentiodynamic polarization and electrochemical impedance spectroscopy (EIS). The CMC with Al^{3+} form an insoluble complex at the beginning of the experiments in every pH that this behavior indicates a very high affinity between CMC and aluminum. A pronounced CMC-induced inhibition was observed in pHs below 9 and it has inhibition efficiency (IE%) of 46% but the presence of CMC in solution with pHs above 9 accelerate the corrosion of Aluminum. This was attributed to the isoelectric point (IEP) of aluminium oxide (pH≈9) which seems to be an important factor controlling corrosion inhibition (and adsorption) of polymers with carboxyl groups.

Keywords: Aluminum corrosion; Carboxymethyl cellulose; electrochemical impedance spectroscopy; plarization

References:

[1] C. G. Lopez, S.E.R., R. H. Colby, P. Graham, J. T. Cabral, J. Polymer. Sci., Part B: Polym. Phys 53 (2015) 492.
[2] Umoren, S., The Open Corrosion Journal 2 (2009) 175.
[3] Franco, A.P., et al., Hydrometallurgy 87 (2007) 178.

Determination of Fractal Dimension of Electrodeposited MnO_2 on Pt wire by Cyclic voltammetry and Electrochemical Impedance Spectroscopy

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It has been recently recognized that fractal analysis may be used to describe the surface morphology and complexity of various materials [1]. The degree of complexity can be illustrated by a parameter that called fractal dimension (D_f). if $D_f = 2$ the surface is entirely smooth, while when $D_f = 3$ the surface is entirely rough and amorphous so the roughness of surface increases when D_f rises from 2 to 3. D_f have been characterized by several methods that can be classified as physical, chemical and electrochemical [2]. Electrochemical methods have been more rarely used, cyclic voltammetry and electrochemical impedance spectroscopy (EIS) methods are one of the most useful and reliable methods for the determination of D_f [3].

In this work, the electrodeposition of MnO_2 was performed in a three electrode cell. Pt wire and Ag/AgCl (saturated with KCl) electrode were used as the substrate and auxiliary, and reference electrode respectively. The effect of deposition potential, temperature, time of deposition and Mn^{2+} concentration on the D_f were studied systematically. The concentration of Mn^{2+} and time of deposition have a direct effect on D_f, but applied potential and temperature have a reverse effect on D_f. By increasing the time of deposition, D_f rised from 2.57 to 2.87. In 0.1M $MnSO_4$ solution, temperature rised from 34 to72 ˚C, then D_f decreased to 2.66.

Keywords: Cyclic voltammetry, Electrodeposition, Fractal dimension.

References:

[1] F. Gobal, K. Malek, M.G. Mahjani, M. Jafarian, V. Safarnavadeh, *Synthetic Metals*, (2000), 15_19.

[2] S. Neves, C. Polo Fonseca, *Electrochemistry Communications*, (2001), 36_43.

[3] E. Coletta, M.F. Toney, C.W. Fran, *Applied Polymer Science*, (2015), 1_13.

A highly improved method for sensitive determination of imipramine in pharmaceutical formulations using a modified carbon paste electrode with copper aceyl acetonate

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Electrochemical analytical techniques can easily solve many problems of pharmaceutical interest with a high degree of accuracy, precision, sensitivity, and selectivity employing this approach. In the last decade the need for high sensitivity and selectivity for the analysis of biomolecules has been increasing. The development of modified electrodes is based on this need. Electrodes can easily be modified either by dispersing the modifier with a paste or by physically adsorbing it to the electrode surface. An alternative way of modifying the electrode is by covalently bonding the modifier to the surface or modification by a lipidic substance.

In this paper the voltammetric behaviours of imipramine which is tricyclic antidepressants, were investigated using a carbon paste electrode, modified by the addition of $Cu(acac)_2$, by adsorptive stripping differential pulse voltammetry as a very sensitive analytical method. A modified carbon paste electrode was simply prepared by adding the $Cu(acac)_2$ to the carbon paste. Voltammograms obtained for imipramine with this electrode were compared with those obtained using a normal carbon paste electrode. It was shown that the current density for imipramine increased with modification of the carbon paste electrode. Effect of various parameters such as pH, amount of $Cu(acac)_2$, accumulation potential and accumulation time was explored. Under optimum conditions, the calibration curve of anodic peak current versus imipramine concentration was linear in the range of 0.5-120 µM with a detection limit of 30 nM.

The method was applied to pharmaceutical preparations of imipramine in real samples and can be used for routine quality control analysis of bulk pharmaceutical and pharmaceutical formulations containing imipramine.

Keywords: imipramine, $Cu(acac)_2$, electrochemistry

Development and application of new carbon paste electrode modified with copper aceyl acetonate for amitriptyline determination

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This work presents a voltammetric study using a modified carbon paste electrode for the evaluation of amitriptyline concentration in pharmaceutical preparations and attempts to optimize the analytical conditions.

Amitriptyline (AMT) is a pharmaceutical belonging to the azepine group of compounds, and it is widely used due to its antipsychotic and sedative activity as well as analgesic properties. It controls psychomotor disturbances such as agitation, excitement, hyperkinetic states, and aggression. However, AMT may cause side effects including heart problems. Therefore, it is extremely important to analyze concentration levels of this chemical substance in commercial formulations and biological samples. Some electrochemical methods for determining AMT and other same-class psychotropic drugs have been reported in the literature.[1] Electrochemical methods may be used for this purpose due to their excellent sensitivity, short analysis time, simplicity, and the low costs involved in the implementation of these powerful tools for measuring different analysts.

Herein, adsorptive stripping differential pulse voltammetry as a very sensitive analytical method was used. Effect of various parameters such as pH, amount of $Cu(acac)_2$, accumulation potential and accumulation time was investigated. Amitriptyline, which was electroinactive with the normal carbon paste electrode, became electroactive on the modified electrode. Under optimum conditions, the calibration curve of anodic peak current versus amitriptyline concentration was linear in the range of 0.1-80 µM with a detection limit of 20 nM. Therefore, the developed method also was successfully applied for the AMT determination in real samples of pharmaceutical formulations and can be used for routine quality control analysis of bulk pharmaceutical and pharmaceutical formulations containing AMT.

Keywords: amitriptyline, $Cu(acac)_2$, electrochemistry

References:

[1] A.C. Pereira, A.S. Santos, L.T. Kubota, Quim. Nova 25 (2002) 1012.

Determination of samarium (III) using carbon paste electrode modified with Sm-ion imprinted polymer nanoparticles

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A sensitive samarium electrochemical sensor was successfully constructed for the detection of samarium ion. It is based on a carbon paste electrode modified with samarium (III) imprintd polymer nanoparticles (IIP-NPs). The IIP-NPs were synthesized by precipitatation polymerization of methyl methacrylate (the functional monomer), ethylene glycol dimethacrylate (the crosslinking monomer), 2,2′-azobis isobutyronitrile (the initiator), 5,7-dichloro-8-hydroxy quinoline and 4-vinylprydine (the samarium binding ligands) and samarium ions (the template) in 2-methoxyethanol solution. Imprinted samarium ion was removed from the polymeric matrix using 1 M hydrochloric acid. The electrochemical performance of the imprinted sensor was investigated by cyclic voltammetry. The modified electrode responds to Sm (III) was linear in the 0.05 nM to 1 nM (with sensitivity of 197.54 nA/nM) and 0.005 µM to 1 µM (with sensitivity of 27.690 µA/µM) concentration ranges. The limit of detection (LOD) of the sensor was 38 pM (at S/N =3). The sensor was successfully applied to the trace determination of Sm(III) in spiked environmental water samples.

Keywords: Samarium, Ion-imprinted polymer, Modified carbon paste electrode, Cyclic voltammetry

Ref erence:

[1] M. K. Bojdi, M. Behbahani, A. Sahragard, B. G. Amin, A. Fakhari, A. Bagheri, *Electrochimica Acta* 147 (**2014)** 108.

Novel electrochemical method for simple and sensitive simultaneous determination of methotrexate and doxorubicin in human serum based on modified carbon paste electrode

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Doxorubicin and methotrexate are two important anticancer drugs, which are widely used in medical practice. As a kind of anthracyclinic compound, doxorubicin can produce regression in disseminated neoplastic conditions such as leukemia, neuroblastoma, sarcomas and carcinoma [1].

An electrochemical nanosensor was adopted through modified carbon paste electrode by graphene nanosheets as an analytical platform for the simple and sensitive simultaneous determination of methotrexate and doxorubicin. This modified electrode was then used for the determination of methotrexate and doxorubicin in pure form and dosage forms using Differential Pulse Voltammetry (DPV). In optimizing step, main experimental parameters such type and concentration of modifier, type and concentration of buffer, pH and salt effect were optimized. Under optimized experimental conditions, the assay was linear in the ranges from 2.75 to 8800 µM and 0.4 to 100.8 µM for methotrexate and doxorubicin determination, respectively. The detection limit was 0.61and 0.15 µM using $3s_b/m$ for methoteraxate and doxorubicin and repeatability of the nanosensor was estimated at 5.5 of methoteraxate and 6.3 µM of doxorubicin resulted in RSD of 4.1 and 8.8 % (n=5) , respectively . The results showed this proposal is simple, cost effective and also has a good sensitivity for electrochemical simultaneous detection of methotrexate and doxorubicin in biological samples.

Keywords: electrochemical sensor, modified carbon past electrode, methotrexate, doxorubicin, geraphen nanosheet.

References:

[1] J.W. Lown, Chem. Soc. Rev. 1993, 22, 165..

Design and Fabrication of Screen-Print Potentiometric NOx Gas Sensor Based on Cathodic Deposition of Nano-structured Polypyrrole

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The coating of nanostructured polypyrrole (PPy) on Cu screen-printed was performed by cathodic electropolymerization of pyrrole in the presence of nitrate ions as dopant anion in aqueous solution by potentiostatic method. The concentration of nitrate ion, applied potential, presence of a transition metal cation as catalyst and time of synthesis were investigated as effective parameters in electrosynthesis. The morphology of the conducting films was examined by field emission scanning electron microscope (FESEM). The PPy film applied as nitrate potentiometric sensor in aqueous solution and potentiometric NOx sensor in gas phase.

The screen-printed sensor responded to nitrate ions in buffered media pH = 7 with nernstian slope of -55.5 ± 2.5 mv per decade within the concentration range 3×10^{-4} - 3×10^{-2} M nitrate ion and good reproducibility (RSD ≤ 5%). We describe the design and fabrication of miniaturized thin-film Ag/AgCl reference electrode that has been integrated with proposed potentiometric nitrate sensor. The proposed sensor can be applied for nitrate analysis in one drop aqueous sample solution. Also this sensor can be used for direct potentiometric analysis of NOx in gas phase by applying 10 microliters of ionic liquid on surface of screen-printed electrodes. This sensor has a detection limit of 108 $mg.L^{-1}$ for NOx in gaseous atmosphere.

Keywords Cathodic Electropolymerization; Nanostructure Conducting Polymer; Screen-Printed Electrodes; NOx Gas Sensor

Determination of doxorubicin in human plasma by carbon paste electrode modified with graphene nanosheet

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Doxorubicin is important anticancer drugs, which is widely used in medical practice. As a kind of anthracyclinic compound, doxorubicin can produce regression in disseminated neoplastic conditions such as leukemia, neuroblastoma, sarcomas and carcinoma[1].

In the present study, a fast, low cost and sensitive method for the electrochemical determination of doxorubicin was proposed based on stripping method. An electrochemical sensor was fabricated using carbon paste electrode modified with graphene nanosheet. A considerable increase was observed in the oxidation signal of doxorubicin at carbon past electrode modified with graphen nanosheet compared with unmodified electrode. After optimizing main experimental parameters such as type of buffer, pH, accumulation time and etc. Two linear reng dependences of the anodic peak current of doxorubicin on its concentration were observed in the range of 0.4-10.08 and 10.08- 100.8µM with detection limit of 9.3×10^{-8} M. The relative standard deviations for 6.3 and 19.8µM Were 5 and 1.6% (n=5), respectively. The proposed sensor was successfully applied to the analysis of doxorubicin in the human plasma.

Keywords: electrochemical sensor; modified carbon past electrod; doxorubicin; geraphen nanosheet

References:

[1] J.W. Lown, Chem. Soc. Rev 22 (1993) 165.

A new genosensor for ALS disease based on Samarium/graphene nano-composite using FFT-SW Voltammetry

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We have made a DNA-hybridization electrochemical biosensor by 20-mer oligonucleotide and it's complementary, non-complementary and mismatches strains. Selected DNA was related to SOD1 Gene witch encodes the Cu-Zn superoxide dismutase (SOD1) enzyme were associated with around 20% of familial *Amyotrophic lateral sclerosis* (ALS). Mutations (over 150 identified to date) in SOD1 have been linked to familial ALS. Usage of Polyaniline and Samarium Graphene nanocomposite for modifying surface of GC electrode provides a new platform for immobilization of ssDNA without any modification on DNA. $[Ru(bpy)_3]^{2+/3+}$ was employed as electrochemical probe that its different interactions with ssDNA and dsDNA can produced distinguished currents. Fast Fourier Transform square wave Voltammetry signals was used as a sensitive detection methods. Our experiment has shown a good linear dynamic range between $1x10^{-8}$ mol L-1 to $1x10^{-13}$ mol L-1. (RSD 3.5%).

The proposed biosensor was successfully applied for the determination of the SOD1 Gene in plasma sample (RSD% 5).

Comparison of various nano-materials effects on the behavior of modified carbon paste electrode with hydroquinone derivative and nano materials for simultaneous determination of hydrazine and phenol

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In the recent years, various nanomaterials have been paid attention due to their unique electrical, optical, catalytic and magnetic properties compared with those of bulk materials [1-3]. In the present paper, construction of a carbon pate electrode modified with hydroquinone derivative (CIT) and different nano materials (nano particles based on silica and carbon) has been reported. A pair of well-defined redox peaks of CIT was obtained at the modified electrode by direct electron transfer between CIT and CPE. Under optimum conditions, some kinetic parameters such as electron transfer coefficient (**α**) and heterogeneous rate constant (**k**) for hydrazine were also determined using electrochemical techniques. Voltammetric peak currents showed a linear response for HZ in the range of 2.2–100.0 µM and 100.0–800.0 µM with a detection limit (based on $3S_b/m$) of 0.5 µM. The main purpose of this paper was the investigation of silica and carbon nano materials effects on the behavior of the designed electrode for hydrazine analysis. The obtained results revealed that using nano materials of SiO_2, RGO, CNT and RGO-CNT (MIX) has a key role in reducing oxidative over voltage and intensively increasing in the peak current of HZ. The novel electrochemical sensor revealed suitable electrocatalytic activities toward the oxidation of hydrazine (HZ) and phenol (PH), simultaneously. The high sensitive, stable, and reproducible electrochemical sensor was applied in the real samples of waste water for determination of HZ successfully, too.

Keywords: Carbon paste electrode; Hydrazine; Hydroquinone derivative; Nanomaterials

References:

[1] H.X. Li, Z.F. Bian, J. Zhu, D.Q. Zhang, G.S. Li, Y.N. Huo, H. Li, Y.F. Lu, J. Am. Chem. Soc. 129 (2007) 8406.
[2] Q. Kuang, C.S. Lao, Z.L. Wang, Z.X. Xie, L.S. Zheng, J. Am. Chem. Soc. 129 (2007) 6070.

Electrochemical determination of codeine in pharmaceutical formulations and human urine using a graphene/gold nanoparticle modified glassy carbon electrode

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A graphene/gold nanoparticle modified glassy carbon electrode was used as a sensitive and selective electrochemical sensor for the determination of codeine by the use of differential pulse voltammetry.

Codeine provided a single well-defined oxidation peak at +1.0 V vs. Ag/AgCl in Britton-Robinson buffer solution at pH 7.0. Using the optimal differential pulse voltammetric conditions , the detection limit of 0.08 µM, the linear response of peak current on codeine concentration in the range from 0.1 to 40 µM (R2 = 0.998, n = 6) and relative standard deviation of 0.7% at 10 µM concentration level (n = 9) were achieved with electrode surface modification. The influence of potential interfering agents on the current response was also studied and the results indicated that the proposed method was sufficiently selective. The method was successfully applied in the determination of codeine in real samples including pharmaceutical tablets and human urine with results similar to those declared by manufacturer and obtained by reference high performance liquid chromatography method, respectively. The typical benefits of the method may be summarized as: rapidity (15 determinations per hour), sensitivity and selectivity and elaborateness, simplicity, wide linear concentration range, low detection limit and excellent repeatability. It might also represent the competitive alternative to the existing analytical methods in monitoring of drug abuse.

Keywords: Codeine, Graphene, Gold nanoparticle, Differential pulse voltammetry.

Reference:

[5] C.F. Thorn, T.E. Klein, R.B. Altman, Pharmacogenetics and Genomics **2009**, 19, 556.
[6] R.S. Irwin, F.J. Curley, F.M. Bennett, Drugs **1993**, 46, 80.
[7] W. Fischer, J. Bernhagen, R.H.H. Neubert, M. Brandsch, European Journal of Pharmaceutical Sciences **2010**, 41, 31.

Simultaneous determination of 6-thioguanine and folic acid using a carbon paste electrode modified with a 2-chloro benzoyl ferrocene and ZnO-CuO nanocomposite

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6-Thioguanine, belonging to the family of anti-metabolites drugs, 6-thioguanine is one of the most important anticancer therapeutic agents used in the clinical treatment of acute childhood lymphoblastic leukemia, inflammatory bowel disease, Crohn's disease, AIDS, and some other pathology [1]. Folic acid has long been recognized as part of the vitamin B complex found in some enriched foods and vitamin pills. It is usually employed in the treatment or prevention of megaloblastic anemia during pregnancy andchildhood [2]. In the present study, a modified carbon past electrode was developed with a 2-chloro benzoyl ferrocene and ZnO-CuO nanocomposite for the electrochemical determination of 6-thioguanine in the presence of folic acid. Square wave voltammetric peak current of 6-thioguanine increased linearly with 6-thioguanine concentrations in the range of 5.0×10^{-8} to 2.0×10^{-4} M and method detection limit of 2.5×10^{-8} was obtained for 6-thioguanine.

Keywords 6-Thioguanine; Folic Acid; Nanotechnology; Carbon paste electrode;

References:

[1] Ensafi, A. A.; Karimi-Maleh, H. J. Electroanal. Chem. **2010**, 640, 75.
[2] Lehninger AL (1982) Principles of biochemistry. Worth, New York.

Electrochemical sensor for determination of Dopamine and Uric acid with MWCNT carbon ceramic electrode modified by $LaMnO_3$ nanoparticle

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Dopamine (DA) as neuro transmitter molecule plays important role in central nervous system in our body. Neurological disorders such as schizophrenia and Parkinson's disease can created due to Low levels of DA.Uric acid (UA) is one of important biomolecule in human body. normal UA levels in serum, are 330–360M for women and less than 420M in men[1] and its abnormal concentration levels will cause several diseases such as gout, hyperuricaemia, pneumonia and leukemia[2].UA and DA are coexisting in our body fluids. Therefore, it is essential to develop simple and rapid methods for simultaneous determination of them in routine analysis. For the first time, electrochemical sensor for simultaneous determination of DA and UA with a carbon ceramic electrode (CCE) modified by $LaMnO_3$ nanoparticl is reported. Due to the excellent catalytic activity, enhanced electrical conductivity and high surface area of the MWCNT-$LaMnO_3$, the simultaneous determination of DA and UA with well-defined peaks were achieved at the MWCNT-LaMnO3 CCE. Comparing with those achieved at the bare CCE, the oxidation currents of DA and UA increased remarkably. The catalytic peak current obtained, was linearly dependent on the DA and UA concentrations in the range of 0.75 – 216.6 and 0.75 – 250.0 μM with sensitivity of 0.036 μM and 0.065 μM, respectively. The detection limits for DA and UA were 0.11μM. The diffusion coefficient for the oxidation of DA and UA at the modified electrode was calculated as $1.71\times10^{-5}$and 1.47×10^{-5}, respectively

Keywords: Electrochemical sensor, Dopamine and Uric acid, nanocarbon ceramic electrode

References:

[1] T.Xu, Q. Zhang, J. Zheng,*Electrochimica Acta*,**2014,**115, 109–115.

[2] D. Lakshmi, M.J. Whitcombe, F. Davis, P.S. Sharma, B.B. Prasad,Electroanalysis23 (2011) 305.

Electrochemical sensor for determination of low concentrations of L-Tyrosine in the presence of Uric acid by using modified carbon paste electrode

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Some oxidizable amino acids such as L-tyrosine (L-Tyr) play important roles in many biochemical processes. L-Tyr is a non-essential amino acid, synthesized from phenylalanine and incorporated into proteins in human body. The lack of L-Tyr may lead to albinism, alkaptonuria, depression, and other psychological diseases, while an overdose of L-Tyr could cause the increase of sister chromatid exchange [1]. Since alteration of Tyr concentration is related to several diseases, its determination in human fluids such as blood serum and urine is much essential. Several methods have been employed to determine the concentration of Tyr. Electrochemical methods has several advantages such as less expensive, more convenient and highly selective and sensitive. The aim of this work is developing of a sensitive and speed method for determination of Tyr using modified carbon paste electrode. However, the AuNPs and CS electrode not only separates the voltammetric signals of L-Tyr and UA with potential differences of 345 mV between L-Tyr-UA. Differential pulse anodic stripping voltammetry (DPASV) is based on electrochemical reduction of Tyr at the working electrode to deposit Tyr on the electrode surface with subsequent anodic stripping by scanning the potential to anodic direction to allow electrooxidation of the deposited Tyr at a characteristic potential of it. This method provides good peak shape and high sensitivity. ***Electrochemical impedance spectroscopy (EIS) were studied*** for characterizing the interface properties of the electrode surfaces during different modifications. The effects of pH on electrochemical response of the AuNPs/Chitosan/CPE towards the measurement of 20 µM L-Tyr in 0.1 M phosphate buffer solution were investigated. For the Electrocatalytic oxidation of L-Tyr, DPASV recorded for the same solution at pH=7 and deposition time=200s, at bare carbon paste electrode (CPE), AuNPs/CPE, Chitosan/CPE and AuNPs/Chitosan/CPE. The calibration curve was linear in the range of 0.01- 200 µmol L^{-1} and detection limit was 0.004 µmol L^{-1}. The preparation of the sensor is simple, short-time and it does not require a special apparatus. The DPASV current responses of L-Tyrosine were increased linearly. The present method was also applied for the determination of L-Tyr in different samples.

Keywords: Carbon Paste Electrode; Anodic stripping voltammetry; L-Tyrosine.

Three dimensional graphene- based gas sensor for sensing trace level of ammonia

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As a result of this study, a new and simple method was proposed for the fabrication of an ultra sensitive, robust and reversible ammonia gas sensor. The sensing mechanism was based upon the change in electrical resistance of a graphene aerogel as a result of sensor exposing to ammonia. Three-dimensional graphene hydrogel was first synthesized via hydrothermal method in the absence or presence of various amounts of thiourea. The obtained material was heated to obtain aerogel and then it was used as ammonia gas sensor. The materials obtained were characterized using different techniques such as Fourier transform infra red spectroscopy (FT-IR), thermal gravimetric analysis (TGA), X-ray diffraction (XRD) and scanning electron microscopy (SEM). The thiourea-treated graphene aerogel was more porous (389 m2 g_1) and thermally unstable and exhibited higher sensitivity, shorter response time and better selectivity toward ammonia gas, compared to the aerogel produced in the absence of thiourea. Thiourea amount, involved in the hydrogel synthesis step, was found to be highly effective factor in the sensing properties of finally obtained aerogel. The sensor response time to ammonia was short (100 s) and completely reversible (recovery time of about 500 s) in ambient temperature. The sensor response to ammonia was linear between 0.02 and 85 ppm and its detection limit was found to be 10 ppb (3S/N).

Keywords: Graphene, Hydrogel , Aerogel, Ammonia, Gas sensor

References:

[1] K.S. Novoselov, A.K. Geim, S.V. Morozov, D. Jiang, Y. Zhang, S.V. Dubonos, I.V. Grigorieva, A.A. Firsov Science 306 (2004) 666.
[2] F. Schedin, A.K. Geim, S.V. Morozov, E.W. Hill1, P. Blake, M.I. Katsnelson, K.S. Novoselov, Nat. Mater. 6 (2007) 652.

Investigation of high capacity of stem cells for removal of mercury using a novel electrochemical system

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Stem cells are often described as the best candidates for cell therapy studies due to their self-renewal capacity and their large differentiation potential. These cells express neuronal markers and present electrophysiological characteristics similar to those observed in mature neurons. Stem cells can serve as sensitive *in-vitro* model systems to test cytotoxicity of drugs and chemicals, and potentially to predict toxicity in humans. The validated embryonic stem cell test (EST) also utilizes mouse embryonic stem cells to identify potential embryo toxic compounds because embryos and fetuses are more sensitive to environmental toxicants than adult cells or tissues.

About the neuron cells, mercury ion (Hg^{2+}) is considered as an important toxic reagent. Mercury has been known as the most toxic heavy metals, can readily enter to live neurons cell, and disturbs their constructions. A discrete molecular mechanism for mercury toxicity in neuronal cells is not well resolved. At a cellular level, mercury causes inhibition of neurotransmitter receptors and calcium ion channels, damage to mitochondria and oxidative stress, inhibition of protein synthesis and microtubule assembly and up regulation of apoptosis genes. In this experiment for the first time a novel electrochemical system has been designed for electrochemical removal of Hg^{2+} in some stem cell environment. This system is considered as appropriate system for removal and filtration of mercury with efficiency to below 1.0×10^{-12} M. This system also seems to be suitable for controlling the matrix of water during the surgery process.

Keywords: Stem cells; Cytotoxicity; Heavy metals; Mercury removal.

Voltammetric detection of diclofenac by a novel electrochemical nanosensor based on multivariate optimization methodology

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Diclofenac (DCF) is a nonsteroidal anti-inflammatory drug (NSAID) that is widely prescribed for the treatment of rheumatoid arthritis, osteoarthritis, musculoskeletal injuries in human and veterinary medicine [1]. It is rapidly absorbed by the organism which by itself and its reactive metabolites may be involved in serious idiosyncratic hepatotoxicity [2]. So it is very important to create a sensitive, accurate, simple and fast method for DCF detection. A simple and sensitive carbon nanoparticles electrode has been used for the electrochemical trace determination of DCF in phosphate buffer solution. This modified electrode was designed by addition of Fe2O3 nanoparticles into the carbon paste electrode (CPE). The nanoparticles was characterized by scanning electron microscopy (SEM) and X-ray diffraction (XRD). The performance of nanoparticles was checked by cyclic voltammetry (CV) and differential pulse voltammetry (DPV). Using DPV, the results showed that this nanoparticles electrode exhibits excellent enhancement effects on the electrochemical oxidation of diclofenac sodium. Under the optimized experimental conditions diclofenac sodium gave linear response over the range of 0.01–100 μmol L− 1. The proposed sensor was successfully applied for the determination of DCF in human plasma.

Keywords: Diclofenac sodium determination; plasma; Iron oxide nanoparticles; Differential pulse voltammetry; Multivariate Optimization.

References:

[1] B. Yilmaz, U. Ciltas, J. Pharm. Biomed. Anal. 5 (2015) 153.
[2] M. Syeda, C. Skonbergb, S. Honoré Hansena. J. Toxi.I.V, In Press 2015.

Determination of Dopamine Using The Indium Tin Oxide Electrode Modified with Direct Electrodeposition of Gold-Platinum Nanoparticles

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Gold–platinum (Au-Pt) alloy nanoparticles with a ratio of 3: 1 solution of chloride salts in the starting electrolyte, were successfully deposited on an indium tin oxide (ITO) surface, using a direct electrochemical method, by 40 successive cyclic voltammetry scans to obtain Au_3Pt_1NPs/ITO electrode. The deposited nanoparticles were characterized by scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX) and electrochemical methods. The SEM result showed that The average size of electrodeposited nanoparticles was 30 nm. the elemental composition of Au_3Pt_1NPs/ITO electrode was determined by EDX. The EDX result showed that the molar ratio of electrodeposited Au/Pt on the modified electrode was of about 86/14. The effect of number of cyclic voltammetry scans in the Electrodeposition of nanoparticles on the size of electrodeposited nanoparticles, was tested. Electrochemical studies revealed that the modified electrode exhibits excellent electrocatalytic activity towards the oxidation of Dopamine (DP). The calibration plot for DP was linear over the concentration range from 0.4 to 350 μM with a correlation coefficient of 0.998. The detection limit of DP was 0.02 μM. It was shown that the Au_3Pt_1NPs/ITO electrode can be used as a sensor with high reproducibility, sensitivity, and long term stability. The interference of potential interfering substances on the determination of DP, were studied, and the results confirm the method selectivity. The modified electrode was used for the determination of DP in injection sample, with satisfactory results.

Keywords: Dopamine, Gold–platinum alloy nanoparticles, Indium tin oxide electrode.

Fabrication of an electrochemical sensor based on graphene nanoplatelets modified platinum electrode for sensitive determination of sunset yellow coloring food in drinks

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Graphene nanoplatelets (GNPs) are the stack of graphene sheets with an overall thickness of about 5 to 25 nm. They have “platelet” morphology with a diameter ranging from 0.5 to 25 µm, resulting in high aspect ratios up to the thousands. This unique size and platelet morphology makes these particles especially effective at providing barrier properties, while their pure graphitic composition makes them excellent electrical and thermal conductors [1].

Food coloring, or color additive, is any dye, pigment or substance that imparts color when it is added to food or drink. Food coloring is used both in commercial food production, domestic, pharmaceuticals and medical devices [2]. Sunset Yellow (SY) is a petroleum-derived orange azo dye used in soft drinks, food, cosmetics, and drugs [3].

In this study, graphene nanoplatelets was dispersed in dimethylformamide (DMF) uniformly and drop casted on a platinum electrode. The fabricate electrochemical sensor was sensitive to sunset yellow in sub micromolar concentrations. Cyclic voltammetry studies shows that the modified electrode has higher sensitivity for oxidation of SY with a pair of peaks at 0.708 and 0.625 V (versus Ag/AgCl) in Britton Robinson buffer (pH 3.0, 0.1 M). Some parameters such as kind of supporting electrolyte, pH, volume of coated graphene nanoplatelets and scan rate have been optimized to get higher sensitivity and selectivity. The fabricated electrochemical sensor can be easily applied to the determination of SY in soft drinks without any pretreatment.

Keywords Graphene nanoplatelets; Platinum electrode; Electrochemical sensor; Sunset Yellow

References:

[1] E. LaZaro, P. J. Lowe, X. Briand, B. Faller, J. Med, Chem 51 (2008) 2009–2017.
[2] CFR Title 21 Part 70: Color Additive Regulations, FDA, retrieved Feb 15, 2012.
[3] FDA December 2009 Color Additive Status List.

Sensitive Voltammetric Determination of Amitriptyline using Multiwall carbon nanotube-Ionic liquid Nanocomposite Electrode

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Depression is a commonly-occurring, highly debilitating, and life-threatening psychosocial and physical impairment. Amitriptyline is one of the most commonly prescribed drugs for the treatment of psychiatric patients suffering from depression. However, even at therapeutic doses, it may provoke many side effects, whereas its overdoses may result in conditions that affect heart rhythms and changes in blood pressure. Therefore, quality control of pharmaceutical formulations is important nowadays [1].

Electrochemical methods may be used for this purpose due to their excellent sensitivity, short analysis time, simplicity, and the low costs involved in the implementation of these powerful tools for measuring different analytes. Carbon ionic liquid electrode (CILE) was introduced in 2006 for the first time as a new and high performance carbon composite electrode [2].

In this work we have employed the unique properties of multi-walled carbon nanotube (MWCNT) modified CILE for fabrication of an amitriptyline electrochemical sensor. Adsorptive stripping differential pulse voltammetry as a very sensitive analytical method was used. Effect of various parameters such as pH, amount of MWCNT, accumulation potential and accumulation time was investigated. Under optimum conditions, the calibration curve of anodic peak current versus amitriptyline concentration was linear in the range of 0.1-100 µM with a detection limit of 20 nM.

Keywords: amitriptyline, multiwalled carbon nanotube, ionic liquid, electrochemistry

References:

[1] E. H. Duarte, W. P. dos Santos, F. F. Hudari, J. L. Bott Neto, E. R. Sartori, L. H. Dall'Antonia, A. C. Pereira, C. R. Teixeira Tarley, Talanta 127 (2014) 26.
[2] N. Maleki, A. Safavi, F. Tajabadi, Anal. Chem. 78 (2006) 3820.

Electrochemical Determination of Imipramine and Desipramine at Carbon Ionic Liquid Electrode

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Imipramine and desipramine are tricyclic antidepressants and belong to the group of dibenzazepine derivatives, consisting of two aromatic rings connected by a seven-member ring which has a propylamino side chain joined to it. Imipramine and its active metabolite, desipramine, are used in the treatment of depressive affective disorders, principally major depression. The therapeutic ranges of desipramine and imipramine are 115–250 and 180–350 ng/mL, respectively, and both become toxic at concentrations higher than 500 ng/mL. Therefore, the detection of their concentration in patients' body fluids becomes an important analytical task. Electrochemical methods may be used for this purpose due to their excellent sensitivity, short analysis time, simplicity, and the low costs involved in the implementation of these powerful tools for measuring different analytes. Only a few reports concern the electrochemical measurements of imipramine or despiramine. Carbon ionic liquid composite electrodes (CILE) have been proposed and used as convenient electrodes for different electrochemical applications. Using IL as a pasting binder in carbon paste electrodes leads to a new generation of carbon composite electrodes with advantages over CPE such as high conductivity, fast electron transfer rates and antifouling properties. In this work, we have employed the unique properties of CILE for fabrication of the sensitive determination of imipramine and desipramine. Adsorptive stripping differential pulse voltammetry as a very sensitive analytical method was used. Effect of various parameters such as pH, amount of IL, accumulation potential and accumulation time was investigated. Under optimum conditions, the calibration curves of anodic peak current versus imipramine and desipramine concentrations were linear in the range of 0.4-110 µM and 0.7-100 µM with a detection limit of 50 nM, 80 nM, respectively.

Keywords: Desipramine; Electrochemical; Imipramine; Ionic Liquid

Differential Pulse Anodic Stripping Voltammetry Determination of L-Phenylalanine by Ninhydrin Addition Based on Modified Carbon Paste Electrode

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Carbon paste electrode modified by synthesized ZnO nanoparticles and Chitosan (ZnO/CS/CPE) was used as a sensor for determination of L-phenylalanine (L-Phe) with the addition of specific concentration of Ninhydrin. We determined L-Phe concentration by recording the interaction between these two compounds. L-Phe is an essential amino acid, is a constituent of many central nervous system neuropeptides. The body uses phenylalanine to make chemical messengers, but it is not clear how phenylalanine might work [1]. Ninhydrin is a chemical used to detect ammonia or primary and secondary amines. When reacting with these free amines, a deep blue or purple color known as Ruhemann's purple is produced. Electrochemical methods are used for the elegant and sensitive properties such as selectivity, reproducibility, low cost and simplicity of this approach. The enzymatic electrochemical biosensors are suffering from very low stability. Because of that, we considered fabricate non-enzymatic, sensitive, simple, rapid and also low cost sensor for determination of low concentrations of L-Phe. CS is a natural polysaccharide which has been extensively studied over the last two decades as a nontoxic, renewable and biodegradable polymer. The advantages of ZnO nanoparticles could be, narrow size distribution, efficient surface modification, and desirable biocompatibility. The cyclic voltammograms of the modified electrode in an aqueous solution displayed a pair of well-defined, stable and irreversible reductive/oxidation redox systems. By using ZnO/CS/CPE we have successfully determined the different concentrations of L-phe on the electrode surface. The performance characterization of the sensor was accomplished by Differential pulse anodic stripping voltammetry (DPASV) and cyclic voltammetry (CV). Under the optimized experimental conditions, L-phe gives linear response over the range of 10-550 µmolL^{-1}. The detection limit was found to be 0.59 µmolL^{-1}. The practical application of the modified electrode was demonstrated by measuring the concentration of L-phe in blood serum and urine samples analysis.

Keywords: Carbon Paste Electrode; Anodic stripping voltammetry; L-Phe; ZnO nanoparticles.

The simultaneous electrochemical determination of guanine and adenine with NiAl-layered double hydroxide/graphene oxide multi wall carbon nanotube modified glassy carbon electrode

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The electrochemical sensor was developed for simultaneous determination of guanine (GA) and adenine (AD) detection by covering a glassy carbon electrode (GCE) with a composite arranged from multiwall carbon nanotubes (MWCNTs) with the hybrid NiAl-layered double hydroxide/graphene oxide (NiAl-LDH/GO) on a glassy carbon electrode (GCE), referred to as MWCNTs/NiAl-LDH/GO/GCE.

Deoxyribonucleic (DNA) acid plays the main role in the storage of genetic information and protein biosynthesis. GA and AD are important components found in DNA, with critical roles in life processes. They have significant effects on the modulation of adenylate cyclase activity, control of blood flow, the prevention of cardiac arrhythmias and the inhibition of neurotransmitter release [1-3].

The effects of different parameters such as pH, accumulation time, accumulation potential, and scan rate on the sensitivity were investigated. Individual and simultaneous determinations were performed by linear sweep voltammetric (LSV) technique. The linear ranges of 0.010-45 mM, with the detection limit of 3 nM for GA, and 0.08-45 mM, with the detection limit of 20 nM for AD, were achieved.

Keywords: Simultaneous determination, Layered double hydroxide, Multiwall carbon nanotubes, Guanine and Adenine.

References

[1] W. Saenger, Ch.R. Cantor, Principles of Nucleic Acid Structure, Springer, New York, 1984.
[2] S.P. Li, P. Li, T.T.X. Dong, K.W.K. Tsim, *Electrophoresis*, 2001, **22**, 144-150.
[3] F.Q. Yang, J. Guan, S.P. Li, *Talanta*, 2007, **73**, 269-273.

Voltammetric determination of bisphenol A using nanostructure modified ionic liquids carbon paste electrode

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Bisphenol A is a chemical compound widely used to make epoxy resins and polycarbonate plastics. Polycarbonate based plastics have many applications such as food and drink packaging and medical devices [1]. On the other hand, epoxy resins are used to metal coating such as bottle tops, food cans, and water supply pipes. Bisphenol A can leach into food produce from the epoxy resin lining of cans and from other products such as food storage containers, polycarbonate tableware, and water and baby bottles. The National Institute of Environmental Health Sciences expects to support more research to determine if bisphenol A in receipts poses a risk to human health. According to the above points, it is very important for preparation of fast and sensitive method for determination of bisphenol A in food samples.

In this work, the electrochemical oxidation of bisphenol A has been studied by CdO nanoparticle ionic liquids carbon paste electrode. Cyclic voltammetry, square wave voltammetry and chronoamperometry were used to investigate the suitability of new sensor for the electro-oxidation of bisphenol A in aqueous solution. The electro-oxidation of bisphenol A occurs at a potential about 50 mV less positive than with the unmodified carbon paste electrode at pH 7.0. The SWV peak currents of the electrode increased linearly with the corresponding bisphenol A concentration in the range of 0.3-650 μM with a detection limit of 0.1 μM. The influence of pH value and potential interfering substances on the determination of bisphenol A were studied. Finally, the proposed novel sensor was also examined as a sensitive, high selective, simple and precise electrochemical sensor for the determination of bisphenol A in food samples.

Keywords: Bisphenol A; Voltammetry; Ionic liquids, CdO nanoparticle

References:

[1] A. Calafat, J. Weuve, Ringer S Environmental Health Perspectives 117 (2009) 639.

Estimation of One-Electron reduction potentials of two compounds extracted from Salvia miltiorrhiza

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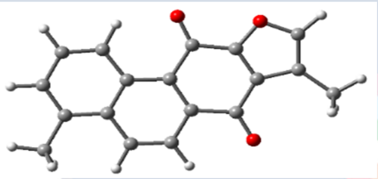
Because of particular electron-accepting abilities, quinones not only are involved in the redox chemistry of living organisms and fulfill important biological functions but also have widespread use in organic and industrial synthesis [1]. The one-electron reduction potentials of Tanshinone (I) and Isotanshinone (II) in DMSO have been calculated in the present work. All structures have been optimized at the M062X/6-311++g (d,p) level by the Gaussian 09 software [2]. The One-Electron reduction potentials are calculated as follow:

$$E_{NHE}\left({}^{Q}/_{Q^{\cdot-}}\right) = E_{NHE}\left({}^{p-BQ}/_{P-BQ^{\cdot-}}\right) + \frac{\Delta G^{*}_{sol}}{F} \qquad (1)$$

Where, E_{NHE} (p-BQ/P-BQ$^{\cdot-}$) is the reduction potential of Para-benzoquinone (P-BQ) in DMSO and F is the Faraday constant [3]. The estimated values of reduction potential for I and II are equal to, -0.3186 V and -0.3185 V, respectively. With respite to the reduction potentials of I and II, both compounds can be suitable reducers with approximately equal activity.



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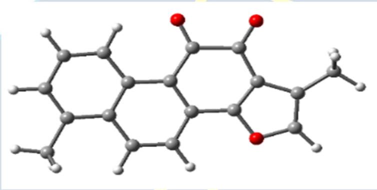

I

Keywords reduction potential; quinones; Tanshinone; Isotanshinone; Para-benzoquinone

References:

[1] J.D. Adams, R. Wang, J. Yang, Chinese Medicine, 1 (2006) 1.
[2] M.J. Frisch, et al., Gaussian 09, Revision A.02, Gaussian Inc., Wallingford, CT, 2009.
[3] X.Q. Zhu, C.H. Wang, C. Zhi Huang, J. Org. Chem, 72 (2010) 5037.

Theoretic analysis of π-π stacking interaction effect on Isotanshinone I One-Electron reduction potential

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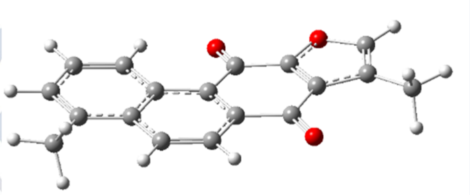
The π–π stacking interactions are weak noncovalent forces that play an essential role in supramolecular chemistry, drug design, biochemistry, crystal engineering and molecular science [1]. The one-electron reduction potentials of Isotanshinone (I) and benzene‖isotanshinone complex (II) have been calculated in DMSO in the present work. All structures have been optimized at the M062X/6-311++g (d,p) level by the Gaussian 09 software [2]. The One-Electron reduction potentials are calculated as follow:

$$E_{NHE}\left({}^{Q}/_{Q^{\cdot-}}\right) = E_{NHE}\left({}^{p-BQ}/_{P-BQ^{\cdot-}}\right) + \frac{\Delta G^{*}_{sol}}{F} \qquad (1)$$

where, E_{NHE} (p-BQ/P-BQ$^{\cdot-}$) is the reduction potential of para-benzoquinone (P-BQ) in DMSO and F is the Faraday constant [3]. The estimated values of reduction potential for I and II are equal to, -0.32 V and -0.30 V, respectively. In fact, π-π stacking interactions between aromatic rings lead to decrease of reduction potential of related quinone.

I



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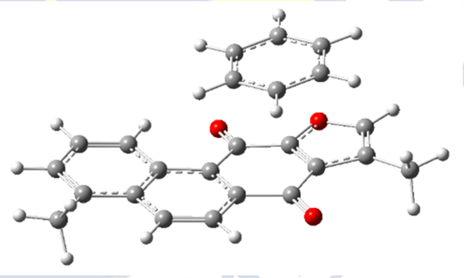

Keywords benzene; Isotanshinone I; Para-benzoquinone; reduction potential; π-π stacking

References:

[1] P.Cysewski,Phys.Chem.Chem.Phys.10,2636(2008).
[2] M.J. Frisch, et al., Gaussian 09, Revision A.02, Gaussian Inc., Wallingford, CT, 2009.
[3] X.Q. Zhu, C.H. Wang, C. Zhi Huang, J. Org. Chem, 72 (2010) 5037.

Multi-Wall Carbon Nanotube-Based Voltammetric Sensor for Sensitive Determination of Food Red No. 14 in Real Samples

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Synthetic colors usually include the compounds with azo bond, benzene and xanthene. Although most food dyes are expected to be safe if their dosages are strictly limited, some studies have indicated carcinogenicity and toxicity related to commonly used food dyes [1]. Food Red No. 14 is a cherry-pink, coal-based food colorant with a poly-iodinated xanthenes structure unique among FDA approved food dyes. It is also used as an exclusion dye and a phosphorescent probe for membrane proteins [2].

In the current study a simple procedure was developed to prepare a carbon paste electrode modified with multi-walled carbon nanotubes (MWCNT-CPE). Then the electrochemical behaviour of Food Red No. 14 was investigated using this electrochemical sensor in phosphate buffer (PBS) at pH = 10.0 using Cyclic voltammetry (CV), chronocolumetry (CHA) and differential pulse voltammetry (DPV) techniques.

After optimizing the experimental conditions, the peak current increased linearly with the Food Red No. 14 concentration within the concentration range of 0.1 to 20.0 µM for DPV. The detection limits (S/N > 3) for Food Red No. 14 was found to be 5.0 nM in phosphate buffer solution (PBS) at pH 10.0. This modified electrode was applied to the determination of Food Red No. 14 in drinks and cosmetic products with good recovery.

Keywords: Food Red No. 14, Multi-walled carbon nanotubes, Voltammetry

References:

[1] Z. Xu, L. Zheng, Y. Yin, J. Wang, P. Wang, *Food Control*, 47 (2015) 472.
[2] L. Ganesan, E. Margolles-Clark, Y. Song, *Biochem. Pharmacol*. 81 (2011) 810.

Nonenzymatic xanthine sensor based on ternary Ag nanoparticles/polypyrrole/graphene oxide nanocomposite

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Xanthine (3,7-dihydro-purine-2,6-dione) is the degradation product of guanine and hypoxanthine and is prevalent in most body tissues, blood, and urine. Until now, xanthine detection methods have involved mainly electro-chemical biosensors based on immobilized xanthine oxidase (XOD), a number of chromatographic methods (HPLC, mass spectrometry, and capillary), enzymatic colorimetric assay and etc [1-3]. Non-electrochemical methods used to determine xanthine often complex and very costly, and sensitivity, selectivity, stability and repeatability is not good. To overcome these problems, it is best to determine xanthine, electrochemical methods used.

In this paper, we reported a non-enzymatic sensor based on graphene oxide/polypyrrole/Ag nanoparticles nanocomposite modified glassy carbon electrode (GCE/GO/Ppy/Ag) for determination of xanthine (XA). The morphology and structure of GO/Ppy/Ag nanocomposites were characterized by scanning electron microscopy (SEM), X-ray diffraction (XRD) and Fourier transform infrared (FT-IR). The incorporation of GO into PPy resulted in a distinctly different and more porous surface morphology than that observed in PPy films synthesized in the presence of conventional counter ions. The GCE/GO/Ppy/Ag-based sensor exhibited excellent electrocatalytic activity and high stability for xanthine oxidation. Under optimized conditions, the linearity between the current response and the xanthine concentration was obtained in the range of 2 µM to 200 µM with a detection limit of 0.8 µM (S/N=3).

Keywords: Ag nanoparticles; non-enzymatic; sensor; xanthine.

Refrences:

[1] X. Zhang, J. Dong, X. Qian, C. Zhao, Sensors and Actuators B, 221 (2015) 528.
[2] M. Dervisevic, E. Custiuc, E. Çevik, Z. Durmus, A. Durmus, Food Control 57 (2015) 402.
[3] B. Dalkiran, C. Kaçar, P. E. Erden, E. Kiliç, Sensors and Actuators B 200 (2014) 83.

Fabrication of non-enzymatic glucose sensor based on graphene oxide/polypyrrole/NiO-Co_3O_4 nanocomposite

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Glucose is one of the indispensable substances for life activities, and it can be ingested directly in the metabolic process to provide energy so as to maintain the normal life activities and the increase of glucose in blood could cause diabetes. Electrically conducting polymers (ECPs) are unique since they are both ionic and electronic conductors. To further improve material properties like stability, conductivity, capacitance, and mechanical strength, ECPs have been fabricated as composites with a wide variety of materials like metal nanoparticles, conventional polymers, and carbon materials like nanotubes and fullerenes [1-3].

In this work we report a simple, one-step method for direct electrochemical incorporation of graphene oxide (GO) into conducting polymer films without the use of any additional dopants. Polypyrrole (PPy) was successfully electropolymerized in as-prepared aqueous GO dispersions using potentiostatic polymerization. Then NiO and Co_3O_4 nanostructures were electrodeposited on the PPy/GO by cyclic voltammetry method. The morphology and structure of RGO/PPY/NiO-Co_3O_4 nanocomposites were characterized by scanning electron microscopy (SEM), X-ray diffraction (XRD) and Fourier transform infrared (FT-IR). The RGO/PPY/NiO-Co_3O_4-based sensor exhibited excellent electrocatalytic activity and high stability for glucose oxidation. Under optimized conditions, the linearity between the current response and the glucose concentration was obtained in the range of 2 μM to 4 mM with a detection limit of 0.7 μM (S/N=3).

Keyword: Glucose, Graphene oxide, NiO and Co_3O_4 nanostructures, Polypyrrole

Reference

[1] T.J. Tsakova, Solid State Electrochem. **2008**, 12, 1421.
[2] C. Lu, Y. Tang, S. Huan, S. Li, L. Li, Y. Wang, Adv. Funct. Mater. **(2010)**, 20, 1714.
[3] K. Xue, S. Zhou, H. Shi, X. Feng, H. Xin, W. Song, Sens. Actuators, B **(2014)**, 203, 412.

Fabrication of Nanoporous Anodic Aluminum Oxide Membrane in Modified Oxalic Acid Electrolyte at Room Temperature and Investigation of Effective Parameters

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Nanoporous anodic aluminum oxide (AAO) has recently attracted the attention of scientists due to their unique properties. These structures used as membrane and template in separation and fabrication of nanostructures. At present study, we were prepared membranes in modified acid Oxalic electrolyte solution and investigated the effect of some parameters (Anodization time, composition of electrolyte solution, composition of stripping solution) on pore structure of membranes. The Anodic aluminum oxide membranes were fabricated by a two-step anodization technique at potentials 25 and 45 V in different times with an acidic stripping step. The electrolyte solutions were 0.3 M Oxalic acid and 0.3 M Oxalic acid with very low concentration of sulfuric acid as modifier at room temperature. This is an advantage for our work because conventional anodization carried out at long times and very low temperatures to prevent from burning phenomenon in the samples but we achieved optimum conditions for prepared membranes and reduced the anodization time in modified electrolyte without sample burning at room temperature. The morphology of the samples was explored by a field emission scanning electron microscopy (FE-SEM). Results showed that produced membranes in modified electrolyte at potential 45 V, anodization time of 60 and 240 min for first and second anodization step respectively and CrO_3/H_3PO_4 stripping solution had very ordered nanoporous structures with large pore diameter and very good pore distribution. In presence of sulfuric acid as modifier, solving speed of pores wall at room temperature was increased and causes widening of pores up to 90 nm and interpore distances were decreased. Also causes that very ordered nanopores were fabricated at short anodization time.

Keywords Anodic aluminum oxide; Modified electrolyte; Nanoporous structure; Pore diameter, Stripping solution.

A novel solid-state electrochemiluminescence biosensor for detection of cytochrome C based on Ceria Nanoparticles Decorated Reduced Graphene Oxide nonocomposite

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A novel reduced graphene oxide decorated cerium oxide / Tris(2,2-bipyridyl) ruthenium(II) /chitosan [CeO2NPs-RGO/ Ru(bpy)$_3^{2+}$/ CHIT] nanocomposites were successfully fabricated and used for the sensitive electrochemiluminescence (ECL) biosensing. The ECL biosensor fabricated with CeO_2NPs- RGO/ Ru(bpy)$_3^{2+}$/ CHIT composite exhibited high ECL intensity, good biocompatibility, long-term stability and was used to detect of cytochrome C (Cyt C). The whole process was characterized by cyclic voltammogram (CV) and Electrochemical impedance spectroscopy(EIS). Experimental parameters such as the amount of CeO_2NPs-RGO, Ru(bpy)$_3^{2+}$ concentration and the pH value of electrolyte solution were studied to investigate the effect on the ECL intensity. Under the optimized conditions, the ECL intensity decreased linearly with the Cyt C concentrations in the range from 2.5 nM to 2μM (R=0.9933, n=9) with detection limit of 0.9 nM. The solid-state ECL quenching biosensor exhibited high sensitivity and good stability and can selectively sense Cyt C from glucose and bovine serum albumin (BSA).

Keywords: Electrochemiluminescence, [CeO_2NPs-RGO/CHIT] nanocomposites, Biosensor

References:

[1] W.J.Miao,Chem.Rev.108 (2008) 2506.

[2] T. Wang, S. Zhang, Biosensors and Bioelectronics (2012),369.

Non-enzymatic glucose nano-biosensor based on copper oxide

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Diabetes mellitus is a serious metabolic disorder caused by insulin deficiency, and about 200 million people worldwide are being afflicted by diabetes mellitus. For these patients, regular testing of physiological glucose level is necessary. The rising demand for glucose sensors with high sensitivity, good reliability, and excellent selectivity has impelled researchers to make tremendous efforts for decades. Many of them were focusing on the development of sensing devices for monitoring the concentration of glucose. Enzymatic biosensing of glucose by glucose oxidase has many problems such as highly cost and instability of this compound [1-4].

In this article, glucose was sensed by a non-enzymatic method in buffer phosphate. The main part of the glassy carbon electrode is made of copper oxide. The nanostructure copper oxide was synthesized by a solvothermal method using a bifunctional organic substance and characterized with FT-IR, XRD and SEM. Results showed that sensitivity of the sensor is 517 µA/cm^{2}mM. Also the sensor detected the glucose without interference from dopamine, fructose and uric acid.

Keywords Non-enzymatic; glucose; nano-biosensor

References:

[1] N. S. Oliver, C. Toumazou, Johnston, D. G. *Diabetic Med*.26 **2009**, 26, 197.

Identification of glucose by a new non-enzymatic nano-biosensor based on CuO/MWCNT and investigation of their interference

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In a new route, controlled synthesis of nano structured copper(II) oxide was carried out by solvothermal method. Sphere morphologies were obtained through the synthetic route. To test its application, CuO nanostructure, formulated by multi-walled carbon nanotube (MWCNT) on glassy carbon electrode (GCE) and was applied as new nanobiosensor for detecting glucose in a simple and inexpensive way without using any expensive glucose oxidase or nafion which was accomplished in a phosphate buffer solution (PBS, pH=7) for CuO/MWCNT/GCE sample. Results showed that in this non-enzymatic biosensor system, obtained spherical CuO has the highest sensitivity with repeatable results. For the mentioned sensor, no interference observed in the presence of dopamine, uric acid and fructose. The detection limit is 0.01 mM toward glucose with good selectivity and stability.

In a typical synthesis, 0.5gr of $CuSO_4$-$5H_2O$ was dissolved in10 mL of distilled water and 10mL Methanol.Reaction mixture was stirred for15 min, followed by the drop-wise addition of aqueous KOH (0.1M) under continuous stirring, a blue precipitate was obtained. Reaction mixture was transferred into a Teflon-lined stainless steel autoclave,and maintained at 150 °c for 20 h. After the reaction, autoclavewas cooled to room temperature. The resulting black precipitatewas filtered and washed with distilled water.

Keywords: Nano structured copper(II) Oxide; Nonenzymatic;Biosensor glucose; Multi-walled Carbon nanotube

References:

[1] J. Yang, L.C. Jiang,W.D. Zhang,S. Gunasekaran, Talanta 82 (2010) 25.
[2] M.U. Anu Prathap, B. Kaur, R.Srivastava, Journal of Colloid and Interface Science 370 (2012) 144.
[3] F. Cao, J. Gong, Analytica Chimica Acta 723 (2012) 39.

Fabrication of a lanthanum cation selective sensor based on dibenzo-18-crown-6 as a supramolecular carrier in polyvinyl chloride membrane

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The development of ion selective electrodes are the well established in most frequent applications in the fields of environmental, agricultural, industrial and clinical analysis. This is due to their several advantages, such as high speed, ease of preparation, simple instrumentation, relatively fast response, wide working concentration range, adequate selectivity and low cost. In this project a lanthanum (III) selective coated graphite electrode based on dibenzo-18-crown-6 as a neutral ionopHore incorporated in polyvinyl chloride (PVC) membrane in tetrahydrofuran (THF) has been fabricated. The best operation obtained in the membrane including: 7.0 mg dibenzo-18-crown-6, 2.0 mg sodium tetra phenyl borate (NaTPB), 61.0 mg dioctyl sebacate (DOS) and 30.0 mg PVC. This electrode had a good selectivity respect to La^{3+} cation, with a nernstian slope of 21.8 $mV.decade^{-1}$ in a linear concentration range of 1.0×10^{-6} M to1.0×10^{-1} M. The detection limit of the electrode was 8.2×10^{-7} M. The proposed sensor had a fast response time of 15 sec and good reproducibility. It can be used for a period of 8 weeks without any significant changes in its potential. The effects of the pH and possible interfering ions were investigated, and it could be used in pH range of 2-12. This sensor was employed as an indicator electrode in potentiometric titrations of lanthanum cation with EDTA solutions and a sharp break in titration curves around the equivalent point was observed. Also this sensor was used for determination of lanthanum (III) in non- aqueous solutions and in real samples.

Keywords: Ion selective electrode; lanthanum (III) cation; dibenzo-18-crown-6; Potentiometric

Homogeneous liquid–liquid microextraction via flotation assistance for determination of atrazinein water samples by gas chromatography-mass spectrometry

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The simple and efficient homogeneous liquid–liquid microextraction via flotation assistance method (HLLME-FA) combined with gas chromatography-mass spectrometry was proposed for determination of trace amounts of atrazine. A special extraction cell was designed to simplify collection of the low density extraction solvent. Air flotation allowed the extraction solvent to be collected from the top of the solution. The parameters affecting the HLLME-FA, such as extraction and homogeneous solvent types and volumes, ionic strength and extraction time were studied. Under optimum conditions, the detection limit of 0.008ng g^{-1}, linear range of 0.05- 50ng g^{-1}, and the precision (RSD%, n = 7) of 3.2 % were obtained. The enrichment factor of 2857.2 was achieved in the process. The proposed procedure showed satisfactory results for analysis of water samples.

Keywords: Atrazine; Flotation assistance; Gas chromatography- mass spectrometry; Homogeneous liquid-liquid microextraction

References:

[1] N. Baroumand, A. Akbari, M. Shirani, Z. Shokri, 226 (2015) 2254.

[2] M. HajiHosseini, M. Rezaee, S. Akbarian, F. Mizani, M. R. Pourjavid, M. Arabieh, Anal.Chim.Acta 762 (2013) 54.

[3] H. Haddadi, M. Shirani, A. Semnani, M. Rezaee, H.A. Mashayekhi, A. Hosseinian, Chromatographia, 77 (2014) 715.

Equilibrium, Kinetic and Thermodynamic Studies on the Adsorption and Photocatalytic Degradation Behaviors of Cationic Dye Basic Violet 16 (BV16) in ZnO-Natural *Ghezeljeh* Nanoclay Composite/ UV-C

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In the present study, ZnO-natural *Ghezeljeh* nanoclay composite was synthesized and its dye removal ability was investigated. Cationic dye Basic Violet 16 (BV16) was used as model compounds. For this purpose, a number of parameters were optimized. *Ghezeljeh* nanoclay in pure and natural form exhibited a cationic exchange capacity, experiences demonstrated a good ability during the photocatalytic reaction cationic dye molecules (BV16); therefore, a combination of *Ghezeljeh* nanoclay and ZnO makes photooxidation effective for the removal of dye compounds from wastewater. The maximum adsorption and photocatalytic degradation are high in acidic medium, and increase in temperature resulted in enhancement of the dye degradation efficiency. The efficiency of adsorption increased from 58.70% to 82.54% and 84.50% in the presence of KI and NaCl, respectively. The adsorption of BV16 decreased significantly in the presence of KCl (18.52%) and Na_2CO_3 (22.83%). Kinetic data revealed that the intraparticle diffusion is not the only rate limiting step, but also other kinetic models may control the rate of adsorption, all of which may be operating simultaneously. The linearity of the plots (R^2) demonstrates that pseudo-second order kinetic model play a significant role in the uptake of the dye and the dye removal isotherm follows the Langmuir isotherm at ordinary temperature and Dubinin–Radushkevich isotherm at upper temperature. The values of ΔG^0 achieved in this study, are suggesting a physical adsorption process. The negative values of ΔG^0 confirm the feasibility and spontaneous nature of the process. The positive values of ΔH^0 indicate the presence of an energy barrier in the adsorption process. Also, the positive values of entropy change (ΔS^0) indicate that the randomness at the solid–liquid interface during the photocatalytic degradation process increases.

Keywords Nanoclay; Adsorption; Photocatalytic; Kinetic; Thermodynamic

Sunset yellow dyes removal from food industry waste by graphene oxide

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The purpose of this article is manufacture and modification of graphene as an absorber to remove Disodium 6-hydroxy-5-[(4-sulfophenyl)azo]-2-naphthalenesulfonate (sunset yellow) from industrial effluent. Due to the high volume of effluents which containing synthetic dyes in industry, providing cost-effective and efficient manner is essential. In this paper, graphene oxide produced by the Hamrz method and after confirming the structure by UV and FTIR and being consistent with graphene oxide standard.the parameters optimized with some items such as absorber(graphene),the initial concentration of analyte (sunset yellow)the environmental conditions of solvent(pH) and extraction time for achieve maximum efficiency to absorb analyte. according to the results absorber is 0.01 germs, absorbent 15mg per litters and extraction time is 4 hours. To evaluate the capabilities of the study for absorb the sunset yellow in industrial effluent from chemical waste in quality control laboratory which is located in Tehran.to perform this test,we could remove the color available in 50 ml sample test with optimized conditions.the results show effluent which contained sunset yellow with 25 ppm concentration reach to 3.26 ppm sunset yellow by graphene oxide after removing.in the other word, removal rate of sunset yellow was 86% . this method has advantages such as simply performance, economic efficiency speed run and the most important items is ability to resuscitation.

Keywords : graphene oxide , sunset yellow , effluent

A novel method based on supramolecular nano solvent-hollow fiber liquid phase microextraction for simultaneous extraction of acidic, basic and amphiprotic pollutants

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The coextraction of acidic, basic and amphiprotic pollutants from various matrixes is a considerable and disputable concept in sample preparation strategies. In this study, for the first time, coextraction of acidic, basic and amphiprotic pollutants was performed using supramolecular nano solvent-based hollow fiber liquid phase microextraction (SS-HF-LPME) as an efficient method followed by high performance liquid chromatography-photo diode array detection. The supramolecular solvent (SUPRAS) is formed from the coacervation of decanoic acid aqueous vesicles in the presence of tetrabutylammonium hydroxide. The results showed 40% SUPRAS in 1-decanol has the best extraction efficiency for three selected model analytes (4-nitrophenol, 3-nitroaniline and 1-amino-2-naphthol). The extraction process was accomplished in two phase mode and the unique interactions between the solvent and polar analytes (hydrophobic, electrostatic, hydrogen bonding and π-cation interactions) resulted in elevated coextraction efficiency. Central composite design methodology combined with desirability function approach was applied to develop predictive models for simulation and optimization of SS-HF-LPME method. The opted conditions were: pH of the sample, 9.0; percentage of SUPRAS in 1-decanol, 40%; extraction time, 30 min; salt concentration, 20% w/w; stirring rate, 1250 rpm. Under the optimum conditions detection limits and linear dynamic ranges were achieved in the range of 0.1-0.2 μg L^{-1} and 0.5-400 μg L^{-1}, respectively. The percent of extraction recovery and relative standard deviations (n = 5) were in the range of 56.1-71.1 and 4.1-6.9, respectively. Finally, the applicability of this method was successfully confirmed by analyzing rain, snow and river water samples satisfactorily.

Keywords*:* Coextraction; Central composite design and desirability function; Hollow fiber liquid phase microextraction; Pollutants; Supramolecular nano solvent.

Effervescent CO_2 flotation after dispersive liquid-liquid microextraction for on-site extraction of polycyclic aromatic hydrocarbons from seawater

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For the first time, effervescent CO2 flotation after dispersive liquid-liquid microextraction (ECF-DLLME) coupled with gas chromatography-mass spectrometry (GC-MS) is presented for the determination of polycyclic aromatic hydrocarbons (PAHs) in aqueous samples. In this method, after injection of a mixture of extraction and disperser solvents into the sample, an effervescent tablet containing sodium bicarbonate and sodium dihydrogen phosphate was applied for phase separation. Thanks to the in-situ generation of carbon dioxide (CO_2), the dispersed extraction solvent was collected to the surface of the aqueous sample. The experimental variables, including volume of extraction and disperser solvents, ionic strength and weight of effervescent tablet, were investigated and optimized by a central composite design (CCD). Under the optimal conditions, the limits of detection were at the range of 0.01 to 0.1 $\mu g\ L^{-1}$ and preconcentration factors were varied between 134 and 406 for different PAHs. The linearity of the method was evaluated using water samples spiked at six different concentrations ranging from 0.05 to 100 $\mu g\ L^{-1}$. The relative standard deviations for the determination of PAHs at the concentration of 10 $\mu g\ L^{-1}$ were less than 11.4% (n=3).To evaluate the proposed method, four environmental samples were examined and relative recoveries were obtained at the range of 80 to 110%. Since there is no need to centrifugation or a special apparatus for the proposed method, ECF-DLLME has the most promise for becoming a quick, simple and economical approach to reduce transportation costs after water sampling in the field.

Keywords: Dispersive liquid-liquid microextraction; Effervescent CO2 flotation; Polycyclic aromatic hydrocarbons

Toxic heavy metals contamination of ground and surface waters around gold extraction factories in Zarshoran area of Takab

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In recent years, gold mining and processing have played a significant role in the socioeconomic life of Takab people but it become unpopular because the source of toxic heavy metal (As, Hg, Pb, Cd and Cr) and cyanide pollution. In the Zarshran area of Takab, large deposits of gold mining and processing wastes, exists around the plants. Weathering of the waste materials is resulted in the release of toxic chemicals into the environment.

Due to the vital importance of harmful heavy metals monitoring, we were interested to study the release of toxic heavy metals owing to activities such as mineral exploitation, ore transportation and refining to the ground and surface waters in Zarshran area of Takab. The sampling sites (n=16) selected around three different gold extraction factories and also out of industrial areas. Water samples were collected from wells, rivers and springs in polyethylene bottles according to standard methods [1] in the mid of every season (2015). The samples were acidified with HNO_3 and kept at 4^oC. The concentration of Hg and As in the water samples was determined using atomic absorption spectrophotometer at hydride generation mode. The concentration of Pb, Cd and Cr were determined by liquid-liquid extraction of their pyrilidine dithiodiethylcarbamate complexes in methyl isobuthyl keton prior to analysis by flame atomic absorption spectrophotometer [1]. The obtained results show that the concentration of As in the studied area is higher than the standard level allowed for drinking water [2] and it is related to the geochemical composition of the soil in studied area. Also it was found that, the concentrations of Hg, Pb and Cr in surface waters decreases with distance from the industrial area so the gold ore processing had positive effect on solubility of the toxic heavy metals.

Keywords: Heavy metals contamination, Gold extraction, Water analysis.

References:

[1] APHA (American Public Health Association), *20th Ed.*, **1998**.

[2] WHO (World Health Organisation), Geneva, WHO, **2007**.

Separation of cyanide ion from water samples using head space liquid phase microextraction and quantitative analysis by spectrophotometry

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Cyanide is widely used in processing of low grade ores (gold and silver), electroplating, and in production of plastics. Its release to the environment from the mentioned sources is very dangerous because cyanide is highly toxic and can be fatal to humans and animals if ingested in sufficient quantity. For quantitative analysis of cyanides in water samples, steam distillation coupled with spectrophotometric methods are advantageous, as simplicity and availability of instrumentation [1,2] but it need high amount of sample and also its repeatability is limited.

In this work, we developed a new head space liquid phase microextraction procedure for separation and pre-concentration of cyanide ion from water samples prior to quantitative analysis. by The sample solution (500 mL) were acidified and liquid phase microextraction was performed from its headspace using a grooved teflon rod which contains extraction phase (250 µL NaOH) in its threads. After liquid phase microextraction, acetate buffer (pH=5) was added and then, the standard spectrophotometric method which is use the Chloramine T as oxidation reagent and Pyridine-Barbituric acid as coloring reagent was used for cyanide determination. Factors relevant to the microextraction efficiency, such as volume of extraction phase, concentration of extraction phase, sample solution temperature and the extraction time were investigated and optimized. Under the optimal conditions the linear dynamic range of cyanide was from 1.0 to 100.0 µg L^{-1} with a correlation coefficient of 0.9991. The relative standard deviation (RSD) was less than 2.21% (n=3) and the recoveries of cyanide was in the range of 98.6±1.9%. Finally the proposed method was successfully applied for the analysis of real water samples collected from around the Aqh Dareh gold processing plant in Zarshran area of Takab.

Keywords: Cyanide microextraction, Water analysis, Spectrophotometry.

References:

[1] P. Nagaraja, M. S. Hemantha Kumar, H. S. Yathirajan, J. S. Prakash. *Anal. Sci.*, **2002**, 18, 1027-1030.
[2] D. Cacace, H. Ashbaugh, N. Kouri, S. Bledsoe, S. Lancaster, S. Chalik, *Anal. Chim. Acta*, **2007**, 589, 137-141.

The Effect of Solvent on Extraction of Crocin from Saffron

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Saffron is the dried stigmas of Crocus Sativus L., belonging to the family of Iridaceae. Iran and especially Khorasan provinces are known as the most important production center for saffron. The main active ingredients of saffron are crocin, picrocrocin and safranal and respectively are responsible for color, taste and aroma. Crocin ($C_{44}H_{64}O_{24}$) is glycoside ester of crocetin ($C_{20}H_{24}O_4$) and considered as color agent of saffron [1]. Different extraction methods have been used for extraction of active components from saffron. Among of the extraction methods, solvent extraction is industrially more common and the selection of solvent is key factor for efficient extraction of active components [2]. In this work, the effect of hudro-alcoholic solvent for extraction of crocin from saffron stigmas has been investigated.

Crocin has been extracted from saffron by different composition of methanol and ethanol (0 – 100 % composition) in water as solvent. For the extraction, 10 mg of powdered saffron was suspended in 20 ml of different solvents and after sonication for 15 min the samples centrifuged and filtered. The performance of solvent for extraction of crocin investigated spectrophotometrically at wavelength 442 nm. The results showed using methanol and ethanol in water considerably increase the extraction of crocin from saffron. By increasing the proportion of alcohol in solvent, the crocin spectra shifted to higher wavelength and absorbance and the extraction efficiency reached to maximum amount at 50:50 (v/v) ethanol-water composition.

Keywords: Saffron; Crocin; Hydro-alcoholic solvent extraction, Spectrophotometry.

References:

[1] H. Caballero-Ortega, R. Pereda-Miranda, F. I. Abdullaev, Food Chem 100 (**2007**) 1126–1131.

[2] H. Sereshti, R. Heidari, S. Samadi, Food Chem 143 (**2014**) 499–505.

Dispersive micro-solid-phase extraction of catecholamines from biological samples based on Fe_3O_4@MIL-100 (Fe) core-shell nanoparticles grafted with pyrocatechol

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Dopamine (DA), epinephrine (EP) and norepinephrine (NE) belong to catecholamines family and exist in the mammalian central nervous system [1,2].The determination of trace concentration of catecholamines and related compounds in biological samples requires highly specific and sensitive methods. Recently, metal-organic frameworks (MOFs), built up from organic linkers and inorganic connectors, as a novel class of nanoporous adsorbents have drawn special interest in SPE.Herein, a selective and sensitive method based on dispersive micro-solid-phase extraction was developed for the extraction of DA, EP and NE from biological samples prior to high performance liquid chromatography (HPLC-UV). The Fe_3O_4@MIL-100 (Fe) core-shell nanoparticles grafted with pyrocatechol were synthesized and characterized using scanning electron microscopy, transmission electron microscopy, vibrating sample magnetometry and infrared spectroscopy. The fractional factorial design and central composite design of response surface methodology were used to the experimental design and optimization of extraction efficiency. Under optimized conditions, calibration graphs of DA, EP and NE were linear in a concentration range of 1-300 μg L^{-1} with correlation coefficients more than 0.9966. Limits of detection and quantification were in the ranges of 0.22-0.36 μg L^{-1} and 0.78-1.20 μg L^{-1}, respectively. This procedure was successfully employed in determining target analytes in spiked biological samples; the relative mean recoveries ranged from 91.4 to 103.4%.

Keywords: Catecholamines; Fe_3O_4@MIL-100 (Fe) core-shell nanoparticles; HPLC-UV; response surface methodology

References:

[1] K. Liu, H. Pang, J. Zhang, H. Huang, Q. Liu, Y. Chu, RSC Adv. 4 (2014) 8415.

[2] V. Carrera, E. Sabater, E. Vilanova, M. A. Sogorb, J. Chromatogr. B 847 (2007) 88.

Development of hollow fiber microextraction with using two immiscible organic solvents for determination of Benzodiazepines in biological samples

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Benzodizepines (BZDs) are a class of psychoactive drugs whose core chemical structure is the fusion of a benzene ring and diazepine ring. BZDs generally viewed as safe and effective for short term use, although cognitive impairment and paradoxical effects such as aggression or behavioral disinhibition occasionally occur. BZDs are now among the most commonly prescribed drugs, which increases their potential for addiction and abuse in cases of crime, driving under the influence of drugs, suicide, and drug facilitated sexual assault. For these reasons, simultaneous analysis of BZDs and their metabolites in complicated matrices is of great interest to clinicians and forensic toxicologists

In this research, three-phase hollow fiber liquid microextraction has been used on the basis of the usage of two immiscible organic solvents in lumen and wall pores of hollow fiber prior to GC-ECD for determination of BZDs in plasma and urine samples. The factors affecting the HF-LPME of target analytes such as type of immiscible solvents, pH of donor and acceptor phases, salt addition, extraction time, stirring rate, and hollow fiber length were investigated using the central composite design (CCD) and the optimal extraction conditions were established. Under the optimum conditions, preconcentration factors in a range of 124 – 433, limits of detection (LODs) as low as 0.01 µg L^{-1}, linear dynamic range in the range of 0.05 – 200 µg L^{-1} and the relative standard deviations of < 9.7% were obtained. Finally, the applicability of the proposed method was evaluated using extraction and determination of the BZD drugs in urine and plasma samples. The results demonstrated that three-phase hollow fiber microextraction based on two immiscible solvents has excellent clean-up and high-preconcentration factor and can be served as a simple and sensitive method for monitoring of BZD drugs in the biological sample.

Keywords: Benzodiazepines; Gas chromatography-electron capture detector; Immiscible organic solvents; Three-phase hollow fiber microextraction.

Application of Response Surface Optimization to Remove Brilliant Green by Magnetic Nanoparticles Functionalized from Water Samples.

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In the past decade, the synthesis of maghemite nanoparticles has been intensively developed not only for its great fundamental scientific interest but also for many technological applications in separation and preconcentration of various anions and cations [1]. Method based on mixed hemimicelles assemblies (hemimicelles/admicelles) has been proposed for the removal of a variety of inorganic and organic compounds from complex environmental matrices [2]. In recent years, optimization is the crucial step to find out the best conditions and maximize the desired responses in any experimental subject [3].

Aliquots of 25 ml of the dye solutions with initial concentrations of 80–600 mg L^{-1} in the pH range of 3.0–11.0. A known dosage of Magnetic Nanoparticles and surfactant in the range of 2–20 mg was added to each solution and the suspension was immediately stirred with a magnetic stirrer. After the mixing time elapsed, the magnetic nanoparticles functionalized were magnetically separated and the solution was analyzed for the residual dye.

Determine of dye-removal efficiency and amount of the dye adsorbed onto absorbent was calculated. Evaluation the equilibrium adsorption; several isotherm models which are essential in designing and optimizing of adsorption processes and effect of solution temperature.

Conventionally, the classical method (one-at-a-time) is the lack of inclusion of the interactive effects among variables. However, it could not lead to real optima in many cases. Consequently, procedures for optimization of factors by multivariate techniques have been encouraged, as they are faster, more economical, and effective and allow more than one variable to be optimized simultaneously. Among the various response surface approaches, Box–Behnken design (BBD) have been utilized for the final optimization of desired processes.

Keywords: Dye removal; magnetic Nanoparticles; Box–Behnken; DOE

Reference:

[1] A. Afkhami, R. Moosavi, J. Hazard. Mater. (2010) , 174, 398.
[2] J.D. Li, Y.Q. Cai, Y.L. Shi, S.F. Mou, G.B. Jiang, J. Chromatogr. A(2007) 1139, 178.
[3]Javad Zolgharnein, Ali Shahmoradi, Jahan B. Ghasemi. J. Chemometrics 2013; 27: 12–20

Development of a greenmicroextractionmethod as hollow fibre based surfactant solution for determination of quercetinin Vegetable juice samples

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A novel and environmental friendly approach, hollow fiber-supported liquid phase microextraction based surfactant solution combined with high performance liquid chromatography (HPLC) was developed for extraction and determination of quercetin in vegetable juice samples. In this method surfactant solution which was used for the first time as a solvent in HF-LPME constitutes a real alternative to organic solvents and has the main advantages of safety, low cost, easily availability of surfactant, and low toxicity compared with classical organic solvents. In present work, quercetin was extracted from aqueous samples (donor phase) into a surfactant solution inside the lumen of the hollow fiber (acceptor phase).After extraction, quercetin was analyzed by injecting the analyte enriched acceptor phase into the HPLC. In order to obtain high recoveries and enrichment factors of the analyte extraction conditions were evaluated, including: donor pH, stirring speed, extraction time, effect of salt and, concentration of acceptor phase.Under the optimal conditions the linearity of the new developed method was 0.5-1000 ng mL^{-1} with coefficient of correlation greater than o.999. The limits of detection and quantification were 0.26 and 0.78 ng mL^{-1}, respectively. The extraction recovery was 95% and the preconcentration factor was 248. While the intra-day and inter-day relative standard deviations (n=3) less than 4% were reported.The method was successfully applied for the extraction and preconcentration of quercetin injuice of Lycopersicum esculentum (tomato) and Allium cepa (onion).The present method provides a simple and inexpensive sample preparation, easy to use and also friendly environment.

Keywords: Hollow fiber; HPLC-UV; Quercetin; Surfactant

Determination of solvent residuals in pharmaceuticals with a novel highly-efficiency layer-by-layer graphene oxide-coated SPME fiber

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A novelrobust, reliable and durable nanocomposite solid-phase microextraction (SPME) fiber was prepared by layer-by-layer coating of 3-aminopropyltriethoxysilane-functionalized graphene(APTS) on a stainless steel wire. Then, the proposed fiber was used for headspace SPME (HS-SPME) and trapping of toluene as a residual solvent in solid penicillin vials followed by gas chromatography-flame ionization detection (GC-FID). It had significant stability and durability and was successfully applied for more than one hundred analyses without any damage or change in its extraction efficiency.

The effects of main experimental parameters affecting the fiber preparation process and the HS-SPME-GC-FID method, including extraction time and temperature, water content of sample, and desorption time and temperature were studied. Under the optimized parameters (i.e., extraction temperature: 50 °C, extraction time: 30 min, water content: 10 µL, desorption time: 1 min and desorption temperature: 250 °C), the proposed method was validated for limit of detection (LOD), limit of quantification (LOQ), linear dynamic range (LDR) and repeatability (relative standard deviation, RSD%) Under optimal conditions, the LDR of the method was obtained in the range of 0.2-10 µg $g^{-1}$with the correlation coefficients greater than 0.99. LOD and LOQ were 60 ng g^{-1} and 200 ng g^{-1}, respectively. RSDs% for the determination of toluene at different concentration levels were lower than 5.2% (n=3). The recoveries, for different drug samples, were obtained in the range of 92.3-108.6%. The results established that the proposed HS-SPME-GC-FID method with APTES nanocomposite fiber could be successfully used for quantitative tracing of solvent residuals in various pharmaceutical drugs.

Keywords: GC-FID; HS-SPME; PHARMACEUTICALS; Solvent residual; Toluene;3-aminopropyltriethoxysilane-functionalized graphene(APTS).

MWCNTs/ATSB fiber for Solid Phase MicroExtraction: Study of benzene-17β-estradiol interaction.

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Endocrine disrupting chemicals are compounds that alter the normal functioning of the endocrine system. Benzene is organic liquid which has more applications in chemical industries. Benzene receives an increasing consideration as potential endocrine disrupters. Physiological estrogens, including 17β-estradiol (E2) fluctuate with life stage, are suggesting specific roles for them in biological and disease processes. Understanding of the interaction processes is the key to describe the fate of benzene in biological media. Solid Phase Micro Extraction fiber containing multi walled carbon nanotubes/Aluminum tri-sec-butylate sol-gel based on copper wire was developed. The objectives of this study were to evaluate total, bound and freely dissolved amount of benzene in presence of 17β-estradiol. The optimum conditions of microextraction process were selected and under optimized conditions, in vitro experiments were conducted utilizing a HeadSpace Solid Phase MicroExtraction (HS-SPME) combined with Gas Chromatography–flame ionization (FID) detector. Scatchard plot, binding constant, binding percentage, the number of binding sites per hormone molecule was determined. Binding percentage, the number of binding sites is 25.21 and $K1=34.58\times10^6$, $K2=0.1181\times10^6$ and 1 respectively. The results confirmed that benzene bound to one class of binding sites on 17β-estradiol. The value range of K suggested the existence of high affinity specific binding for E2.

Keywords: Benzene; 17β-estradiol; Interaction; MWCNTs; solid phase microextraction.

References:

[1] A. Costantini, G. Gorini, D. Consonni, L. Miligi, L. Giovannetti, M. Quinn, Tumori, 95 (2009) 8.
[2] H. Bahadar, S. Mostafaiou, M. Abdollahi, Toxicol. Appl. Pharmacol, 276 (2014) 83.
[3] Z. Es’haghi, M. Ebrahimi, M.S. Hosseini, J. Chromatogr. A, 1218 (2011) 3400.

Development of New graphene oxide nanosheet/$ZrOCl_2$ coating for Solid Phase MicroExtraction and its application for the analysis of Aliphatic Chlorinated Solvents

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Solid phase microextraction (SPME) has been used as an in situ sampling technique for a wide range of volatile organic chemicals. This paper presents a study on the graphene oxide nanosheet/ $ZrOCl_2$ coated on piece of copper wire used as extraction fiber for head space solid phase microextraction (HS-SPME) combined with Gas chromatography (GC) with electron capture detector (ECD) and applied to an extended monitoring survey of five volatile aliphatic chlorinated solvents (dichloromethane, carbon tetrachloride, chloroform, trichloroethylene and tetrachloroethylene). For quantitative purposes SPME was validated. Calibration curves were constructed for aliphatic chlorinated solvents in the concentration ranges of 0.5–1900 $\mu g.mL^{-1}$ with correlation coefficients (r) 0.9839–0.9990 for analytes. Important parameters influencing the extraction efficiency such as extraction temperature and time, desorption temperature and time and addition of salt were optimized. The optimized conditions were 20 min extraction time at 40 °C without salt addition. This fiber is stable up to 250 °C and demonstrated high sensitive and fast sampling of aliphatic chlorinated solvents. Wide linear dynamic ranges, Low detection limits, good reproducibility (RSD% 1.04–4.43) and high mechanical durability are some of advantages of the new fiber.

Keywords chlorinated solvents; ECD detector; Gas chromatography; graphene oxide nano sheet; head space solid phase microextraction.

Ctylpyridinium Chloride Modified Graphene Oxide for Solid Phase Extraction-Spectrophotometric Determination of Metoclopramide

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Metoclopramide, 4-amino-5-chloro-2-methoxy-N-(2- diethylamino-ethyl)benzamide (MCP) is a freely soluble drug and is rapidly absorbed from the gastrointestinal tract. It is used for the management of gastrointestinal motility disorders and gastrointestinal reflux and for the prevention of cancer chemotherapy-induced emesis at much higher doses [1].

Graphene oxide was prepared from graphite powder and then was characterized. Graphene oxide was modified in-situ with cetylpyridinium chloride, and then was used for enrichment spectrophotometric determination of MCP. MCP was diazotized with nitrite in acidic media, and then the formed diazonium cation was coupled with 1-naphthol in basic media to produce an azo dye derivative. It seems that formation of hemimicelle-admicelle like structures on the surfaces of graphene oxide nano-sheets helps extraction of the azo dye derivative. The preconcentrated azo dye was eluted by a low volume of basic ethanol, and the ethanolic solution was monitored at 553 nm, spectrophotometrically. The optimum condition for the reactions, extraction and back-extraction was obtained, and the calibration graphs were obtained in the concentration ranges of 4–45 and 45-1100 ng mL^{-1} of MCP. The limit of detection for MCP was obtained 2.8 ng mL^{-1}. The relative standard deviations for 10, 45, 400 and 1000 ng mL^{-1} of MCP were 4.8, 1.6, 0.5 and 0.4, respectively; with recoveries in the range of 98.6-104.9%. Also, the interfering effects of a large number of diverse species were studied. The method was successfully applied for the determination of MCP in various environmental and biological samples.

Keywords Metoclopramide; Solid phase extraction; Modified graphene oxide

References:

[1] Nawal. A. Al-Arfaj, Talanta, 62 (2004) 255–263.

Determination of NSAIDs in biological samples using three-phase hollow fiber microextraction based on two immiscible organic solvents

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Non-steroidal anti-inflammatory drugs (NSAIDs) are a type of pain reliever that are used to treat a variety of conditions that cause pain and inflammation. Although the concentrations of these drugs are relatively low in water (ngL^{-1} to μgL^{-1}), continuous release and chronic exposure to these substances, because of their toxicity, can affect the intestinal, hematopoietic, and renal systems which can be a harmful to human health. Therefore, development of a simple and robust method for the determination of these is necessary for toxicological and therapeutic purposes.

In the present study, three-phase hollow fiber microextraction based on two immiscible organic solvent sprior to GC-MS was developed for extraction and determination of four common NSAIDs, including ibuprofen, naproxen, ketoprofen, and diclofenac from human biological samples. Injection-port derivatization was carried out using N-Methyl-N-(trimethylsilyl) trifluoroacetamide(MSTFA) in order to protect the COOH functional group of NSAIDs. In order to obtain high extraction efficiency, the parameters affecting HF-LPME such as pH of the donor phase, and the type of the acceptor phase and supported liquid membrane solvent were optimized firstly using one variable at a time method and other effective parameters such as the HF length, the extraction time, salt addition, and stirring rate were optimized using the central composite design (CCD) as an authoritative tool. Finally, the applicability of the proposed method was successfully confirmed by extraction and determination of drugs in water and various animal food samples. Comparing to the traditional methods, the proposed method exhibits high sensitivity and high preconcentration factors as well as good precision.

Keywords: Non-steroidal anti-inflammatory drugs; Hollow fiber microextraction; Gas chromatography-mass spectrometry.

Dispersive liquid-liquid microextraction (DLLME) method for determination of tramadol in human urine samples using high performance liquid chromatography

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A rapid and sensitive method has been established for the determination of Tramadol in the urine sample by using dispersive liquid–liquid microextraction (DLLME) coupled with high-performance liquid chromatography with UV detection. A mixture of extraction solvent and dispersive solvent were rapidly injected into 5.0 mL sample containing tramadol, and a cloudy solution was formed. After extraction of the analyte into the fine droplets of extractant, phase separation was performed by centrifugation and the enriched analyte in the sedimented phase was determined by HPLC-UV. Parameters that affect the extraction efficiency, such as the kind and volume of the extraction and disperser solvent, extraction time, and salt addition were investigated and optimized. Under the optimum conditions, the linearity of the method was obtained in the range of 5-20ng mL^{-1} with the correlation coefficients(r) 0.9995. The limit of detection and limit of quantitation were 0.693 and 2.1 $ngmL^{-1}$ and relative standard deviation(RSD) was 4.40% (n=5).The relative recoveries of tramadol from urine sample at spiking level 10 ng mL^{-1} was 93.8%. In this paper, a simple, rapid, and sensitive DLLME technique coupled with HPLC -UV has been developed for the determination Tramadol. The method can provide a good repeatability, high enrichment factor, and good recovery with a short analysis time. The comparison of the proposed DLLME method with other extraction methods such as SPME, LPME, and SPE indicates that DLLME can offer advantages of speed, simplicity, ease of operation, and a low consumption of organic solvent[1].

Keywords: Dispersive liquid-liquid micro extraction, HPLC, Tramadol

Reference:

[1] Q.a. Wu, X. Zhou, Y. Li, X. Zang, C. Wang, Z. Wang, Anal BioanalChem, 393 (2009) 1755.

A sol-gel based amino-functionalized coating on steel fiber for headspace solid-phase microextraction of 2-phenylethanol from rose water

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Solid-phase microextraction (SPME) is a preconcentration technique with many advantages which has been applied to the extraction of analytes from different matrices [1-3]. A method based on headspace solid-phase microextraction (HS-SPME) and gas chromatography flame ionization detection (GC–FID) for the determination of 2-phenylethanol in aqueous samples was developed. A sol-gel based coating on stainless steel wire was prepared using 3-(trimethoxysilyl propyl) amine as precursor. Important parameters influencing the efficiency of SPME process, such as extraction time, extraction temperature, ionic strength, pH, desorption time, and desorption temperature were optimized and an extraction time of 30 min at 50 °C gave maximum peak area, when NaCl (30% w/v) was added to the aqueous sample. The linear range for determination of 2-phenylethanol was between 0.1 and 1000 µg.mL^{-1}. Limit of detection was 0.01 µg.mL^{-1}, and the interday and intraday relative standard deviations at 1.0 µg.mL^{-1} concentration level (N= 5) using a single fiber were 5.4% and 18.2%, respectively. The fiber-to-fiber RSD% (N=3) was 5.40% at 1.0 µg.mL^{-1}. The developed method was successfully applied to various rose water samples. The relative recoveries were determined after spiking a rose water sample at three concentration levels from 1 to100 µg.mL^{-1}. The recoveries found varied from 93.7 to 103%

Keywords: Gas chromatography- flame ionization detector; 2-Phenylethanol; Sol-gel; Solid-phase microextraction

References:

[1] H. Bagheri, A. Aghakhani, A. Es-haghi, Chromatographia, 66 (2007) 779.
[2] D. Wang, S.L. Chong, A. Malik, Analytical Chemistry, 69 (1997) 4566.
[3] M. Behzadi, E. Noroozian, M. Mirzaei, Talanta, 108 (2013) 66.

A New Method to Identify and Removal of Antidegradants from Polymer Vulcanizates by Solvent Extraction

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Antidegradants in tire play an important role in protecting rubber from the outside or inside environment such as ozone, oxygen, ultraviolet ray, and heat. These rubber chemicals interrupt identification of oil type by FT-IR techniques.

To eliminate antidegradants from polymer compound, each sample was cut into 1 mm^3 in size. About 0.1 g of sample is weighted and extracted with 1.5 ml acetonitrile (ACN) in a vial at oven for 4h.The qualitative and quantitative analysis of antidegradants was performed by GC. The retention time is the one reaching from injection to the peak and characteristic of the chemicals. The area produced for each peak is proportional to its concentration. Dibutyl phthalate (DBP) as the internal standard is used to determine the amount of antidegradants. After dissolving antidegradants in raw with ACN, it was identify that the retention time. It was known that extraction of antidegradants with ACN from polymer was independent of the effect of temperature. Therefore all sample were extracted at 80˚C oven for 4h.The extracted materials are DBP (0.31), TMDQ (11.24), and a trace of oil by GC. These chemicals must be eliminated completely as described in the effect of temperature on extraction. In result qualitative and quantitative analysis of antidegradants was performed by GC.

Keywords ACN; Antidegradant; GC; Polymer; Solvent extraction

References:

[1] R.W. Keller, Rubber Chem.Technol., 637 (1985) 58.
[2] P.J. Dimauro, H.L. Paris, M. A. Faith, Rubber Chem.Technol 973 (1979) 52.
[3] M.S. Kim, K.S. Sohn, I.S.Kim, Aero Technology Research Institute. (2012) 395.

Preparation and investigation of electrospun CH_3MOF-5/PAN composite nanofibers as Solid-Phase Extraction adsorbent for the preconcentration of trace levonorgestrel and megestrol acetate in biological samples

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The miniaturization of sample preparation device was successfully fabricated by packing 5 mg electrospun composite nanofibers of methyl-modified metal–organic framework-5/ Polyacrylonitrile (CH_3MOF-5/PAN) into mini-disc cartridges for pre-concentration and separation of two estrogenic drugs, Levonorgestrel and Megestrol acetate, in urine samples. A simple, cheap, and accessible electrospining method was employed to prepare a water stable CH_3MOF-5/PAN composite nanofibers. The nanofibres were characterized by scanning electron microscopy, thermogravimetric analysis, Fourier transform infrared spectroscopy, X-ray diffraction and N_2 adsorption-desorption experiments. Seven important parameters, affecting the extraction efficiency of Levonorgestrel and Megestrol acetate, including: type of eluent and its volume, sorbent amount, pH, ionic strength and sample volume were investigated and optimized. The Optimum extraction conditions were obtained as: 150 µL methanol for type of eluent and its volume, 5 mg for sorbent amount, 5 for pH value, 4 % (w/v) for NaCl concentration and 80 mL for sample volume. Under the optimized condition, the calibration curves were linear ($R^2 > 0.999$) in the range of 0.05 to 100 µg L^{-1}. Limit of detection for both of the analytes were 0.02 µg L^{-1}. The applicability of the method was examined by analyzing the analytes in urine samples. The recoveries of the analytes were in the range of 82.8% to 94.8% that show the capability of the method for determination of the drugs in biological fluids.

Keywords Electrospining; CH_3MOF-5/ PAN; composite nanofibers; Levonorgestrel; Megestrol acetate

Development of multivariate analytical figures of merit for quantitative measurements using comprehensive two-dimensional chromatography

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In the present contribution, multivariate analytical figures of merit (AFOM) were developed according to the new definition of sensitivity (SEN) [1] for comprehensive two-dimensional chromatographic systems (CTDC) with multivariate detectors (i.e., GC×GC-MS and LC×LC-MS) [2]. On this matter, multivariate curve resolution-alternative least squares (MCR-ALS) and parallel factor analysis (PARAFAC) as frequently used second-order calibration algorithms for CTDC were used to obtain pure component profiles (elution profiles in both chromatographic columns and mass spectra), to build calibration curves and to calculate SEN, selectivity (SEL) and limit of detection (LOD) for sought analytes [3]. For this purpose, various two-component systems with calibrated components in calibration set and interferences in test set were simulated with different levels of chromatographic artifacts (i.e., homoscedastic noise (0-10%), heteroscedastic noise (0-10%) and random shifts in two chromatographic columns (0-10%)). Additionally, a new strategy was developed to estimate the noise level using variance-covariance matrix of residuals. Inspection of the results showed that in the absence of noise and shifts, the multivariate AFOMs for MCR-ALS and PARAFAC are similar. However, in the presence of noise and shifts, there was a clear difference of their AFOMs due to the superiority of bilinearity of MCR-ALS relative to trilinearity and quadrilinearity of PARAFAC. As an instance for two-component chromatographic system with 0.1% noise and 1% shift, the SEN, SEL and LOD for MCR-ALS are respectively 0.46, 0.55, and 0.000273 (a.u.) and respectively 0.45, 0.57, and 1.57 (a.u.) for PARAFAC. Finally, the proposed strategy in this work was confirmed by the analysis of GC×GC-MS data of heavy fuel oils.

Keywords: Two-dimensional chromatography; Figures of merit; MCR-ALS; PARAFAC.

References:

[1] A. Olivieri, *Chem. Rev.*, 114 (2014) 5358-5378.
[2] J.V. Seeley, S.K. Seeley, *Anal. Chem.*, 85 (2013) 557-578.
[3] H. Parastar, R. Tauler, *Anal. Chem.*, 86 (2014) 286-297

High-Submicellar Liquid Chromatographic Separation of mono and disaccharides Labeled by UV Detection

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Carbohydrates are the most abundant biological molecules in nature. Carbohydrates lack a light-absorbing chromophore, which makes direct UV detection impossible unless a derivatization procedure is involved prior to analysis.Therefore,the analysis of carbohydrates is very challenging.Carbohydrate analysis by HPLC or other separation techniques coupled to UV detectors is made difficult by the absence of effective chromophores or fluorophores. In this study, a simple and sensitive HPLC-based method for reducing sugar analysis is developed. Condensation with an active methylene group is a quite different type of reaction requiring no acid catalyst. In this study, the condensation was performed with 1-phenyl-3-methyl-5-pyrazolone (PMP) under alkali condition. The reaction could be performed under mild conditions, requiring no acids catalyst and causing no desialylation and isomerization. The labeled monosaccharides were separated by high-submicellar chromatography (HSC) technique.. The mobile phases were prepared with acetonitrile and an aqueous solution of sodium dodecyl sulphate according to the Box-Behenken experimental design. The considered factors in modeling were SDS concentration, mobile phase pH and volume percentage of acetonitrile.The PMP derivatives showed strong UV absorbance at 245 nm. Optimization of separation condition was followed by experimental design and MLR modeling. The effects of considered factors were investigated upon retention time and resolution. The result showed that retention time became shorter as pH increased, but alteration of elution order was not observed. Also, in the pH region of 4.5-5.5, resolution became the highest for most combinations. The best conditions for derivatization were: reaction temperature 70 ^{o}C, reaction time 60 min, reagent concentration 0.5 M, concentration of sodium hydroxide 0.3 M. The PMP-labeling chemistry used is simple and highly sensitive and reproducible. All monosaccharides and disaccharides were resolved by a single chromatographic step. This method can be conveniently employed in biological and biochemical laboratories, where GC and high-pH anion-exchange chromatography or refractive index detector may not be readily available.

Keywords*:* Reducing Carbohydrates, High submicellar liquid chromatography, 1-phenyl-3-methyl-5-pyrazolone (PMP)

A novel extraction technique based on hyperbranchedpolyglycidol/ graphene oxide nanocomposite reinforced hollow fiber solid/liquid microextraction for the measurement of ibuprofen and naproxen in hair and waste water samples

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A new design of hyperbranchedpolyglycidol/ graphene oxide nanocomposite reinforced hollow fiber solid/liquid phase microextraction (HBP/GO -HF- SLPME) coupled with high performance liquid chromatography was used for extraction and determination of ibuprofen and naproxen in hair and waste water samples. The graphene oxide first, synthesized from graphite powders by using modified Hummers approach. Graphene oxide was functionalized with hyperbranchedpolyglycidol using direct polycondensation with thionylchloride. The prepared nanocomposite was applied to extract the target analytes indirect immersion sampling mode. After extraction, the analytes were desorbed with methanol, and then detected by high performance liquid chromatography (HPLC).The main factors influencing the extraction of the analytes: pH of the aqueous feed solution, amount of the sorbent, extraction time, aqueous feed volume, agitation speed, and desorption conditions have been examined in detail. Under the optimized conditions, the linearity was observed in the range of 5-30000 ng mL^{-1} for ibuprofen and 2-10000 ng mL^{-1} for naproxen with correlation coefficients of 0.9968 and 0.9925, respectively. The limits of detection were 2.95 ng mL^{-1} for ibuprofen and 1.54 ng mL^{-1} for naproxen. The relative standard deviations (RSDs) were found to be less than 5% (n = 5).

Keywords: Graphene oxide, Hyperbranchedpolyglycidol, Ibuprofen, Naproxen

Determination of the Diphenylamine in Propellants using Thin-Layer Chromatography-Image Analysis Method

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Nitrocellulose based propellants undergo chemical changes during storage due to autocatalytic decomposition of nitrate esters. The stabilizers (e.g. diphenylamine (DPA)) are added to single base propellants to decelerate the autocatalytic decomposition of nitrocellulose in propellants. In fact, stabilizers act by binding the nitrogen oxides, so that the autocatalytic decomposition of nitrate esters is inhibited. The high performance liquid chromatography (HPLC), an expensive and time consuming method, is used conventionally for quantitative analysis of stabilizer and its nitro derivatives in propellants. In this study, a simple thin layer chromatographic (TLC)-image analysis method was developed for rapid detection and quantitation of DPA in propellants.

Suitable amount of propellant samples were dissolve in acetonitrile. After complete dissolving, 5 µL were transferred on the silica gel TLC plate. Variety of mixture of solvents were tested for separation of DPA from propellant matrix. Finally, a mixture of benzene/carbon tetrachloride/l, 2-dichloroethane with the ratios of 50:30:25 selected as the mobile phase for this purpose. Among visualization reagents that were introduced for aromatic amines, Mandelin’s reagent (Ammonium monovanadate/sulfuric acid), was obtained as suitable reagent to visualize the DPA spots. Image analysis of the scanned TLC plates were performed using the codes written in MATLAB software to quantify the amount of DPA. Based on optimized conditions, the linear range and detection limit of measurements were calculated 0.01-2%w/w $_{\text{(propellant)}}$ and 50 ng respectively. The contents of DPA in real propellant samples were successfully determined by this method that were in good agreement with those obtained by HPLC.

Keywords: Diphenylamine; Image Analysis, Propellant stabilizer; Thin-Layer Chromatography

Dispersive Liquid-Liquid Extraction Combined With Gas Chromatography-Mass Spectrometry for Determination of tri-Ethylene Glycol Dimethacrylate in a nitrocellulose Polymeric Composite

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Tri-Ethylene Glycol Dimethacrylate(tri-EGDMA) is mostly used as deterrent into nitrocellulose based propellants in order to slow down their initial burning rate. a simple method is presented for extraction and determination of tri-EGDMA in solid propellants. At first, propellant grain is dissolved into acetonitrile by shaking/stirring for a minimum of 4 hours. then the nitrocellulose content, which can interfere in GC-MS analysis, is precipitated using aqueous $CaCl_2$ solution. then, for removing water interfering in GC-MS analysis, tri-EGDMA content is extracted into the second organic solvent from mix of water/acetonitrile using dispersive liquid-liquid extraction(DLLE) technique. Parameters affecting the extraction efficiency, including a choice of appropriate second organic solvent, volume of solvents, amount of aqueous $CaCl_2$, initial sample weight, and the extraction time were examined and optimized. the consideration of extraction efficiency showed that 30mg propellant grain, 5 cc acetonitrile, 2cc aqueous $CaCl_2$ solution 2%W/V and 0.5cc Normal Hexane as second organic solvent and extraction time of 10 min are optimized conditions for this purpose. the recovery and the limit of detection of the method obtained 85-93% and at $ng/g_{(propellant)}$ level respectively. the method was successfully applied for determination of tri-EGDMA in propellants.

Keywords Dispersive Liquid-Liquid Extraction; Propellant; Tri-Ethylene Glycol Dimethacrylate

Investigation of the Potential of Amic Acid Compounds as Extractant in Intra-group Separation of Rare Earths

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Liquid-liquid extraction of ions La(III), Eu(III) and Er(III) ions using 4-(dibutyamino)-4-oxobut-2-enoicacid (HL) was comprehensively investigated. Slope analysis demonstrated that the transfer of Ln(III) with HL proceed through a proton-exchange reaction, by formation 1:3 metal ion/ligand extracted complexes[1]. The effect of the parameters influencing the extraction efficiency including kind of the organic diluent, extractant concentration, type of the electrolytet used for ionic strength adjustment, contact time and temperature was evaluated and discussed. Under optimized conditions (aqueous phase: 5 mL, lanthanide ions concentration 1×10^{-4} M, pH5, sodium chloride 0.1 M; organic phase: 5 mL dichloromethane, ligand concentration 0.01M), extraction of lanthanide ions was achieved, after 20 min. magnetically stirring of the phases, at25 °C. The extracted lanthanideions were stripped from the organic phase by diluted nitric acid (0.1 M) solution[2].

It was also found that the cooperative extraction of the studied lanthanides with the mixture of HL and 2-thenoyltrifluoroacetone (HTTA) in the acidic media, augments the extraction of La(III) and Eu(III) ions. Such effect was diminished by increasing the pH of the aqueous phase, revealing the participation of HTTA as an ion exchange extractant, rather than solvating agent as its role was approved in the lower pH region. Such synergistic effect was observed for the extraction of europium ions by the mixture of HL and Tris(2-ethyl)hexyl phosphat, in the all examied pH values (1-6).

Keywords: Amic acid extractant, Intra-group separation, Lanthanide ions, Liquid-liquid extraction, Synergism.

References:

[1] K. Shimojo, N. Aoyagi, T. Saito, H. Okamura, F. Kubota, M. Goto, H. Naganawa, Anal. Sci., 30 (2014) 263.

[2] H. Soltani, M.R. Yaftian, A. Zamani, M. Ghorbanloo, Anal. Bioanal. Chem. Res., 2 (2015) 91.

Cooperation of reduced graphene oxide and Triton X-114 for amelioration of electromembrane-microextraction of Pramipexole

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Pramipexole as a dopamine agonist is prescribed for the treatment of signs and symptoms of Parkinson's disease and restless legs syndrome [1]. A variety of methods have been reported for determination of Pramipexole. Among these methods are spectrophotometric methods [2] which do not provide sufficient sensitivity for trace analysis of this drug. The sophisticated methods such as GC-MS [3] and HPLC-MS [4] are very expensive. Therefore, development of simple, rapid and accurate preconcentration methods followed by conventional analytical methods for determination of Pramipexole is important. The present communication reports a novel electromembrane-microextraction (EME) coupled with HPLC for determination of trace amounts of Pramipexole in urine samples. The combination of reduced graphene oxide (RGO) in the membrane and Triton X-114 in the receiving phase augments the extraction-preconcentration of Pramipexole by EME. RGO was dispersed in the organic solvent (NPOE) which was held in the pores of the fiber wall by capillary forces and sonification. Immobilized RGO acts as a powerful sorbent and affords an additional pathway for analyte transport. The presence of Triton X-114 in donor phase promotes effective migration of ionic analytes across the organic solvent membrane. The optimized experimental conditions included; application of NPOE as the organic solvent, 150 V as the driving force and 0.01 %w/v Triton X-114 with pH 3.5 in the donor and pH 2.0 in the acceptor solutions with stirring rate of 1000 rpm after 15 min. The linear range and enrichment factor was 0.1–1000 ng mL^{-1} and 240, respectively. Intra- and inter-day relative standard deviations were less than 3.8 %. The developed method was used to Pramipexole level monitoring in the urine samples.

Keywords: Pramipexole, Preconcentration, Determination, HPLC, Urine samples.

References:

[1] E. Ghasemi, S. Kheradmand, O. Ghorban-D, Biomed.Chromatogr 28 (2014) 486.
[2] B. Thangabalan et al., J. Pharm. Res 4 (2011) 813.
[3] G. P. Jayesh et al., Biomed. Chromatogr 25 (2011) 524.

Assessment of Quality Control of Echinacea Purpurea Extract by Analytical Methods

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Based on WHO reports, about 80% of world population uses herbal medicines for some aspects of their primary health care. Therefore increasing awareness for ensuring quality and safety of medicinal plants has been concerned. Standardization and quality control of herbals is the process of physicochemical evaluations such as macro and microscopic examination, foreign organic matters, ash values, moisture content, extractive values, qualitative chemical evaluation, chromatographic examination and toxicological studies.

Echinacea is among the most frequently utilized medicinal herbs around the world that are used for cold, flu, sore throats and many other ailments. Quality of Echinacea plant and their extracts are related to contamination such as toxic metal, pesticides residuals and microbes. Complexity of the ingredient in herbal medicines is another source that affects quality of herbal medicine.

In this study extraction of cichoric acid as biomarker from aerial part of echinacea has been achieved and the experimental parameters optimized. Moisture content, ash content, elemental analysis, swelling index, extractive values, pesticide residuals and microbial contamination of herb and its extract have been evaluated. Elemental analysis, extractive values and pesticide residuals determined by analytical methods such as ICP-OES, HPLC, GC-ECD and GE-MS respectively. The results of this study were compared with international standards and showed the content of pesticides, toxic metals, ash content, moisture content were less than permitted level in US and British pharmacopeia.

Keywords: Echinacea purpurea extract; ICP-OES; HPLC; GC-ECD; GE-MS.

Periodic mesoporous organosilica with 4, 4′-bipyridine framework as a novel fiber coating for headspace solid-phase microextraction of phenols environmental samples

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In this work, inorganic hybrid nanocomposite, SBA@BiPy^{2+} 2Cl^{-} was synthesized, and used as a novel fiber for solid phase microextraction (SPME) of four phenols (phenol, 2-nitrophenol, 4-nitrophenol, and 2,4,6-trichlorphenol) in environmental water and soil samples, followed by gas chromatography-flam ionization detection (GC-FID). For synthesize nanocomposite, SBA@BiPy^{2+} 2Cl^{-} , first, N, N′ bis (triethoxysilylpropyl)-4,4′-bipyridinium dichloride, $(TEOS)_2BiPy^{2+}2Cl^{-}$ precursor was synthesized by the reaction of 3-chloropropyltriethoxysilane with 4,4′-bipyridine. The organic– inorganic hybrid nanocomposite, SBA@BiPy^{2+} 2Cl^{-}, was then synthesized by hydrolysis and polycondensation of the precursor and tetraethyl orthosilicate in the presence of poly (ethylene oxide)-b-poly (propylene oxide)-b-poly(ethylene oxide), Pluronic P123. These fibers was characterized by scanning electron microscopy (SEM), FT-IR spectrometer and thermogravimetric analyzer (TGA), transmission electron microscopy (TEM), X-ray diffraction (XRD). Under optimized conditions, a linear relationship was obtained between the peak area and the concentration of phenols in the range of 0.1–40 μgL^{-1}. The detection limits were lower 0.028 for phenols. Intra-day and inter-day precisions for the analysis of analytes were in the range of 1.1–1.9%. This procedure was successfully applied with satisfactory results to the determination four phenols in waters samples. The relative mean recoveries of in waters samples ranged from 92.0% to 101.0%.

Keywords: Phenolic pollutants, SBA@BiPy^{2+} 2Cl^{-} nanocomposite, Solid-phase microextraction, GC-FID.

References:

[1] A. Bashti, A.R. Kiasat, B. Mokhtari, RSC Adv5 (2015) 25816.
[2] W. Du, F. Zhao, B. Zeng, J Chromatogr A 1216 (2009) 3751.
[3] M.M. Abolghasemi, V. Yousefi, J Chromatogr A 1345(2014) 9.

Determination of nicotine in biological samples by GC-FID after its extraction and preconcentration by headspace solid-phase microextraction using a stainless steel fiber coated by polypyrrole nanosorbent

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Polypyrrole (PP) and its derivatives as conductive polymers, due to their different interesting properties, have attracted great interest by scientists for development of chemical sensors, electrochemically controlled devices, and stationary phases for separation and extraction of polar and ionic compounds.

In this research, a stainless steel wire was coated by PP nanosorbent by using an appropriate electrophoretic deposition (EPD) method and applied for headspace solid-phase microextraction (HS-SPME) and preconcentration of nicotine in aqueous samples, followed by gas chromatography-flame ionization detection (GC-FID). The effects of different experimental parameters on the extraction efficiency of the proposed HS-SPME-GC-FID method, such as pH of sample solution, extraction temperature and time, stirring rate, and salt concentration were investigated and optimized. Under the optimum experimental conditions, the calibration curve for nicotine was linear over the range of 0.1-20 μg mL^{-1}. Relative standard deviation (RSD, n= 6) was found to be 7.6%. The proposed HS-SPME-GC-FID method was finally applied for the extraction and determination of nicotine in biological samples. Comparison of the proposed procedure with a validated standard method showed good agreements between the results of HS-SPME-GC-FID and those obtained by the standard method.

Keywords: headspace solid-phase microextraction; Nicotine; GC FID; Polypyrrolenanosorbent; Electrophoretic deposition.

References:

[1] M. Moradi, M. Kaykhaii, A.R. Ghiasvand, S. Shadabi, A. Salehinia, Phytochemical Analysis, 23 (2012) 379.

[2] C. L. Rainey, D.E. Bors, J.V. Goodpaster, Anal. Chem, 86 (2014) 11319.

Extraction and Determination of Stabilizer in a Double-Base Propellant for Estimation of Shelf Life

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The propellant formulations contain ingredients such as nitrocellulose (NC). This nitrate ester tends to decompose over time, releasing nitrogen oxides. If nitrogen oxides are not removed, they act catalytically to accelerate the nitrate ester's degradation. Stabilizers such as centralites (MC and EC) are added to retard the autocatalytic decomposition of NC in double-base propellants.

Chemical interactions in propellants cause dissociation and decomposition of their internal structure. So propellants like other materials has life time which after that, using them has uncertainty. Tracing of stabilizer consumption, is the most important method for determination of chemical life time in propellants. In this article extracting the stabilizer of a double base propellant after tolerating accelerated ageing condition is done, by a new extraction method which has been developed in our laboratory. Under the optimum conditions, recoveries of extraction in samples ranged between about 90.0 and 98.0%.

Gas chromatography was once used as a leading method to determine the stabilizer content in propellants. However, the limitation of the GC method is the inability to separate centralites and their main derivatives, which is thermally decomposed in the GC inlet port. There is no such a problem with high performance liquid chromatography (HPLC) method because of its lower operating temperatures. In this work the stabilizer value determinated by a new HPLC method which has been developed for the quantitative analysis of methyl centralite (MC). Life time is estimated by kinetic parameters from NATO method, zero order, first order and second order kinetic models. The results respectively are 105, 467, 722 and 1478 years.

Keywords: Accelerated Ageing; Double Base Propellant; Stabilizer Consumption; Shelf Life, High Performance Liquid Chromatography (HPLC)

References:

[1] L. Jelisavac, M. Filipovic, Chromatographia 55 (2002) 239.

Extraction and determination of polycyclic aromatic hydrocarbons using polyacrylonitrile / magnetic zeolite composite nanofibers as a new sorbent

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Polycyclic aromatic hydrocabons are persistent organic pollutants which have two or more fused benzene rings. They originate from the incomplete combustion or pyrolysis of organic compounds and are carcinogenic, mutagenic and teratogenic. Therefore, determination of these compounds in environmental samples is very important.

In the present work, a novel magnetic solid phase extraction (MSPE) sorbent, polyacrilonitrile/magnetic zeolite nanofiber, was synthesized by electrospinning method. These electrospun fibers were utilized for extraction of polycyclic aromatic hydrocarbons (PAH_s) in water samples. The PAHs were quantified by GC with flame ionization detection. To reach the optimum extraction efficiency, affecting parameters, including the amounts of sorbent, volume of desorption solvent, sorption and desorption time were investigated by a central composite partial design. The optimum amounts were 41 mg, 0.5 mL, 15.5 and 5 minutes, respectively.

Calibration curves in the range of 30-5000 $ngmL^{-1}$ for naphthalene, acenaphthylene, anthracene, phenanthrene are linear and linear range for acenaphthene is 300-5000 $ngmL^{-1}$. Under the optimum conditions, detection limits were in the range of 0.008–0.2 $ngmL^{-1}$ and the limits of quantification were between 0.03–0.66 $ngmL^{-1}$. The reproducibility was obtained using relative standard deviations (RSDs) less than 13 % by various sorbents and inter- and intra-day precision evaluation. As real samples, several water samples were collected from different areas. Recovery percent of PAH_S were in range of 92 -115%.

Keywords: Electrospinning; Magnetic solid phase extraction; Nanofiber; Polycyclic aromatic hydrocarbons

Application Electromembrane Extraction (EME) for separation Anti-HIV drug zidovudine

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Electromembrane extraction (EME) as a simple, efficient, and low cost analytical method, with minimum environmental impact and compatibility of its acceptor solutions with many of general analytical instruments, was introduced as a novel microextraction technique by Petersen-Bjergaard *et al.*, in 2006. The basic principle of this method relies on electrically induced transfer of charged species from one aqueous solution (donor), across thin layer of a water immiscible solvent (membrane), into a second aqueous solution (acceptor). Two working electrodes are placed into donor and acceptor solutions. Application of DC electric potential in EME significantly increases the extraction speed of species. Compared to other extraction methods, additional extraction selectivity is achieved in EME, since only charged species can be transferred. Several reports were released in the past for describing possible theoretical models of the EME transfer mechanism as well as numerous reports reviewing its latest instrumental developments and applications. The main variables affect the EME efficiency include pH, ionic strength and volume of donor and acceptor solutions, volume and nature of membrane, time extraction, and DC electrical potential. In this research, for the first time, EME was carried out for extraction and preconcentration of zidovudine, as a basic anti-HIV drug. The analyte was transferred through an organic solvent membrane, from an acidified aqueous solution (donor) into the other aqueous solution (acceptor), under a constant DC potential. The efficiency of extractions was evaluated by UV-Vis spectrophotometric determination of analyte in the acceptor solution. Different important experimental variables affect the efficiency of the developed EME method was studied and optimized as; EME device: a narrow Teflon clear tube with I.D.=2.5 mm, working electrodes: 2×30 mm Al strips, donor: 20 µL aqueous solution (pH=4), liquid membrane: 20 µL dichloroethane, acceptor: 20 µL aqueous solution (0.01 M HNO_3), extraction time: 20 min, and DC potential 200 V. The linear dynamic range (LDR) for zidovudine was found to be in the range of 0.001-40 µg mL^{-1} (R^2>0.997).The limit of detection (LODs) obtained 0.05 ng mL^{-1}. The recovery of the proposed EME-UV method was calculated 93%. The relative standard deviation (RSD%) for five repeated analyses of 5 µg mL^{-1} zidovudine was calculated 1.36%. Finally, the proposed EME-UV procedure was successfully applied for the recovery and determination of zidovudine in pharmaceutical product.

Keywords*:* Electromembrane extraction (EME); Anti-HIV drug; Zidovudine; UV-Vis spectrophotometry.

Ionic liquid loaded hollow fiber membrane as a fiber for headspace solid-phase microextraction of aromatic hydrocarbons from water samples

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The headspace solid-phase microextraction (HS-SPME) method with new coating based on 1-vinyl-3-hexyl-imidazolium hexafluorophosphate ([VMIM][PF_6]) ionic liquids loaded on hollow fiber membrane pores using sol-gel formulation coupled with gas chromatography–flame ionization detector (GC–FID) was proposed for the microextraction of benzene, toluene, ethyl benzene and xylenes (BTEX) as model analytes. The extraction temperature, extraction time, effect of salt addition, desorption temperature, desorption time and stirring rate were optimized. Under the optimized conditions, linear dynamic ranges were 0.1 to 100 μgL^{-1} for ethyl benzene and xylenes and 0.3 to 100 $\mu gL^{-1}$for benzene and toluene, the RSD was below 4.8% and limit of detections (LODs) were between 0.04 and 0.15μgL^{-1}. The proposed HS-SPME-GC-FID method was successfully applied for the analysis of BTEX compounds from river and well water samples.

Keywords: Hollow fiber membrane; Ionic liquid; Sol-gel; Solid-phase microextraction

References:

[1] C.L. Arthur, J. Pawliszyn, Anal. Chem. 62 (1990) 2145.
[2] M.A. Farajzadeh, A. A. Matin, Chromatographia, 68 (2008) 443.
[3] A.A. Matin, P. Biparva, M. Gheshlaghi, J. Chromatogr. A, 1374 (2014) 50.

Application of air-assisted liquid-liquid microextraction for determination of lead with flame atomic absorption spectrometry

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Lead is a toxic element and has deleterious effects on multiple organs of the human body. So, much interest and effort have been devoted to its determination in biological fluids [1]. Flame atomic absorption spectrometry (FAAS) is commonly used for this purpose. However, in many cases due to the concentrations lower than detection limits and/or the interferences from the matrix of biological samples, pre-concentration and/or separation processes are inevitable [2]. Microextraction techniques are very useful and popular for the pre-concentration and separation of organic and inorganic analytes at trace levels due to their advantages like simple procedure, high extraction efficiency and low consumption of toxic organic solvents.

In this study, a recently reported technique namely air-assisted liquid-liquid microextraction (AALLME) [3] was investigated for extraction and pre-concentration of trace amounts of Pb^{2+} ions before determination of it by FAAS. O, O- diethyl dithiophosphoric acid was used as a chelating agent to form a hydrophobic complex. AALLME is similar to dispersive liquid-liquid microextraction but in this method there is no need to use a disperser solvent. Some effective parameters on the microextraction and the complex formation were investigated including extraction solvent type and its volume, pH, concentration of the chelating agent and extraction time. Finally, the proposed method was successfully utilized for the pre-concentration and determination of Pb^{2+} ions from different samples to achieve high EFs extraction recoveries nearly 100%, and low detection limits.

Keywords: lead; atomic absorption spectrometry; air-assisted liquid-liquid microextraction

References

[1] M. Soylak, E. Yilmaz, Desalination, 2011, 275, 297–301.
[2] M. H. Sorouraddin, L. Khoshmaram, J. Chinese Chem. Sci., 2010, 57, 1-7.
[3] M.A. Farajzadeh, L. Khoshmaram, Food Chem., 2013, 141, 1881–1887.

Determination of Sodium Benzoate, Potassium Sorbate and Natamycin in Yoghurt samples produced in Khuzestan

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Preservatives are such chemical compounds which are intentionally added to food products in order to cease or postpone undesirable microbiological activities within the extension of product shelf life. In recent years, application of preservatives is restricted due to their detrimental effects on the foods. Because dairy products, and specially yogurt, have a significant role in the food basket of Iranian people; in this study, the yogurt produced in dairy factories of Khuzestan province (South western of Iran) was assessed to determine the presence of preservatives. Therefore, to determine preservatives including sodium benzoate, potassium sorbate and natamycin, 69 yogurt samples from 11 dairy factories located in Khuzestan were collected (in 2014-2015). Evaluation of the preservatives was performed by high performance liquid chromatography equipped with UV-Vis. detector, and chi-square and fischer tests were applied to statistical analyses of the results. The obtained results showed that 98.6% (for sodium benzoate), 72.5% (for potassium sorbate) and 95.7% (for natamycin) of the samples were in good agreement with definite governmental regulations levels. According to Iranian rules, addition of preservatives is prohibited. Also, the investigation reveals that there was no significant difference between the seasons of the sampling year and the existence of preservatives in the samples.

Keywords: Yogurt ; Sodium benzoate; Potassium sorbate; Natamycin; High performance liquid chromatography

Determination of Pb and Cd ions in contaminated water using FAAS after preconcentration by dithizone-modified cellulose acetate polymeric membranes

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This investigation proposes a new method for the determination of lead and cadmium ions from contaminated waters by dithizone-modified cellulose acetate polymeric membranes. This method is fast, cost-effective and eco-friendly. Quantitation of analytes was performed by flame atomic absorption spectrometry technique (FAAS). The method is based on the retention of Pb and Cd by an adsorbent which its effective component is dithizone, a strong chelating ligand with lead and cadmium ions. Some important parameters affecting the analytical performance of the method such as pH, flow rate of the sample solution and eluent; concentration and volume of the eluent were studied. Maximum adsorption capacities of adsorbent for Pb(II) and Cd(II) were 787 and 195 mg g^{-1}, respectively. LODs (3σb) of Pb(II) and Cd(II) were 0.012 and 0.001 mg L^{-1}, respectively. Linear range of calibration curves were 0.044-1.047 and 0.006-0.113 mg L^{-1} for lead and cadmium ions, respectively. RSD% of the method in optimized conditions was below than 5% for lead (0.25 mg L^{-1}) and cadmium (0.025 mg L^{-1}) ions. Enrichment factors of the method were more than 19 and 17 for Pb and Cd ions, respectively.

Keywords: Lead; Cadmium; Dithizone-modified cellulose acetate polymeric membranes; Solid phase extraction; Determination

Mechanical stir-bar sorptive extraction (MSBSE) coupled by gas chromatography as a new method for determination of polycyclic aromatic hydrocarbons in water samples

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In the present work, A new and highly sensitive analytical technique based on mechanical stir bar sorptive extraction followed by gas chromatography-flame ionization detector (MSBSE-GC-FID) for the simultaneous determination of five polycyclic aromatic hydrocarbons (PAHs) in water samples was developed. A polypyrrol-polyaniline nanocomposite conducting polymers was used as extraction phase. Experimental parameters controlling the performance of MSBSE process, were optimized using response surface methodology (RSM) based on central composite design (CCD). Under optimum conditions, the calibration curves showed high levels of linearity (R2 > 0.9922) for PAHs in the range of 0.04-0.45 µg mL−1. Limits of detection (LODs) and limits of quantification (LOQs) were 0.02-1.10 ng mL-1 and 0.06-3.33 ng mL-1, respectively. The relative standard deviations (RSD%) for five analyses at a concentration of 20 ng mL-1 were less than 10%. The recoveries of those compounds in spiked water samples at a concentration of 50 ng mL-1 were obtained from 86% to 100%. High recovery, short extraction time, ease of use and acceptable merit figures compared to other methods are advantages of the new proposed method.

Keywords: Mechanical stir bar sorptive extraction; Polypyrrol-polyaniline; Nanocomposite; Polycyclic aromatic hydrocarbons; Central composite design.

Extraction of trace Vanadium (V) usingoctadecyl silica membrane disks modified Graphene oxide with covalently linked porphyrin (GO–H_2P) in water samples

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Vanadium is a trace element of highly critical role in biochemical processes and of significant importance in environmental, biological and industrial analysis due to itstoxicity. Vanadium is an essential oxygen carrier for marine organism [1,2]. A simple, highly sensitive, accurate and selective method for determination of trace amounts of Vanadium (V) in water samples is presented. a novel Graphene oxide with covalently linked porphyrin solid-phase extraction adsorbent was synthesized by covalently linked porphyrin onto the surfaces of graphite oxides. the rapid extraction and determination of trace amounts of Vanadium (V) ions using octadecyl-bonded silica membrane disks modified by Graphene oxide with covalently linked porphyrin (GO–H_2P)and Atomic Absorption Spectrometry is presented. The method is based on complex formation on the surface of the ENVI-18 DISKTM disks followed by stripping of the retained species by minimum amounts of appropriate organic solvents. In the present study, we report the application of preconcentration techniques still continues increasingly for trace metal determinations by flame atomic absorption spectrometry (FAAS) for quantification of Vanadium (V) in water samples. The maximum capacity of the disks was found to be 389± 4 µg for Vanadium (V) .The limit of detection of the proposed method is 3ng per 1000mL.The method was applied to the extraction and recovery of Vanadium (V) in different water samples.

Keywords: Vanadium (V) ;SPE;Octadecylslica disks; AAS ; Graphene oxide with covalently linked porphyrin (GO–H_2P).

Reference

[1] D.C. Crans, J.J. Smee, E. Gaidamauskas, L. Yang,Chem. Rev. 104 (2004) 849.
[2] A.Moghimi, M.Shabanzadeh, J.Chem Health Risks. 2(2), (2012) 7-18.

Graphen oxide for solid phase extraction-spectrophotometric determination of trace amounts of sulfasalazine

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Sulfasalazine (SZ) was developed in the 1950s specifically to treat rheumatoid arthritis. It was believed at the time that bacterial infections were the cause of rheumatoid arthritis.

Solid-phase extraction (SPE) is a powerful tool to preconcentrate and purify analytes of interest from a great variety of sample matrices. Considering the superior properties and high chemical stability of grapheme oxide (GO), it thus may serve as a good adsorbent for SPE. GO contains polar moieties, such as hydroxy, expoxy, and carboxy groups. The extraction can be carried out with a SPE cartridge/column, or simply by dispersing GO sheets in sample solutions followed by collecting the analyte-adsorbed GO sheets by centrifugation.

GO adsorbent was prepared from graphite powder using the modified Hummer’s method. Then, GO was used for solid phase extraction of SZ. SZ was extracted by GO in hydrochloric acid medium, and then was eluted by a low volume of sodium hydroxide solution. The eluate was monitored spectrophotometrically at 457 nm. The optimum condition for the extraction and elution was obtained, and the calibration graph was obtained in the concentration range of 12–2000 ng mL^{-1} of SZ for ten mL of the aqueous solutions. The limit of detection for SZ was obtained as 8 ng mL^{-1}. The relative standard deviation and recovery for 80 and 160 ng mL^{-1} of SZ solutions¸ were obtained as 3.5 and 1.3%, and 97.5 and 102%, respectively. The selectivity of the method was also evaluated and the method was successfully applied to the determination of SZ in various soil and water samples.

Keywords: Graphene oxide; Solid phase extraction; Spectrophotometry; Sulfasalazine

References:

[1] Q. Liu, J. Shi, J. Sun, T. Wang, L. Zeng, G. Jiang, *Angew. Chem. Int. Ed.* 50 (2011) 5913

Separation and Preconcentration of trace amounts Co (Π) in water samples using Polyhydroxybutyrate-b-polydimethyl siloxane

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In the recent years, pollution of the environment by heavy metals has received considerable attention. These elements accumulate in living organisms and are of high toxic potential. Their wide technological use (fertilizers, mining, pigments), as well as their production from burning oil and coal and incineration of waste causes an extensive anthropogenic contamination of soil, air and water [1]. Several analytical techniques such as flame atomic absorption spectrometry (FAAS) are available for the determination of trace metals with enough sensitivity for the most applications [2].A simple, sensitive and selective method for exteraction of trace amounts of Co(II) in water samples based on the adsorption of Polyhydroxybutyrate-b-polydimethyl siloxane. A new technique using a solid phase extraction (SPE) cartridge with Polyhydroxybutyrate-b-polydimethyl siloxane as sorbent was developed for the preconcentration of trace amounts of Co and was determined by flame atomic absorption spectrometry (FAAS). Some of the important parameters on the preconcentration and complex formation were selected and optimized. Under the optimized conditions the limit of detection (LOD) and limit of quantification (LOQ)were 0.167,0.562 and theproposed methodhas a good reproducibility 0.81% (RSD %).The enrichment factor was 200 and the percentage of recovery was in the range of 95-100% .The method was successfully applied to the recovery of Co2+in different type of water samples. Polyhydroxybutyrate-b-polydimethyl siloxane in this study is full of potential to use as an excellent adsorbent in the extraction method like solid phase extraction(SPE) and solid phase micro extraction(SPME).

Keywords: Polyhydroxybutyrate-b-polydimethyl siloxane; SPE; Preconcentration; FAAS; Co^{2+}

References:

[1] Izatt R.M., Bradshaw J.S., Bruening R.L. 1996. Pure Appl. Chem. 68,1237-1242.
[2] A Moghimi, Russian Journal of Physical Chemistry A ,(2013)87 (11), 1851-1858.

Extraction of Co(II) by Graphene oxide with ethylenediamine adsorbed on surfactant coated C_{18} before determination by FAAS

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Recently, Co has attracted great interest of scientists and researchers worldwide. Co is considered a toxic metal that can accumulate through the food chain, ending in the human body. Co accumulation may Co to haematological disorders and the disturbance of metabolic processes [l,2]. The method is based on (GO–EDA) of Co(II) on surfactant coated C18, modified with a porphyrin -treated graphite oxides (GO–EDA). The retained ions were then eluted with 4 ml of 4 M nitric acid and determined by flame atomic absorption spectrometry (FAAS) at 283.3 nm for Co. The influence of flow rates of sample and eluent solutions, pH, breakthrough volume, effect of foreign ions on chelation and recovery were investigated. 1.5 g of surfactant coated C18 adsorbs 40 mg of the Schiff's base which in turn can retain 15.2±0.8mg of each of the two ions. The limit of detection(3σ) for Co(II) was found to be 3.20 ng l -1. The enrichment factor for both ions are 100. The mentioned method was successfully applied on determination of Co in different water samples. The ions were also speciated by means of three columns system.

Key Words: Determination of Co, Preconcentration, Graphene oxide with ethylenediamine (GO–EDA), FAAS.

References:

[1] Gama, E.M., Lima, AS., and Lemos, VA, J. Hazard. Mater., 2006, vol. 136,757.
[2] A Moghimi, Russian Journal of Physical Chemistry A ,(2013)87 (11), 1851-1858.

Determination of amitraz and carbaryl residues in vegetable oils using liquid–liquid extraction and dispersive liquid–liquid microextraction followed by gas chromatography–flame ionization detection

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Vegetable oils are very common materials in today's marketplace and are commodities in our daily life. The analysis of vegetable oils is of increasing importance in forensic casework and better analytical techniques have been investigated and required.

A simple, fast and economical method has been developed for the determination of amitraz and carbaryl in vegetable oils. The method is based on a dispersive liquid–liquid microextraction (DLLME) technique after a preliminary liquid–liquid extraction step, which is followed by a gas chromatography–flame ionization detection. Initially oil samples were partitioned in a dimethylformamide (DMF)–hexane mixture and then DMF was removed and used as a disperser solvent in the following DLLME procedure in which µL-level of chloroform was used as an extraction solvent. Neither significant matrix effects nor interferences were observed by employing the proposed treatment in analysis of oil samples. The method was successfully applied in determination of target analytes in different sunflower, colza and olive oils.

Keywords: Amitraz, Carbaryl, Dispersive liquid–liquid microextraction, Gas chromatography, Vegetable oils

References:

[1] J. Gromadzka, W. Wardencki, Pol. J. Food Nutr. Sci. 61 (2011) 89.
[2] M. A. Farajzadeh, L. Khoshmaram, A. A. Alizadeh Nabil, J. Food Compost. Anal. 34 (2014) 128.
[3] J. Beltran, F. J. López, F. Hernández, J. Chromatogr. A. 885 (2000) 389.

Development and validation of HPLC method for determination of Bortezomib and assessment of impurities in API samples

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A new, simple, isocratic NP-HPLC method was developed for the separation of Bortezomib (BZB) enantiomers and quantitative determination of (1S,2R)-enantiomer of BZB in active pharmaceutical ingredient (API) samples.BZB is an anticancer drug which is recommended for the treatment of relapsed multiple myeloma [1,2]. Enantiomeric separation was performed on a Chiralpak AD-H column. The mobile phase consisted of a mixture of n-hexane, ethanol, 2-propanol, methanol and TFA (82/8/8/2/0.5 v/v). The developed method was validated as per ICH guidelines and it was proved to be accurate, precise, robust and suitable for the intended purpose. The calibration curve for (1S, 2R)-enantiomer was found to be linear in the concentration range of 0.238-5.360 mg/L with regression coefficient (R^2) of 0.9997. The LOD and LOQ were 0.072 and 0.218 mg/L, respectively.Also, a gradient RP-HPLC method was developed and validated for determination of BZB in API samples. In this regard, a Waters Symmetry Shield RP18 column using a gradient mode elution with mobile phasesA (water/acetonitrile/formic acid, 71.5/28.5/0.1, v/v/v) and B (methanol/water/formic acid, 80/20/0.1, v/v/v) was utilized. The R^2 was 0.9997in the concentration range of 0.256-1026 mg/L. The LOD and LOQ were 0.074 and 0.221 mg/L respectively. The performance of two common integration methods for drawing the baseline between two adjacent peaks (i.e., the drop perpendicular and valley to valley methods) were investigated for the determination of diastereomeric impurity (Imp-D) in the BZB-API samples. The results showed that valley to valley method outperform the drop perpendicular method for calculation of Imp-D peak areas.

Keywords: Bortezomib; Enantiomeric separation; NP-HPLC; Pharmaceutical.

References

[1] S.E. Walker, L.F. Charbonneau, S. Law, CJHP, 67 (2014) 102.
[2] M.E. Bosch, F.S. Rojas, C.B. Ojeda, IJPBS, 2 (2012) 344.

Novel TiO_2/SO_4^{-2} Nano composite for separation of lysozyme from egg white

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Lysozyme is a commercially valuable enzyme which has bactericidal and bacteriostatic properties. It is widely used in food industry as an anti-microbial agent and food preservative and recently has been reported to be used for wound healing and inhibiting angiogenesis and tumor growth. Since, Lysozyme has remarkable application in medical and industrial, and chicken egg white is a rich resource of lysozyme, separation techniques of lysozyme from chicken egg white have been attracted more attention. In this work, TiO_2/SO_4^{-2} nanoparticles (NPs) were synthesized and then characterized by transmission electron microscopy (TEM), scanning electronic microscope (SEM), Brunauer-Emmett-Teller (BET) and Fourier transform infrared spectrometer (FTIR) analysis. The prepared TiO_2/SO_4^{-2}-NPs were used for adsorption and separation of lysozyme from aqueous solutions. The effect of pH, ionic strength, adsorption time and initial lysozyme concentration on the adsorption of lysozyme from aqueous solutions was investigated using batch adsorption process. Also, Amount of lysozyme in solutions was determined by UV-Visible spectroscopy at 280 nm. In optimum condition which equilibrium time=240 min, pH=8.4 and ionic strength=0, the adsorption and separation of 0.2 mg/ml lysozyme in 6 ml aqueous solutions was completely achieved. The relative standard deviation (RSD %) value with three replicates under optimized conditions was 5.3 %. Finally, the performance of the prepared Nano particles for adsorption and separation of lysozyme from egg white was investigated. Results of SDS–PAGE analysis demonstrated that adsorption of lysozyme from egg white is efficient.

Keywords TiO_2/SO_4^{-2} nanoparticles, Lysozyme separation, Egg white.

Cotton coated by silica/graphene oxidenanocomposite as sorbent for needle trap device for extraction of PAHs in contaminated solid samples followed by GC-FID determination

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In this research, a novel sorbent was prepared using cotton coated by silica/graphene oxide (Si/GO) nanocomposite. The synthesized C-Si/GO nanocomposite sorbents was characterized by scanning electron microscopy (SEM) and Fourier transfer infrared spectrometry (FT-IR). Then the sorbent was packed in a needle trap device (NTD) and coupled with gas chromatography-flame ionization detection (GC-FID) for the extraction and determination of seven representative polycyclic aromatic hydrocarbons (PAHs). Different affecting experimental variables in the efficiency of the proposed NTD-GC-FID method, including sample temperatures, desorption time and temperature, flow rate, and moisture content of sample were studied and optimized. Under the optimized experimental conditions linear dynamic ranges (LDRs), for seven PAHs were obtained over the ranges of 2.00 and 400.00 ng mL^{-1}, respectively. For six replicated analysis of 10.00 ng mL^{-1} PAHs, the relative standard deviations (RSDs) were calculated in the range of 10.7-19.7%.

Finally, the prepared nanocomposite NTD was carried out for determination of PAHs in polluted soil samples, collected from different gas stations. Comparison of the results with different NTDs, packed by traditional sorbents, showed the priority of the proposed nanosorbent relative to commercial sorbents.

Keywords: Needle trap device; Cotton-silica/graphene oxide nanocomposite; PAHs; GC-FID.

References:

[1] Y. Wen, L. Chen, J. Li, D. Liu, L. Chen, TrAC Trends in Anal. Chem. 59 (2014) 26.
[2] M. H eidari, A. Bahrami, A.R. Ghiasvand, M.R. Emam, F.G. Shahna, A.R. Soltanian, Talanta 131 (2015) 142.

Application of Hydroxypropyl alpha cyclodextrin (HP-α-CD) as chiral selector in capillary electrophoresis (CE) for quantification of tetrabenazine enantiomers in commercial tablets

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Chiral molecules are constituents of a large proportion of therapeutic agents. The separation of enantiomers is of great interest to the pharmaceutical industry since more than half of pharmaceutically active ingredients are chiral. A simple, accurate, precise and sensitive method using cyclodextrin for separation of enantiomers of tetrabenazine in the commercial tablets has been established. Several types of CD were evaluated. For development of a stereoselective CE method, various effective parameters on the enantioseparation were optimized. The best results were achieved on an uncoated fused silica capillary at 25°C using phosphate buffer (100 mM, pH 3) containing 7% w/v hydroxypropyl-α-CD. The UV detector was set at 214 nm and a constant voltage of 18 kV was applied. The method has shown adequate separation for tetrabenazine enantiomers from its degradation products. The range of quantitation for both enantiomers was 5–100 mg/L. Intra- and inter-day RSD (n = 6) was < 4%. The limit of quantification that produced the requisite precision and accuracy was found to be 5 mg/L for both enantiomers. The method was applied for the quantification of tetrabenazine enantiomers in commercial tablets.

Keywords: Capillary electrophoresis, Enantioseparation, Hydroxypropyl-α-CD, Tetrabenazine

References:

[1] A. R. Fakhari, S. Nojavan, S. Haghgoo, A. Mohammadi, Electrophoresis 29 (2008) 4583–4592.

[2] S. Nojavan, S. Pourmoslemi, H. Behdad, A. R. Fakhari, A. Mohammadi, Chirality 26 (2014) 394–399.

[3] S. Nojavan, A. R. Fakhari, J. Sep. Sci. 33 (2010) 3231–3238.

Application of Lawsone nanodispersion in dispersive liquid-liquid microextraction for spectrophotometric determination of Cholesterol

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Lawsone (2-hydroxy-1,4-naphthoquinone), also known as hennotannic acid, is a red-orange dye present in the leaves of the henna plant. Lawsone has been found to exhibit antifungal, antibacterial and dermatological properties. Despite having several benefits, Lawsone suffers from low aqueous solubility. Nanonization is one of processes that can help to overcome this drawback [1]. Cholesterol is an important biomarker for various diseases. It acts as a major structural constituent of plasma membranes and is a precursor of biological substances, such as bile acid, vitamin D and steroid hormones [2,3]. In this work, Lawson nanodispersions as a natural compound are introduced in a dispersive liquid-liquid microextraction (DLLME) method for spectrophotometric determination of Cholesterol. The effect of chemical variables such as pH of sample solution, type and volume of dispersing solvent, type and volume of extraction solvent and extraction time on the DLLME procedure was studied and optimum conditions were established. The calibration curve was linear in the range of 5-200 mg L^{-1} (r= 0.9980) with a limit of detection 4.1 mg L^{-1}. The relative standard deviation for 8 replicate determinations of 25 mg L^{-1} and 150 mg L^{-1} of cholesterol were 3.96 % and 1.52 %, respectively. The proposed method was successfully utilized to determine cholesterol in several blood serum, egg and yoghurt.

Keywords: Lawsone nanodispersion, Cholesterol, Spectrophotometric, Dispersive liquid-liquid microextraction

References:

[1] F. Shahidi, Antinutrients and Phytochemicals in Food, ACS Symposium Series; ASC, Washington, DC, 1997.
[2] S. Nantaphol, O. Chailapakul, W. Siangproh, Sens. Actuators, B, 207 (2015) 193.
[3] J. John, A. Reghuwanshi, U. K. Aravind, C.T. Aravindakumar, J. Food Drug Anal., 23 (2015) 219.

Magnetic solid phase extraction coupled with dispersive liquid-liquid microextraction for determination of hydrophobic and hydrophilic drugs

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In this work cetyltrimethyl ammonium bromide (CTAB)-coated Fe_3O_4@decanoic acid was synthesized as an efficient sorbent for coextraction of hydrophobic and hydrophilic drugs. To achieve high preconcentration factors (PFs), efficient clean-up and low detection limits (LODs) the method was coupled to dispersive liquid-liquid microextraction (DLLME) procedure. The combination of these extraction methods with GC-FID was applied for simultaneous extraction and determination of venlafaxine (VLF) as a hydrophilic drug and desipramine (DESI) and clomipramine (CLO) as hydrophobic drugs in urine samples. Different parameters influencing the extraction efficiency including: sample pH, amount of sorbent, sorption time, CTAB concentration, elution solvent and its volume, salt content, elution time, extraction solvent in DLLME step and its volume were optimized. The calibration curves were linear in the concentration range of 5-5000 $\mu g\ L^{-1}$. The LODs were achieved in the range of 1.5-3.0 $\mu g\ L^{-1}$ for DESI, 1.2-2.5 $\mu g\ L^{-1}$ for VLF and 2-4 $\mu g\ L^{-1}$ for CLO, respectively. The percent of extraction recoveries and relative standard deviations (n = 5) were in the range of 82.4-95.9 and 6.1 for DESI, 60.5-92.8 and 6.9 for VLF and 57.2-58.0and 5.5 for CLO, respectively. Ultimately, the applicability of the method was successfully confirmed by the extraction and determination of DESI, VLF and CLO in water and human urine sample.

Keywords: Dispersive liquid-liquid microextraction;Hydrophobic and hydrophilic drugs; Solid phase extraction.

References:

[1] A.A. Asgharinezhad, N. Mollazadeh, H. Ebrahimzadeh, F. Mirbabaei, N. Shekari, J. Chromatogr. A, 1338 (2014) 1.

A novel Organic Gas Steam-Liquid Extraction (OGS-LE) Method as a Development in Liquid- Liquid Extraction Method for the Selective Extraction of Cobalt from Water Samples and Determination with Inductive Coupled Plasma Optical Emission Spectrometry

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In this work, for the first time, organic gas steam- liquid extraction (OGS-LE) was developed as a promotion in liquid- liquid extraction (LLE) method, by use of a special home- made extraction cell that was designed to facilitate traditional LLE method without emulsification with high recovery of extraction by a small amount of organic solvent in one step. This method was used as a fast, simple and efficient method for selective extraction of cobalt(II) from water samples and determination with inductively coupled plasma-optical emission spectrometry (ICP-OES) after back extraction. The saline aqueous sample (20 ml) and organic solvent (5 ml, methyl isobutyl ketone) were injected into the dedicated column in the extraction cell. Organic solvent column was warmed up with heating chamber by a circulator. Using N_2 flotation into organic solvent, gas steam of organic solvent was transferred to the aqueous column. N_2 bubbles in the aqueous column from the bottom upward move and its interaction with aqueous sample. Organic gas steam along with N_2 bubbles after solvation in aqueous sample and supersaturating was collected in the surface of aqueous sample. In this procedure, low density organic solvent was used and no centrifugation was required. 4-(2-pyridylazo) resorcinol (PAR) and tributyl ammonium bromide (TBAB) were used as a complexing ligand and ion- pair reagent, respectively in aqueous sample. The optimized levels of effective parameters were found based on one variable at a time approach. The effects of various cationic and anionic interferences on the percent recovery of Co^{+2} were also studied. Under the optimized conditions, the detection limit, the precision and linearity of the method were found 8.8 µg L-1, 7.62 % (RSD, 0.1 mg L^{-1}, n=6) and 20-1000 µg L^{-1}, respectively. The method performance was studied with determination of Co^{+2} in different water samples. Percentage of extraction was over 90%, the efficiency of the OGS-LE was compared with traditional LLE method. The OGS-LE showed higher efficiency than LLE method.

Keywords Organic gas steam- liquid extraction; Liquid- liquid extraction; Cobalt; Water sample; Inductive coupled plasma optical emission spectrometry

Quantitative Lipid analysis in Nano Liposome as Drug delivery Vehicles by HPLC-UV; Simple, Accurate and low-cost Method

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Nano liposomes are used as ideal vehicles in drug delivery systems (for drug delivery recently) because of their biocompatibility and ability to encapsulate a large amount of drugs. Also they can improve drug potency and efficiency and reduce the side effects or toxicity [1]. There are some design and application problems with nanoliposomes as drug delivery systems that influence stability, time of release, cost of preparation, short shelf life, and poor interaction with certain drugs in which the lipid composition is very important because of its direct effect on entrapment efficiency. Maximum UV absorbance wave length for lipids is (~200–210 nm) that causes difficulties in HPLC-UV method development for quantitative lipid analysis. So, HPLC method coupled with refractive index (RI) or evaporative light scattering detection (ELSD) is applied for lipid analysis [2, 3]. Like mass spectrometry, RI and ELSD have a number of disadvantages including the laborious optimization of a number of operating parameters, destruction of the sample and variable detector response necessitating the use of an internal standard. The refractive index has the disadvantages of being sensitive in temperature, pressure, flow rate and mobile phase composition that cause limitation in application. In this study, a simple, rapid and cost effective HPLC method based on isocratic elution and UV detection has been developed for simultaneous quantification of α-(3-O-cholesteryloxy)-δ-(N-ethylmorpholine)-succineamide (MoChol), cholesteryl-hemisuccinate (Chems) and Cholesterol in nano iposomes containing anti-BCL-2 DNA oligonucleotide. A Full method validation of the proposed method was done based on International Conference on Harmonization (ICH) guidelines.

Keywords Nanoliposome, Lipid Analysis, HPLC-UV, MoChol, Chems and Cholesterol.

References:

[1] D. C. Drummond, O. Meyer, K. Hong, D. B. Kirpotin, , D. Papahadjopoulos, *Pharmacological reviews*, **1999,** 51, 691-744.
[2] K. W. Y. Lee, C. J. Porter, B. J. Boyd, *AAPS PharmSciTech*, **2013**,14, 927-934.
[3] B. Sas, E. Peys, M. Helsen, *Journal of Chromatography A*, **1999**, 864, 179-182.

Application of dithiocarbamate-functionalized SBA-15 as an adsorbent for solid phase extraction of cadmium ions from aqueous sample

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The heavy metals are nonbiodegradable that can accumulate in living tissues which cause cancers and neural problems in human. From an environmental health point of view, it is therefore necessary to remove them from aqueous solution and wastewater. In this study, at first nanosorbent SBA-15 was synthesized from surfactant (P123) and tetraethyl orthosilica (TEOS) and then was functionalized by 3-aminopropyl trimethoxy silane and dithiocarbamate. After that, the functionalized nanosorbent was used for extracting cadmium from water sample. The flame atomic absorption spectrometry was used for determining cadmium ions amount in solution. Functionalized nanosorbent was characterized using elemental analyses, thermogravimetic analysis, FT-IR, BET and XRD.

Effect of different parameters influencing the extraction efficiency such as pH, sorbent dosage, the volume of sample, the type, volume and concentration of the eluting acid was investigated and optimized.

The detection limits (LOD) of the method under optimized condition was 11 µg/L. The relative standard deviation (RSD) (n=6) at a concentration level of 0.5 mg/L was obtained 7.560 %. The calibration curve of cadmium showed linearity in the range of 0.01-1 mg/L. The proposed method was successfully applied to the extraction from spiked well water, river water, sea and waste water samples and relative recoveries were higher than 54/54% for cadmium.

Keywords: SBA-15; cadmium; Water samples; Flame Atomic Absorption Spectrometry

Solid phase extraction-spectrophotometric determination of Lorazepam using magnetic $MnFe_2O_4$ nanoparticles as extractor in biological samples

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This work investigates the potential of magnetic $MnFe_2O_4$ nanoparticles as an adsorbent for separation and preconcentration of trace amounts of Lorazepam in aquatic and biological samples, prior to spectrophotometric determination. The magnetic Manganese ferrite nanoparticles ($MnFe_2O_4$) were synthesized by mixing of $FeCl_3$ and $MnCl_2$. The possible parameters affecting the enrichment were optimized. It is shown that the novel magnetic nano-adsorbent is quite efficient for fast adsorption of Lorazepam in pH =1.0. Various parameters affecting the adsorption of Lorazepam on $MnFe_2O_4$, such as pH of solution, the effect of SDS, desorbing reagent, amount of adsorbent effects, have been investigated. The calibration graph for the determination of Lorazepam was linear in the range of 0.01-0.22 $ngmL^{-1}$. The limit of detection, defined as LOD = $3S_b/m$ was 0.039 $ngmL^{-1}$ of Lorazepam. The relative standard deviation (RSD) was below 0.09% for Lorazepam. The preconcentration factor of 50 was achieved in this method. The proposed procedure has been successfully applied to the determination of Lorazepam in biological samples such as human plasma.

Keywords Lorazepam; Determination; Nanoparticles; SPE; Spectrophotometric

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References:

[1] S. Veyseh, A. Niazi, *Talanta*, **2016,** 147, 117-123.
[2] A. Scott, *Chemical Geology* **1990**, 82, 159-186.

Fast derivatization and air assisted liquid liquid microextraction of ultra trace aliphatic aldehydes in human exhaled breath, followed by gas chromatographic analysis

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Volatile organic compounds (VOCs), such as aliphatic aldehydes are an issue of major concern for many scientists worldwide. Pentanal, hexanal, octanal and nonanal when present in human breath exhales are important lung cancer markers. Their monitoring at trace levels inhuman breath exhales can be used for non-invasive early diagnosis of lung cancer. The aim of this work is to use the effective and newly developed extraction method (co-liquefaction, followed by derivatization and air assisted dispersive liquid-liquid micro-extraction (AALLME)) for the isolation of C3-C9 from lungcancer patient exhaled breath and their ultra-trace analysis by GC-FID.

1000 mL of lung cancer patient exhaled breath sample was taken in the specially fabricated extraction device. 1.4 mL of methanol was added. The extraction device was exposed to ultrasonic bath for the evaporation of solvent and then co-liquefaction at -18ºC with any VOCs present in exhaled breath.0.4 mL of derivatization reagent (MBTH) solution, 0.4 mL of phosphate buffer (pH=5.5) and 0.2 mL H_2O was added into collected metanolic solution. The extraction of derivatizedaldehydes was performed using air assisted dispersive microextraction with 0.1 mL 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 0.2-10 ng mL^{-1}, with correlation coefficients> 0.9975. The limits of detection (LODs) and the limits of quantitation (LOQs) were ranged from 0.04 to 0.11 ng mL^{-1} and 0.1 to 0.3 ng mL^{-1}, respectively. The relative standard deviations (**n**=3) 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.

Keywords: Aldehydes, Co-liquefaction, Derivatization, AALLME, Lung cancer, Gas chromatography

Separation and preconcentration trace amounts of lead ion by using modified nanofibers sorbent

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In recent years pollution of the environment by large amount of toxic elements has been considered as a result of human activities [1]. Therefore, the determination of various toxic metals such as lead in environmental samples is very important task. Lead is one of the most toxic elements, has an accumulative effect and is an environmental priority pollutant. The harmful effects on the human health, caused by the lead contamination, are well-known and among them, the reduction of the enzymatic activity, the kidneys function and the neuromuscular difficulties have been reported [2].

Functionalized nylon-6 nanofibers have been obtained through electrospinning and modification with 5-(4-Dimethylamino-benzyliden)-rhodaninand its performance were evaluated as a sorbent for preconcentrationof trace amounts of lead ions in water samples. Nylon-6 was dissolved in 75% formic acid to yield a solution of 20 wt % nylon-6.The solution was heated at 60 °C and stirred until a homogeneous solution was obtained. The 5-(4-Dimethylamino-benzyliden)-rhodanin was impregnated in the nylon-6 polymer solution and then was electrospun to form composite nanofibers. The composite nanofibers membrane was characterized by SEM and FTIR.Batch adsorption experiments were carried out to study the sorption behavior of lead ions as a function of pH, contact time and initial concentration.The calibration curve was linear from 0.1µg mL^{-1} to 1.0µg mL^{-1}. The proposed method was successfully applied for separation and determination of lead in sea, drinking, river, well water and wastewater samples.

Keywords: Nanofibersnylon-6, Separation, Lead preconcentration, Sorbent.

References:

[1] M. Soylak, M. Elci, L. Divrikli, U. Dogan, Talanta 56 (2002) 565.
[2] A.L.D. Comitrea, B.F. Reis, Talanta 65 (2005) 846.

Extraction of benzodiazepines based on nano structured supramolecular solvent microextraction in biological samples prior to their determination by HPLC with UV detection

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Supramolecular solvent microextraction namely SUPRAS-ME is an extraction technique that provides very high pre-concentration factors. SUPRASs offer a number of interactions for analyte solubilisation. This property makes them suitable for the extraction of organic compounds with a wide polarity range [1]. In this study, a simple versatile extraction method by using of SUPRASs is propsed for extraction of four benzodiazepine drugs (oxazepam, diazepam, alperazolam and clonazepam) from biological samples. The enriched analytes in the surfactant-rich phase were separated and determined by high-performance liquid chromatography with UV detection (HPLC-UV). Different Parameters that affect the extraction efficiecy of the analytes by SUPRASs method (i.e. pH of sample solution, amount of vesicle, ultrasonic time and salt effect) were investigated and optimized. Under the optimal conditions, the preconcentration factors were obtained in the range of 102–176. LDR of the method was determined to be in the range of 0.05–200.0 μg L^{-1} for alperazolam and diazepam, 0.1–100.0 μg L^{-1} for clonazepam and 0.5–100.0 μg L^{-1} for oxazepam with coefficient of determination (R^2) ranging from 0.9961 to 0.9993. The limits of detection for the target benzodiazepines were in the range of 0.02–0.15 μg L^{-1} (based on an S/N ratio of 3). The method was successfully applied for extraction and determination of the drugs in plasma and urine samples and relative recoveries of the compounds studied were in the range of 90.0–98.8%. The intraday (n=5) and interday standard deviations were calculated by extracting the analytes from biological samples through supramolecular solvent microextraction. Interday RSDs% 6.3% and intraday RSDs% 5.7% were obtained. Finally, the proposed method was successfully utilized for the extraction and detremination of benzodiazepines in biological samples.

Keywords: Benzodiazepines; High performance liquid chromatography; Supramolecular solvent microextraction.

References

[1] V.C. nosa, M.L. Lunar, S. Rubio, *J.Chromatography A*, **2011**, *1218* , 8996–9002.

Determination of naproxen in biological fluids using dispersive liquid liquid microextraction followed by corona discharge ion mobility spectrometry with the aid of experimental design

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A fast, simple and sensitive sample preparation procedure based on dispersive liquid-liquid microextraction(DLLME) is proposed for the determination of naproxen in biological samples. The variables of interest, such as pH, the volume of extraction and disperser solvent, salt effect, centrifugation time, centrifugation speed and extraction time in the DLLME process, were optimized with the aid of response surface methodology and experimental design (RSM). Firstly, Plackett-Burman design (PBD) was used to choose the significant variables for the optimization. Secondly, the significant factors were optimized by using a Box-Behnken design (BBD) and the quadratic model between the dependent and the independent variables was built. The proposed method showed good agreement between the experimental data and predictive value, and it has been successfully employed to determine naproxen in biological samples. By using the experimental conditions, obtained in the optimization step, the method allowed naproxen determination in the linear dynamic range of 10–1200 ng.mL^{-1} The limit of detection was 3.8 ng mL^{-1} and, repeatability of the method, described as relative standard deviation, was lower than 4.4% (*n* = 5).

Keywords Dispersive liquid-liquid microextraction . Naproxen . Ion mobility spectrometry . Experimental design

References:

[1] X.L. Cheng, L.X. Zhao, M.L. Liu, J.M. Lin, Anal. Chim. Acta 558 (2006) 296.
[2] N. Alizadeh, A. Mohammadi, M. Tabrizchi, J. Chromatogr. A 1183 (2008)21.
[3] H.A. Mashayekhi, P. Abroomand-Azar, M. Saber-Tehrani, S.H. Waqif, Chromatographia 71 (2010) 517.

Fabrication and modification of cellulose acetate nanofiltration membrane using polyaniline-montmorillonite nanocomposite: Morphology, characterization and performance in removal of pesticides

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Nanocomposite membranes containing cellulose acetate (CA) modified polyaniline-montmorillonite nanocomposite (PANI/MMT) were prepared by a combination of sonication dispersion and wet-phase inversion methods and accordingly, the effect of PANI/MMT addition to the properties and performance of fabricated nanofiltration membranes was investigated. The membranes were characterized by contact angle measurement, scanning electron microscopy (SEM), atomic force microscopy (AFM), X-ray diffraction (XRD), mechanical strength evaluation, thermogravimetric analysis (TGA).

The performance of the membranes was elucidated by the removal of pesticides (methoxyfenozide) in different pHs. The hydrophilicity of the membranes was strongly enhanced by increasing the PANI/MMT concentration. The SEM and AFM images showed that addition of PANI/MMT to the casting solution resulted in nano-structure membranes with a thinner skin layer and a smaller surface pore size. The addition of PANI/MMT improved the mechanical properties and thermal stability of the membranes. Moreover, the pure water flux, permeation and, rejection of methoxyfenozide were significantly improved. The performance of fabricated NF membranes in removal of MF varied depending on the solute and membrane properties as well as solution condition. Finally, concentration of methoxyfenozide in permeation flux was determined by HPLC –UV.

Keywords: cellulose acetate; PANI/MMT nanocomposite; Pesticide; nanofiltration

References:

[1] V. Vatanpour , S. S. Madaeni , R. Moradian, S. Zinadini, B. Astinchap, J. Separation, Purification Technology, 90 (2012) 69.
[2] N. Ghaemi, S.S. Madaeni, A. Alizadeh, P. Daraei, V. Vatanpour, M. Falsafi. Desalination, 290 (2012) 99.

Encapsulation of pistachio green hull extract in nanoliposomes

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Natural extracts are receiving increasing attention due to high level of antioxidant and antimicrobial activities. One of these extracts is the pistachio (*Pistacia vera* L.) green hull extract that has great amount of phenolic compounds. Despite their beneficial effects, the use of plant extracts in foods has been limited because of significant effects on taste and flavor, instability, low bioavailability and so on. To overcome such problems, extract encapsulation could be used. The present study focused on preparation of pistachio green hull extract (500, 750 and 1000ppm) loaded into nanoliposomes by soy lecithin (1%) and evaluation of their physicochemical characteristics involving particle size, size distribution, zeta potential, morphology and encapsulation efficiency. Pistachio green hulls (*Ahmadaghaei* cv) were obtained from the Yazd Agricultural Research Center of Iran and total phenolic content was determined in purified water extracts by the Folin–Ciocalteu method. Extrusion technique was applied to obtain large uni lamellar vesicles (LUVs). Our data showed that amount of phenolics in pistachio green hull extract was 382.2 mg gallic acid equivalent/g extract. The empty capsules had a mean diameter of 99.29 nm and significantly ($p < 0.05$) decreased with the addition of extract. But, the size of nanoliposomes showed no statistically significant difference with the increase of extract concentration. The polydispersity index (PDI) of the samples displayed values from 0.098 to 0.119, indicating homogenous populations ($PDI < 0.3$) of vesicles. The surface potentials of nanoliposomes were in the range of -42.5 to -50.1 mV with no significant difference between treatments, suggesting stable liposome system. The highest encapsulation efficiency (52.93%) was achieved from 1000 ppm of extract. In terms of morphology, atomic force microscopy (AMF) images revealed the lamellae and spherical shaped vesicles. Moreover, AFM size value of nanoliposomes was larger than the same vesicles obtained through the light scattering measurements. Therefore, it was found that liposomes could serve as a suitable system for encapsulation of pistachio green hull extract.

Keywords Encapsulation; Nanoliposome; Phenolic compounds; Pistachio green hull extract

Application of modified nanocomposite for simultaneous extraction and determination of trace amounts of Cd, Cu and Zn ions in food and natural water samples

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The first study on the high efficiency of modified nanocomposite as a new sorbent solid phase extraction (SPE) has been reported. Sorbent modified nanocomposite was used to simultaneous preconcentration and separation Cd, Cu and Zn in food and water samples. A microsample introduction system was employed for the nebulization micro-volume of diluted solution into FAAS. Some effective parameters on extraction and complex formation, such as pH, concentration and volume of the chelating agent, adsorbent dosage, eluent concentration and volume, extraction time, salt effect and sample volume have been optimized. The calibration graph was linear range between 10-500 ng mL^{-1} for Cu (II), between 1-100 ng ml^{-1} for Zn (II) and between 20-800 ng ml^{-1} for Cd (II) and the detection limits were respectively 2.31, 0.43 and 8.93 ng ml^{-1}. Relative standard deviation (RSD) of Cu, Zn and Cd were 1.54%, 2.67% and 1.31% respectively The proposed method has been applied to the determination of cadmium, copper ans zinc ions at ng mL^{-1} levels in real samples sush as tomatoes, potato, wheat flour, red beans, oat, tap water, river water and sea water with satisfactory results.

Keywords: Solid phase extraction, Preconcentration, simultaneous.

Reference:

[1] H. Tahermansouri, Y. Aryanfar, Bulletin of the Korean Chemical Society. 34(2013)149.
[2] K. Yang, M. Gu, Y. Guo, X. Pan, G. Mu, Carbon. 47(2009)1723.

Amino-Functionalized Iron Oxide Magnetic Nanoparticles for Efficient Ultrasound-Assisted Dispersive Magnetic Solid Phase Extraction of Melamine from Aqueous Phases

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Presented is a simple, fast, and efficient solid phase extraction method for determination of melamine in aqueous samples by utilizing amino-functionalized magnetic nanoparticles (AMNPs) as highly effective sorbents. AMNPs were synthesized and characterized through characterization analyses including: FT-IR, XRD, TGA, SEM, TEM, and VSM. While XRD and VSM results confirm the formation of Fe_3O_4 nanoparticles, FT-IR studies certify the modification of these MNPs with an amino layer that is chemically immobilized on their surface. SEM images reveal the spherical morphology of particles with the sizes in the range of 35-60 nm and TEM images show the core-shell structure of synthesized MNPs which are coated with a thin layer of organic phase. The characterized MNPs were utilized to develop a magnetic solid phase extraction method for determination of melamine, a potentially toxic chemical that may be found in adulterated food and dairy products. Affecting parameters on the extraction recovery of melamine were optimized through an orthogonal rotatable central composite design (CCD). Under optimum extraction conditions of melamine (pH= 7, amount of MNPs = 10 mg, sample volume = 30 ml, sonication time = 1 min, and 500 µL of methanol as desorbing solvent), the extraction recovery of 97.4% was obtained via five replications with relative standard deviation of 2.9%. The method was successfully utilized for determination of melamine in aqueous real samples including milk and some dairy products. Regarding the method calibration graphs in sample matrices which are spiked in the observed linear range of 0.01– 600 µg. L^{-1}, pre-concentration factor of 173, method detection limit (MDL) of 0.27 µg. L^{-1}, and lower limit of quantification of 0.9 µg. L^{-1} were obtained. The method exhibits good potentials to be a fast, efficient and reliable method for melamine monitoring in aqueous samples.

Keywords: Solid phase extraction; Magnetic nanoparticles; Melamine; Response surface methodology; Aqueous samples

A novel process for preparation of agarose-coated Fe_3O_4/SiO_2 nanoparticles modified with sodium dodecyl sulfate and their application in separation and determination of phenazopyridine in biological samples

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Agarose-coated Fe_3O_4/SiO_2 nanoparticles modified with sodium dodecyl sulfate as anionic surfactant were synthesized for application in mild separation, enzyme immobilization, etc. For this propose, NPs of Fe_3O_4 were synthesized via a chemical precipitation method with addition of ammonium hydroxide to solutions of Fe^{2+} and Fe^{3+} and then magnetite nanoparticles (Fe_3O_4) homogeneously incorporated into silica spheres using the modified Stober process. The surface of silica coated Fe_3O_4 was modified with addition of sodium dodecyl sulfate as an anionic surfactant and modified nanoparticles were covered with the outer shell of agarose by a layer-by-layer assembly process. The obtained particles were characterized by scanning electron microscopy (SEM), energy dispersive X-ray analysis (EDAX), fourier transform infrared spectroscopy (FT-IR) and the applicability of the synthesized NPs for separation and determination of phenazopyridine as a cationic drug from aqueous solutions was investigated. The effects of different parameters on the separation efficiency of phenazopyridine such as volume of sample, amount of adsorbent, pH of solution, and contact time were optimized by a central composite design (response surface) method and effect of volume and type of eluent and desorption time were studied by a one-at-a-time procedure. The method was successfully applied to the determination of phenazopyridine in biological samples.

Keywords: Sodium dodecyl sulfate, agarose-coated Fe3O4/SiO2, phenazopyridine

Determination of Capsaicin in Hot Chili Sample using High Performance Liquid Chromatography

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Capsaicinoids are the compounds responsible for the pungency of pepper fruits and their products. The various peppers are widely used in many parts of the world for their valued and characteristic sensory properties: color, pungency and aroma.Pungency, a commercially important attribute of peppers, is due to the presence of chemicals from the characteristic capsaicinoids group [1]. Capsaicin content of peppers is one of the major parameters that determine its commercial quality [2]. The first test developed to measure pungency was the Scoville test, which developed in 1912 by Wilbur Scoville [3]. There are five levels of pungency classified using Scoville heat units (SHU): non-pungent (0–700 SHU), mildly pungent (700–3,000 SHU), moderately pungent (3,000–25,000 SHU), highly pungent (25,000–70,000 SHU) and very highly pungent (>80,000 SHU) [4].

The aim of the present study was to determine the content of capsaicin in a one kind hot chili sample that collected from city markets in Karaj,and calculate their pungency in Scoville heat units (SHU).

Extraction of capsaicinoids was done using ethanol as solvent, while high performance liquid chromatography (HPLC) was used for separation, identification and quantitation of the components. Concentration of capsaicin in hot chiliwas 1412.5 ± 140 µg/g and the pungency level was22600SHU.Therefore, this hot chili sampleusing Scoville heat units (SHU),classified in moderately pungent.

Keywords: Capsaicin; Scoville Heat Units (SHU);Pungency;Extraction; High Performance Liquid Chromatography (HPLC)

References:

[1] Perucka, I.; Materska, M. Food Sci. Emerg. Tech. 2 (2001) 189.
[2] Hachiya, S.; Kawabata, F.; Ohnuki, K.; Inoue, N.; Yoneda, H.; Yazawa, S.; Fushiki, T. Biosci. Biotechnol. Biochem. 71 (2007) 671.
[3] Scoville, W.L. J. Am. Pharm. Assoc. 1 (1912) 453.

Reversed-Phase Dispersive Liquid–Liquid Microextraction with Multivariate Optimization for Sensitive Ion ChromatographicDetermination of Anions in Olive Oil.

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A reversed-phase dispersive liquid-liquid microextraction (RP-DLLME) method coupled to ion chromatography (IC) was developed for the preconcentration and determination of NO_3^-, SO_4^{-2}, Cl^-, and Br^- in virgin olive oil. The proposed RP-DLLME method overturns the solvent polarity in the ordinary (normal-phase) DLLME and replaces the toxic solvents with water.In this technique, a small volume of water (or an aqueous buffer solution) is dispersed in a lighter-than-water organic solvent with the aim of a moderately polar solvent as the dispersre. A glass test tube with lengthened conical bottom was fitted inside a centrifuge tube in this work for more efficient withdrawal of the sedimented phase with a microsyringe. Using this method, direct extraction of anions from the oil sample into an aqueous micro-drop for its direct injection into the ion chromatography column was achieved. Volumes of water (solvent) and ethylacetate (disperser), pH of water and centrifugation time as four effective parameters on the extraction were optimized by a central composite design (response surface) method. The method was successfully applied for the determination of NO_3^- SO_4^{-2}, Cl^- and Br^- in olive oil samples.

Keywords: Cenrtal composite design (CCD); Ion choromatography; Olive oil; Reversed-phase dispersive liquid-liquid microextraction (RP-DLLME)

Simultaneous Determination of Pioglitazone and Its Two Active Metabolites in Cow's Milk by Liquid Chromatography Tandem Mass Spectrometry

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Pioglitazone (PIO) hydrochloride is known as an oral antidiabetic agent which is used for the treatment of human type 2 diabetes mellitus [1] and reduces insulin resistance at target tissues. Several studies have indicated the advantage of PIO in ruminant species, but there is no available data about oral administration and bioavailability of this drug in ruminant's milk. PIO is also extensively metabolized by hydroxylation and oxidation. Keto and hydroxy metabolites of PIO are pharmacologically active in animal models of type 2 diabetes [2]. As the milk containing PIO can be guaranteed diabetes patients health, it is needed to its metabolization process by hydroxylation, oxidation and rumen microorganisms- be investigated due to the high potency of rumen microbes involved in feed degradation. Furthermore, determination of pioglitazone and its two active metabolites can lead to optimal dosage of drugs in ruminants's milk. In this study a simple, selective and robust high performance liquid chromatography–electrospray ionization-tandem mass spectrometry (HPLC-ESI-MS/MS) method is developed and fully validated for simultaneous quantitation of PIO, hydroxy pioglitazone (OH-PIO) and ketopioglitazone in cow's milk. A quick, easy, cheap, effective, rugged, and safe (QuEChERS) liquid–liquid partitioning followed by a solid phase dispersion method was applied for sample preparation. The sample extract was analysed by HPLC-ESI-MS/MS in MRM mode. A method was linear ($r^2 > 0.999$) was in the concentrations range of 1- 750 ng/mL for PIO in cow's milk. The method detection and quantitation limits were 0.2 ng/mL and 1ng/mL respectively. The inter- and intra-day RSD% were found to be less than 9%. The developed method was successfully applied to the monitoring of analyte and its metabolites in cow’s milk.

Keywords: HPLC-ESI-MS/MS; Metabolites; Pioglitazone; QuEChERS

References:

[1] B. Jagadeesh et al., J. Chromatogr. B, 930 (2013) 136.
[2] Zh. J. Lin et al., J. Pharm. Biomed. Anal., 33 (2003) 101.

Ultrasound-Assisted Dispersive Liquid-Liquid MicroextractionFollowed High-Performance Liquid Chromatography for the Simultaneous Determination of Theophylline and Caffeine

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Dispersive liquid- liquid microextraction (DLLME) is a new extraction method that usesµL volumes of extraction solvent along with a few mL of dispersive solvents.A cloudy solution is formed when an appropriate mixture of extraction and dispersive solventsis injected into an aqueous sample containing the analytes of interest [1]. The DLLME has several advantages including simplicity, low cost and ease of method development [2].Onemode of DLLME involvesthe use of ultrasonication instead of organic dispersive solvent.

A new, rapid and simple ultrasound-assisted dispersive liquid-liquid microextraction(UA-DLLME) was developed for preconcentration of theophylline and caffeine prior to their determination by high-performance liquid chromatography (HPLC). In this study, the mixture of extraction solvents (170 µL chloroform:decanoic acid 80:20) was rapidly injected into the aqueous sample (5mL) containing theophylline and caffeine by syringe and sample was subjected to ultrasound for 6 min and a cloudy solution was formed in the test tube. Cloudy solution was centrifuged at 4000 rpm for 6 min to separate the phases.Organic phase in the bottom of test tube was injected into HPLC for analysis.Various factors that affected the extraction efficiency were investigated such as type and volume of extraction solvents, pH, type and volume of buffer and extraction time. Under optimized conditions, the calibration curves were linear and ranged from 2 to 200 ng mL^{-1} (r = 0.9992 and 0.9994) and the limits of detection were 0.35 and 0.56 ng mL^{-1} for theophylline and caffeine respectively.The proposed method was successfully applied to the determination of theophylline and caffeine in drinks such as tea and cola.

Keywords: Caffeine; Dispersive liquid-liquid microextraction; Theophylline

References:

[1] A. Sarafraz-Yazdi, A. Amiri, Trend Anal Chem, 29 (2010) 1.
[2]A. Zgoła-Grześkowiak, T. Grześkowiak, TracTrend Anal Chem, 30 (2011) 1382.

Application of synthesized room temperature ionic liquid for separation/preconcentration of Naproxen by in situ solvent formation microextraction

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Naproxen is a nonsteroidal anti-inflammatory drug (NSAID). It works by reducing hormones that cause inflammation and pain in the body. It acts by reducing the levels of prostaglandins, chemicals that are responsible for pain, fever and inflammation. Determination and preconcentration of naproxen to reduce its toxicity in biological fluids is important and therefore sensitive analytical teqnique is required for its detection. Several microextraction methods, such as liquid-phase microextraction (LPME), dispersive liquid–liquid microextraction (DLLME) have been developed to miniaturize the LLE procedure and to reduce the amount of organic solvent as well. Ionic liquids (ILs) are being recently considered as replacement solvents in sample preparations, due to their unique chemical and physical properties. This work is aimed at developing a microextraction technique against very high content of salts, and a new mode of homogeneous liquid-liquid microextraction (HLLME) based on ILs, termed in situ solvent formation microextraction (ISFME) is reported.

This work is based on the use of 1-Butyl-3-methylimidazolium Bromide ionic liquid as extraction solvent. To 1 mL sample solution containing Naproxen added 100 mg of the IL. The mixture was transferred into a conical centrifuge tube, shaken the mixture and 1 mL counter ion $NTf2^-$ was added, upon which a cloudy solution was appeared. The resulted solution was then centrifuged for 6 min at 5000 rpm, the two phases were separated and the organic phase was analyzed for Naproxen content by spectrophotometric detection at 232 nm.

The parameters like sample pH, amount of IL, amount of counter ion and effect of centrifuge conditions were investigated to find the effective ones, and optimized as 3, 100mg, 0.05 mol L^{-1} and 6 min at rate of 5000 rpm respectively.

The IL, $[Bmim]^+[Br]^-$ as extraction solvent and $NTf2^-$ as ion-pairing agent could efficiently phase transfer the Naproxen.

Keywords: Ionic liquid; ISFME; Naproxen; Spectrophotometry

Application of Box-Behnken Design for Optimization of Vortex-assisted Liquid–liquid Microextraction for Determination of Uranium in Water Samples

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Uranium is an important element not only in industrial application but also in energy and environmental problems. It is known to cause acutetoxicological effects in mammals and its compounds are potential occupational carcinogens [1]. Uranium and its compounds are highly toxic which cause progressive or irreversible renal injury. The appraisal of water pollution, which depends on the presence of radionuclide in the ground, is of major environmental concern [2]. In this work, vortex-assisted liquid–liquid microextraction (VALLME) coupled with spectrometry is proposed for the rapid determination of uranium in water sample. In the proposed method, arsenazo is used as a chelating agent. A four-factor, three-level Box-Behnken experimental design which combined the response surface modeling was used to optimize VALLME. Four independent variables, including pH, amount volume of extraction solvent, vortex time and concentration of arsenazo were studied and optimized. Optimum conditions were 4 of pH, 150 µL of volume of carbon tetrachloride, 1.5 min of vortex time, 5.5×10^{-4} mol L^{-1} of concentration of arsenazo. Under the optimum conditions, the calibration graph was linear in the range of 10.0-220.0 ng mL^{-1} and the relative standard deviation (RSD%) was found to be 1.42%. The method was evaluated using synthetic data as well as experimental data and good results were obtained.

Keywords: Box–Behnken design; Uranium; Vortex-assisted liquid-liquid microextraction

References:

[1] V.K. Jain, R.A. Pandya, S.G. Pillai, P.S. Shrivastav, Talanta 70 (2006) 257.

[2] Q. Fana, P.Li, Y. Chena, W.Wu, J. Hazard. Mater 192 (2011) 1851.

HPLC Modeling and Scale-Up for Celecoxib and its isomer Separation

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Celecoxib (Celebrex), a non-steroidal anti-inflammatory drug which its synthesis process is accompanied by its isomers and there are some reports on separation of celecoxib stereoisomers by HPLC [1].The HPLC method development for preparative targets is a time-consuming and costly process. These processes could be improved by applying theoretical based applications to save time, solvent and experimental efforts [2]. Thus, contributed by ESI-MS, The DryLab® software was applied to model the separation of synthesized celecoxib and its co-eluted compounds. Then maximum loadability (2 mg) was gained by touching-band overloading method on the analytical 10 µm C18 4.6×250 mm column. Simple scale-up factor was calculated and 50 mg crude was loaded on 21×250 mm column, which was packed with the same packing, and its accuracy was confirmed by peak shapes.Two interested peaks were collected, rotary evaporated, and freeze dried to complete the removal of methanol and water. More than 95% recovery and 99% products purity were approved with weighing and additional analyze were carried out by analytical HPLC.

Keywords: Celecoxib; HPLC Modeling;Touching Band Overloading; Scale-Up; DryLab

References:

[1] Satyanarayana, U., Sreenivas Rao, D., Avindra Kumar, Y., Moses Babu, J., Rajender Kumar, P., Tirupathi Reddy, J.,*J. Phar. and Biomed. Anal.*(**2004**), *35*, 951-957.
[2] Sandford, L., Shelver, G., *S-Matrix Corporation, Fusion AE Method Development Application Note* (**2009**), 002-09.

Evaluation of acrylate polymer with monolithic nanostructure for extraction of losartan and valsartan from plasma using HPLC and LC-MS/MS

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Losartan (LOS) and valsartan (VAS) are effective agents for the treatment of hypertension and heart failure. Different sample preparation methods such as liquid liquid extraction, solid phase extraction, solid phase microextraction, and protein precipitation were used for their extraction from biological samples. Stir bar sorptive extraction (SBSE) technique has become an important trend topic in sample preparation of biological analysis due to its simple operation, high efficiency and biocompatibility. In this study, a monolithic acrylate polymer as sorptive phase was used for extraction and determination of LOS and VAS in plasma at therapeutic levels through SBSE-high performance liquid chromatography (HPLC) method. After optimization, methanol was selected as desorption solvent that sonicate during 10 min at 45 °C. With the aim of optimizing the extraction step, several factors including ionic strength, extraction time and temperature, and pH of sample were evaluated using design of experiments (DOE).The optimized extraction conditions were fixed in the following values: pH of the conditioning 2, Extraction temperature 70◦C, extraction time 120 min and NaCl25%.The separation was performed on a monolithic column Chromolith® RP-18 (4.6 mm id × 100 mm). Acetonitrile/acetate buffer with pH 3.8 (30:70 v/v) was used as mobile phase at flow rate of 1.0 mL min^{-1}. Detection was performed at 220 nm wavelength. Linear dynamic range of calibration curve in plasma was obtained in the range of 24–1000 ngmL^{-1} (r^2=0.9998), 91–1000 ngmL^{-1} (r^2=0.9971) with limits of detection of 7 and 27 ngmL^{-1} for LOS and VAS, respectively. The average recoveries were obtained 104%, and intra- and inter-day precision were also found with a relative standard deviation <9%. The proposed method was successfully capable to analyze the free drug concentration of LOS and VAS in two volunteer patients, so that the concentration was estimated 11 and 107 ng mL^{-1}, respectively. Also, these results were confirmed using LC-MS/MS.

Keywords: Monolithic SBSE; Monolithic column; LC-MS/MS; Losartan; Valsartan

References:

[1] I. Muszalska, A. Sobczak, A. Dołhań, A. Jelińska, J. Pharm. Sci. 103 (2014) 2.

Air-assisted liquid-liquid microextraction followed by liquid chromatography for determination of aristolochic acid I in urine, flour, and Aristolochiaceae fruit

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Aristolochic acids (AAs), powerful mutagenic and carcinogenic compoundsare structurally related to nitrophenanthrene carboxylic acids.They are not only responsible for tumor development but also for the destructive fibrotic process in the kidney, leading to permanent kidney damage in a short period of time.A number of methods have been developed for the determination of AAs, including CE,HPLC coupled with MS,UV, and FLD.While HPLC–FLD allowed sensitive detection with a low detection limit, a derivatization procedure is required to convert NO_2 groups as fluorescence quenching agents to fluorescence agents, such as NH_2. HPLC–UV is the most economical method for the determination of AAs.Appropriate isolation and purification of the analytes of interest is always a challenging step in the development of analytical methods for complex matrices. SPE and LLE are widely-accepted and increasingly used sample preparation techniques. However, they are time-consuming and use considerable amounts of organic solvents. In order to reduce or eliminate the use of organic solvents and improve the extraction processes, new sample preparation methods, such as pressurized liquid extraction, microwave-assisted extraction,hollow fiber–liquid-phase microextraction, and cloud point extraction have been developed for the extraction of AAs. One type of LPME is AALLME. In this microextraction method, an extraction solvent is transferred into an aqueous sample solution, and then the mixture of organic extractant and aqueous solution containing the target analyte is sucked into a glass syringe and pushed into the test tube several times. This action produces a cloudy solution owing to the dispersion of the organic solvent into the aqueous solution. AALLME is very simple, low cost, enables a significant reduction in the consumption of organic solvents, and does not require high-cost fibers or controlled pressure, temperature, or other conditions that are required in the above-mentioned preparation methods.

This work focuses on developing a simple, effective, and reliable method to quantify for AA I by HPLC–UV determination. The chromatographic separation was performed on a C_{18} column and mobile phase consist of 15% methanol, 20% acetonitrile, and 65% aqueous acetate buffer solution (pH=5.3). Flow rate of 1 mL min^{-1} and wavelength of 254 nm were used in analysis. The LODs and LOQswere obtained as 0.16 and 0.53 µg L^{-1}, respectively. Intra- and inter-day RSDs were obtained as 0.66% and 0.72 % for 10 µg L^{-1}, respectively.

Keywords: Aristolochic Acid, Flour, Fruit, Microextraction, Urine

Microelectromembrane extraction of trace amounts of Cr(VI) based on free liquid membrane

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This contribution describes properties and utilization of free liquid membranes (FLMs) in microelectromembrane extraction (μ-EME) of Cr(VI) from water samples with complex matrices. A FLM was formed as a plug of a selected organic solvent, 1-nonanol, 1-octanol, 1-heptanol, 1-hexanol and 2-ethyl hexanol, in a capillary tube was sandwiched between a plug of aqueous donor and aqueous acceptor solution. The FLM acted as a phase interface that enabled selective transfer of Cr(VI) from donor to acceptor solution. The FLM of Cr(VI) was studied using an ionic carrier enhanced by the application of an electric field. Following the μ-EME, Cr(VI) ions were determined by electrothermal atomic absorption spectrometry. The transportation of Cr(VI) oxoanions across the FLM was explored via the ion-exchange process and electrokinetic migration. The type of FLM, type of acceptor solution, pH of acceptor and donor phase, electrical potential and thickness of FLM were investigated and optimized using MilliQ water. A mixture of an anion exchange carrier (methyltrialkyl-ammonium chloride, Aliquat 336) in the FLM facilitated the transportation of Cr(VI) oxoanions. The best performance was 1-heptanol mixed with 5% Aliquat 336 with 0.5 M $NaClO_4$ as the acceptor. Linearity was obtained in the working range of 0.5–14 μg L^{-1} Cr(VI) (R^2>0.98) at 75V with a 5 min extraction time. The limit of detection was below 0.057 μg L^{-1}. The relative standard deviation was equal to 12.3%. The method was applied to drinking water samples. The recoveries of spiked Cr(VI) in drinking water samples were in the range of 69-94% based on the standard addition method.

Keywords: FLM, μ-EME, Cr(VI), trace, atomic absorption spectrometry.

Dispersive liquid–liquid microextraction coupled with surface plasmon resonance of silver nanoparticles for the determination of captopril in biological sample

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In recent years, nanoscience and nanotechnology have attracted worldwide research interests. In this field, metal NPs such as Au and Ag have established numerous fundamental studies and applications in a various scientific research. AgNPs are probably the most important metal NPs which offer excellent surface plasmon resonance properties exhibiting strong and well-defined colors and easy visualization of color change between individual and wellspaced NPs compared to aggregate ones; yellow to brown. This phenomenon leads to new competencies for chemical sensing that are both useful and extraordinarily sensitive for detection of various species.

In this work a new method was developed for the determination of trace levels of captopril by combination of dispersive liquid-liquid microextraction (DLLME) and microvolume spectrophotometry. In this method surface plasmon resonance of silver nano particles (AgNPs) was used as a colorimetric probe. The AgNPs as a colorimetric probe were synthesized according to a simple method and used in DLLME procedure along with carbon tetrachloride as extraction solvent and ethanol as disperser. The microscopic characterization of the prepared AgNPs showed that by the control of the experimental conditions, it was possible to synthesize highly dispersed AuNPs with an average size of 7 nm. The presence of captopril was affected on plasmon resonance of AgNPs in sedimented phase which was used as a sensing probe for captopril assay. The effect of different variables such as CTAB, sodium hydroxide and ascorbic acid concentration, type and volume of extraction and disperser solvent was investigated and optimized by response surface methodology. The calibration curve was linear in the range of 0.77 to 22.50 nmol L^{-1} of captopril, limit of detection was 0.51 nmol L^{-1} and the relative standard deviation for 11.54 and 19.23 nmol L^{-1} of captopril was 2.12 and 0.72 %, respectively. The method was applied to the determination of analyte in the pharmaceutical, human serum and urine samples.

Keyword: Spectrophotometric, Silver nanoparticles, Surface plasmon resonance, Captopril, Dispersive liquid-liquid microextraction

In situ forming of label -free gold nanoparticles as colorimetric probes using ascorbic acid for determination of zineb after dispersive liquid-liquid microextraction

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Zineb(Zinc(II) ethylenebisdithiocarbamate) is one of the ethylenebisdithiocarbamates (EBDTCs) pesticides that prevents, kills, or repels a pest or acts as a plant regulator,a desiccant, a defoliant, a synergist, or a nitrogen stabilizer. The increasing applications of this pesticide in agriculture result in being released into the environment with hazardous effects that requires the control of the concentration of this compound at trace level in underground and surface waters [1-3].

In this study the label free gold nanoparticles(AuNPs) were used as an extracting probe in a DLLME procedure for zineb assay. The method is based on combination of microextraction approach for sample preconcentration and a sensitive colorimetric assay based on AuNPs probe. The label-free AuNPs with strong plasmon resonance signal at 532 nm were synthesized according a simple and rapid procedure by applying ascorbic acid as reducer and cetyltrimethylammoniumbromide(CTAB) as stabilizer, at room temperature. Absorbance of AuNPs at 532 nm was decreased with increasing of zineb concentration. In order to find the appropriate conditions for DLLME, different experimental parameters such as pH, volume of buffer, effect of stabilizer and effect of reducing agent were studied.The presented method is capable of determining zineb over a range of 0.8–20.0ngml^{-1} with a limit of detection 0.5ngml^{-1}. The relative standard deviation for eight replicate measurements of 16 ngml^{-1}and 4ngml^{-1}of zineb was 1.6% and 4.5%, respectively.This method was applied to determine zineb in natural waters.

Keywords: Dispersive Liquid-Liquid Microextraction ,Dithiocarbamates, Gold nanoparticles, Zineb

References:

[1] M. Giannoulis, L. Giokas, Z. Tsogas, Talanta, 2014, 119, 276-283.
[2] D. Amorello, S. Orecchio, Microchemical Journal, 2013, 110, 334–339.
[3] S. Eustis, Mostafa A. El-Sayed. Chemical Society Reviews, 2006, 35, 209–217

Cooling-assisted in-tube solid-phase microextraction with electropolymerized aniline-grafted multi-walled carbon nanotube for analysis of PAHs in polluted soils

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A novel cooling-assisted in-tubesolid-phase microextraction (CA-IT-SPME) technique was developed byelectropolymerizetion of polyaniline grafted multi-walled carbon nanotube (PANI-MWCNT) sorbent inside a stainless steel needle. This method, coupled with gas chromatography-flame ionization detection (GC-FID) was carried out to analyze polycyclic aromatic hydrocarbons (PAHs) in solid samples. The nanocomposite sorbent was deposited on the interior surface of the stainless steel needle from an aqueous solution by applying a constant DC potential and its structure wascharacterized using FT-IR and SEM instruments.In this cooling-assisted SPME strategy, to enhance the extraction efficiency, the sample is heated to high temperature and simultaneously the nanosorbent cooled to low temperature. This fact causes a significant increase in the matrix/extraction phase partition coefficients for the analytes.

Different important experimental variables on the extraction efficiency of the proposed CA-IT-SPME-GC-FID method were studied. Under the optimal conditions (i.e., extraction temperature:120°C, extraction time: 15 min, sorbent temperature:0°C, desorption time: 4 min,and desorptiontemperature: 280 °C), the limits of detection (LODs) werefound to be 10^{-6} µg mL^{-1}. Linear dynamic ranges (LDRs) for the calibration curves of five analytes were obtained over the range of 0.01-25 µg mL^{-1}. Relative standard deviations (RSDs%) for recovery of 1.0 µg mL^{-1}of PAHs using six replicated analyses, were calculated 9.8%.The developed CA-IT-SPME-GC-FID technique, coupled with gas chromatography-flame ionization detection (GC-FID) was carried out to analyze polycyclic aromatic hydrocarbons (PAHs) in contaminated soil samples.

Keywords: Cooling-assisted in-tube solid-phase microextraction; Polyaniline grafted MWCNT; PAHs; GC-FID; Polluted soil.

Reference:

[1] S.H. Haddadi, J. Pawliszyn, J. Chromatogra. A 1216 (2009) 2783.
[2].H.C. Menezes, Z. de Lourdes Cardeal, J. Chromatogra. A 1218 (2011) 3300.
[3] J. Merib, G. Nardini, J.N. Bianchin, A.N .Dias, V. Simão, E. Carasek, J. sep. sci (2013).

Extraction, Isolation and Identification of Flavonoids From Albizzia Lebbeck Leaves

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The herbs and plant products have been used for combating diseases since ancient. It has been reported that *Albizzia lebbeck* shows antibacterial, anti-inflammatory and antioxidant activity. Ethanolic extract of leaves possess anticancer properties. [1]Flavonoids are polyphenolic compounds that are responsible for the color of the leaves and are present in many plants and are responsible for their antioxidant properties. In this research the ethanolic extract of *Albizzia lebbeck* leaf was prepared using maceration by 70% ethanol. After evaporating the solvent, by distillation under reduced pressure using a rotary evaporator, chlorophyll content was removed by petroleum ether and the residue was re-extracted using liquid-liquid extraction. Finally the solution was injected into a packed chromatographic column with silica gel using wet method. Then 32 solvent systems were tested and the appropriate eluent was selected using TLC. The column parameters were optimized and the best height, diameter and flow rate were selected. Four fractions were isolated using optimized conditions. The obtained GC-Mass chromatograms showed the purity of products. The flavonoids were identified by IR and NMR spectroscopy techniques. The antioxidant activity and [2]total flavonoid content of each fraction was also determined by folin-ciocalteau reagent according to modified colorimetric and spectophotometic method at 765 nm, respectively.

Keywords: Column chromatography; ethanolic extract; Flavonoids; GC-MS

References:

[1] M.D. Amani, El Mousallamy, Phytochemistry, 48 (1998) 759.
[2] J.Y. Lin, C.Y. Tang, Food Chemistry 101 (2007)141.

Development of microfluidic-chip system for liquid–phase microextraction based on two immiscible organic solvents for the extraction and preconcentration of hormonal drugs

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In the present research, for the first time, an on chip liquid phase microextraction (LPME) coupled with high performance liquid chromatography was introduced for the analysis of Levonorgestrel (Levo), Dydrogesterone (Dydo) and Medroxyprogesterone (Medo) as model analytes in biological samples. The chip based LPME setup was composed of two microfabricated polymethyl methacrylate (PMMA) plates with a microporous membrane sandwiched between them in order to separate the sample solution and acceptor phase channels. These channels were used as a flow path for the sample solution and a thin compartment for the acceptor phase. The new setup provides effective and reproducible extractions by using sample solution with low sample volumes. Efficient parameters on consecutive electromembrane extraction of the model analytes were optimized using one variable at a time method. Under the optimized conditions, the new setup offered a good linearity in the range of 10.0–500.0 μg L^{-1} with coefficient of determination (R^2) higher than 0.9909. The relative standard deviation (RSD %) and LOD values were less than 6.5% based on five replicate measurements and 5.0 μg L^{-1} for the model analytes, respectively. The preconcentration factors higher than 18.8-fold were obtained. Finally, the proposed method was successfully applied for determination and quantification of the model analytes in urine and plasma samples.

Keywords Microfluidic chip; Chip-based liquid phase microextraction; Levonorgestrel; Dydrogesterone; Medroxyprogesterone; Microextraction.

References:

[1] N. Petersen and S. Pedersen-Bjergaard, Microfluid Nanofluidics, 9 (2010) 881.
[2] S. Seidi, M. Rezazadeh, Y. Yamini and S. Esmaili, Analyst, 139 (2014) 5531.

Effective on chip electromembrane extraction coupled with UV-Vis spectroscopy and RGB method to detection and quantification of metamphetamine-type drugs

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In the current research, a simple and portable on chip electromembrane extraction analysis device (CEME-AD) was designed for the first time in order to extract and determine methamphetamines as the model analytes.

The chip consists of two polymethyl methacrylate parts which a microfluidic channel is craved in each part as flow path for the sample solution and acceptor phase. The ionized analytes migrate from sample solution through the porous sheet membrane into the acceptor phase. The acceptor phase was collected and added to a micro-tube containing 1,2-naphthoquinone-4-sulphonic acid sodium salt (NQS) solution and therefore, the formation of a reddish-brown compound due to reaction of NQS with methamphetamine was a sign of the presence of methamphetamine in the sample solution. Next, digital picture of the micro-tube contents was analyzed by investigating its Red-Green-Blue (RGB) components. Efficient parameters on CEME-AD of the model analytes were optimized using one variable at a time method. Under optimized conditions, the calibration curve was linear in the range of 10.0–1000 mg L^{-1} with coefficient of determination (r^2) more than 0.9717. The relative standard deviations (RSD %) were less than 9.8% based on four repeated measurements. LODs less than 5.0 mg L^{-1} were obtained. The preconcentration factors higher than 9.2-fold were obtained. Accuracy of the proposed method was validated using UV-visible spectrophotometry and high performance liquid chromatography as a reference methods.

Keywords: On chip extraction; Electromembrane; RGB; Methamphetamine.

References:

[1] N. Petersen and S. Pedersen-Bjergaard, Microfluid Nanofluidics, 9 (2010) 881.
[2] S. Seidi, M. Rezazadeh, Y. Yamini and S. Esmaili, Analyst, 139 (2014) 5531.

Determination of lead and cadmium in real sample with ionic liquid-based ultrasound-air-assisted liquid–liquid microextraction

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A ionic liquid-based ultrasound- air-assisted liquid–liquid microextraction(IL-US-AALLME) was developed for the determination of Pb(II) and Cd(II). Fine organic droplets were formed by sucking and injecting of the mixture of aqueous sample solution and extraction solvent with a syringe for several times in a conical test tube. The application of ultrasound irradiations and AALLME can lead to the rapid formation of fine droplets of the IL in the sample solution, and the contact surface between both immiscible liquids is significantly enhanced. Also the mass transfer of analytes is promoted into the extractant. Under the optimum extraction conditions, the detection limits 0.7 and 0.2 μg L^{-1} with a good relative standard deviation of 1.85 and 2.40 % at 50 μg L^{-1} for Pb(II) and Cd(II) were obtained respectively (n = 10). The method was applied satisfactorily for the preconcentration of Pb(II) and Cd(II) in real samples with relative recoveries 96.6 and 101.0%.

Keywords: Ultrasound; Air-assisted liquid–liquid microextraction; Real samples.

Temperature-Controlled Ionic Liquid-Based DispersiveLiquid Phase Microextraction forUltratrace Spectrophotometric Determination of Uranyl Ion

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Uranium and its compounds are well known as environmentalcontaminants in theearth.Uranyl ion, UO_2^{2+}, is considered to be one of the most soluble species of uranium inaqueous solutions.Therefore, the development of reliable, low cost andsimple methods for uranium determination is highlyrecommended.

A simple and reliable UV-Vis spectrophotometric method associated with temperature-controlled ionic liquid-based dispersive liquid phase microextraction (TCIL-DLPME) has been developed and applied for ultratrace determination of UO_2^{2+}in water samples. The method was based on formation of uranyl complex with 1-(2-pyridylazo)-2-naphthol, (PAN) which isextractable into the ionic liquid phase. Room temperature ionic liquid 1-hexyl-3-methylimidazolium hexa fluorophosphate ($[C_6MIM][PF_6]$) was used as the extracting solvent. Factors affecting extraction efficiency, such as type and volume of ionic liquid, pH, concentration of the chelating agent, dissolution temperature, cooling as well as centrifugation times, and aqueous phase volume were optimized.

Under optimum experimental conditions, the calibration curve was linear in the concentration range of 5-600 μg $L^{-1}UO_2^{2+}$.Preconcentration factor was found to be 200.Limits of detection and quantification were found to be 0.29 and 0.97μg $L^{-1}UO_2^{2+}$, respectively. Wheneverrequired, EDTA or KCN were used to remove interferences of foreign cations. The method was successfully applied to the analysis of some real water samples through spiking known amounts of UO_2^{2+} and acceptable recoveries were achieved.

Keywords; Ionic liquid; PAN;TCIL-DLPME; Uranyl ion; Water samples

References:

[1] M. Kaykhaii, E. Ghasemi, Anal. Methods, 5 (2013) 5260.

A Facil Synthesis of Green SnO_2 and Its Application for the Solid-Phase Extraction of Cu^{2+} Ions

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By the facile and elegant methodology, invoking the principles of Green Chemistry, porous tin dioxide nanoparticles were successfully fabricated. The uniform, and monodispersed porous nanospheres with remarkably high surface area and porosity were synthesized by use of glucose. Glucose acts not only as structure modifying and reducing agent but also plays a role in the formation of spherical aggregates and prevents the spontaneous aggregation. Among all the metal oxides, (SnO_2) is regarded as a promising candidate to serve as the sorbent material for use in the removal of environmental pollutants due to its high purity, large specific surface area and unique adsorption property. The morphology and structure of the prepared SnO_2 were characterized by using the scanning electron microscopy, powder X-ray diffraction, infrared spectroscopy. SnO_2 nanoparticles were used in a solid phase extraction procedure for the separation and preconcentration of Cu^{2+} ions. The heavy metal is then measured by flame atomic absorption spectroscopy. Parameters affecting the adsorption of Cu^{2+} were optimized by one variable at-a-time methodology. The optimum conditions were obtained to be 30 mg of sorbent, pH of 8, 15 min for adsorption time, 5 mL of HNO_3 (0.5 mol L^{-1}) as the eluent and 250 mL for breakthrough volume. Under the optimized conditions, the limit of detection was 10.6 µg L^{-1} and a good linear range of the method was obtained from 32 to 200 µg L^{-1} with relative standard deviation of 2.2%. Ultimately, the applicability of the proposed method for trace analysis of Cu^{2+} was investigated in seawater samples and good recoveries (91%) were acquired. It indicated that the interfering ions in real sample had no significant effect on the extraction efficiency of Cu^{2+} ions.

Keywords: Green synthesis, Solid phase extraction, Seawater sample, Tin dioxide

Application of Supported Liquid Hollow Fiber Membrane for Preconcentration of Ivermectin in Some Dairy Products

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Ivermectin is one of the veterinary drugs commonly used for animal husbandry. For reasons of consumer safety, in recent years its use in animals from which milk is produced for human consumption is mostly unauthorized by European Union (EU) and other food organizations. Among the miniaturized extraction methods such as liquid–phase microextraction (LPME) [1] and solid phase microextraction (SPME) techniques, hollow fiber based LPME technique offers lots of efficient alternatives due to high selectivity and high enrichment factors, as well as simplicity and flexibility [2]. Herein, a two-phase HF-LPME method was used for determination of ivermectin in some dairy products such as milk and yogurt. All the experiments were monitored at λ max =245nm using a simple double beam UV-Vis spectrophotometer. A Taguchi experimental design with an OAD_{16} (4^5) matrix was employed to optimize the affecting parameters. At optimum conditions, values of variables were set as following: di-hexyl ether as an organic solvent (SLM), stirring rate of 900 rpm, pH 12, 45 min extraction time, without addition of salt and 7 ml as the volume sample. The developed method was successfully applied for separation and determination of ivermectin from milk and yogurt samples. The calibration curve was obtained linear in the range of 0.6-5000.0 µg $L^{-1}$and the limit of detection (S/N=3) was 0.۱۹ µg L^{-1} respectively. The relative standard deviation (RSD %) at a 50 µg L^{-1} concentration level (n = 5) was 0.23%.

Keywords: Dairy products; Ivermectin; Supported liquid membrane; Taguchi experimental design

References:

[1] A. Sarafraz Yazdi, M. Y. Khuhawar, P. C. Uden. J. Chromatogr. 594 (1992) 395-399.
[2] L. Xia, B. Hu, Y. Wu, J. Chromatogr A. 1173 (2007) 44-51.

Fe_3O_4/RGO NanocompositeReinforced with Hollow Fiber Membrane as a Highly EfficientAdsorbent for Preconcentration of Ketamine

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In this work is presented a novel and simple preconcentration method calledas: hollow fiber membrane stir bar sorptive microextraction (HF-SBSME).In this technique,Fe_3O_4/RGO nanocomposite as a high performance adsorbentwas prepared by a one-pot solvothermal reaction using GO and $FeCl_3$ as starting materials [1] and immobilized in the pores of hollow fiber through the sol-gel technology [2]. Also, astainless steel rod immersed into the lumen of hollow fiber membrane which played the role of stirring bar. The as-made nanocomposite was characterized by fourier transform infrared spectroscopy (FTIR), field emission scanning electron microscopy, and X-ray diffraction (XRD). The scanning electron microscopy characterization with the related acquiring EDX results indicated that Fe_3O_4 nanoparticles were successfully decorated onto the surfaces of graphene sheets during the solvothermal reaction process.In the following,the applicability of the fabricated device was investigated for preconcentration and determination of trace amounts of ketamine as one of the most widely used club drugs,using gas chromatography (GC)-flame ionization detector (FID).In order to optimize the extraction conditions through affecting parameters (pH, stirring rate, salt addition, extraction time and volume of donor phase), response surface methodology (RSM) was employed as a powerful statistical technique.Theapplication of proposed method to analysis of ketamine in urine samples resulted in a linear concentration range and limit of detectionof 1.1 - 7500.0 µg L^{-1} ($r^2 = 0.997$) and 0.56 µg L^{-1}, respectively.

Keywords: Fe_3O_4/GO nanocomposite;Hollow fiber membrane; Ketamine; Urine

References:

[1] K. Zhou, Y. Zhu, X. Yang, Ch. Li, New J. Chem., 34 (2010) 2950.
[2] S.Vo. Duy, P.B. Fayad, B. Barbeau, M. Pre´ vost, S. Sauve, Talanta 101 (2012)337.

Quantitative removal of ferric and chromate ions from aqueous solutions by using prepared activated carbon adsorbent in laboratory

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Adsorption process is very effective and simple to removal the different species and pollutants from aqueous solutions. Many adsorbents have been used in this process but activated carbon is traditional and low cost adsorbent. Preparation of activated carbon from natural raw materials is very interests nowadays.

In this study, the activated carbon has been prepared in the laboratory from oak shell raw material and used to remove Fe (III) and $Cro_4^=$ ions from aqueous solutions through batch method. SEM images and porosity measurements had been taken to evaluation the structural properties of adsorbent. The results showed that prepared adsorbent have a porous structure with high amount of surface area (520 m^2/g). The effective parameters such as adsorbent dosage, time, and concentration of studied ions and pH of solutions had been optimized. Spectrophotometry method has been used to measurement the adsorption capacity of adsorbent by measuring the absorption signal of ion solutions before and after the contact with adsorbent. In optimum conditions, quantitative removal of Fe (III) and $Cro_4^=$ have been done with 87.3 and 47.4 mg g^{-1} adsorption capacity respectively. Also the experimental equilibrium data were analyzed and fitted to the Langmuir model with highest correlation coefficients related to other tested adsorption models. Also kinetic studies showed that the pseudo-second-order kinetic model is best model to description the kinetic of removal process.

Keywords: Spectrophotometry, Activated carbon, Adsorbent, Removal ions, Oak shell, Ferric, Chromate

Production of new adsorbent activated carbon fromwild cherry core native of Kurdistan: application in removal of three acidic dyes from aqueous solution

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Pollution of waters with various hazardous pollutants such as dyes from textile and printing industries and etc is a serious problem of modern life. Adsorption process is very effective and simple to removal the different species and pollutants from aqueous solutions. Many adsorbents have been used in this process such as activated carbon as traditional and low cost adsorbent. Preparation of activated carbon from natural raw materials is very interests nowadays.
In this study, the wild cherry core native of Kurdistan state was used to production of activated carbon by thermo chemical method. The core of the fruit after washing and crushing, were meshed by sieve mesh standard. Zinc chloride as chemical activator was mix with different amounts of selected raw material. The prepared samples were converted to activated carbon in electrical furnaces under inert nitrogen atmosphere. After cooling the chamber furnace the samples were out and powder. Removing of acid orange 10 was selected as indicator the best proportion of chemical activator to raw material. The results showed that the 1:1 proportion was best. SEM and BET techniques for structural analysis of produced activated carbon samples were used. These results also showed the 1:1 proportion has been best. In after step the application of produced adsorbent to removing three acidic dyes (acid orange 10, acid blue 113,and acid red 18) were investigated. The amount of adsorbent, time, concentration of dyes and pH were optimized in optimum conditions in aqueous solutions. The adsorption capacity were calculated 30, 50, 33/33 mg/g for acid orange 10, acid blue 113, acid red 18 respectively. Also the thermodynamics were done to determine the adsorbent isotherms the Langmuir isotherm was fitted with high Correlation coefficient to all optimum date. The second order kinetic equation was best to pseudo-second-order kinetic model to explain the kinetic process of adsorbent.

Keywords: Oak fruit, Activated carbon, Acidic dye, Adsorption isotherm, Dye removal

Magnetic Nanocellulose/Halloysite Nanotubes Composite M(NC/HNTs) as Nanoadsorbent for Removal of Nickel Ion from Aqueous Solution

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In this study, magnetic nanocellulose/halloysite nanotubes composite M(NC/HNTs) was performed for Nickel ions removal from aqueous solution. In the first step, magnetic iron oxide (Fe_3O_4) nanoparticles were prepared by a chemical co-precipitation method and then, M(NC/HNTs) composite was synthesized. The prepared nanocomposite was characterized by Fourier transform infrared spectroscopy (FT-IR), scanning electron microscopy (SEM), X-ray diffraction (XRD) teqniques. The magnetization values of magnetic nanoparticles were measured with vibrating sample magnetometer (VSM). After that the mentioned nanocomposite was used to remove Nickel and measurements were performs by Atomic Absorption Spectroscopy(AAS). Effect of operating parameters effecting the removal of Nickel ions onto M(NC/HNTs) agitation speed and temperature were investigated and optimized. The results showed that at the optimal conditions, nano-adsorbent Nickel removal from aqueous solution with removal efficiency %95. The M(NC/HNTs) nanocomposite was stable and easily recovered. The synthesized nanocomposite can be a good candidate for Nickel removal from aqueous solution and industrial wastewater.

Keywords: Magnetic; Nanocellulose; Halloysite nanotube; Nanoadsorbent; Nickel

References:

[1]- A. H. Lu, E. L. Salabs, F. Schuth, *Angew. Chem. Int. Edit.* 46, (**2007**), 1222.
[2]- M. Faraji, Y. Yamini, M. Rezaee, *J. Iran. Chem. Soc*. 7, (**2010**), 37.
[3]-S. H. Sun, H. Zeng, D. B. Robinson, S. Raoux, *Chem. Soc*. 126, (**2004**), 273.

Quantitative assessment of the adulteration of peanut in almond powder samples using gas chromatographic fatty acid fingerprinting and chemometrics

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Adulteration of food products, involving the replacement of high-cost ingredients with cheaper substitutes, is one of the most popular types of economic fraud. Adulteration currently is a growing concern in the food industry, especially for high-priced products and there is a need for rapid and simple detection methods for detection of adulteration.

Almond (Prunus amygdalus) is one of the most popular nuts on a worldwide basis. Its seeds are typically used as snack foods and its powder as ingredients in a variety of processed foods, notably bakery and confectionery products. The most frequent adulteration in almond powder is carried out with peanut because of its lower price. Regarding the chemical composition of almond and peanut, fatty acid fingerprinting could be applied as a means of investigation of peanut adulteration in almond powder samples. Therefore, the main aim of this study was to establish a reliable model using multivariate calibration methods and GC fingerprinting for detection and determination of peanut adulteration in almond powder samples. For this purpose, the fatty acid profiles of almond samples adulterated with different weight ratios of peanut (5-90% (w/w)), were considered to generate chromatographic fingerprints. Principal component analysis (PCA) was used to investigate the discrimination of the samples, linear discriminant analysis (LDA) applied to detection of pure and adulterated almond samples and partial least squares regression (PLS) was investigated to detect and quantify the adulterant. The proposed method successfully detected adulteration of peanut in almond powder samples from 90% down to 5% (w/w) of adulterant and accurately determined the degree of adulteration (i.e, root mean square error of calibration and prediction of 1.15 and 2.14, respectively for PLS model).

Keywords: adulteration; almond; chemometrics; GC fingerprinting

Magnetic Nanocellulose/Halloysite Nanotubes Composite M(NC/HNTs) as Nanoadsorbent for Removal of Cadmium Ion from Aqueous Solution

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In this study, magnetic nanocellulose/halloysite nanotubes composite M(NC/HNTs) was performed for Cadmium ions removal from aqueous solution. In the first step, magnetic iron oxide (Fe_3O_4) nanoparticles were prepared by a chemical co-precipitation method and then, M(NC/HNTs) composite was synthesized. The prepared nanocomposite was characterized by Fourier transform infrared spectroscopy (FT-IR), scanning electron microscopy (SEM), X-ray diffraction (XRD) teqniques. The magnetization values of magnetic nanoparticles were measured with vibrating sample magnetometer (VSM). After that the mentioned nanocomposite was used to remove Cadmium and measurements were performs by Atomic Absorption Spectroscopy (AAS). Effect of operating parameters effecting the removal of Cadmium ions onto M(NC/HNTs) agitation speed and temperature were investigated and optimized. The results showed that at the optimal conditions, nano-adsorbent Cadmium removal from aqueous solution with removal efficiency %95.The M(NC/HNTs) nanocomposite was stable and easily recovered. The synthesized nanocomposite can be a good candidate for Cadmium removal from aqueous solution and industrial wastewater.

Keywords: Magnetic; Nanocellulose; Halloysite nanotube; Nanoadsorbent; Cadmium

References:

[1]- A. H. Lu, E. L. Salabs, F. Schuth, *Angew. Chem. Int. Edit.* 46, **2007**, 1222.
[2]- M. Faraji, Y. Yamini, M. Rezaee, *J. Iran. Chem. Soc*. 7, **2010**, 37.
[3]-S. H. Sun, H. Zeng, D. B. Robinson, S. Raoux, *Chem. Soc*. 126, **2004**, 273.

Central Composite Design for the Optimization of Hydrogel-Fe_3O_4 nanocomposite based Sorbent to remove the methylene blue from wastewater samples

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In this work a new sorbent based on Hydrogel-Fe_3O_4 nanocomposite was synthesized. The used hydrogel (poly (styrene-alt-maleic anhydride)) was modified by melamine. The hydrogel has the strong ability to remove some organic and inorganic compounds like methylene blue from water samples. Fe_3O_4 nanoparticles have the magnetic character that could help to the separation of hydrogel from the water after removal process by a magnet. The morphology of the hydrogel, Fe_3O_4, and hydrogel-Fe_3O_4 was examined by scanning electron microscope (SEM). The structure of hydrogel and presence of the Fe_3O_4 particle in the hydrogel nanocomposite and were verified by FT-IR spectroscopy. The synthesized sorbent was used to remove methylene blue from wastewater samples. Central Composite Design (CCD) and response surface method were used to optimize some parameters that affect magnetic character, removal ability and removal efficiency, so the time of removal, pH and concentration of hydrogel as important parameters were optimized by designed experiments. Determination of removal efficiency was done by spectrophotometric method. The removal efficiency of methylene blue from waste water by synthesized sorbent was between 50- 92 % that in the optimized condition it was almost 90 %. Relative standard deviation (RSD) for 5 replicate the removal of methylene blue with synthesized sorbent was 4 %.

Keywords: Modified hydrogel, Fe_3O_4 magnetic particles, nanocomposite, Central composite design (CCD), Methylene blue removal

References:

[1] Sh. Jahangiri, M. Bahram*, Kh. Farhadi and R. Hasanzadeh, Anal. Bioanal. Chem. Res., 1(2014) 29-37.
[2] Dimitri R. Kioussis, Peter Kofinas, Polymer 46 (2005) 9342–9347.

Simultaneous Detection of Ammonia, Ethylamine and Butylamine by a designed portable system based on packed column/ nano-sized polypyrrole gas sensor

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A designed portable system based on packed column/ nano-sized polypyrrole gas sensor with relatively high sensitivity and fast response–recovery was developed for simultaneous detection of ammonia, ethylamine and butylamine. The gas-sensitive thin film was prepared using chemical polymerization, and characterized by scanning electron microscopy. The resistive response of the PPy gas sensor to amines were in the order of ammonia > ethylamine > butylamine. The possibility of applying Dispersive liquid-liquid microextraction (DLLME) for the determination of analytes in trace levels is demonstrated. DLLME combined with designed system has been developed for simultaneous determination of analytes. The reproducibility of this method is suitable and good standard deviations were obtained. RSD value is less than 6% for all analytes. Finally, the method was successfully applied to the extraction and determination of analytes in water samples.

Keywords: Polypyrrole, Nano-sized, Gas sensor, Portable systems, Water sample, amines, simultaneous determination

References:

[1] Sajad Pirsa, Naader Alizadeh, Mohsen Zandi, Hadi Almasi, and Hassan Heidari, SENSOR LETTERS 12 (2014) 1–8.
[2] Sajad Pirsa, Naader Alizadeh, Mohsen Zandi and Hadi Almasi, Nanoscience & Nanotechnology-Asia 5 (2015) 176

Flow-Through Analysis of Antibiotics by Fe_3O_4 Nanoparticles

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In the current study, an in-tube solid phase microextraction (SPME) approach based on Fe_3O_4 nanoparticles packed tube for microextraction and detection of fluoroquinolones has been reported. In this regard, the Fe_3O_4 nanoparticles (NPs) were prepared by a batch synthesis and were introduced into a stainless steel tube. Afterward, a strong magnet was placed around the tube, so that the Fe_3O_4 NPs were retained in the tube and the tube was used in the in-tube SPME-HPLC for the analysis of fluoroquinolonesin urine samples, which sodium dodecyl sulfate (SDS) was used as bridging agent between the Fe_3O_4 NPs and fluoroquinolones. The operational conditions such as uptake and release times, flow rate and pH of solution were investigated and optimized. Calibration curves were linear ($r^2 > 0.990$) in the range of 0.1-1000 μg L^{-1} for ciprofloxacin, 0.1-5000 μg $L^{-1}$for moxifloxacin, and 0.5-500 μg L^{-1} for enrofloxacin and ofloxacin, respectively. LODs for all studied fluoroquinolones ranged from 0.01 to 0.05 μg L^{-1}.Simplicity and facile automation, rapid analysis, high sensitivity, wide linear range, and fully sorbent collection after analysis are the main advantages of the method.

Keywords: Sodium dodecyl sulfate; Fe_3O_4 nanoparticles; In-tube magnetic solid phase microextraction; Antibiotics;

References:

[1] A. H. Kumar, V. Sudha, R. Srinivasan and G. Ramachandran, J. Chromatogr. B, 879 (2011) 3663.
[2] F. J. Lara, M. del Olmo-Iruela and A. M. García-Campaña, J. Chromatgr. A, 1310 (2013) 91.
[3] A. V. Herrera-Herrera, J. Hernández-Borges, T. M. Borges-Miquel and M. Á. Rodríguez-Delgado, J. Pharm. Biomed. Anal., 75 (2013) 130.

Electrochemically EnhancedIn-Tube Solid Phase Microextraction of Non-Steroidal Anti-Inflammatory Drugs

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An in-tube solid phase microextraction approach named electrochemically controlled in-tube solid phase microextraction (EC in-tube SPME) has been reported. This approach which combined electrochemistry and in-tube SPME, led to decrease in total analysis time and increase in sensitivity. Pyrrole was elctropolymerized on the inner surface of a stainless steel tube. Then, this polypyrrole (PPy)-coated tube was coupled on-line to liquid chromatography (HPLC) to achieve automated in-tube SPME-HPLC analysis. After the completion of EC-in-tube SPME-HPLC setup, the PPy-coated tube was used as working electrode for uptake of diclofenac and naproxen. Extraction ability of the tube in presence and in absence of applied electrical field was investigated. It was found that, under the same extraction conditions, the extraction efficiency could be greatly enhanced by using the constant potential. The detection limits (S/N = 3) for naproxen and diclofenac were 0.07 and 0.1μg L^{-1}, respectively.

Keywords: Electropolymerization; Electrochemically enhanced in-tube solid phase microextraction; polypyrrole;

References:

[1] J. Wu, Z. Mester, J. Pawliszyn, Anal. Chim. Acta 424 (2000) 211.
[2] J. Wu, J. Pawliszyn, Anal. Chem. 73 (2001) 55.
[3] J. Pawliszyn, Solid-Phase Microextraction: Theory and Practice, Wiley-VCH, New York, 1997.

Trace determination of mercury (II) ions in food and environmental samples using ultrasound-assisted dispersive liquid–liquid microextraction and graphite furnace atomic absorption spectrometry

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In the present study, ultrasound-assisted dispersive liquid–liquid microextraction (UA-DLLME) followed by graphite furnace atomic absorption spectrometry (GFAAS) was developed for the extraction, preconcentration, and determination of mercury (II) ions in food and environmental samples. The method is based on complex formation of the mercury (II) ions with low cost complexing agent of 2-aminothiophenol that can be transferred into the carbon tetrachloride after fine dispersion via ultrasound and detected by GFAAS. The influences of various parameters, including pH, extraction as well as disperser solvent types and their volumes, concentration of 2-aminothiophenol, salt effect, vortex, and ultrasonic time were investigated and optimized. Under the optimum conditions, a linear range of 5–100 μg L^{-1} with a correlation coefficient of 0.9975, a limit of detection ($3S_b/m$) of 0.9 μg L^{-1}, and a high enrichment factor of 603 were obtained from 5 mL of sample. The relative standard deviation for six replicates of 5.0 μg L^{-1} mercury (II) solution was 6.2%. The proposed method might be considered as a simple, rapid, and cost-effective method for mercury (II) ions determination in water, and porgy fish samples. Satisfactory recoveries were obtained in the range of 97.2 – 107%. Our method was also successfully applied to the analysis of the rice quality control reference material in good agreement with the assigned values.

Keywords UA-DLLME; Mercury (II) ions; GFAAS; 2-aminothiophenol; Preconcentration

Reference:

[1] B. Albero, C. Sánchez-Brunete, L. Tadeo, *Trends Anal.Chem.*, (**2015**), 71, 110–118.

Combination of micro liquid-liquid extraction and dispersive liquid phase microextraction for quantification of some phenolic antioxidants in edible oil by gas chromatography-flame ionization detector

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Phenolic antioxidants are widely used as food additives to prevent deterioration and rancidity of food products. Some phenolic antioxidants such as butylated hydroxyanisole (BHA), t-butyl hydroquinone (TBHQ) and butylated hydroxyl toluene (BHT) are used in edible vegetable oil frequently [1]. However, the safety of these antioxidants was questioned due to their potential risk for people health [2]. In this research combination of micro liquid liquid extraction with dispersive liquid phase microextraction was used for determination of BHA, BHT and TBHQ in edible oils. At first, target compounds were extracted by a polar solvent (extraction solvent) and finally dispersive liquid phase microextraction was used for preconcentration of analytes in non-polar solvent (preconcentration solvent). Derivatization of BHA and TBHQ should be done, for better peak shapes, between two extraction procedures. Acetic anhydride was applied as a derivatization reagent. Different effective parameters such as type and volume of extraction and preconcentration solvent, extraction time and derivatization conditions were evaluated and optimized. Under the optimum conditions, the method yielded a linear calibration curve ranging from 0.1 to 50 mg L^{-1} for different analytes, with determination coefficients (R^2) varying from 0.9907 to 0.9981. The relative standard deviation (RSD) for the extraction and determination of two levels of target antioxidants was less than 7.1% (n=5). Finally, the proposed procedure was successfully applied for the determination of the studied antioxidants in different commercial edible oil.

Keywords: Micro liquid-liquid extraction; Dispersive liquid phase microextraction; Phenolic antioxidant; Gas chromatography- flame ionization detector

References:

[1] L. Xiu-Qin, J. Chao, S. Yan-Yan, C. Xiao-Gang, Food Chemistry 113 (2009) 692.
[2] T. Okubo, Y. Yokoyama, K. Kano, Food Chem. Toxicol. 41 (2003) 679.

Preconcentation of palladium in real samples with air assisted liquid phase microextraction

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A switchable-hydrophilicity solvent in combination with air-assisted liquid–liquid microextraction (AALLME) called AA-SHS-LPME, has been applied for microextraction palladium. A water-immiscible solvent, Triethylamine (TEA), as green switchable solvent was solubilized by using CO_2 as a stimulus for triggering the transformation to the water-miscible form and removal of CO_2 to achieve the reverse in sample solution. Separation is induced by the addition of sodium hydroxide, which produces a change on the ionization state of the amine. The cloudy state was accelerated by pulling in and pushing out the mixture of sample solution and extraction solvent for several times using a 10-mL glass syringe. AA-SHS-LPME provided a limit of detection 0.07 μgL^{-1} with preconcentration factor of 64 and the relative standard deviation (RSD, n=10) 3.5 % were achieved. The recoveries of the analytes in water and road dust samples were in the range of 96–104%.

Keywords: Air-assisted liquid–liquid microextraction; Water and road dust samples; Switchable-hydrophilicity solvent

Preparation of magnetic nanoparticles modified with imine base ligand as a novel sorbent for magnetic solid-phase extraction of organochlorine pesticides (OCPs)

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This work describes the synthesis and application of an attractive magnetic sorbent modified with imine base ligand to preconcentration and extraction of some organochlorine pesticides (OCPs) including heptachlor, aldrin, dieldrin, Dichlorodiphenyldichloroethylene (DDE), 4,4-dichlorodiphenyltri-chloroethane (DDT) from seawater sample and their determination by gas chromatography with electron capture detection. The magnetic new sorbent showed good dispersibility, high efficiency and effective interaction with OCPs, which provided plenty sites to extract the target analytes. The sorbent were characterized by using the techniques of transmission electron microscopy (TEM), Fourier transform infrared spectroscopy (FT-IR) and energy-dispersive X-ray spectroscopy (EDX). Experimental parameters, such as sample volume, amount of the magnetic sorbent, volume of the eluent solvent, adsorption and desorption times, and salt content of the sample were properly optimized. Under the optimum conditions - limit of detections (LODs) were between 0.0010-0.0046. The enrichment factors (EFs) for the target analytes were different from 84.13 to 99.93. The good linearities in the ranges of 0.05-50 µg L^{-1} and 0.05-75 µg L^{-1} were also obtained for heptachlor and other analytes, respectively with the correlation coefficient (R^2) of $0.990 \leq R^2 \leq 0.999$ for all the analytes. The relative standard deviations (RSDs) were less than 8.3% for the OCPs in seawater sample. Ultimately, the magnetic new sorbent was successfully applied for the rapid extraction of trace quantities of OCPs in seawater samples and high recoveries (79.3 to 109.3%) were obtained.

Keywords: Imine base ligand**,** Ligand modified, Magnetic solid-phase extraction, Organochlorine pesticides (OCPs), Seawater

Magnetic graphene-carbon nanotubes nanocomposite for the preconcentration of organophosphorus pesticides from water samples prior to determination by HPLC-UV

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Sample preparation methods generally involve a solvent- or solid-phase-based extraction technique [1]. The objective of sample preparation is to transfer the analyte from the sample matrix into a form that is pre-purified, concentrated and compatible with the analytical system. In recent years, a new procedure for SPE, based on the use of magnetic or magnetically modified adsorbents called magnetic solid-phase extraction (MSPE), has been developed. It adopts magnetic particles as adsorbents, which endow some unique features in extraction and solve some problems associated with ordinary SPE. Magnetic particles can be coated with a protective layer of different materials to improve their stability and to introduce new surface properties and functionalities [2]. Recently, graphene and carbon nanotubes show many outstanding advantages, such as remarkable thermal and chemical stability, good mechanical strength, high surface-to-weight ratios and low production cost [3].

In this study, magnetic solid phase extraction method coupled to HPLC-UV was proposed for the determination of Organophosphorus Pesticides (OPPs) at trace levels in environmental water samples. The ternary nanocomposite of graphene - carbon nanotube -Fe_3O_4 (G-CNT-Fe_3O_4) has been synthesized via a simple solvothermal process and the resultant material was characterized by X-ray powder diffraction (XRD), transmission electron microscopy (TEM), scanning electron microscopy (SEM) and Fourier transform infrared (FTIR). Significant factors that affect the extraction efficiency, such as amount of magnetic nanocomposite, extraction time, ionic strength, solution pH and desorption conditions were carefully investigated. The results demonstrated that the proposed method had a wide dynamic linear range (0.005-500 $\mu g\ L^{-1}$), good linearity (R^2 = 0.9955-0.9997) and low detection limits (1.4-11 $ng\ L^{-1}$). High enrichment factors were achieved ranging from 930 to 1510. The results show that the developed method is suitable for trace level monitoring of OPPs in environmental water samples.

Keywords: Graphene-carbon nanotube-Fe_3O_4 nanocomposite; Magnetic solid phase extraction; Organophosphorus pesticides; Environmental water samples.

A ceramic-magnetic graphene nanocomposite as effecting sorbent for solid-phase microextraction fiber for determination of organophosphorus pesticides in environmental water samples

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Over 80% of the total analysis time is generally spent on the sampling and sample preparation steps. Recent trends in sample preparation are clearly towards miniaturization [1]. Minimizing sample preparation steps is effective, not only in reducing sources of error but in reducing time and cost. Solid-phase microextraction (SPME), is a new and effective sampling and sample preparation method. The main advantages of SPME are simplicity, rapidity, solvent elimination, high sensitivity, small sample volume, relatively low cost and easy automation. New trend in SPME are focused on development of new sorbent [2]. The extraction efficiency and selectivity of SPME can be improved by the development of new coating materials [3]. In this study, a novel solid phase microextraction (SPME) fiber coated with ceramic-magnetic graphene (C-G/Fe_3O_4) nanoparticles on glass tube was prepared by sol-gel technology. Scanning electron micrographs of the fiber surface revealed a three dimensional structure of the C-G/Fe_3O_4 nanoparticles which is suitable for SPME applications. Application of the C-G/Fe_3O_4 nanoparticles coated fiber was evaluated through the extraction and determination of the four Organophosphorus pesticides (OPPs) in water samples followed by HPLC-UV detection. Several experimental parameters affecting the extraction efficiency such as extraction time, stirring rate, desorption conditions, salinity and pH were investigated and optimized. The results revealed that this procedure is a simple technique for the preparation of SPME fibers coated with magnetic nanoparticles. Under the optimized conditions, the linear response for the analytes was observed in the range from 0.05 to 400 µg L^{-1} with the correlation coefficients (R) ranging from 0.9944 to 0.9969 and the limits of detections between 5 and 60 ng L^{-1}. The extraction procedure based on CG/Fe_3O_4 SPME fiber was successfully used for the determination of OPPs in spiking water samples, resulting average recoveries of 85-102.2% and RSD values of 8.8-13.9%.

Keywords Ceramic-magnetic graphene nanoparticles; Organophosphorus pesticides; Sol–gel; Solid–phase microextraction

References:

[1] C.L. Arthur, J. Anal. Chem. 62 (1990) 2145-2148.
[2] C. Dietz, J. Sanz, C. Cámara, J. Chromatogr. A 1103 (2006) 183-192.
[3] H. Zhang, H.K. Lee, J. Chromatogr. A 1218 (2011) 4509-4516.

Removal of three anionic dyes using amine functionalized kit-6 mesoporous magnetite nanocomposites

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In this study, kit-6 silica mesoporous was chemically synthesized on the surface of silica coated magnetite core and functionalized by amine group to form $Fe_3O_4@SiO_2@kit\text{-}6/NH_2$. The synthesized nanocomposite was used as sorbent for removal of three anionic dyes from aqueous samples. The characterization of the synthesized nanocomposites were evaluated by Transmission electron microscopy (TEM), Fourier transform infrared spectroscopy (FT-IR), X-ray diffraction (XRD) and Brunauer–Emmett–Teller (BET) measurments[1]. For dyes removal, all of the experimental factors affecting the removal efficiency were investigated using L_{16} Taguchi orthogonal array desing. Adsorption data were studied using Langmuir and Freundlich models. Also, the sorption kinetics were investigated and the best fit was achieved by pseudo second order kinetic model. The results showed very fast kinetics and high removal efficiency of sorbent that makes it as a recoverable sorbent for removal of these anionic compounds.

Keywords Adsorption; Kit-6; Magnetite nanocomposites; Mesoporous

References:

[1] M. Khabazipour, Sh. Shariati, F. Safa, "SBA and KIT-6 mesoporous silica magnetite nanoparticles: Synthesis and characterization", Synthesis and Reactivity in Inorganic, Metal-Organic, and Nano-Metal Chemistry, (2015) Article in press.

Solid phase microextraction with Magnetite-Reduced Graphene Oxide Compositesfor removal of organophosphorus pesticidesby gas chromatography–mass spectrometry

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In this paper, a graphene-based magnetic nanoparticles zero-valentiron (G-Fe MNPs) was used as the magnetic sorbent for solid-phase microextraction of some organophosphorus pesticides (Sevin, Fenitrothion, Malathion, Parathion and Diazinon) in environmental water samples followed by gas chromatography–mass spectrometry. The effects of the amount of the extractant composite employed, extraction time, pH values and desorption conditions were investigated.Under theoptimum conditions, Response is linear in the concentration rangefrom 0.02-0.07 to 60-80μg L^{-1} for five pesticides with the correlation coefficients (r^2) upper than 0.995.The suggested method was successfully applied to the determination of organophosphorus pesticides in the real samples with relative standard deviation RSD:4-7%. Accuracy of this method was investigated through the recovery experiments of the mixture standard reference material (KDWR003, Accustandard).

Keywords: Dispersive solid-phase microextraction;Graphene; zero-valent iron; OrganophosphorusPesticides

References:

[1] M.J. Allen, V.C Tung, ChemRev, 110 (2010) 132.
[2] G. Giakisikli, A.N. Anthemidis, Anal. Chim. Acta, 789 (2013) 1.
[3] X. Zhang, H.B Yang, Biosens Bioelectron, 41 (2013) 669.

Dispersive microsolid phase extraction of Nickel and Cobalt with Magnetic-graphene oxide followed by Furnace Atomic Absorption

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In this paper a new method for sample preparation using magnetic-graphene oxide (MGO) as a novel sorbent was developed for the preconcentration of trace amounts of Co(II), Ni(II) with assisted by ligand followed by Furnace Atomic Absorption. The proposed preconcentration procedure is based on dispersive micro-solid phase extraction (DMSPE). It means that MGO was dispersed in aqueous samples containing trace elements to be determined. The factors affecting the separation and preconcentration of nickel and cobalt were investigated and optimized. The pH of the analyte solution, the amount of sorbent, the sample volume, the contact time are discussed in this paper. Under the optimized conditions, the method exhibited a linear dynamic range of 0.01–10.0μgL^{-1} with a detection limit of 2ngL^{-1} and 1.7ngL^{-1} and an enrichment factor of 270 and 320 for Nickel and Cobalt respectively. The relative standard deviations of 2.4% and 3.4%(n=6) were obtained for Nickel and Cobalt respectively. The proposed method successfully applied for certified reference material NIST 1643e.

Keywords Cobalt; dispersive micro-solid phase extraction; Furnace Atomic Absorption ;magnetic-graphene oxide; Nickel

Magnetic solid phase extraction of cadmium ion from environmental water samples with sulfated metal organic framework loaded on iron oxide nanoparticles

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A new magnetic solid phase extraction (MSPE) method using sulfated metal organic framework loaded on iron oxide nanoparticles (S-Fe_3O_4@MOF-235(Fe)) has been developed for separation and preconcentration of cadmium ions prior to its determination by flame atomic absorption spectrometry. The S-Fe_3O_4@MOF-235 (Fe) sorbent was characterized by FTIR, and X-ray diffraction (XRD) and thermogravimetric analyses. The method is based on the sorption of cadmium ion on magnetic S-Fe_3O_4@MOF-235(Fe) nanostructure due to sharing an electron pair of O and S groups of S-Fe_3O_4@MOF-235(Fe) with cadmium ion. The experimental parameters affecting on the extraction of cadmium such as solution pH, type, concentration and volume of the eluent, amount of the sorbent, and extraction time have been investigated and optimized. Under the optimized conditions, the limit of detection and the enrichment factor of the method were found to be 0.3 ng/mL and 192, respectively. The relative standard deviation (RSD) for five replicate measurements of 25 µg/L Cd (II) was 1.4%. The method was successfully applied for the determination ofcadmium environmental water samples.

Keywords: Cadmium; Flame atomic absorption spectrometry; Metal organic framework; Magnetic solid phase extraction; Preconcentration

Magnetic framework composite as novel adsorbent combined with high performance liquid chromatography for the determination of benzoylurea insecticide in juice fruit

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Metal–organic frameworks (MOFs), as a new class of crystalline porous materials, have received great attention in the past decade because of their intriguing structures [1]. In this work,two metal–organic frameworkshave been synthetizedby mechanosynthesisas a convenient, rapid, low-cost, solventless, and green process. The studies conducted revealed that, among the two MOFs, TMU-8 had a more adsorption efficiency for benzoylurea insecticide than the other MOFs. Afterwards, magnetic TMU-8 was fabricated by using core shell. Subsequently, magnetic core shell was applied as an efficient sorbent for the extraction and preconcentration of benzoylurea insecticide followed bytheir determination by High Performance Liquid Chromatography (HPLC-UV). In this study, the best possible performance of magnetic solid phase extraction (MSPE) has been achieved using a combination of central composite design (CCD) and Bayesian regularized artificial neural network (BRANN) technique.Under the optimal conditions, preconcentration factors in range of 317-420 were obtained. The figures of merit of the method was studied in terms of linear ranges (LRs from 0.5 to 250 µg L^{-1}), linearity ($R^2 \geq 0.996$), precision (RSD %≤5.7) and limits of detection (LODs in the range of 0.15–0.3µg L^{-1}).Finally, the potential applicability of the proposed method was evaluated for the extraction and determination of benzoylurea insecticidein fruit juice samples.

Keywords: Metal–organic frameworks;Magnetic solid phase extraction; Bayesian regularized artificial neural network;Benzoylurea insecticide

References:

[1] O.M. Yaghi, M. O'Keeffe, N.W. Ockwig, H.K. Chae, M. Eddaoudi, J. Kim, Nature, 423 (2003) 705.

Accelerated Hydrolysis and Precolumn Derivatization for Complete Amino Acid Analysis of Decapeptide Cetrorelix Acetate by Reversed Phase HPLC

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The decapeptide cetrorelix (Ac-D-Nal–(p-Cl)-D-Phe–D-Pal–Ser–Thy–D-Cit–Leu–Arg–Pro–D-Ala–NH_2),is used to treat hormone-sensitiveprostate and breast cancers, infertility and benign prostatichypertrophy[1].Hydrolysis of peptides is necessary for the analysis of their amino acid content. The current study introduces a fast and additive free method for the hydrolysis of cetrorelixto prevent residues from degradation which normally happens in conventional hydrolysis methods. Using only HCl 6 M, this hydrolysis process is completed in 30 min at 150 ˚C. This fast hydrolysis method followed by pre-column derivatization of the released amino acids with 4-N,N-dimethylaminoazobenzene-4′-sulfonyl chloride (DABS-Cl) which takes only 20 min, enables the detection and quantification of the amino acids by reversed phase HPLC in less than 2 hours. The conventional methods for amino acid analysis take at least 24 hours. The highly stable colored DABS-Cl derivatives can be detected in 436 nm by a simple UV-Vis detector, which eliminates spectral interferences to a great extent. The amino acid analysis of cetrorelix acetate including hydrolysis, derivatization and chromatographic analysis was validated in terms of specificity, system suitability, linearity, accuracy, precision, LOD and LOQ according to International Conference of Harmonization (ICH) guidelines.

Keywords: Cetrorelix acetate; Hydrolysis; Amino acid analysis; Reversed phase HPLC; DABS-Cl

References:

[1] M. Ludwig, A. Katalinic, K. Diedrich, Arch. Gynecol. Obstet., 265 (2001)175.

Optimizing the simultaneous removal of lead, cadmium, nickel and copper from environmental samples by using graphene oxide sorbent modified with amine groups

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Novel, highly ordered layered graphene oxide (GO) functionalized with Amine Dipyridyl ligands (DPA) was synthesized successfully and was used as adsorbent for the simultaneous removal of Cu^{+2} , Cd^{+2} , Ni^{+2} and Pb^{+2} . The adsorbent was characterized by Fourier Transform Infrared spectroscopy (FT-IR), X-ray Diffraction (XRD), Atomic Force Microscopy (AFM), Energy Dispersive Spectroscopy (EDS), carbon (C), hydrogen (H) and nitrogen (N) elemental analysis (CHN) and Scanning Electron Microscope (SEM) respectively. For this process, we utilized Experimental Design methods to determine how to calculate the tests and the number of them, also calculation the optimum adsorption condition more accurately.

The effect of pH, contact time, dose of sorbent and initial metal ions concentration were investigated carefully. The simultaneous adsorption process for these metals follows the pseudo-second order equation and Langmuir isotherm. The maximum adsorption capacity was 355mg/g for Pb (II), 342 mg/g for Cu (II), 248mg/g for Cd (II) and 167mg/g for Ni (II) at 2 min and pH 5.

The results demonstrated that the graphene oxide has a promising application for heavy metal removal from water.

Keywords: Eexperimental design, Heavy metals ions, Modified graphene oxide, Simultaneous adsorption

Determination of carboxylic acids in nonalcoholic beer samples by a dispersive micro-solid phase extraction based on Ni/Cu-Al layered double hydroxide nanocomposites followed by gas chromatography

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Magnetically separable layered double hydroxide Ni/CuAl-LDH nanocomposites were synthesized and employed as dispersive micro-solid phase extraction (D-µSPE) sorbent to extract several carboxylic acids (propionic, butyric, pentanoic, hexanoic, heptanoic, octanoic, decanoic) from nonalcoholic beer samples. Dispersive micro-solid-phase extraction is based on the dispersion of adequate amount of micro or nano-adsorbents in the aqueous solution in order to absorption of target analytes. Micro or nano-sorbents offer a significantly higher surface area-to-volume ratio and a shorter diffusion route than conventional sorbents, resulting in high extraction capacity, rapid extraction dynamics and high extraction efficiencies. Ni/CuAl-LDH sorbent was characterized by fourier transform-infrared (FTIR) spectroscopy, transmission electron microscopy (TEM) and vibrating sample magnetometry (VSM). Effective variables such as amount of sorbent (mg), pH and ionic strength of sample solution, volume of eluent solvent (µL), vortex and ultrasonic times (min) were investigated via fractional factorial design (FFD). The significant variables were optimized by a Box-Behnken design and combined by a desirability function (DF). Under optimized conditions, the calibration graphs of analytes were linear in a concentration range of 0.05-100 µg/mL, and with correlation coefficients more than 0.997. The limits of detection and quantification were in the ranges of 16-40 µg/L and 53-133 µg/L, respectively. This procedure was successfully employed in the determination of target analytes in spiked beer samples; the relative mean recoveries ranged from 87 to 110%.

Keywords: Box-Behnken design, Dispersive micro-solid-phase extraction, Fractional Factorial design

Modified Magnetic Nanoparticles as a Sorbent for the Extraction of Benzaldehyde and Cinnamaldehyde from Fruit Juice Based on Dispersive Micro-Solid-Phase Extraction: Response Surface Methodology

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Benzaldehyde and cinnamaldehyde are compounds widely used for the manufacture of odorants and flavoring chemicals. They are also employed as starting material for some pharmaceu-ticals, such as ampicillin and pesticides [1,2]. Herein, a selective and sensitive method was developed based on dispersive micro-solid-phase extraction for the extraction of benzaldehyde and cinnamaldehyde from fruit juice samples prior to gas chromatography-flame ionization detection (GC-FID). Fe_3O_4 and modified Fe_3O_4 nanoparticles were synthesized and characterized through the use of scanning electronic microscopy, energy dispersion X-ray analysis, vibrating sample magnetometry and infrared spectroscopy. Effective variables such as the amount of sorbent (mg), pH and ionic strength of sample solution, the volume of eluent solvent (μL), vortex and ultrasonic times (min) were investigated. The significant variables optimized by a Box-Behnken design, were combined by a desirability function (DF). Under optimized conditions, the calibration graphs of benzaldehyde and cinnamaldehyde were linear in a concentration range of 0.5-300 mg/L, and with correlation coefficients more than 0.998. The limits of detection for benzaldehyde and cinnamaldehyde were 0.4 and 0.3 mg/L, respectively. This procedure was successfully employed in determining target analytes in spiked fruit juice samples; the relative mean recoveries were more than 85% and relative standard deviation were less that 5%.

Keywords: Dispersive micro-solid-phase extraction, GC-FID, modified Fe_3O_4 nanoparticles, Box-Behnken design

References:

[1] J. A. González, C. A. Tristán, I. G. de la Fuente, Fluid phase Equilibr, 366 (2014) 61.
[2] M. Katayama, Y. Mukai, H. Taniguchi, Analyst, 1159 (1990) 9.

Preparation and investigation of electrospun CH_3MOF-5/PAN composite nanofibers as Solid-Phase Extraction adsorbent for the preconcentration of trace levonorgestrel and megestrol acetate in biological samples

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The miniaturization of sample preparation device was successfully fabricated by packing 5 mg electrospun composite nanofibers of methyl-modified metal–organic framework-5/ Polyacrylonitrile (CH_3MOF-5/PAN) into mini-disc cartridges for pre-concentration and separation of two estrogenic drugs, Levonorgestrel and Megestrol acetate, in urine samples. A simple, cheap, and accessible electrospining method was employed to prepare a water stable CH_3MOF-5/PAN composite nanofibers. The nanofibres were characterized by scanning electron microscopy, thermogravimetric analysis, Fourier transform infrared spectroscopy, X-ray diffraction and N_2 adsorption-desorption experiments. Seven important parameters, affecting the extraction efficiency of Levonorgestrel and Megestrol acetate, including: type of eluent and its volume, sorbent amount, pH, ionic strength and sample volume were investigated and optimized. The Optimum extraction conditions were obtained as: 150 µL methanol for type of eluent and its volume, 5 mg for sorbent amount, 5 for pH value, 4 % (w/v) for NaCl concentration and 80 mL for sample volume. Under the optimized condition, the calibration curves were linear ($R^2 > 0.999$) in the range of 0.05 to 100 µg L^{-1}. Limit of detection for both of the analytes were 0.02 µg L^{-1}. The applicability of the method was examined by analyzing the analytes in urine samples. The recoveries of the analytes were in the range of 82.8% to 94.8% that show the capability of the method for determination of the drugs in biological fluids.

Keywords: Electrospining; CH_3MOF-5/ PAN; composite nanofibers; Levonorgestrel; Megestrol acetate

Removal of Congo Red from Aqueous Solutions Using Biodegradable Hollow Zein Nanoparticles

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The removal of Congo red (CR) from water samples by using biodegradable hollow zein nanoparticles, with diameters less than 100 nm, has been described. Corn zein is generally recognized as a safe biomaterial that has characteristics including biocompatibility, biodegradability and low toxicity with hydrophobic property and unique solubility.Ease of fabrication, high dye sorption and biodegradability make zein nanoparticles ideal for azo dyes removal from wastewaters. The CR is a water soluble diazo dye and widely used in textile, paper, printing, leather and plastic industries. It is an irritant to skin and eye, and induces somnolence and respiratory problems. Characterization of the hollow zein nanoparticles was achieved by transmissionelectron microscopy. Batch experiments were performed to investigate the adsorption conditions. Several experimental factors such as pH, type of buffer, amount of nanoparticles, buffer concentration, contact and centrifugation periods and breakthrough volume were optimized. The results showed that the nanoparticles could quantitatively remove CR under the optimum experimental conditions of 2.5 ml nanoparticles dispersion, 2.5ml phosphate buffer (0.15 mol L^{-1}), pH=3, contact and centrifuging times of 1and 3 min, respectively. The maximum adsorption capacity for nanoparticles was found to be 476.19 mg g^{-1}, which was higher than those recently reported for CR removal.

Keywords: Congo red; Hollow zein nanoparticles; Waste water

References:

[1] C. Srilakshmi, R. Saraf, Microporous Mesoporous Mater 219 (2016) 134.
[2] H. Xu, Q. Jiang, N. Reddy, Y. Yang, J. Mater. Chem 21 (2011) 18227.

Application of In situSurfactant-Based Solid PhaseExtraction for Preconcentration and Determination of Nystatin

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In situ Surfactant-based solid phase extraction method(ISS-SPE) has been employed for preconcentration and determination of nystatin with spectrophotometric detection. Nystatin is an efficient antimicrobial agent against a broad spectrum of saprophytic and pathogenic fungi.InISS-SPE, a cationic surfactant with a proper alkyl group is dissolved in the aqueous sample and then a proper ion pairing agent is added. Due to interaction between surfactant and ion-pairing agent, very fine solid particles are formed.Extraction occurs via hydrophobic bonding of alkyl groupof the sorbent with the hydrophobic part of the extractedanalyte.The influences of surfactant as well as ion pairing agent type, pH, buffer concentrations, surfactant and ion pairing agent concentrations, dissolving-agent nature and its volume, contact and centrifugation time periods, and influences of coexisting ions were investigated. After optimizing the operational conditions,linear ranges of 0.07-1.0 and 1.0-2.1 µM and detection limit(n=10) of 8.35 nM were obtained. Intraday and interday precisions were performed at three different concentration levels of nystatin and RSDs were 2.84 % and 2.64 %, respectively. The proposed method showed some advantages for determination of nystatin over the other methods including low consumption of reagents, using environmentally friendly solvent and surfactant, availability in terms of materials and instrument, simplicity, low cost of the extraction device, producing a clean extraction phase and fast experimental process.The large surface area of the sorbent led to short extraction time and high extraction recovery.

Keywords: In situ Surfactant-based solid phase extraction; Nystatin; surfactant

Simultaneous Removal of Titan Yellow and Eosin Y from Aqueous Solutions through Biosorption Using Hollow Zein Nanoparticles

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Azo dyes have extensive applications in industrial activities such as paper, textiles, additives and leathers. The removal of dyes from wastewaters is of great concern because the presence of trace amounts of dyes can affect water quality. Recently, the nanoparticles have been considered as new adsorbents for removal of dyes [1]. In this study, the biodegradable hollow zein nanoparticles with diameters less than 100 nm were synthesized and characterized by transmission electron microscopy (TEM). Then, the biosorption of two anionic dyes, Titan Yellow and Eosin Y, from aqueous solutions, was investigated in a batch mode using hollow zein nanoparticles as adsorbent. Several experimental factors affecting extraction process such as pH, type of buffer, volume of hollow zein nanoparticles and buffer concentration were optimized. Experimental results indicated that these nanoparticles could remove more than 98 % of each dye under optimum experimental conditions of 2.5 ml hollow zein nanoparticles dispersion and 2.5 ml phosphate buffer (0.2 mol L^{-1}), pH=2, plus contact times of 1.0 and 2.0 min, respectively for Eosin Y and Titan Yellow. The centrifuging time for both dyes was 5 min. The Langmuir isotherm model has been used to evaluate the ongoing adsorption kinetic equations. The results revealed that high dye sorption, dyeing process, simple fabrication, and biodegradability of hollow zein nanoparticles make them ideal for azo dyes removal from wastewaters.

Keywords: Azo Dye; Eosin Y; Hollow Zein Nanoparticles; Titan Yellow

References:

[1] V. Belessi, G. Romanos, N. Boukos, D. Lambropoulou, C. Trapalis, J. Hazard. Mater. 170 (2009) 836.

Modification of Silica-coated Fe_3O_4 Nanoparticles by Graphene oxide as a Sorbent for Removal of Tetracycline from Water Samples

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The removal of tetracycline (TC) as antibiotic from water samples is described. Silica-coated Fe_3O_4 nanoparticles modified with graphen oxide(Fe_3O_4/SiO_2-GO) were synthesized and used as adsorbent. Characterization of the nanoparticles was achieved by Fourier transform infrared spectra, transmition electron microscopy and X-Ray diffraction. Batch adsorption experiments were performed to investigate the adsorption conditions and reusability of the adsorbent. The influences of several parameters such as nanoparticles dosage, pH of the solution, TC concentration, contact time, temperature, and ionic strength were studied. Experimental results indicated that the Fe_3O_4/SiO_2-GO nanoparticles were able to quantitatively remove (RSD =1.4%, n=6) TC under the optimum experimental conditions of a nanoparticles dosage of 20.0 mg, a pH of 6.0, and a contact time of 7.0 minutes when initial TC concentrations of 2.0-40.0 mg L^{-1} were used. The kinetics of adsorption fits pseudo-second-order model perfectly. The reusability of the adsorbent in several successive separation processes was tested and the results showed that the nanoparticles could be recycled and reused for8 times without significant reduction in its removal efficiency. The results also revealed that GO was stable for a period of at least 8 months at the surface of Fe_3O_4/SiO_2. Finally, the proposed nanoparticles was successfully utilized for removal of TC from water samples.

Keywords: Adsorbent; Graphene oxide; Fe_3O_4magnetic nanoparticles; Tetracycline; Water samples

Hollow fiber liquid-phase microextraction followed by high performance liquid chromatography for speciation and determination of chromium in natural waters

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Hollow fiber liquid-phase microextraction (HF-LPME) offers an efficient alternative to classical techniques for sample preparation and preconcentration [1]. Features include high selectivity, good enrichment factors, and improved possibilities for automation.In this work, Cr(VI) and Cr(III) react with ammonium pyrrolidinedithiocarbamate (APDC) to produce hydrophobic and detectable complexes, which are subsequently extracted into the fine droplets of organic phase in the lumen of hollow fiber then the extracting organic phase was injected into the separation column of HPLC for simultaneous analysis of both chromium species. The best possible performance of HF-LPME has been achieved by using of central composite design (CCD).The effect of different extraction conditions in each method (i.e. type of acceptor phase, hollow fiber length, ionic strength, stirring rate, and extraction time) on the extraction efficiency of the chromium was investigated and optimized. Under optimized conditions, the analytes were quantified by HPLC-UV instrument, with acceptable linearity ranging from 0.5 to 100 µg L^{-1} (R^2 values≥ 0.998), and repeatability (RSD) ranging between 6.2% and 7.4% (n = 3). Also, preconcentration factors of 550–680 that corresponded to recoveries ranging from 94% to 105% were achieved for Cr(III) and Cr(VI), respectively. The estimated detection limits (S/N ratio of 3:1) were less than 0.15 µg L^{-1}.).Finally, the proposed procedure was successfully applied to the speciation and determination of chromium species in different water samples and satisfactory results were obtained.

Keywords: Hollow fiber liquid phase microextraction; Chromium speciation; High performance liquid chromatography

References:

[1] M. Ghambarian, Y. Yamini, A. Esrafili, Microchimica Acta 177 (2012) 271.

Dispersive Micro-Solid Phase Extraction of Rhodamine B using Zein Nanoparticles as Extracting Sorbents by Spectrophotometric Method

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Application of zein nanoparticles, as sorbent, has been introduced in dispersive micro solid phase extraction (DMSPE) for sensitive and selective determination ofrhodamine B inaqueous samples. A UV visible spectrophotometr at 556 nm was used as detection system. Combination of DMSPE procedure based on zein nanoparticles, as a sample preparation method, offers important advantages such as providing environmentally friendly condition as well asfast, easy, safe, and inexpensive procedure. The effects of various experimental factorson extraction efficiencyof rhodamine B such as solution pH, buffer type, buffer concentration, concentration of salt, amount of zeinnanosorbent, contact time, centrifuges time**,** dissolving-agent nature and its volume, and influences of coexisting ions wereoptimized. Under the optimum experimental conditions, the calibration graph was linear over the concentration range of 0.02-0.9 mg L^{-1}rhodamine Bwith a limit of detection (n=10) of1.4 µg L^{-1}.Intraday precision was performed five times in one day at three different concentration levels of 0.06, 0.5 and 0.9 mg L^{-1}rhodamine B.The mean value of RSD was 1.74 %.The interday precision was performed over five days at three different concentration levels of 0.06, 0.5 and 0.9 mg L^{-1}rhodamineB. The mean value of RSD was 1.85%.Finally, the proposed method was successfully utilized to determine rhodamine B in lipstick and hand washing liquid soap samples.

Keywords: Dispersive micro solid phase extraction; Hand washing liquid soap sample; Lipsticksample; Rhodamine B; Zein nanoparticles

Alcoholic assisted dispersive liquid-liquid microextraction combined with liquid chromatography for determination of fluoxetine and citalopram in biological samples using an experimental design

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An high performance liquid chromatography method was developed for the determination of some frequently prescribed selective serotonin re-uptake inhibitors (SSRI) – citalopram and fluoxetine- in human plasma and urine samples, using a previous stage of alcohol assisted liquid-liquid microextraction (AA-DLLME). In this method, cloudy solution is formed after injecting the appropriate mixture of extraction solvent with lower density than water and disperser solvent into the aqueous sample by syringe and process can be speed-up by centrifugation. AA-DLLME method developed the applicability and compatibility of the DLLME procedure to RP-HPLC that use alcoholic solvents for both extraction and disperser solvents. This method has less toxicity and environmental greenness. A Plackett-Burman design and a Box-Benken design were applied to evaluate the alcoholic-assisted dispersive liquid–liquid microextraction procedure. The effective parameters (extraction time, stirring speed, pH, ion strength and volume of extraction and dispersion solvent) on the extraction recovery were studied utilizing Plackett-Burman design. Next, Box-Benken design was applied to obtain optimal condition. The best recovery was achieved using 1-octanol as the extraction solvent and methanol as the dispersive solvent. The results showed that volume of dispersive solvent, extraction time and stirring time had no effect on the recovery of analytes.

In optimized conditions, five replicates of experiment gave the average of extraction recoveries equal to 89.42 % and 90.15% and detection limits were obtained 7.63 and 7.15 μgL^{-1} for citalopram and fluoxetine, respectively. The relative standard deviations for the determination of citalopram and fluoxetine at different concentration levels were less than 10%. The developed method was successfully applied for the determination of citalopram and fluoxetine in biological samples.

Keywords: selective serotonin re-uptake inhibitors; Alcoholic-assisted dispersive liquid–liquid microextraction; Experimental design; HPLC

Synthesis and characterization of a new surface modified magnetic nanoparticle and its application as an efficient sorbent for ultrasound-assisted dispersive magnetic solid phase extraction of Berberine

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A new surface modification of iron oxide magnetic nanoparticles (MNPs) was carried out by immobilizing p-Naphtholbenzein as a hydrophobic compound on the surface of pre-amino functionalized MNPs. Fabrication of p-Naphtholbenzein-coated MNPs (PNB-MNPs) was confirmed by characteristic analyses such as: FT-IR, XRD, TGA, VSM, SEM, and TEM. XRD and VSM analyses confirmed the formation of superparamagnetic Fe_3O_4 nanoparticles. While SEM images revealed the spherical morphology of MNPs in the range of 40- 60 nm, the TEM results showed the core-shell structure of synthesized MNPs. Regarding the TGA results, approximately about 29 percent of the total weight of PNB-MNPs is consisted of the modifying organic layer. The characterized PNB-MNPs were utilized to develop a dispersive magnetic solid phase extraction of Berberine, an important chemical with a leading structure for designing new drugs. Affecting parameters on the extraction recovery of Berberine were optimized through an orthogonal rotatable central composite design (CCD). Under optimum extraction conditions of Berberine (pH= 4.5, amount of MNPs = 5 mg, sample volume = 30 ml, sonication time = 1 min, and 500 µL of methanol as desorbing solvent), the extraction recovery of 98.2% was obtained via five replications with relative standard deviation of 3.7%. The method was successfully utilized for determination of Berberine in human plasma and urine samples. Regarding the method calibration graphs in plasma and urine matrices, which were spiked in the range of 0.01–200 µg L^{-1}, pre-concentration factors of 67 and 63, method detection limit (MDL) of 0.34 and 0.36 µg L^{-1}, and lower limit of quantification of 1.13 and 1.2 µg L^{-1} were obtained for plasma and urine samples, respectively. The method exhibits good potentials to be a fast, efficient and reliable method for determination of Berberine in human biological samples.

Keywords: Solid phase extraction; Magnetic nanoparticles; Berberine; Response surface methodology; Biological samples

Optimizing the Conditions for Removal of Mercury (II) and Methylene Blue from Environmental Samples by Using Modified Graphene Oxide as a New Sorbent

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Heavy metal ions and dye pollutants are toxic and dangerous for human health. They are carcinogenic and toxic to the ecosystem and strongly threaten the survival of organisms. Therefore, the elimination of these hazardous pollutants and the refinement of wastewater by a reasonable route is vital. Adsorption has been found to be an efficient, accessible route for this aim. In this work, grapheme oxide modified with pyridine thiosemicarbazone as ligand (GO/2-PTSC) was used for removal of methylene blue and mercury ion. The prepared GO/2-PTSC was characterized by Fourier transform infrared spectroscopy (FT-IR), X-ray powder diffraction (XRD), atomic-force microscopy (AFM) and elemental analysis. The experimental design methodology was used to determine and calculate the tests and the number of runs. It should be noted that, by this approach the optimum conditions can be obtained more accurately. The influences of the analytical parameters including pH, contact time, adsorbent dosage and initial concentration of solution were investigated. The maximum adsorption capacity of MB and Hg (II) was 712 and 520 mg/g at pH =7 and 6, respectively. Notably, the removal time of these contaminants was decreased to 3 min by ultrasonic bath. The proposed method has been successfully applied for MB and (GO/2-PTSC) uptake in some real samples such as natural water samples.

Keywords: Modified graphene oxide, Methylene blue, Mercury, Experimental design Removal

References:

[1] L. Han, X. Zhou, L. Wan, Y. Deng and S. Zhan, J. Environ. Chem. Eng., (2014), 2, 123.
[2] D. Lu, Y. Zhang, S. Lin, L. Wang and C. Wang, J. Alloys Compd.,(2013), 579, 336.

Removal of Trihalomethanes (THMs)from water samples using Iron nano particles coupled head space method by GC- MS

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THMs (chloroform,bromoform,dichloro bromo methane and dibromo chloro methane) are one of the most persistent groups of organic micropollutants present in the environment. Their presence in the environment is a result of uncontrolled release of solid/liquid effluents as well as industrial atmospheric discharges .Hence ,studing methods for micro extraction ,analyzing and especially removal them from water is very necessary. [1]

Removal of some chlorinated hydrocarbons from water samples was investigated using laboratory synthesized zero-valent nano iron (ZVNI) particles. . Iron is inexpensive, nontoxic and environmentally compatible. Researchers showed that ZVNI has been successfully used to Removal of chlorinated hydrocarbons from water samples The synthesized ZVNI particles were characterized as nanoscale sized by scanning electron microscopy (SEM). [2]

In this article Static Headspace analysis combined with high-resolution gas chromatography and detection by mass spectrometry was evaluated for the analysis of samples.

Several conditions such as contact time between ZVNI powder and sample, weight of sorbent, concentration of chloroform in sample and PH were optimized. The suggested method was successfully applied to the determination of chloroform in the real samples. The standard reference material was (THMs standard 38407 AccuStandard).

The adsorption equilibrium data fitted very well to the Langmuir and Freundlich adsorption isotherm models.The adsorbent capacity qmax (mgg-1) is108.14 and constant separation factor or equilibrium parameter RL in different concentration is between 0.02 and 0.07

Keywords laboratory synthesized zero-valent nano iron particles (ZVNI);Static Headspace; Trihalomethanes (THMs).

References:

[1]V.I. Safarova, S.V. Sapelnikova, E.V. Djazhenko, G.I. Teplova,G.F. Shajdulina, F.Kh. Kudasheva,J.ChromB.800 (2004) 325–330
[2] E.J.Petersena, R.A Pinto, X. Shi, Q.Huang, J.Hazard. Mat. 243(2012) 73–79.

Solvent exchange method as facile, simple and fast procedure for preparation of nanocomposites coated stir bars for sorptive extraction methods

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A novel method for preparation of stir bar coating based on various nanocomposites is introduced. In this method, nanocomposites are easily coated on a stainless steel substrate using solvent exchange method. The solvent exchange method is based on a phenomenon that a solid polymer film forms at the interface between an aqueous solution and a solution of a water-insoluble polymer upon their contact [1]. In this procedure the nanofiller was dispersed in a polymeric solution, the substrate was immersed in this solution and after deposition of a layer of polymeric solution on it, it is immersed in water which leads to the formation of a nanocomposite layer coated on a substrate. Various nanocomposites coated stir bars can be prepared using this procedure concerning the different polymeric matrix and different nanofillers in order to sorptive extraction of different analytes with different polarity. In this regards, the nanocomposites based on reinforcing of multiwalled carbon nanotubes (MWCNTs) and graphene oxide (GO) in polyamide (PA) were prepared as stir bar coating. The morphology and surface characteristic of PA, CNT/PA and GO/PA coated stir bars were investigated using scanning electron microscopy. The stir bar coated by CNT/PA nanocomposite was used as an extraction device for stir bar sorptive extraction (SBSE) of bisphenol A from aquatic environment followed by high pressure liquid chromatography-UV-Vis (HPLC-UV-Vis) detection . Additionally it was applied to SBSE of naproxen from biological samples followed by spectrofluorimetric determination. The GO/PA coated stir bar was applied to extraction of tramadol from biological samples followed by spectrofluorimetric detection. Important factors influencing the extraction and desorption processes were studied and optimized using response surface methodology applying central composite design. In order to evaluate the developed methods, Limits of detection, the methods precision, the linearity of the methods and relative recovery percentages were obtained.

Keywords: stir bar sorptive extraction; solvent exchange method; carbon nanotubes; graphene oxide; nanocomposite.

References:

[1] Y. Yeo, A.U. Chen, O.A. Basaran, K. Park, Pharm. Res. 21 (2004) 1419.

Ultrasound-assisted dispersive liquid–liquid microextraction followed GC-Mass for the determination of Organochlorine pesticides in water samples

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The control of pesticides in surface, drinking and groundwater is nowadays a real necessity. Hence a simple and rapid ultrasound-assisted dispersive liquid–liquid microextraction (USA-DLLME) coupled with High sensitive techniques like Gas chromatography-Mass spectrometry (GC-MS) was developed for the extraction and determination of 12 organochlorine pesticides (Alpha.-Lindane, Beta-lindane, Delta-Lindane, Heptachlor, Aldrin, Epoxyheptachlor, Endosulfan I, Endosulfan II, Dieldrin, 4,4'-DDE, 4,4'-DDD, 4,4' DDT).[1]

Microextraction techniques, such as dispersive liquid-liquid microextraction have many advantages such as minimal consumption of harmful solvents, and typically, the high enrichment factor. And it is readily combined with GC/MS. [2]

In this method, 300uL of disperser/ extracting solvent (chloroform/acetone)was rapidly injected into a 10.00mL of the sample was placed in a 20mL glass test tube with a conical bottom by a 1000 uL syringe and the mixture was sonicated for 4 min. Then, the mixture was centrifuged at 2500 rpm for 5 min. the extractant phase deposited at the bottom of the test tube was manually injected into the GC–MS system (GC-MS Shimadzu QP -2010 plus) for analysis.

The suggested method was successfully applied to the determination of these OCPs in the real samples. The standard reference material was (Pesticide mix 163 Dr Ehrenstrofer).Extraction efficiency (such as type and volume of extraction and dispersive solvent, extraction time, ultrasonic time, and centrifuging time) were evaluated. Under the optimum condition, good linearity was obtained in a range of 2-400 ppb for all analytes with the correlation coefficient R2=0.9986.Average recoveries at three spiking levels were over the range of 93-112% with RSD less than 9%.

Keywords: Acetone; Chloroform;.Organochlorine pesticides (OCPs); ultrasound-assisted dispersive liquid–liquid microextraction (USA-DLLME)

References:

[1] A. Alves, M. Gonçalves, M. Bernardo, B. Mendes, J Sep Sci. 35-19 (2012) 2653.

[2] M. Rezaee, Y. Yamini, M. Faraji, J. Chrom A. 1217 (2010) 2342.

Modified multi-walled carbon nanotubes as solid phase extraction sorbents for determination of metformin hydrochloride in real samples

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A new method based on the combination of solid-phase extraction and spectrophotometric determination was developed for isolation and preconcentration of metformin hydrochloride from real samples using sodium dodecyl sulfate (SDS) coated Modified multi-walled carbon nanotubes(MWCNT) as an adsorbent. Various parameters influencing the extraction efficiency of metformin hydrochloride including the amount of MWCNT and SDS, pH value, sample volume and type and amount of Desorption solvent were optimized. Under optimized conditions, the method was successfully applied to the extraction of metformin-HCL from human plasma and wastewater samples and monitored spectrophotometrically at λ_{max} = 230 nm. The calibration curve for the determination of metformin-HCL was linear in the range of 0.03-1.52 µgmL^{-1} with r^2 = 0.9965. The limit of detection (LOD) of the proposed method was 0.009 µgmL^{-1}. The relative standard deviations for the determination of metformin in wastewater samples and human plasma were less than 3.0% (n=5). The method was successfully applied to determine metformin hydrochloride in biological fluids and equatic samples and satisfactory recoveries were obtained.

Key words: solid phase extraction; metformin; multi-walled carbon nanotubes; SDS

Preconcentration and determination of trifluoperazine hydrochloride using multi-walled carbon nanotubes

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A solid phase extraction procedure using multi-walled carbon nanotubes (MWCNTs) as sorbents combined with UV spectrometry was developed for preconcentration and determination of trifluoperazine hydrochloride. Several key factors including pH value, amount of MWCNTs , sample volume,type and amount of elution solvent were investigated to achieve optimal SPE recoveries and efficiency. Under optimized conditions trifluoperazine was extracted and measured spectrophotometrically at λ_{max} = 260 nm. The method was successfully applied to the extraction of trifluoperazine-HCL from human urine and wastewater samples. The obtained recoveries in human urine and equatic samples were values of 82% to 91% . The calibration graph for the determination of trifluoperazine-HCL was linear in the range of 0.08-1.7 μgmL^{-1} with $r^2 = 0.9938$. The limit of detection (LOD) of the proposed method was 0.024 μgmL^{-1}. The repeatability and reproducibility (R.S.D.) of the mentioned method were 1.25% and 1.9% respectively. The whole procedure showed to be conveniently fast , efficient and economical for extraction of triluoperazine hydrochloride from real samples.

Keywords: solid phase extraction; trifluoperazine; multi-walled carbon nanotubes

Development of a solid phase extraction by using Fe_3O_4 / PANI nanocomposite coupled with HPLC for the preconcentration and determination of chlordiazepoxide and diazepam

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Chlordiazepoxide (CZP) and diazepam (DZP) are two psychoactive drugs belonging to the benzodiazepines (BZN) that widely used for the treatment of anxiety and insomnia, as well as other psychological disorders. Intoxication can be associated with behavioral disinhibition, generating hostility or sexual aggression. The effect is perhaps most common when BZD are taken in combination with alcohol [1].

One of the efficient preconcentration method is dispersive solid phase extraction which has some advantageous such as low organic solvent usage and extraction time for sample preparation. In this work Fe_3O_4 / polyaniline nanocomposite was used as solid sorbent for extraction of CZP and DZP in biological samples.

The effect of several parameters on the extraction efficiency including PH, amount of absorbent, type and volume of desorption solvent, extraction time and ion strength were studied. Under the optimum conditions, the linear dynamic range of the proposed method were 0.01-5.00 and 0.01-5.30 mg L^{-1} for CZP and DZP respectively. The method detection limits were 7.27×10^{-3} and 4.6×10^{-3}mg L^{-1} for CZP and DZP respectively. Finally the proposed procedure has been successfully applied for the preconcentration and sensitive determination of chlordiazepoxide and diazepam in biological samples.

Keywords: Chlordiazepoxide, Diazepam, Dispersive solid phase extraction, Fe_3O_4/PANI

References:

[1] P. Fernandez, C. Gonzalez, M. T. Pena, A. M. Carro, R. A. Lorenzo, Chim. Acta, **2013**, 767, 88-96.
[2] V. Camel, spect. Chim. Acta part B, **2003**, 58, 1177-1233.

Application of nanocomposite of Fe_3O_4 / PANI as sorbent followed by high performance liquid chromatography for preconcentration and quantification of Nitrazepam and alprazolam

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Benzodiazepines (BZN) belong to a type of drug that acts on the neurotransmitter _-amino butyric acid (GABA) receptors, resulting in sedative, hypnotic, and anxiolytic properties. Nitrazepam (NTZ) and alprazolam (APZ) are two psychoactive drugs belonging to the benzodiazepines (BZN) which are sedative, hypnotic, and anxiolytic drugs [1]. The sedative effects of these drugs have been subjected to abuse in the recent years. Thus screening and detection of these drugs may be necessary under the therapeutic aspects as well as in connection with the forensic toxicology.

In this study, a simple and fast method based on the using of new nanocomposite such as Fe_3O_4 / polyaniline as solid sorbent was used for preconcentration of the studied drugs. Also, the extracted drugs were analyzed by HPLC.

Some parameters affecting on the extraction efficiency including pH, amount of nanocomposite, type and volume of desorption solvent, extraction time and salt effect were investigated. The linear dynamic range of the proposed method were 0.01-5.30 and 0.01-5.00 mg L^{-1} for NTZ and APZ respectively under optimum conditions with good correlation coefficient. Also the method detection limits were 0.01 and 8.96×10^{-3} mg L^{-1} for NTZ and APZ respectively. Finally the proposed method was successfully applied for preconcentration and quantification of NTZ and APZ in biological samples.

Keywords: Alprazolam, Dispersive solid phase extraction, Fe_3O_4/PANI, Nitrazepam

Synthesis and characterization of magnetic nanocomposite beads based on chitosan for removal of Cu(II) ions from aqueous solution

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Significant efforts have been made to develop highly efficient adsorbent for removal of Cu(II) ions pollutant from domestic and industrial wastewaters. In this study, nanoparticles of iron oxide was first synthesized and then imprinted in the network of chitosan containing nanoclay and thus the novel magnetite nanocomposite beads were synthesized. Then, they were characterized using Fourier transform infrared spectroscopy (FTIR), X-ray diffraction analysis (XRD), scanning electron microscopy (SEM), and energy-dispersive X-ray spectroscopy (EDX). The prepared magnetite nanocomposite beads containing several different functional groups were utilized as an adsorbent of copper ions from an aqueous solution. The effect of various experimental conditions such as time, pH, initial concentrations of adsorbate solutions, temperature, and amounts of adsorbent on adsorption capacity of nanocomposite beads were explored. In addition, the kinetic, isotherm and thermodynamic of adsorption were investigated for the description of adsorption process. The maximum Cu^{2+} ions adsorption capacity of the prepared magnetite nanocomposite beads was found to be 292.6 $mg.g^{-1}$ in the optimized conditions. The mechanism of adsorption was well followed a pseudo-second-order kinetic model. Furthermore, the Langmuir seems to produce better fit in comparison with the Freundlich adsorption isotherm.Finally, thermodynamic studies suggest that the Cu^{2+} ions endothermic adsorption process is spontaneous and thermodynamically favorable.

Keywords: nanocomposite, iron oxide nanoparticles, magnetic bead, chitosan, nano-clay

Application of deep eutectic solvent in hollow fiber liquid phase microextractionfor extraction and preconcentrationof steroidal hormones from biological fluids

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The sample preparation is a critical step in an analysis. Hollow fiber liquid-phase microextraction (HF-LPME) offers an efficient alternative to classical techniques for sample preparation and preconcentration [1]. Within the framework of green chemistry, non-toxic, biodegradable, recyclable and low price solvents occupy a strategic place. The present study, introduces a novel solvent as acceptor phase for HF-LLLME based on using two immiscible organic solvents, this new solvent called deep eutectic solvent (DES). DESs are generally composed of two or three cheap and safe compounds that mixture of them has melting point lower than each individual component *[2]*. Here, an organic solvent (*n*-dodecane) is immobilized in the pores ofthe hollow fiber, providing a supported liquid membrane (SLM), and DES is filled within its lumen andservesas theacceptorphase. This method coupled with HPLC-UV-Vis detection was applied for extraction and determination of dydrogesteroneand cyproteronein biological samples. The effects of different parameters such as type of acceptor phase, composition of SLM and acceptor phase, ionic strength, stirring rate, fiber length and extraction time on the extraction efficiency of the analytes were investigated and optimized. Under the optimum condition, preconcentration factors in the range of 421-428 were obtained. The performance of the proposed method was studied in terms of linear ranges (LRs from 1.5 to 800 ng mL^{-1}), linearity ($R^2 \geq 0.998$), precision (RSD % ≤6.05) and limits of detection (LODs in the range of 0.5-2 ng mL^{-1}). In addition to preconcentration, HF-LLLME also served as a technique for sample clean-up.

Keywords: Hollow fiber; Deep eutectic solvents; Steroidal hormones

References:

[1] M. Ghambarian, Y. Yamini, A. Esrafili, Microchim. Acta 177 (2012) 271.
[2] Q. Zhang, K.D.O. Vigier, S. Royer, F. Jérôme, Chem. Soc. Rev. 41 (2012) 7108.

Simultaneous Determination of Triacetin, Diacetin and monoacetin in Gasoline by reverse Micelle Procedure and Gas Chromatography

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Triacetin is an artificial chemical compound that commonly used as a fuel additive as a antiknock agent which can reduce engine knocking in gasoline. A simple, fast and sensitive sample preparation based on reverse micelle ultrasonic back-extraction of TritonX-114 reverse micelles by a water-toluene binary system and gas chromatography with flame ionization detection (GC-FID), was proposed for determination of triacetin, diacetin and monoacetin in gasoline. Reversed micelles are formed by dissolving a surfactant in an organic solvent, the aggregates have been visualized as spherical with the polar head groups of amphiphiles shielded from the solvent by hydrocarbon tails[1]. After the mixing of the gasoline and Triton X-114, an aliquot of acetonitrile, as a modifier, was added to the mixture to form a cloudy state. The surfactant-rich phase was obtained by centrifugation and treated with a mixture of water and toluene as extraction solvent. The analyst back extracted in the toluene phase by ultrasonication. After the centrifugation, the upper toluene layer was withdrawn by a microsyringe and injected into the GC-FID. Influence of several important parameters on extraction efficiency of analyst was evaluated. Under optimized conditions a linear relationship was obtained between the peak area and the concentration of analyst. The calibration graphs were linear in the range of 1.0-30 mg.L^{-1}, and the correlation coefficients were more than 0.994.The limit of detection for triacetin, diacetin and monoacetin were 0.06, 0.15 and 0.18mg.L^{-1} respectively, and the recoveries were more than %93. This procedure was successfully applied with satisfactory results to the determination of triacetin, diacetin and monoacetin in real sample.

Keywords: Gasoline, GC-FID, Reverse micelle

References:

[1] E.Ruckenstein, R. Nagarajan, J. Phys. Chem. 84 (1980) 1349.

A new method for Identification and determination of tri (ethylene glycol) dimethacrylate deterrent in single-base gun propellants

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Propellants burn so in some cases rapidly that the initial rise of pressure in weapons may be faster than desired rate and amount. To avoid this unwanted effect, burning rate of the propellants is controlled and moderated by applying a surface coating agent. Coating agents are usually called deterrents (moderants). The interior ballistic properties of propellants can be significantly improved by the application of deterrents. However, the diffusion of the deterrents from the surface into the propellant grains during long-time storage may significantly reduce the propellants ballistic life. Therefore determination of the diffusion and rate of deterrents helps in development of propellants with more stable ballistic performance. Accordingly identification and determination of deterrent in gun propellants should be done. Using different analytical methods presence of (tri-EGDMA) deterrent was determined. Methods include gas chromatography-Mass (GC-MS), FTIR microspectroscopy and High Performance Liquid Chromatography (HPLC). Different instrumental methods have been applied to determine the content of the deterrent in propellants. Experimental results indicated that GC-MS analysis is an appropriate method for this work. Under the optimum conditions, the determination of deterrent in one kind of single base propellant is done and its value was 3.4 percent. The detection limits of deterrent in propellant samples were reported 0.010 mg g^{-1}. Linear dynamic range of deterrent is 0.04–10.00 mg g^{-1} with R^2 of 0.9982. This method (GC-MS analysis) was successfully applied for determination of (tri-EGDMA) deterrent in gun propellants.

Keywords: Propellant, Interior ballistic performance, Deterrent, Tri(ethylene glycol) di-methacrylate .

Nano structured star-like poly ionic dendrimer as sorbent for microextraction in packed syringe (MEPS)

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In this study, a new adsorbent based on star-like poly ionic dendrimer which bonded on nano silica particles was prepared and used as sorbent for microextraction in packed syringe(MEPS) coupled with HPLC-UV for determination of bisphenol A in water samples. The surface morphologies of the sorbent was studied by scanning electron microscopy (SEM). Ionic liquids (ILs) are organic salts consisting bulky organic cations together with an organic or inorganic anion as counter ion with melting points lower than 100 °C. Unique physico-chemical properties of ionic liquids make them suitable for various applications in chemistry like solvents for synthesis [1], catalyst for chemical reactions [2] and separation media for extraction process. [3]. Dendrimers are a class of macromolecules, constituted of branches which pull out radially from a central core. Important parameters influencing extraction and desorption processes including desorption solvent, elution volume, pH effect and amount of sorbent were optimized. The developed method was successfully applied for determination of bisphenol A in water samples which packed in plastic bottles.

Keywords: Star like poly ionic dendrimer; microextraction in packed syringe; high performance liquid chromatography

References:

[1] M.J. Earle, K.R. Seddon, Pure Appl. Chem. 72 (2000) 1391.
[2] A. Kumar, S.S. Pawar, J. Mol. Catal. A: Chem. 208 (2004) 33.
[3] E. Stanisz, J. Werner, A. Zgola-Grzeskowiak, TRAC-Trend. Anal. Chem. 61 (2014) 54.

Preconcentration and microextraction of Safranin O by SM-DLLME-SFO prior of spectrophotometric determination

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In this research, a simple, rapid and environmentally friendly method was applied for the microextraction, preconcentration and determination of ultratrace quantities of safranin O in some water and wastewater samples by supramolecular dispersive liquid–liquid microextraction based on the solidification of floating organic droplet (SM-DLLME-SFO) coupled with spectrophotometry Uv-vis .The SM solvent selected was made up of reversed micelles of decanoic acid dispersed in tetrahydrofuran (THF)-water. THF plays double role, not only acts as a disperser solvent but also causes self-assembly of decanoic acid. Effective factors on the microextraction efficiency, such as pH, type and volume of extraction and disperser solvents, ionic strength, sonication and centrifuge time were investigated and optimized. Under the optimized conditions, the calibration curve was linear in the range of 0.25 to 400.00 μg L^{-1} for method. The detection limit, enrichment factor and preconcentration factor were obtained 0.22 μg L^{-1}, 39 and 33.33 respectively. The relative standard deviation for four replicate determination of 100 μg L^{-1} safranin O was ±2.11%. In addition, the effects of some (RSD) foreign species including cation, anions and dyes were investigated. The method was successfully applied to the extraction and determination of safranin O in some water and wastewater samples.

Keyword: Dispersive liquid–liquid microextraction, Solidification of floating organic droplet, Supramolecular solvent, Safranin O.

A Novel Nanosorbent Based on Polystyrene and Magnetite Nanohybrid for Solid-Phase Extraction of Silver Ion from Environmental Samples

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A nanohybrid based on polystyrene derivatives and magnetite was introduced as a new sorbent for pretreatment and analysis of the trace silver in environmental samples. Flame atomic absorption spectrometry was used for detection of the analyte after desorption of the extracted analytes by hydrochloric acid solution. Different variables affecting the separation/pre-concentration conditions of the analyte, including pH of the sample solution, buffer concentration, amount of the sorbent, sample volume, extraction and desorbtion times, and elution conditions were investigated and optimized. Under the optimized conditions, linear calibration graph was obtained in the range of 0.01–0.11 mg L^{-1} silver, with the correlation coefficient of 0.998. The enrichment factor of 50 was achieved, leading to limit of quantification of 10 µg L^{-1}. The relative standard deviation for the determination of silver was 2.37% (n=6, silver concentration; 80 µg L^{-1}).The method was successfully applied to determine silver in natural waters and satisfactory recoveries were obtained in the range of 94–105%.

Keywords: Nanohybrid, Magnetite, Polystyren, Magnetic solid phase extraction, Sample pretreatment

References:

[1] V. Stefanova, D. Georgieva, V. Kmetov, I. Roman, A. Canals, J, Anal. At.Spectrom, 27(2012) 1743.
[2] K. Aguilar-Arteaga, J.A. Rodriguez, E. Barrado, Anal. Chim.Acta, 674 (2010) 157-165.
[3] G. Giakisikli, A. N. Anthemidis, Anal. Chim.Acta, 789 (2013)1185–1189.

Synthesis of sulfonic acid functionalized SBA-15 magnetic nanocomposite for removal of Methyl green dye

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In the present study, SBA-15 magnetic nanocomposite functionalized with sulfonic acid was synthesized and after characterization by XRD, FT-IR, EDX and SEM, its effectiveness as an adsorbent for the removal of methyl green from aqueous solutions was evaluated. Experimental factors affecting the dye removal efficiency were studied and optimal conditions were obtained. The results revealed that more than 97% removal efficiency of methyl green was obtained in optimal conditions. The kinetic studies showed the second order kinetic model with $R^2 = 0.9999$, $Q_{eq}= 5.567$ mg/g and $K_2 = 1.570$ which shows chemisorptions process. Also, the Langmuir and Freundlich isotherms were investigated and dye adsorption equilibrium data were fitted well to the Langmuir isotherm rather than Freundlich isotherm. The results of this study, suggest the high ability of synthesized mesoporous magnetic nanocomposite as a good sorbent for complete removal of methy green.

Keywords Mesoporous SBA-15, magnetic nanocomposites, sulfonic acid, Methyl green

Study of biogenic volatile organic compounds released from *Clostridium* Tetani by HS-SPME coupled to GC-MS

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Microbial species produce a wide range of volatile organic compounds (VOCs), and identification of pathogenic species through analysis of secondary microbial metabolites is possible as early as the 1960s. Various odors and associated biomarker VOCs have been identified from cultures of a number of parasitic and pathogenic microbes. The unique biomarkers are a useful key for studied the microorganism genus and control the growing behavior.

A novel and efficient method based on headspace solid-phase microextraction (HS-SPME), followed by gas chromatography–mass spectrometry (GC-MS), was developed to study the VOCs emerged by *Clostridium Tetani* (C. Tetani). C. Tetani was cultured in different media and SPME was conducted from them. SPME was performed by PDMS coated fiber prepared by sol-gel method followed by GC-MS for analysis.

About fifty constituents were identified and the main compounds detected include sulfur compound like dimethyldisulfide, dimethyltrisulfide, and dimethyltetrasulfide. These sulfur volatiles are derived from two different L-methionine catabolism pathways, which probably coexist in this bacterium.

The developed HS-SPME-GC-MS method allowed to determine the chemical fingerprint of *C. tetani* volatile constituents, thus providing a new and reliable tool for the control growth phase of microorganism in bioreactor for vaccine production.

Keywords: Biogenic volatile organic compounds, clostridium tetani, HS-SPME, GC-MS.

References:

[1] Z. Zhang, G. Li, Microchem. J. 95 (2010) 127.
[2] T. Sawoszczuka, J. Syguła-Cholewińskaa, J. M. del Hoyo-Meléndezb,J. Chromatogr. A1409 (2015) 30.

Gamma irradiation effect on the total phenolic and flavonoids contents of Persian hogweed (Heracleum persicum)

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Gamma irradiation is used in treating dried spices, herbs, and vegetable seasonings to reduce pathogens and spoilage microorganisms [1-3]. *Heracleum persicum,* commonly known as Golpar or Persian Hogweed, is recommended in traditional medicine as a cure for numerous diseases. The objective of this work was to assess the effect of gamma irradiation on total phenolic and flavonoids contents as natural antioxidants compounds in *Heracleum persicum*. Gamma irradiation was performed with a cobalt-60 irradiator at doses of 1, 3, 5, 10, 15, 20 and 25 kGy. The irradiated and nonirradiated plant samples were first ground to powder and then extracted with water and methanol (80%). To extract with water, 0.5 g of the fine powder was treated with 10 ml of ultra-filtered water at 100 °C for 30 min. To extract with methanol, 0.5 g of the powder was treated with 10 ml of 80% methanol at 40 °C for 24 h. The samples were then cooled down to room temperature and centrifuged at 4500 rpm for 15 min. Total phenolic and flavonoids contents in supernatants were determined by Folin Ciocalteu method and aluminum chloride colorimetric assay, respectively. The results showed that gamma radiation does not significantly affect total phenols and flavonoids contents of *H. persicum* over the entire employed range from 0.5 to 25 kGy.

Keywords Gamma irradiation; Heracleum persicum; Total phenolic content; Flavonoids extraction

References:

[1] M Jamshidi, M Barzegar, MA Sahari, Iranian Journal of Nutrition Sciences & Food Technology 7 4 (2013) 73-82.

[2] S. Taheri, T.L Abdullah, E. Karimi, E. Oskoueian and M. Ebrahimi, International Journal of Molecular Sciences 15 (2014) 13077-13090.

[3] M. Rousta, A.A. Sadeghi, P. Shawrang, M. Aimn Afshar and M. Chamani, Iranian Journal of Applied Animal Science 4 4 (2014) 723-731.

The effect of electric field geometry on the performance of electromembrane extraction systems: footprints of a third driving force along with migration and diffusion

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The distribution of electric field vectors was first calculated for electromembrane extraction (EME) systems in classical and cylindrical electrode geometries. The results showed that supported liquid membrane (SLM) has a general field amplifying effect due to its lower dielectric constant in comparison with aqueous donor/acceptor solutions. The calculated norms of the electric field vector showed that a DC voltage of 50 V can create huge electric field strengths up to 64 kV m^{-1} and 111 kV m^{-1} in classical and cylindrical geometries respectively. In both cases, the electric field strength reached its peak value on the inner wall of the SLM. In the case of classical geometry, the field strength was a function of the polar position of the SLM whereas the field strength in cylindrical geometry was angularly uniform. In order to investigate the effect of the electrode geometry on the performance of real EME systems, the analysis was carried out in three different geometries including classical, helical and cylindrical arrangements using naproxen and sodium diclofenac as the model analytes. Despite higher field strength and extended cross sectional area, the helical and cylindrical geometries gave lower recoveries with respect to classical EME. The observed decline of the signal was proved to be against the relations governing migration and diffusion processes, which means that a third driving force is involved in EME. The third driving force is the interaction between the radially inhomogeneous electric field and the analyte in its neutral form.

Keywords: Electric field inhomogeneity; Electromembrane extraction; Electrode geometry; Inhomogeneous electric field-dipole interaction

New Synthesis of silver oxide nano particle and applied in extraction and determination of Diazepam.

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Nano materials are new solid materials that have attracted to SPE methods substantially due to their special properties. Recently, silver oxide nanoparticles as adsorption materials have been employed for preconcentration of trace metal and drug analytes from real samples. In this work introduces an approach, silver oxide nanoparticles modified with SDS was synthesized. We developed an efficient and cost-effective method for the preconcentration of trace amount of Diazepam in human plasma samples using this novel magnetic solid phase in pH =1.0. The possible parameters affecting the enrichment were optimized. It is shown that the novel silver oxide nano-adsorbent is quite efficient for fast adsorption of Diazepam. Various parameters affecting the adsorption of Diazepam on silver oxide nanoparticle, such as pH of solution, desorbing reagent, adsorption isotherms, amount of adsorbent and matrix effects, have been investigated. The calibration graph for the determination of Diazepam was linear in the range of 0.05-5.0 ng mL^{-1}. The limit of detection, defined as LOD= $3S_b/m$ was 0.003 $ngmL^{-1}$ (n=3) of Diazepam. The relative standard deviation (RSD) with n=3, was below 0.08%. The preconcentration factor of 50 was achieved in this method. The method was applied to an assay of Diazepam in human plasma.

Keywords: Biological sample; Diazepam; Silver oxide nanoparticles; Solid phase extraction; Spectrophotometric

References:

[1] R. Smith, *J.Chromatog . A* 1000 (2003) 30.
[2] H. Lord, J. Pawliszyn , *J.Chromatogr . A.* 902 (2000) 17.
[3] E.Baltussen, P. Sandra, F. David, C. Cramers, *J. Microcol.* Sep. 11 (1999) 737.

Metal-organic framework-199/graphite oxide hybrid composites coated on stainless steel fiber for headspace solid-phase microextraction -gas chromatography of polycyclic aromatic hydrocarbons in water

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In this paper, the potential applications of hybrid material of a copper-based metal-organic framework (MOF-199) and graphite oxide (GO) as fiber coatings for the solid-phase microextraction (SPME) of polycyclic aromatic hydrocarbons (PAHs) in water samples were explored. The prepared composite was immobilized onto a stainless steel wire by functionalized surface stainless steel wire and using 3-amino-propyltriethoxysilane (APTES) as the cross-linking agent for fabrication of the SPME fiber. In order to firstly surface pretreatment of stainless steel fiber and then fibers dipped into APTES for 5 min, pulled out and immediately immersed into the powder of MOF/GO composite. After fibers were taken out and placed into an oven at70 ^{0}C for .These fibers was characterized by scanning electron microscopy(SEM), FT-IR spectrometer and thermogravimetric analyzer(TGA), transmission electron microscopy (TEM), X-ray diffraction(XRD). Under optimized conditions, a linear relationship was obtained between the peak area and the concentration of phenols in the range of 0.1–200 μgL^{-1}. The detection limits were lower 0.041 for polycyclic aromatic hydrocarbons (PAHs). Intra-day and inter-day precisions for the analysis of analytes were in the range of 1.57–2.30%. This procedure was successfully applied with satisfactory results to the determination four phenols in waters samples. The relative mean recoveries of in waters samples ranged from 93.0% to 103.0%.

Keywords: Progesterone, Testosterone, molecularly imprinted, Solid-phase microextraction, plasma, serum, HPLC.

References:

[1] A. Eshaghi, V. Hosseininasab, H. Bagheri, Anal. Chim. Acta 813 (2014) 48–55.
[2] Y.Wang, Y. Wu, H. Ge, H. Chen, G. Ye, X. Hu, Acta 37 (2001) 395.
[3] N. Li, Q. Zhu, Y. Yang, J. Huang, X. Dang, H. Chen, Talanta 132(2015)713–718.

Polyethylene glycol grafted flower-like cupric nano oxide for hollow fiber solid phase microextraction of hexaconazole, penconazole and diniconazole in vegetable samples

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In this research, poly (ethylene glycol) - poly (ethylene glycol) grafted flower-like cupric oxide nano particles (PEG-PEG -g- CuO NPs) were synthesized using sol–gel technology. PEG acts as a template for the CuO flower-nanostructures formation. This novel nanocomposit was developed for hollow fiber solid-phase microextraction (HF-SPME) of the pesticides: hexaconazole, penconazole and diniconazole from cucumber, lettuce, bell pepper, cabbage and tomato samples with HPLC–UV. Main parameters affecting microextraction were evaluated and optimized. In optimal conditions, detection limits and precision were measured between 0.003 and 0.097 ng mL^{-1} (n=8), and 2.98 – 6.17% (n = 3) respectively. Linear ranges were within 0.5-50000 ng mL^{-1} for hexaconazol; 0.012 - 50000 ng mL^{-1} for penconazol and 0.02 - 50000 ng mL^{-1} for diniconazol. The constructed method has been developed and successfully used to the analysis of vegetable samples with relative recoveries from 85.46 to 97.47%.

Keywords Hollow fiber Solid-phase microextraction; Flower-like cupric oxide nano particles; Sol–gel technology; Fungicide; Vegetable samples

References:

[1] Z. Es'haghi, M. Ahmadi-Golsefidi, A. Saify, Anal. Chim. Acta, 689 (2011) 122–128.
[2] N.H. Hung, N. Thanh, Mater. Sci. Semicon. Proc., 26 (2014) 18-24.
[3] A. Sarafraz-Yazdi, A. Zendegi-Shiraz, Z. Es'haghi, M. Hassanzadeh-Khayyat, J. Chromatogr. A, 1418 (2015) 21–28.

Antioxidant and Anti microbial Properties of Various Extracts of Menthalongifolia M.amphilema and M.pulegium from Iran

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Antioxidants are the great interest because they may help to protect the body against damage by free radicals. Excessive free radical production and lipid peroxidation are known to cause several pathological conditions Including atherosclerosis, diabete, cancer. Therefore, antioxidants with free radical scavenging activities could have great relevance as prophylactic and therapeutic agents in diseases in which oxidants or free radicals are implicated. A number of synthetic antioxidants such as butylhydroxytoluene (BHT) were extensively added to foodstuffs, although their use has begun to be questioned because of their toxicity. Consequently, there is considerable interest in preventive medicine and in food industry in the development of natural antioxidants from plants.The present study was conducted to evaluate antioxidant activity of the methanolic extracts and their butanol, chloroform and water subfractions of M.amphilema and M.pulegium by using the DPPH assay (Inhibition of free radical 2,2-diphenyl-1-picrylhydrazil). The butanolic subfractions was able to reduce the stable free radical (DPPH) with IC50=10/09 ± 0/05$\frac{\mu g}{Ml}$, which was lower than that of synthetic antioxidant, BHT(IC50= 24/0 ± 0/3$\frac{\mu g}{Ml}$). The antioxidant activity can be attributed to high levels of phenolic extracts. The total phenolics of extracts was determinded by Folin-Ciocalteu Method, Galic acid equivalent . The total phenolic constituent of the butanolic subfractions was 2240 ± 70mg/l for M.amphilema and 2896± 80mg/l for M.pulegium. These extracts have medium Anti microbial activity by disk diffusion method. The chloroform extract of the M.pulegium with MIC= 7/5 gr/ml , IZ =15 mm and methanol extract of M.amphilema with MIC=15 gr/ml , IZ =9 mm showed better activity than other extracts.The chemical composition of a hydro-distilled essential oil of M.logifolia was analyzed by a GC and GC/MS system. Here are 21 compounds were found in the essential oil; piperitenone oxide(49/17|%), piperitone oxide(35/35%), limonene (2/34%), β-caryophyllene(1/82%) were the main components comprising(88/68%)of the oil.

Results presented here may suggest that essential oil and extracts of M.longifolia have anti oxidant activity, and therefor, they can be used as a natural preservative ingredient in food and products.

Keywords: Anti microbial; Anti oxidant ; DPPH; Mentha longifolia

Extraction optimization of polycyclic aromatic hydrocarbons by novel solid/liquid phase microextraction technique and their determination by HPLC using experimental design

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The new extraction and pre-concentration technique, hollow fiber solid/liquid phase microextraction (HF-SLPME) based on multi walled carbon nanotubes (MWCNTs) reinforced sol-gel was applied to determination of poly aromatic hydrocarbons: pyrene, phenanthrene, anthracene, naphthalene, fluorene, fluoranthene and acenaphthene from water samples. MWCNTs were fixed porous wall of hollow fiber. In this microextraction mode organic solvent as liquid microextraction medium and MWCNTs as solid microextraction one will work together. The analytes were subsequently analyzed with high performance liquid chromatography and UV detection. The influences of microextraction parameters such as pH, amount of salt, stirring rate, kind of desorption solvent, donor phase volume, extraction and desorption time were investigated utilizing Plackett-Burman design (BBD). Next, Central Composite design was applied to obtain optimal condition. The optimized conditions were obtained at 5-min stirring of 10mL aqueous sample with 1250 rpm and other parameters had no effect on the recovery of PAHs. Optimal HPLC conditions were C_{18} reversed phase column for separation and mobile phase consisted of water-methanol-THF (40:57:3) and maximum wavelengths for detection were 220 and 270nm.

The method was evaluated statistically and linearity was observed over a range of 0.002-0.060 μgL^{-1} with detection limits between 0.002 - 0.008 μgL^{-1}. The relative recoveries in the real samples ranged from 80% to 91%. Result showed significant improvement with respect to HF-LPME convenience.

Keywords polycyclic aromatic hydrocarbons; solid/liquid phase microextraction; Hollow fiber; Multi-walled carbon nanotubes

References

[1] Song, X.Y, Shi, Y.P, Chen, Talanta100 (2012)153.

Nano magnetic graphene oxide application for analysis of pharmaceutical and personal care products in environmental aquatic samples

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Graphene, because of its exceptional properties such as good mechanical, thermal and chemical stability, electron rich structure and large specific surface area could be utilized as an extraordinary wonderful adsorbent in sample preparation field. Benefiting the magnetic graphene oxide in magnetic solid phase extractions (MSPE) process could overcomes the limitations of SPE in extraction rate and consumed solvent volume.

In this study, nano magnetic graphene oxide was used as an adsorbent in MSPE for extraction of seven pharmaceutical and personal care products consist of Ethyl Paraben, Propyl Paraben, Buthyl Paraben, Diclofenac, Ibuprofen, Benzophenone-3 and 4-Methylbenzylidene camphor (4-MBC) in environmental aquatic samples. The synthesized nano composite sorbent was characterized employing FT-IR, XRD and SEM. To achieve the optimum conditions of MSPE procedure toward target analytes, some parameters affecting the clean-up efficiency including the amount of the adsorbent, desorption solvent volume and desorption time were investigated and optimized using Central Composite Design (CCD). Under the optimized situation, the selected pollutants were analyzed employing high performance liquid chromatography with diod array detection (HPLC-DAD). The acceptable recoveries and figures of merit values demonstrated that the proposed method was successful for determination of pointed analytes in real samples.

Keywords: Magnetic graphene; MSPE; Central composite design; HPLC-DAD

References:

[1] Y.B. Luo, G.T. Zhu, X.S. Li, B.F. Yuan, J. Chromatogr. A, (2013), 1299, 10-17
[2] R.A. Perez,B.Albero,J.L.Tadeo, E.Molero, Anal.Bioanal. Chem. (2015), 407, 1913–1924
[3] A.Samadi,M.Amjadi, ,Microchim.Acta, (2015), 182, 257–264

Electrochemical Hydride Generation coupled with Automated Dynamic Headspace Liquid-phase Microextraction: A novel sample preparation method to improve spectrophotometrics ultramicro-analysis of Antimony(III)

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Antimony (Sb(III)) is an emerging element of environmental concern because of its alarming concentration is increasingly observed during the last years. This is due to the current extensive industrial use of antimony. In this study, an automated dynamic headspace liquid phase microextraction technique is coupled with electrochemical hydride generation to determine trace amount of antimony (Sb) by UV–Vis spectrophotometry. This method is subsequently based on electrochemical reduction of Sb to stibine (SbH_3) and reaction of SbH_3 with silver diethyl dithiocarbamate (AgDDC) -as the acceptor phase in headspace- to give a red complex. The electrochemical hydride generator consisted of a cathode cell separated from the anode cell by a porous glass frit and was operated with a constant direct current. A platinum disk was used as the anode and a pre-activated graphite rod as the cathode. A 100 µL syringe assisted with a homemade syringe pump has been used for dynamic micro extraction. Multi factor optimization of process was performed by simultaneous varying of influencing parameters (Current, Electrolysis time, Extraction time, catholyte –HCl- Concentration, Sample Volume) with the aid of response surface methodology (RSM). Under the optimized operating conditions, the detection limit has been measured to be 0.39 µg (39 ng ml^{-1}).The calibration curve was linear in the range of 120–1500 µg L$^{-1.}$ The relative standard deviations at different concentration levels were less than 5.4 %(n=5). To evaluate applicability of the proposed method, Sb(III) was measured in different environmental samples. To sum up, this research shows that dynamic head space is a successful technique for green chemical sampling of electrolytic metal-hydride generated associated with high concentration capability and good replicability. In the other words a selective, efficient, highly sensitive, and ultramicroscale sample preparation and analytical technique is developed to analysis of Sb(III).

Keywords: Automated dynamic headspace microextraction; Design of experiments; Electrochemical Hydride Generation; Sb(III).

A novel solid phase microextraction coating based on polypyrrole/ZnO nanorods for determination of pesticide residue in water samples

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The results of an innovative study on a new and highly efficient stationary phase based on ZnO/PPy nanocomposite coating on platinum wire have been reported in this paper. This nanocomposite was prepared by a two step process. In the first step, oriented ZnO nanorods (ZNRs) were in situ hydrothermally grown on platinum wire surface [1], and followed by oxidative vapor phase polymerization of pyrrole on $FeCl_3$ impregnated ZnO nanorods as a porous polypyrrole film, in the second step [2]. Scanning electron microscopy (SEM) study revealed that a thin layer of PPY was found to cover the ZNRs, which can enlarge the effective surface area of the composite coating. In fact, this organic/inorganic nanocomposite with combine of hydrothermal deposition and vapor phase polymerization methods has created a good combination of organic and inorganic materials properties. This coating has merged the merits of both ZNRs and PPY, thus, has several advantages over that of sole PPY film and ZNRs coating such as improved extraction efficiency, enhanced mechanical stability and longer service life.

The extraction properties of the coating were investigated using solid phase microextraction coupled with gas chromatography- mass spectrometry detection for residue of amitraz and teflubenzuron pesticides. The effects of various parameters affecting SPME efficiency have been optimized and evaluated. The obtained optimal conditions were: extraction temperature, 65°C; extraction time, 30min; sample pH, 6.5; and salt concentration, 5%w/v. The detection limits were calculated for amitraz and teflubenzuron, 0.05 and 0.08 ng mL^{-1}, respectively. The limits of quantification for both pesticides were 2 ng mL^{-1}. Proposed procedure was successfully applied in the analysis of agriculture water samples with spiked concentration and satisfactory results were obtained.

Keywords: Amitraz, Teflubenzuron, Vapor Phase Polymerization, ZnO nanorods.

References:

[1] R. Alizadeh, N. Mashkouri Najafi, S. Kharazi, *Analytica Chimica Acta* 689 (2011) 117-121.
[2] J.S. Do, S.H. Wang, *Sensors and Actuators B* 185 (2013) 39- 46.

Amine functionalized superparamagnetic multiwall carbon nanotube as adsorbent in magnetic dispersible solid phase extraction (MDSPE) coupled with chemometric method (principal component artificial neural networks (PC-ANNs)), for high selective simultaneous determination lysine, isolysine and valine in bodybuilding athletes serum

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The combination of a extraction technique ,Magnetic dispersive solid-phase extraction (MDSPE) as a simplified, fast and low cost clean-up technique of biological sample extracts for Branched-Chain amino acids (BCAA) and a chemometric method based on kinetic spectrophotometric determination coupled with principal component artificial neural network (PC-ANN) has been proposed for simultaneous determination lysine**,** isolysine and valine in bodybuilding athletes serum for the first time. Multiwall carbon nanotube/magnetic nanocomposite ($MWCNT_S/Fe_3O_4$) were prepared and functionalized with 3-aminopropyltrimethoxysilane (APTS) to creat a dispersible adsorbent with magnetic property , high capacity and sensibility to branched-chain amino acids. The amine- functionalized $MWCNT_S/Fe_3O_4$ (APTS- $MWCNT_S/Fe_3O_4$) were characterized and confirmed by Fourier transform infrared spectra (FT-IR), X-ray diffraction spectrometry (XRD), transmission electron microscopy (TEM) and scanning electron microscopy (SEM). Kinetic spectrophotometric studies was performed by the amino acids reaction with a 1,2-naphthoquinone-4-sulfonate (NQS) in slightly basic medium. On the basis of the difference in the rate between the two reactions, these three amino acids can be determined simultaneously in triplex mixtures. Afterwards reliable, sensitive and cost-effective PC-ANNs method for the determination of amounts of lysine**,** isolysine and valine was developed. The main factors affecting extraction efficiency and kinetic studies, including the pH of the sample solution, extraction and desorption time, desorption conditions, sample volume, amount of magnetic adsorbent, NQS volume investigated.The method was successfully applied to determine lysine, isolysine and valine (BCAA) in bodybuilding athletes serum and satisfactory recoveries were obtained in the range of 99-101%.

Keywords: APTS- $MWCNT_S/Fe_3O_4$nano composite, PC-ANN, BCAA, MDSPE, simultaneous determination

Offering a novel and sensitive method according to restricted access material-molecularly imprinted polymers for selective solid-phase extraction of residual pesticides in fruit juice samples and simultaneous kinetic spectrophotometric determination by chemometric method (PC-ANNs)

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In this method for first time a novel restricted access materials molecularly imprinted polymers (RAM-MIPs) as a new approach for extraction and preconcentration of residul pestiside in fruit juice samples combined to a kinetic spectrophotometric method based on the reaction of potassium ferricyanide ($K_3Fe(CN)_6$) with pestisudes including dimethoate,glufosinate, glyphosate and propetamphos coupled with artificial neural networks (ANNs) has been proposed for simultaneous determination of dimethoate, glufosinate, glyphosate and propetamphos. Kinetic methods are often useful for the determination of multicomponent mixtures.The RAM-MIPs has been synthesized by using dimethoate as template molecule and glycidilmethacrylate (GMA) as pro-hydrophilic co-monomer, methacrylic acid (MAA) as functional monomer, ethylene glycol dimethacrylate (EGDMA) as crosslinking agent and 2,2-azobisisobutyronitrile (AIBN) as the initiator. The prepared RAM-MIPs were characterized and confirmed by FT-IR, XRD, TEM and SEM. RAM-MIPs were used as the adsorbent enclosed in solid phase extraction column and several important extraction parameters were comprehensively optimized to evaluate the extraction performance. Under the optimum extraction conditions, RAM-MIPs exhibited comparable or even higher selectivity with greater extraction capacity toward four kinds of organophosphorus pesticides compared with the MIPs and commercial solid phase extraction columns.The RAM-MIPs solid phase extraction coupled with kinetic spectrophotometric method based on principal component artificial neural networks (PC-ANNs) was successfully applied to simultaneously determine four kinds of organophosphorus pesticides from food sample. This modeling shows a powerful potential for the considered system without the prior knowledge of the kinetic rate constant and reaction order. It was demonstrated that RAM-MIPs solid phase extraction with excellent selectivity and restricted access function was a simple, rapid, selective, and effective sample pretreatment method.

Keywords: RAM-MIPs, PC-ANNs, organophosphorus pesticides, simultaneous determination, Solid phase extraction

Fast derivatization and air assisted liquid liquidmicroextraction of ultra trace aliphatic aldehydes in human exhaled breath, followed by gas chromatographic analysis

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Volatile organic compounds (VOCs), such as aliphatic aldehydes are an issue of major concern for many scientists worldwide. Pentanal, hexanal, octanal and nonanal when present in human breath exhales are important lung cancer markers. Their monitoring at trace levels inhuman breath exhales can be used for non-invasive early diagnosis of lung cancer.The aim of this work is to use the effective and newly developed extraction method (co-liquefaction, followed by derivatization and air assisted dispersive liquid-liquid micro-extraction (AALLME)) for the isolation of C3-C9 from lungcancer patient exhaled breath and their ultra-trace analysis by GC-FID.

1000 mL of lung cancer patient exhaled breath sample was taken in the specially fabricated extraction device. 1.4 mL of methanol was added. The extraction device was exposed to ultrasonic bath for the evaporation of solvent and then co-liquefaction at -18ºC with any VOCs present in exhaled breath.0.4 mL of derivatization reagent (MBTH) solution, 0.4 mL of phosphate buffer (pH=5.5) and 0.2 mL H_2O was added into collected metanolic solution. The extraction of derivatizedaldehydes was performed using air assisted dispersive microextraction with 0.1 mL 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 0.2-10 ng mL^{-1}, with correlation coefficients> 0.9975. The limits of detection (LODs) and the limits of quantitation (LOQs) were ranged from 0.04 to 0.11 ng mL^{-1} and 0.1 to 0.3 ng mL^{-1}, respectively. The relative standard deviations (**n**=3) 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.

Keywords: Aldehydes, Co-liquefaction, Derivatization, AALLME, Lung cancer, Gas chromatography

Determination of Ag^+ by GFAAS after extraction and preconcentration with HLLME using water/tetra butyl ammonium bromide/chloroform ternary component system

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Methods of sample preparation has always been one of the most important challenges for analysis of various species in the complex samples and particular biological tissues. Liquid -liquid extraction, usually as one of methods of sample preparation use to measurement of different species. This method has advantages like simplicity and low-order facilities need that make it useful for measurements and analysis of different species [1]. Homogeneous liquid-liquid micro-extraction technique based on a three-component system and it's adjustable by phase graphs. By disturb the conditions of a homogeneous three-component system, the system will be convert to a two phase mode and phase separation will be done within the solution. As a result, this can be used to claim that in this method, specific area is so high or in other words it's limitless. therefore, the time required for extraction of the analyte was very low and there is no need to stir the solution. In this work, we use a ternary component system to analyte preconcentration. three component include: water, chloroform, tetra butyl ammonium bromide. Before extraction, the pH of solution fixed at a point proportionate to analyte pk_a (pH=4). Then complexing agent (dithizone), chloroform and tetra butyl ammonium bromide added to solution respectively, then sodium perchlorate solution was added to solution as a phase separator. The chloroform aggregate in the bottom of centrifuge tube. The aggregated chloroform volume was in the micro liter range and the analyte (Ag^+) concentrated in this phase. So the aggregated chloroform injected to graphite furnace atomic absorption spectrometer and absorption was read. In this research, we optimum some variable: pH, tetra butyl ammonium bromide and chloroform volume, complexing agent and sodium perchlorate amount. After calibration curve preparation, we analysis a real sample, tap water.

Keywords; Ag^+ analysis; HLLME; GFAAS; Ternary component extraction system.

References:

[1] Anthemidis, A.N., Zachariadis, G.A., Farastelis, C.G., Stratis, J.A., 2004, Talanta 62, 437–443.

Carbon nanotubes@silicon dioxide nanohybrids coating for solid-phase microextraction of organophosphorus pesticides followed by gas chromatography–corona discharge ion mobility spectrometric detection

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A high efficiency solid-phase microextraction (SPME) fiber coated with porous carbon nanotubes–silicon dioxide (CNTs-SiO_2) nanohybrids was synthesized and applied for the determination of some organophosphorus pesticides (OPPs) in vegetable, fruits and water samples. Gas chromatography–corona discharge ion mobility spectrometry was used as the detection system. Glucose, as a biocompatible compound, was used for connecting CNT and SiO_2 during a hydrothermal process. The electrospinning technique was also applied for the fiber preparation. The parameters affecting the efficiency of extraction, including stirring rate, salt effect, extraction temperature, extraction time, desorption temperature and desorption time, were investigated and optimized. The developed CNTs@SiO_2 fiber presented better extraction efficiency than the commercial SPME fibers (PA, PDMS, and PDMS–DVB). The intra- and inter-day relative standard deviations were found to be lower than 6.2 and 9.0%, respectively. For water samples, the limits of detection were in the range of 0.005–0.020 µg L^{-1} and the limits of quantification were between 0.010 and 0.050 µg L^{-1}. The results showed a good linearity in the range of 0.01-3.0 µg L^{-1} for the analytes. The spiking recoveries ranged from 79 (±9) to 99 (±8). The method was successfully applied for the determination of OPPs in real samples.

Keywords: Carbon nanotubes@SiO_2, Solid-phase microextraction, Gas chromatography–ion mobility spectrometry, Water, fruit and vegetable samples

Ultrasound–Assisted Emulsification Microextraction Followed by High Performance Liquid Chromatography for Biotin Determination

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Asimple, fast and efficient microextraction technique followed by high performance liquid chromatography (HPLC) analysis was developed for the determination of Biotin (vitamin B7) concentration in pharmaceutical samples. This method was based on ultrasound-assisted emulsification microextraction (USAEME) by a low density solvent as an extraction solvent. In this procedure, 100μL of pantanolwas injected slowly into a 10 mL acidified aqueous sample of biotin placed inside an ultrasonic water bath. The resulting emulsion was centrifuged and then 20μL of the organic phase was injected into HPLC system.To obtain the best conditions for the quantification of biotin,the effective extraction parameters were optimized. Under the optimal conditions, linearity was in the range of 50 to 500 $\mu g L^{-1}$ corresponding to the limit of detection (LOD) 15$\mu g\ L^{-1}$in water samples. The repeatability of the proposed method was evaluated in terms of the relative standard deviation (RSD), which was<10% ($n = 4$). The proposed method presented an acceptable LOD for biotin analysis in pharmaceutical samples with satisfactory RSD.

Keywords: Biotin; Ultrasound-assisted Emulsification Microextraction; High performance liquid chromatography.

Vitamin K3 Determination by Ultrasound-AssistedEmulsification Microextraction Combined with High Performance Liquid Chromatography

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The aim of this research was to apply ultrasound-assisted emulsification microextraction (USAEME) as an effective and simple method for determination of vitamin K3 in some pharmaceutical products. High performance liquid chromatography (HPLC) equipped with the UV/VIS detector was used for analysis. In this technique, 100 µl of chloroform was slowly injected into the special designed extraction cell containing 10 mL of sample solution. The mixture was sonicated for 30 seconds and then centrifuged for separation of organic solvent from the aqueous sample solution. Then 20 □L of separated chloroform containing extracted vitamin K3 was injected into the HPLC system for analysis. To obtain the highest sensitivity, the influences of the different parameters affecting the microextraction procedure such as the nature and volume of extraction solvent, ionic strength were evaluated to optimize the efficiency of the microextraction process. Under the optimum extraction conditions, the calibration curve was linear in the range of 5 to 500 □g L^{-1} with correlation coefficient of $R^2 \geq 0.999$. The repeatability of the method in terms of relative standard deviation (RSD%) was found ≤11% and the preconcentration factor was found 350 corresponding to the limits of detection 1.5 □g L^{-1} in water sample. Finally, the proposed method as a simple, fast, efficient and environmentally friendly procedure was successfully applied for the determination of vitamin K3 in some pharmaceutical products.

Keywords: Vitamin K3; Ultrasound assisted emulsification microextraction; High performance liquid chromatography.

A novel dispersive liquid microextraction with back microextraction step prior to gas chromatography with micro electron capture detector for highly sensitive determination of benzodiazepines

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Benzodiazepines (BZDs) are psychoactive drugs widely used for the treatment of anxiety and insomnia, as well as other psychological disorders. The BZDs abuse is partially related to the toxic effects that they produce and also to their widespread availability.

The aim of this study was the introducing a novel DLLME with a back-microextraction step (DLLME-BME) for extraction of four BDZs. In this work, through DLLME procedure the BDZs were transferred to extraction solvent then mixed with organic solvent as acceptor phase for precocentration of the target drugs. Gas chromatography with electron capture detector (GC-μECD) was applied for separation and determination of the drugs. Several parameters affecting the extraction efficiency were optimized. Under the optimal conditions, the preconcentration factors were obtained in the range of 16–497. Linearity of the method was determined to be in the range of 0.01–200.0 ng mL^{-1}. The limits of detection for the target benzodiazepines were in the range of 0.005 – 1 ng mL^{-1}. This procedure created better clean up and sensitivity through fast extraction even than the three phase HF-LPME. The method was successfully applied for extraction and determination of the drugs in water, plasma and urine samples.

Keywords: Back-microextraction; Benzodiazepines; Gas chromatography; Urine; Plasma

Refrences:

[1] P. Fernández, Cristina González, M. T. Pena, A. M. Carro, R. A. Lorenzo, Anal. Chim. Acta 767 (2013) 88.

Cloud Point Extraction and Preconcentration with using ECR for Determination of Combination for Copper (II) Ion in Juice Samples by Flame Atomic Absorption Spectrometry

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A cloud point extraction procedure was presented for the preconcentration of copper(II) ion in Juice samples. After complexion by **eriochrome cyanine R**(ECR),copper(II) ionswere quantitatively recovered in Triton X-114 after centrifugation. 0.5 ml of methanol acidified with 1.0 mol.L^{-1} HNO_3 was added to the surfactant-rich phase prior to its analysis by flame atomic absorption spectrometry (FAAS). The influence of analytical parameters including ligand, Triton X-114 and HNO_3concentrations, bath temperature, heating time, centrifuge rate and time were optimized. The effect of the matrix ions on the recovery of copper(II) ions was investigated. The detection limit (*n*=10) of 0.3 ngmL^{-1} along with preconcentration factor of 30 and enrichment factor of 43.2 with R.S.D. of 1.7% for Cu was achieved. The proposed procedure was applied to the analysis of natural Juice samples.

Keywords: Cloud Point Extraction; Eriochrome cyanine R; Preconcentration; Spectrophotometry; Triton X-114

References:

[1] K.A.Venkatesan, P.R.VasudevaRao. Physicochem.Eng. Aspects, 180 (2010) 277.
[2] C. D. Stalikas, Trends Anal. Chem, 21 (2012) 343.
[3] W.L. Hinze, E. Pramauro, Crit. Rev. Anal. Chem., 24 (2013) 133.

Ion-imprinted polydopamine-coated magnetic graphene oxide as a novel nano-sorbent for selective extraction and determination of nickel by flame atomic absorption spectrometry

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In this research, an ion-imprinted polydopamine-coated magnetic graphene oxide [GO@Fe_3O_4@PDA] was synthesized by a simple method at controlled pH conditions. The size, morphology and surface coating of the obtained nanosorbent were characterized by powder X-ray diffraction, scanning electron microscopy and Fourier transform infrared spectroscopy. The feasibility of using GO@Fe_3O_4@PDA as a nano-sorbent in magnetic solid phase extraction (MSPE) was explored for the separation of Ni^{2+} ions from aqueous solutions. The preconcentrated Ni^{2+} ions were eluted and determined by flame atomic absorption spectrometric detection. The effects of various factors were optimized that the optimize pH was 8 to absorbtion and contact time for absorb was 15 min, initial sample volume was 500 ml , type and volume of the desorbing solvent was 3 ml of acetic acide. The accuracy of the method was confirmed by analyzing a standard reference material. The method was applied for the determination of Ni^{2+} ions in natural waters.

Keywords: Graphene oxide, Ionic imprinted polymer, Nano-sorbent, Magnetic solid-phase extraction, Flame atomic absorption spectrometry

References:

[1] L. Zheng, L. Xiong, Y. Li, J. Xu, X. Kang, Z. Zou , S. Yang, J. Xia, “facile preparation of polydopamine-reduced grapheme oxide nanocomposite and its electrochemical application in simultaneous determination of hydroquinone and catechol”, *Sensors and Actuators B*, 177 (2013) 344.

[2] F. Yang, B. Zhao, “Adhesion Properties of Self-Polymerized Dopamine Thin Film”, *The Open Surface Science Journal*, 3 (2011) 115.

Design and performance of nanostructured supramolecular solvent based on gemini surfactant for microextraction of parabens from cosmetics

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Supramolecular solvents (SUPRAs) are produced from amphiphile solutions by a sequential self-assembly process occurring on two scales, molecular and nano, and constitute a valuable strategy to replace organic solvents in analytical extraction processes. Double-chain amphiphiles, called gemini surfactants, contain two hydrophilic groups (ionic head) connected with a spacer and two hydrocarbon tails. These surfactants are superior in comparison withconventional single-chain surfactants because of very lower CMCs and better dispersing and emulsifying properties. In this work, a novel SUPRA based on gemini surfactant in propanol was synthesized and its potential for extraction of some parabens in cosmetics was investigated.

The methyl and ethyl paraben were extracted using novel SUPRA. The extracted analytes were injected into HPLC-UV for separation and detection of the analytes. Several parameters affecting the SUPRA process including propanol:water ratio, concentration of surfactant, salt effect and time of ultrasonic and centrifugation were investigated and optimized. Under the optimized conditions the linearity of the method in the range of 2-200 μg L^{-1} for both of parabens, with correlation of determination (r^2) 0.9996 and 0.9997 were obtained respectively. The method was successfully applied for extraction of the parabens from cosmetic samples and reasonable results were obtained.

Keywords: Gemini surfactant, Propanol, Microextraction, Parabens, Cosmetics

Extraction and separation of essential oil from cumin (Cuminum cyminumL.) seeds using traditional solvent extraction method

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In recent decade, due to the growing use of medicinal plants, extraction and separation of essential oil have been widely investigated by researchers. Cumin (Cuminum cyminumL.) is one of the most popular spice used in many dishes from around the world food and used as as appetite stimulant. It is rich in cuminaldehyde, which benefits the digestive system and promotes oral health. Cumin essential oil can act as a highly antifungal agent against various pathogenic fungi and also as sources of natural antimicrobial microbial agent with potential application in food and pharmaceutical industries. The anticancer and anti-diabetic effect of cumin essential oil has been extensively studied. Cumin essential oil should be produced with such a high quality for medical applications. The purposes of the present work are (1) extraction of essential oil from cumin seeds using three methods including; microwave, clevenger and soxhlet methods, (2) determination of the chemical composition of the essential oil through gas chromatography (GC), (3) evaluating the effect of the applied extraction method on the chemical composition of the extracted essential oil and (4) evaluating the The total phenolic content of control plants is estimated by the Folin–Ciocalteu method and radical scavengering activity of the extracted essential oil to study the possible application of these essential oil as food preservatives. GC results revealed that the oil contains a complex mixture of components while the major compounds detected were cuminaldehyde, γ-terpinene, o-cymene, limonene and β-pinene. The morphology of cumin seeds before and after oil extraction was studied using scanning electron microscopy (SEM) to compare the damaging effect of the applied extraction techniques on the microstructure of the seeds. Results showed that the chemical composition of the extracted essential oil changed as the type of the applied extraction technique changed. The highest weight percentage of the cuminaldehyde was detected in the essential oil extracted using microwave method. Evaluating the antioxidant and radical scavenging activity of the extracted essential oils showed that the essential oil produced by microwave methods has the highest antioxidant and radical scavengering activity. This was attributed to the highest weight percentage of cuminaldehyde in this sample.

Keywords cumin; essential oil; gas chromatography (GC); separation

Trace in situ purification and determination of Zinc and Copper by a novel hollow fiber solid/liquid phase microextraction (HF-SLPME) - pencil graphite electrode (PGE) and experimental design via response surface method (RSM)

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For the first time, in this research a single-use electrochemical sensor, incorporating a three electrodes configuration was developed, using ionic liquid mediated hollow fiber-graphite working electrode. These electrodes coupled with differential pulse voltammetry (DPV) provided a screening tool for in-situ SLPME pre-concentration and determination of trace levels of Zn(II) and Cu(II). In this design, a two centimeter piece of porous polypropylene hollow fiber membrane was impregnated with homogeneous mixture of three type of ionic liquid such as: (1-ethyl-3-methylimidazolium tetrafuoroborate), (1-butyl-3-methylimidazolium hexafluorophosphate) and (1-butyl-2,3-dimethylimidazolium hexafluorophosphate) afterwards a graphite rod was located inside the fiber lumen. Also, synthesized graphene nanoparticles dispersed in the ionic liquid by soncation and were used for one-step simultaneous purification, pre-concentration and determination of Zn(II) and Cu(II) ions from water samples.. The response surface method was applied as a design of experiment to determine optimum conditions for zinc and copper ions removal. Various parameters that more affected in separation part of our study such as: molar mass of used ionic liquids, amount of nanoparticle and sonication time were investigated. The effect of all the input parameters on the output responses was analyzed using analysis of variance (ANOVA) and RSM contouer plots. The results revealed that the metal removal was influenced by the molar mass of used ionic liquids, amount of nanoparticle and sonication time respectively. The performance characteristics of the developed method were evaluated by assessing response linearity and precision. The method was suitable for the quantitation of Zn(II) and Cu(II) ions in the concentration range of 0.1–1050 ng.mL^{-1} and 10–1300 ng.mL^{-1} for Zn(II) and Cu(II) ions respectively. The detection limits recorded for Zn(II) and Cu (II) were 0.53 and 2.05 ng.mL^{-1} with relative standard deviation (RSD) of 3.2%, and 1.8%, respectively. Moreover, successful applications of the sensing device to real water samples were demonstrated.

Keywords: Zn(II); Cu(II); Hollow Fiber Solid/Liquid Phase Microextraction - Pencil Graphite Electrode; Design of Experiment; Surface Response Method.

Headspace-solid phase microextraction based on polypyrrole nanowire coupled with ion mobility spectrometry for determination of bisphenol A in canned food samples

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A novel solid phase microextraction (SPME) fiber was prepared based on nanowire of polypyrrole and the efficiency of this fiber for the extraction of bisphenol A (BPA) from canned food samples was evaluated as the adsorbent in head-space SPME (HS-SPME) coupled with ion mobility spectrometry (IMS). This fiber was synthesized by electrochemical oxidation of the monomer in aqueous solution. The fiber characterization by scanning electron microscopy (SEM) revealed that the new fiber exhibited one-dimensional structures with a nanowire morphology (a highly porous structure). Under the optimum conditions, the linearity of 10-150 ng mL^{-1} and limit of detection (LOD) of 1 ng mL^{-1} were obtained for BPA. The repeatability (n=5) expressed as the relative standard deviation (R.S.D %) was 6.3 %. At the end, the proposed method was successfully applied to determine BPA in different canned food samples (peas, corns, beans). Method validation was conducted by comparing our results with those obtained through HPLC-fluorescence method. Compatible results indicate that the proposed method can be successfully used in BPA analysis. The proposed method is much more simple and cheaper than chromatographic methods, with no need of extra organic solvent consumption and derivatization prior to sample introduction.

Keywords: bisphenol A; Canned food; Headspace solid phase microextraction; Polypyrrole nanowire; Ion mobility spectrometry.

References:

[1] N. Alizadeh, M. Jafari, A. Mohammadi, Journal of hazardous materials 169 (2009) 861
[2] M. Kamalabadi, E. Ghaemi, A. Mohammadi, N. Alizadeh, Food chemistry 181 (2015) 72.
[3] X. Zhang, D. Zhu, C. Huang, Y. Sun, Y.-I. Lee, Microchemical Journal 121 (2015) 1

Dispersive solid phase nanoextraction coupled to GC/MS as a novel technique for extraction of opiate drugs from biological samples

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Dispersive solid phase nanoextraction is presented as an alternative technique for extraction and preconcentration of two opiate drugs including Methadone and Tramadol from serum samples. This novel approach –that we have named dispersive solid phase nanoextraction (DSPNE)– is based on strong affinity between selected drugs and carboxylated–carbon nanotubes (CCNT). Total extraction experimental procedure takes less than 20 min. Final analysis of selected drugs performed by using gas chromatography–mass spectrometric (GC/MS) detection. Different parameters affecting the extraction efficiency, such as the sample volume, extraction solvent type and volume and amount of the adsorbent were investigated and optimized for this method. Firstly extraction parameters were optimized for drugs from water samples, then optimized conditions were used for extraction of drugs from biological (serum) samples. Results show that 1000 µl sample volume, 0.001 g sorbent (CCNT), N,N-dimetylformamide (DMF) as desorbent solvent type and finally 40 µl DMF as desorbent solvent volume are optimized conditions in this technique. The striking features of this technique are correlated to the small volume of sample (200–1000 µl) and adsorbent and finally small volume of organic solvent for analysis. The results showed that dispersive solid phase nanoextraction is a quick, relatively inexpensive and environmentally friendly alternative technique for extraction of BTEX from water samples.

Keywords: Dispersive solid phase nanoextraction, Opiate drugs, Carbon nanotube, gas chromatography-mass spectrometry.

References:

[1] H. Wang, Sh. Yu, A. D. Campiglia. Analytical Biochemistry 385 (2014) 249–256.

Polyacrylonitrile /zeolite Nano-fibers as a New Coating in Solid- phase Microextraction

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In the present work, polyacrilonitrile/zeolite nano-fibers were synthesized by electro- spinning method. These nano-fibers were coated on the steel wire and used as a new coating for extraction of some polycyclic aromatic hydrocarbons (PAHs) in aqueous samples by SPME/GC/FID.

Some important factors in electro-spinning process were optimized such as voltage،electro-spinning distance and concentration of polymer and zeolite. At optimum conditions, the diameter of nano-fibers were about 70 nm. Affecting factors on extraction of PAHs including extraction time and temperature, ionic strength and desorption temperature were investigated and optimized. The detection limits of the method under optimized conditions ranged from 0.1 to 1 ng mL^{-1}. The relative standard deviations of the method were between 4.1 and 12.1 %, at a concentration level of 50 ng mL^{-1}. Calibration curves of PAHs showed linearity in the range of 0.030– 5 µg mL^{-1} with $r^2>0.0999$. As real samples some PAHs extracted in rain water and well water, successfully.

Keywords: Electro-spinning; Nano-fiber; Polycyclic aromatic hydrocarbons; Solid- phase Microextraction;

Spectrophotometric determination of arsenic based on supramolecular dispersive liquid–liquid microextraction-solidified floating supramolecular layer

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The exposure of millions of people to unsafe levels of arsenite (As^{III}) and arsenate (As^{V}) in drinking waters calls for the development of low-cost methods for monitoring these two arsenic species in waters. Herein, in this study a novel dispersive liquid–liquid microextraction based on solidification of floating supramolecular layer for the preconcentration and speciation analysis of inorganic arsenic species has been developed. The method is based on the well-known formation of arsenomolybdate, followed by reduction to heteropoly blue having an absorbance maximum at 815 nm. The blue color was produced from two involved reactions in which the MoO_4^{-2} and AsO_4^{-3} in sample have reacted in acid medium to form arsenomolybdate complex, then the obtained complex was reduced by ascorbic acid liberating the colored molybdenum blue species of heteropoly blue (Mo^{V}). A supramolecular solvent made up of reverse micelles of 1-dodecanol in tetrahydrofuran (THF) was injected into the aqueous sample solution. Reverse micelle coacervate were produced in situ through self-assembly processes. Vortex-mixed accelerated mass transfer of the target analyte into the supramolecular solvent phase. Various significant parameters affecting the extraction such as type and volume of the extraction solvent, acidity, volume of the disperser solvent, vortex-mixed time and salt concentration were investigated.

Under the optimal experimental conditions, detection limit, linear range, and relative standard deviation (RSD) of arsenate were 0.04 ppb, 5-200 ppb and 2.9% (for 50 ppb), respectively.

The proposed method was successfully applied to the colorimetric limit for As detection near 5 ppb, which easily meets the requirements imposed by the revised the World Health Organization (WHO) threshold levels for As in drinking water.

Keywords Arsenic speciation; Molybdenum blue; Supramolecular solvents; Microextraction

References:

[1] F.J. Ruiz, S.d Rubio, D. Pe´rez-Bendito, Anal. Chem. 79 (2007) 7473-7484.

[2] J. Ma, M. K. Sengupta, D. Yuan, P. K. Dasgupta, Anal. Chim. Acta 831 (2014) 1–23.

[3] L. B. Escudero, E. M. Martinis, R. A. Olsina, R. G. Wuilloud, Food Chemistry 138 (2013) 484–490.

Mesoporous carbon as adsorbent for effervescence-assisted dispersive micro-solid phase extraction of some herbicides

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The residues of herbicides are dangerous to man and the environment, therefore the identification and accurate measurement of them is important [1]. Sample preparation is a critical part of the herbicides analysis. Solid-phase extraction is becoming highly popular as a sample preparation method, due to its simplicity and economy in terms of time and solvent [2]. In this work synthesis of mesoporous carbon as adsorbent for pre-concentration and extraction of herbicides by effervescence-assisted dispersive micro-solid phase extraction was performed. Factors affecting the extraction efficiency, such as amount of adsorbent, salt content, type and amount of desorption solvent, the amount of analyte solution, pH and ultrasonic dispersion time were examined. The optimum conditions include: 2 mg of adsorbent and 75 mg of salt mixture to make tablets, 300 μl tetrahydrofuran as desorption solvent, 25 ml of the sample solution containing 0.1 M Tris buffer with pH = 8 and 280 seconds sonication. At the optimum conditions, calibration curves were plotted for each of the herbicides and the results showed that all curves are linear in the range of 25 -500 $\mu g L^{-1}$ (R^2>0.9991). Using the calibration curves the method's figures of merit including precision (RSD<3.85), accuracy (% recovery>85.1) and the limit of detection (< 8.3 $\mu g\ L^{-1}$) were evaluated. Finally, the herbicide content of a farm water sample were tested using this method.

Keywords: High performance liquid chromatography, effervescent assisted dispersive micro solid phase extraction, herbicides, mesoporous carbon

References:

[1] J. L. Tadeo, C. Sánchez-Brunete, L. González, in Analysis of Pesticides in Food and Environmental Samples, ed. J. L. Tadeo, CRC Press, Boca Raton, FL, 2008, ch. 1, pp. 1-35.
[2] J. Płotka-Wasylka, N. Szczepańska, M. de la Guardia, J. Namieśnik, TrAC Trends in Anal. Chem. 73 (2015) 19.

Chemometrics Assisted Peak Tracking and Peak Grouping in a Series of HPLC-DAD Sunscreen Data Sets with Different Complexities

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Peak tracking from one chromatogram to another is often problematic, especially in the case of overlapping peaks. Indeed, peak matching for assigning peaks can be accomplished, while it does not require any prior knowledge of the mixture composition. It is expected to define peaks under poor separation conditions with varying intensities and also missing components. Iterative key set factor analysis (IKSFA), abstract factor analysis (AFA) and spectral correlation are the algorithms that can be used for mixture components detection. With the mentioned methods, it is easy to find out how many components two samples have in common, and it is also convenient to track peaks in optimization of chromatographic conditions. Furthermore, elution order of each component can be distinguished with one injection, even when peaks overlapped seriously.

In the present study, the potential of independent component analysis (ICA) [1], which statistically assumes the independency of source signals, is investigated for tracking and grouping of numerous sunscreen products with different complexities. The quality of results through presenting a high probability of recovered components while differentiating from noise, artifact and co-eluting components have been compared with other well-established approaches.

Keywords Peak tracking; Independent component analysis; Sunscreen products; Overlapping peaks

References:

[1] B. Debrus, P. Lebrun, A. Ceccato, G. Caliaro, E. Rozet, I. Nistor, R. Oprean, F. J. Ruperez, C. Barbas, B. Boulanger, P. Hubert, Anal. Chim. Acta 691 (2011) 33.

Determination of Secondary Metabolites in Melissa officinalis. L using Surfactant Assisted liquid Phase Microxtraction and Spectrophotometric Measurement of Their Antioxidant Activities

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In this work surfactant-assisted extraction was applied for extraction of Secondary Metabolites from Melissa officinalis). Herbs of Melissa officinalis L. were harvested in the growing culture of Eilam, Taleghan, Golestan and the wild bee balm plant collected from pasture west of Eilam. After the powdering 0.10g of the leaves, ultrasonic assisted solvent extraction was used to prepare the extracts. Then a chemometrics approach was applied for the optimization of the extraction parameters such as volume and concentration of aqueous solution of CTAB, percentage and type of acid and vortex time. The extraction yield acted as the comprehensive evaluation index. Total phenolic compounds, total flavonoid compounds, and antioxidant activity were used to evaluate these extracts. The individual phenolic compounds found in the extracts were characterized and quantified by HPLC.

The wild bee balm plant extract showed the highest total phenolic and flavonoid values, at 43.17 mg GAE/g and 38.97 mg RE/g, respectively. The HPLC results have shown that the levels of rosmarinic, gallic, syringic, caffeic, ferulic, chlorogenic acid, luteolin and apigenine were as follows: 56.801, 0.008, 0.627, 0.810, 2.037, 0.016, 2.410 and 3.179 mg/g, respectively. Under the optimum conditions, the values of intra and inter day RSD were in the range of 4.21–5.96% and 7.19–09.38%, respectively. The limits of detection (LODs) ranged between 3.71 - 9.02 ngmL^{-1} respectively. The method was successfully applied for the preconcentration of phenolic compounds in Melissa officinalis L leaves. Moreover, these experimental values were higher than those obtained from previously reported. This study suggests that surfactant assisted liquid phase microextraction can be utilized as sustainable and safe extraction method for natural product extractions.

Keywords: Antioxidant Activities; Melissa officinalis. L; Secondary Metabolites; Surfactant Assisted liquid Phase Microxtraction

Application of nano-cucurbituril as a super adsorbent for removal of dyes from aqueous ecosystems

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Cucurbiturils are macrocyclic molecules made of glycoluril monomers linked by methylene bridges which it are particularly interesting to chemists because they are suitable hosts for an array of neutral and cationic species. In this paper, we applied a specific nano cucurbituril for adsorption and removal of some dyes from aqueous solutions. The adsorbent was synthesized and characterized using powder X-ray diffraction, SEM, TEM and FT-IR spectroscopy. The removal procedure was studied in batch mode and effects of important parameters such as pH of aqueous medium, dye dosages, adsorbent amount and interfering ions on the adsorption were investigated and optimized. The equilibrium data were fitted to the Langmuir, Freundlich and Temkin isotherm models. Langmuir isotherm describes the adsorption data better than Freundlich isotherm and Temkin. The proposed method is capable for removal of anionic dyes including, aniline blue, tartrazine, congo red and methyl blue with adsorption capacity higher than 100 mg g^{-1}. The method was successfully applied to the removal of mentioned dye from wastewater samples.

Keywords: Nano-cucurbituril, Anionic dye, Removal, Batch procedure.

References:

[1] K. I. Assaf, W. M. Nau, *Chem. Soc. Rev.*, (**2015**), 44, 394
[2] S. Lim, H. Kim, N. Selvapalam, K. Kim, S. Cho, G. Seo,K. Kim, *Angew. Chem.*, **(2008)**, 120: 3400–3403.

Electrochemically Co-Deposited Sol-Gel/Cu Nanocomposite as a high performance Solid Phase Microextraction Fiber for Determination of Methadone in Urine Samples

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Electrochemically co-deposited sol-gel/Cu nanocomposite was introduced as a novel, simple and single step technique for preparation of solid phase microextraction adsorbent to extract Methadone (a synthetic opioid) in urine samples. The porous surface structure of the sol–gel/Cu nanocomposite coating was revealed by scanning electron microscopy. A detailed investigation was conducted to evaluate the remarked performance of the newly developed nanocomposite fiber. Direct immersion-solid phase microextraction (DI-SPME) followed by HPLC–UV determination was employed. The factors influencing the SPME such as the salt (NaCl) effect (0-30 w/v %), desorption solvent type (methanol, acetone, chloroform, hexane), pH (1-12), and equilibration time (5-50 min), were optimized. The calibration graphs for urine samples showed a good linearity. The detection limit was about 0.1 ng ml^{-1}. Also, the novel nanocomposite fiber has higher extraction efficiency for Methadone in comparison with commercial poly(dimethylsiloxane) and carbowax–divinylbenzene-coated fibers.

Keywords: solid phase microextraction, nanocomposite, electrochemical co-deposition, sol-gel, Methadone.

References:

[1] Aleksa K, Walasek P, Fulga N, Kapur B, Gareri J, Koren G. Forensic Sci Int 2012: 218: 31-6.
[2] Tehrani MS, Aberoomandazar P, Mohammadiazar S. J Chromatogr A 2013:1278:1-7.

Application of modified magnetite molecularly imprinted nanoparticles based on grafting polymerization for selective extraction of naproxen from aqueous and urine samples

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In this study, an analytical procedure for the selective solid-phase extraction and spectrophotometric determination of naproxen (NAP) in urine and aqueous sample was investigated by using of molecularly imprinted polymer on the surface of magnetic nanoparticles (MNPs). The iron oxide magnetic nanoparticles were modified by tetraethyl orthosilicate (TEOS) and 3-methacryloxypropyl trimethoxysilane (MPTS) before imprinting. The molecularly imprinted polymer (MIP) was polymerized at the surface of modified MNPs by using of methacrylic acid (MAA) as functional monomer, NAP as template and ethylene glycol dimethacrylate (EGDMA) as cross-linker. The resulting MMIP showed high adsorption capacity, proper selectivity and fast kinetic binding for the template molecule. It was characterized by Fourier transform infrared (FT-IR) analysis, scanning electron microscopy (SEM) and transmission electron microscopy (TEM) methods. The assay exhibited a linear range of 25–1000 μg L^{-1} for NAP with the correlation coefficient (R^2) of 0.995. The relative standard deviations (RSD) for the recoveries were less than 5.2%. The proposed method was successfully used in analysis of NAP in urine and aqueous samples.

Keywords: Molecularly imprinted polymer; Magnetic nanoparticles;Naproxen; Urine

References:

[1] Ester Caro, Rosa M. Marc,, Peter A.G. Cormack, David C . Sherrington, Francesc Borrull, *Journal of Chromatography B, 813 (**2004**) 137–143*.

[2] Tao Jing, Hairong Du, Qing Dai, Huan Xia, Jiwei Niu, Qiaolin Hao, Surong Mei, Yikai Zhou, *Biosensors and Bioelectronics* 26 (**2010**) 301–306.

[3] Ali Mehdiniaa,, Tohid Baradaran Kayyalb, Ali Jabbari, Mohammad Ovais Aziz-Zanjani, Ehsan Ziaei, *Journal of Chromatography A*, 1283 (**2013**) 82– 88.

A novel polyamide magnetic nanocomposite as a highly efficient medium for isolation naproxen from Aqueous and biological samples

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In this paper, the polyamide/magnetic nanocomposite was synthesized via electrospun technique and used as the new adsorbent for the isolation of naproxen in aqueous and biological samples. The prepared polyamide/Fe_3O_4 nanocomposite were analyzed by scanning electron microscopy and Fourier transfer infrared analysis. The magnetic nanocomposite adsorbent containing naproxen could easily remove from aqueous samples by applied external magnetic field. After the adsorption, the analyte were desorbed and then determined by spectrofluorometric detection at 357 nm. Parameters affecting the morphology and capability of the prepared magnetic nanocomposites including the Fe_3O_4 content, coating time, flow rate of pump, polyamide concentration and applied voltage were investigated. In addition, various experimental parameters affecting the extraction/desorption process were investigated. Under optimized experimental conditions, the repeatability value (relative standard deviation, RSD %) using a new sorbent at magnetic solid phase extraction for a double distilled water spiked with the naproxen at 5 μgL^{-1} was 3% (n = 5) and the limit of detection for the studied analyte was 0.5 μgL^{-1}. Also, linear calibration curve in the range of 5 - 1000 $\mu g\ L^{-1}$ (R^2= 0.9997) was obtained. The applicability of method was extended to the determination of naproxen in tap water and human urine and plasma samples. The relative recovery percentages for these samples were in the range of 66-96%.

Keywords: Polyamide magnetic nanocomposite; Spectrofluorimetric; Naproxen; Electrospun technique, biological and aqueous samples

References:

[1] Y.W. Wu, J. Zhang, H.Z. Yuan, et al. Spectrosc. 32 (2011) 41.
[2] Y. Song, Sh. Zhao, P. Techounwou,et al. J. Chromatogr. A 1166 (2007) 79.
[3] Z.L. Lei, X.L. Pang, et al. J. Mater. Process. Technol. 209 (2009) 3218.

Polythiophene-chitosan magnetic solid phase extraction coupled with Spectrofluorimetric determination for isolation and indication of fluoxetine in environmental and biological samples

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We have developed a fast method for isolation and determination of the fluoxetine, a model compound, from biological and aqueous sample via Fe_3O_4 magnetic nanoparticles were modified with polythiophene and chitosan. The synthesized magnetic nanoparticles, chitosan magnetic and polythiophene/chitosan magnetic nanocomposite were characterized by scanning electron microscopy (SEM) and Fourier transform-infrared (FT-IR) spectroscopy. Several variables affecting the extraction efficiency of fluoxetine such as desorption condition, amount of magnetic nanocomposite sorbent, salt concentration, sample pH and extraction time conditions were investigated and optimized. The best working conditions were as follows: NaCl concentration, 0% (w/v); sample pH,7; amount of sorbent, 25 mg; extraction time, 10 min; and 1.5mL of methanol for desorption of the analyte within 3 min. Under the optimum conditions, good linearity was obtained within the range of 15–1000μg $L^{-1}$for fluoxetine, with correlation coefficients 0.9994. Furthermore, the method was successfully applied to the determination of fluoxetine in urine and human blood plasma samples. Compared with others methods, the current method is characterized with high easy, fast separation and low detection limits.

Keywords: Magnetic micro-solid phase extraction; Fe_3O_4 nanoparticles; polythiophene/Chitosanmagnetic nanocomposite; Spectrofluorimetric; fluoxetine

References:

[1] Z.B. Li, D.N. Huang, et al. J. Chromatogr. A 1218 (2011) 6232.
[2] X.L. Zhang, H.Y. Niu, et al. Anal. Chem. 82 (2010) 2363.
[3] I. Román, A. Chisvert, A. Canals, J. Chromatogr. A 1218 (2011) 2467.

Low temperature dissolution of biological samples by a new alkaline digestion method for extraction of PAHs followed by HPLC-FL detection

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A novel sample preparation method based on the complete dissolution of marine biological samples in a non-alcoholic alkaline media was developed for fast and efficient extraction of 6 polycyclic aromatic hydrocarbons (PAHs) using minimum volumes of hexane/acetone. The extracted PAHs were purified and then measured by high performance liquid chromatography-fluorescence detector (HPLC-FL). In this method a solution composed of NaOH/Urea/ Thiourea at optimized ratio was used for complete dissolution of about 0.25 g of dry and powdered fish samples within 15 min. Compared to the currently used extraction methods which apply heat and/or pressure to accelerate the dissolution process, the proposed method can be conducted at 10 °C, at atmospheric pressure. The operation at considerably low temperature provided an opportunity to simultaneously extract the target analytes from their matrices by adding the extracting solvent in the initial steps of the dissolution. The effect of the key parameters on the extraction recoveries and precision was investigated. Depending on the analyte, the developed method was linear over the calibration range 0.5–100, 1.0–100, and 2.5–100 ng g^{-1}, with $r^2 > 0.996$. The intra-day and inter-day precisions (based on relative standard deviation, n=5) of the spiked PAHs at concentration level of 25 ng g^{-1} were better than 3.12% and 3.17 %, respectively. Individual PAH recoveries from the spiked marine fish samples were in the range of 91.0 to 100.4%. For comparison, the spiked samples were also subjected to the Soxhlet extraction and methanolic alkaline methods.

Reference

[1]- J.A. Nóbrega, M.C. Santos, R.A. de Sousa, S. Cadore, R.M. Barnes, M. Tatro, Spectrochim. B 61 (2006) 465–495.

Application of carbonated nano-structure hydroxyl apatite modified with trithiocyanoric acid for preconcentration of lead ions in environmental water samples

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A new preconcentration method for solid phase extraction of lead ions from seawater samples on a mini-column of carbonated nano-structure hydroxyl apatite modified with trithiocyanoric (CNHAP-TTC) is presented. The honeycomb structure of the nano-pores of the sorbent was confirmed by various spectral tests such as SEM, TEM, and XRD. The nano-structure provided a high surface area which increased the retention of free ions as well as lead complexes on the sorbent, efficiently. After preconcentration, the retained lead ions were completely eluted from the column with 3 mL of 3 mol L^{-1} nitric acid and measured by flame atomic absorption spectrometry. The effect of the key parameters on the extraction recoveries and precision such as the pH, solution flow rate and volume, eluent solution, and interfering ions, were examined. The results showed that the optimal conditions for quantitative recovery of the metal ions by adsorption and elution on CNHAP-TTC was achieved by employing a flow rate of 10 mL min^{-1} at pH of 5.0 for the sample solutions. The detection limit of this method for Pb ions was 0.30 µg L^{-1} (n = 10). The proposed method was successfully applied to the determination of analytes in seawater and river samples.

Reference

[1] K. Ghanemi, Y. Nikpour, O.Omidvar, A. Maryamabadi, Talanta 85 (2011) 763–769.

Magnetic spinel zinc ferrite nanocomposite as an efficient adsorbent for the removal of tetracycline from aqueous solutions: Kinetic and equilibrium studies

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As one of the most important antibiotics, tetracycline (TC) is the second most widely used antimicrobial in the world, with applications in human therapy and the livestock industry. In this study, $ZnFe_2O_4$ magnetic nano composite was synthesized using a simple chemical coprecipitation procedure and was used as an adsorbent for the removal of tetracycline (TC) from aqueous solution. The materials were characterized using X-ray powder diffraction (XRD), scanning and transmission electron microscopy (SEM) and Fourier transform infrared spectrometer (FT-IR). Sufficient amount of this adsorbent added into sample containing tetracycline. After 1 hour (under stirring condition) magnetic nanoparticle collected with magnet and bottom solution determined with spectrophotometer at 360 nm. The effects of various parameters such as initial TC concentration (10–30 mg L^{-1}), pH solution (3.0–11) and amount of adsorbent (0.02–0.07 g) were investigated. The magnetic nanocomposite was effective for tetracycline (TC) removal from water and the maximal adsorption capacity was 41.1 mg g^{-1} at pH 3.0. Under the optimal conditions, the synthesized nanoparticles showed an excellent efficiency for removal of tetracycline (>98%) from water samples. The TC adsorption followed pseudo-second-order kinetic model. The experimental data were analyzed by the Langmuir and Freundlich models of adsorption. Equilibrium data fitted well with the Langmuir model. All these results showed that the prepared nanocomposite had the potential to be used as adsorbents for the removal of TC from water samples.

Keywords: $ZnFe_2O_4$ nanoparticles; Adsorption; Tetracycline; Efficient removal; Langmuir and Freundlich models

Synthesis of Micrometer-sized Mesoporous Silica Spheres for Separation of Pyridine Derivatives by RP-HPLC

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Mesoporous silica is used in different areas, especially those with 3-10 µm diameters, which are very promising chromatography supports in HPLC. It has attractive properties such as high specific surface area, large mesopore volume, adjustable pore diameter, narrow pore size distribution and regular pore structures; so it is expected to improve the retention capacity, separation slectivity, separation kinetics and the column permeability. It can be easily functionalized and used as promising stationary phase in HPLC. Columns with spherical shaped or spheroidal (almost spherical) mesoporous silica particles are superior for chromatographic applications, because spherical particles provide higher efficiency, better column stability and lower back-pressures compared to irregularly shaped particles.

Mesoporous silica microspheres were prepared via a two-step synthesis process by using a triblock copolymer as template in combination with a cosurfactant and a cosolvent. They were characterized by SEM and BET. To obtain mesoporous silica spheres with particle sizes about 3-7 µm (obtained by SEM), specific surface area of 674 m^2/g and pore sizes of 7 nm, parameters of synthesis were optimized. After surface functionalization with C_{18}, they were used as a stationary phase in RP-HPLC for separation of 2-aminopyridine, pyridine, 2-methylpyridine, 2,4-dimethylpyridine and 2-benzylpyridine at two different pH. It has been shown that the synthesized C_{18}-modified mesoporous silica can be used as a good packing for separation of pyridine derivatives.

Keywords HPLC; mesoporous silica; pyridine derivatives; reversed-phase; sphere

References:

[1] H. Wan, L. Liu, C. Li, X. Xue, X. Liang, *J. Colloid Interface Sci*, **2009**, 337,420-426.

[2] J. Gañán, S. Morante-Zarcero, D. Pérez-Quintanilla, I. Sierra, *Microchem. J*, **2014**, 114, 53-58.

Preparation and evaluation of 5,17-bis(carbonyl-N-L-alanine methyl ester)-25,27-dipropoxy-26,28-bis(prop-2-en-1-yloxy)calix[4]arene-bonded silica gel as a new HPLC stationary phase for chiral separation

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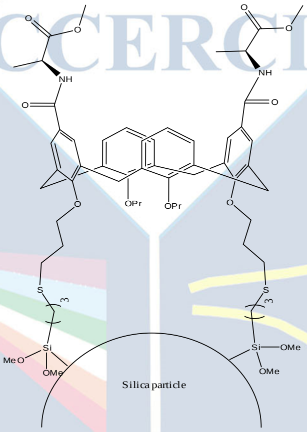
Calix [4] arene is a stable macrocyclic compound composed of phenol units linked by methylene bridges at positions ortho to the hydroxyl groups; this build beaker-shaped hydrophobic cavity at the upper rim is a π-basic cavity [1]. Since calix[4]arene has similar cavity structure and metal/ammonium cation binding properties as crown ethers and cyclams [2], it is of interest to us to prepare Calix[4]arene functionalized at the upper rim with L-alanine units as stationary phase as new chiral stationary phase (CSP) in liquid chromatography and to study their selectivity in chiral separation. The synthetic stationary phase is characterized by means of elemental analysis. The chromatographic behavior of this stationary phase was studied with some racemic amino acid derivatives and chiral drug compounds.



Keywords: Calix[4]arenes; Chiral stationary phase; Chiral compound; High performance liquid chromatography; HPLC

References:

[1] A. Ikeda, S. Shinkai, Chem. Rev. (1997) 1734.
[2] R. Abidi, M. Baker, J. Harrowfield, D. Ho, W. Richmond, B.W. Skelton, Inorg. Chim. Acta, 246 (1996) 275.

Evaluation of three dimensional high nitrogen doped graphene as an efficient sorbent for the preconcentration of BTEX compounds in environmental samples

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Introducing a new class of sorbents is an interesting work and this issue is a hot topic in the field of sample preparation. In this study, for the first time, three dimensional high nitrogen doped graphene (3D-HND-G) was synthesized as a new sorbent and then it was successfully applied for the quantification of BTEX compounds in environmental samples using gas chromatography. Firstly, the extraction efficiency of various carbon nanostructures including graphene (G), graphene oxide (GO), nitrogen doped graphene (ND-G), high nitrogen doped graphene (HND-G), and 3D-HND-G were compared. The results revealed that 3D-HND-G had higher efficiency for the extraction of BTEX compounds. Better dispersibility and higher surface area of 3D-HND-G rather than other carbon nanostructures may be the main reason of this phenomenon. Box–Behnken design methodology and the response surface methodology were applied to find out the optimal experimental conditions. The Optimized extraction conditions were: sorbent amount, 70 mg; sorption time, 8 min; salt concentration, 6.5% w/v; type and volume of the eluent, 255 µL methanols. Under the optimized conditions, the enrichment factors were obtained within the range of 328–376, which corresponds to extraction recoveries of 82–94%. The limit of detection and quantification were in the range of 0.5-1 ng mL^{-1} and 1.5-3 ng mL^{-1}, respectively. The method was reproducible since the intra and inter day precision (RSDs%, n = 5) were less than 6.2%. Finally, the proposed method was successfully applied to determine the concentration of BTEX as hazardous materials in the environmental samples.

Keywords: Carbon nanostructures; Environmental samples; Experimental design; Gas chromatography; Nitrogen doped graphene.

Highly sulfated and natural maltodextrins as chiral selectors in capillary electrophoresis: Prediction of chiral separation for basic compounds

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Prediction of chiral separation for a compound using a chiral selector is an interesting and debatable work [1]. In this study, for the first time, highly sulfated maltodextrin (HS-MD) was synthesized as a new anionic chiral selector and 23 chiral basic pharmaceuticals with different chemical structures were selected as model analytes and the influence of their chemical structures on the enantioseparation in the presence of sulfated and natural MD (as chiral selectors) was investigated. For chiral separation, a 100 mM phosphate buffer solution (pH 3.0) containing 10% (w/v) MD with dextrose equivalent (DE) of 4-7 or 1% HS-MD as chiral selector at the temperature of 25°C and voltage of 20 kV was used. Under this condition, baseline separation was achieved for nine chiral compounds, partially separation was obtained for other six chiral compounds while no enantioseparation was obtained for remaining eight compounds. Results showed there are some structural conditions for chiral separation. Enantioresolved solutes contained a chiral center with at least two aromatic rings or cycloalkanes and an O or N atom or a –CN group directly bonded to this chiral center. It means in the case that one ring and a –CN group or two rings and no O or N atom or –CN group directly bonded to the chiral center, a partial resolution expected and without any ring at the chiral carbon, resolution would be disappeared. With the aim of obtained results in this study, this is enough for user to investigate (look at) chemical structure of desired chiral basic compound. If the chiral compound has above condition, it would be separated with MD and if not, it would not be separated with this kind of chiral selector. This prediction will reduce the number of preliminary tests required for enantioseparation and will cause to a save in time and costs.

Keywords Capillary electrophoresis; Chiral separation; Maltodextrin; Prediction.

References:

[1] M. Blanco, I. Valverde, Trends Anal. Chem. 22 (2003) 428.

Characterization of tropane alkaloids in *Hyoscyamus* species using HPLC

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Due to a more prospective wide range of medicinal use of the two tropane alkaloids namely scopolamine and L-hyoscyamine, as selective antagonists of cholinergic receptors, this study aims to both quantitatively and qualitatively analyze these alkaloids in crude extract of different *Hyoscyamus* species from the Solanaceae family using HPLC after the detection of these compounds in plant extracts. Specimens from five different *Hyoscyamus* species (*H. niger* L., *H. reticulatus* L., *H. kurdicus* L., *H. pusillus* L. and *H. senecionis* L.) which in terms of ecology are cosmopolitan were dried and pulverized into powder, then the extraction processes were performed using an ultrasonic water bath. External standards and plant extracts with various concentrations were injected into the HPLC column via a 50 µL sample loop to identify (retention times) and quantify (peak heights) the mentioned alkaloids in the samples. From the acquired chromatograms peak heights, peak areas and mean retention times were measured with UV detection and processed using Chromgate to demonstrate the coefficient of determination and calibration curves. Calibration curves were linear over the studied ranges of concentrations. Results show that there was a significant difference in the amount and ratio of alkaloids. The main tropane alkaloid in all the studied species except for *H. niger* is L-hyoscyamine, which is significantly higher ($P<0.001$) in *H. senecionis* compared to the other samples. Thus, *H. senecionis* contains the highest amount of both scopolamine and L-hyoscyamine (0.64 and 0.91 mg/g dw, respectively). Furthermore, this study revealed that sample extracts of *H. pusillus and H. kurdicus* had the lowest amount of both alkaloids in comparison to the specimens from other species. It has been revealed that analytical HPLC is a reliable method to identify and estimate the amount and concentration of organic compounds such as scopolamine and L-hyoscyamine in plant samples in order to chemically differentiate their species. These findings suggest that unlike the common use of *H. niger* as a source of hyoscine and atropine, *H. senecionis* could be a promising naturally-abundant source of the mentioned tropane alkaloids which can be commercially available in pharmaceutical industry.

Keywords: HPLC, *Hyoscyamus*, L-hyoscyamine, Scopolamine, Tropane alkaloids

Comparison of Vancomycin chiral columns based on two different types of silica gel

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There are two procedures, Sol-gel and Polyethoxysiloxane (PES) procedures, for synthesizing of silica gel, which are used as support in liquid chromatography stationary phase [1]. In the first step of this research, silica was prepared by sol-gel method, and characterized by N_2 adsorption–desorption isotherms BET and BJH. The BET plot shows the pore size is about 120 Å, and also surface area is 445 m^2g^{-1}. Other characterization such as SEM, IR and optical microscopy of this silica are available. Another type of silica is SBA, which was synthesized by Polyethoxysiloxane (PES) method. By partial hydrolysis of tetraethoxysilane, silica micro beads were synthesized, and characterization was done same as pervious silica gel. Consequently, BET test shows mesopores with high surface area. According to employment of chiral chromatography to immobilize chiral selectors on silica gel in 10- 25 cm columns [2], one of macrocyclic glycopeptides (Vancomycin) was bonded onto two kinds of silica gel in order to preparation of chirobiotic HPLC columns. For assessing the validity of these columns, Enantiomeric separation of racemic compounds was done and the results of separations were compared.

Keywords: silica gel, sol- gel method, polyeyhoxysiloxane method, chiral stationary phase, vancomycin

References:

[1] K.K. Unger, Porous silica, Journal of chromatography library, volume 16, Elsevier, 1979.
[2] C.L. Barhate, M.F. Wahab, Z.S. Breitbach, D.S. Bell, D.W. Armstrong, Anal. Chem. 898 (2015) 128.

Identification of adulterations in commercial peppermint essential oils for evaluation of their authentication

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Nowadays essential oils have valuable benefits in many industries such as food, aromatherapy, fragrance, etc. Thanks to their remarkable importance, particularly in huge trade and transactions, many companies have started to insert impurities into essential oils in favor of extra profit. Common types of adulterations used in essential oil industry are the addition of cheaper essential oils, racemic synthetic compounds, oils and fats as the filler, and prohibited compounds published by IFRA organization. As an instance, there is a great possibility of adulteration for *Mentha piperita* L. which is one of the highly demanded mentha species, reputed for commercial peppermint oil. This study was conducted to evaluate authenticity of four industrial peppermint oils and the possibility of their adulterations using techniques including GC, GC-MS and NMR, as well as comparison of the obtained results with international standard references (e.g. BP, USP, ISO). Results of GC, GC-MS and NMR revealed that amount of propylene glycol and menthol in sample A were 12.4 and 64.27 %, respectively. Higher amount of menthol in comparison with ISO, USP and BP standards could be attributed to addition of synthetic menthol. Also propylene glycol was used as additive in this sample. Relative amounts of 1,8-cineol, Isomenthone, Isopulegol, etc in sample B are compatible with those in another species of mint, *Mentha arvensis*, which suggests that it might be used instead of peppermint oil. According to the acquired information from mass spectra, N,N-diisopropyl-1,2,2-trimethyl cyclopropanecarboxamide was detected in sample C, which could belong to the category of cyclopropanecarboxamide-based herbicides. After applying volatility test for sample D followed by appearance of some peaks at the end of GC-MS chromatogram, we realized that addition of heavy oils as filler is the type of adulteration used for this sample. Consequently, these four commercial peppermint oils obviously displayed different types of adulterations. Since addition of racemic synthetic compounds might be harmful for human health, application of two dimensional gas chromatography technique (2D-GC) could be considered as a powerful and beneficial approach for identification and quantification of such chiral compounds.

Keywords: 2D-GC, Adulteration, Peppermint oil

References:

[1] Tien do and et al, Trends in Anal. Chem. 66 (2015) 146.

Producing and Designing Protein-A affinity Medias for antibody purification

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Immunoglobulin G (IgG) is one of the most important drugs in the biopharmaceutical industry, so researchers attempt to design and investigate different purification methods for this critical drug. The industry has responded in several ways, among them protein-A affinity chromatography exhibited the highest capacity and purity. In this research we immobilize protein-A on porous silica by using 3-glycidoxy propyltrimethoxysilane for utilizing in High Performance Affinity Chromatography (HPAC). We minimized non-specific interactions by maximizing surface coverage. PBS used as binding buffer and Glycine-HCl (pH=3) used as elution buffer. The column purified IgG with purity of more than 90% and recovery of 51% from human serum. IgG purity evaluated by size exclusion chromatography, silver-stained gels following SDS gel electrophoresis and mass spectroscopy of elution peak. The binding capacities of matrice was determined using a purified Human IgG antibody. Static binding capacity and Dynamic binding capacity for IgG was 2.34 mg IgG/gr silica and 4.5 mg IgG, respectively.

Also we used reaction of carbon disulfide (CS2) with amine group of protein-A as a new method for immobilizing protein-A instead of using carbodiimides and succinimides which are common methods in industry. As a result we immobilized protein-A on porous silica and purified IgG with binding capacity of 2 mg IgG/gr silica.

Keywords: High performance affinity chromatography (HPAC), Protein-A, Immunoglobulin G (IgG)

References:

[1] Katoh, Shigeo and et al, Journal of Chromatography A 1161.1 (2007) 36.
[2] Niu, Yu and et al., Langmuir 28.51 (2012) 17718.

Design of experiments accompany multivariate curve resolution for gradient modeling of Preparative HILIC of five major alkaloids

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HILIC is the most popular mode of HPLC after reversed phase especially on the silica bare surfaces and has some advantages for preparative targets such as higher loadability, stationary phase longer life time, possibility of regeneration of packing and more solubility of compounds in injection solvent. But development of a gradient method for preparative targets always is not facile. Therefor design of experiment (DOE) as a statistical modeling that is case independent can be a proper choice for preview of preparative HPLC. However use of multivariate curve resolution (MCR) besides DOE is not avoidable because need to accurate calculation of R_s and α as experimental design responses. For starting to scale-up, 2 g silica gel 10 µm that slurry packed in a 4.6 × 250 mm stain less steel column and different concentration of five major alkaloids (morphine, codeine, thebaine, papaverine and noscapine) as very important drugs and scaffolds in medicinal and forensics was prepared in order to preparation of pure standards by HILIC. Central composite design presented 30 tests based on four factor of pH, ammonium acetate molarity, ACN in start, and decrease of ACN in 30 min beside nine responses that was four R_s, four α, and RT that were inserted in DOE space were achieved after MCR. Comparison of some experiments with DOE depicted results according to different optimization of responses showed very adaptation of them and accuracy of method development. Not only gained equations are applicable for every arbitrary optimization and scale-up but also give an overview of importance of every parameter in HILIC separation of narcotics. Robustness of this process was approved by further simple scale-up on a homemade preparative 21× 250 mm column with the same silica gel 10 µm packing.

Keywords: HILIC, Narcotic, HPLC modeling, Preparative HPLC, Experimental design

Effect of cellulose substitutions on orient of chiral interactions in indoxacarb enantiomers

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Indoxacarb is an active ingredient for crop protection and a chemical compound from the group of oxadiazines which is insoluble in water. The technical product is a 3:1 mixture of the (S)-enantiomer which is effective as an insecticide and the (R)-enantiomer is inactive. Recently there are some papers about enantioseparation and enantioselective degradation of indoxacarb enantiomers in water, soil and plants by chiral HPLC columns that show importance of its chiral interactions [1, 2, 3]. In this work two chiral stationary phases (CSPs) bases on cellulose carbamate was homemade by coating of triethoxy-3-amino-propylized silica gel 10 µm with cellulose phenyl carbamate and the other with cellulose 3,5-dimethyl phenyl carbamate that are nominated OC and OD, respectively. CSPs were slurry packed in two 0.46×25 cm stainless steel HPLC columns and to comparing of CSPs independence of mobile phase same mobile phase was optimized for both CSPs (Hexane-2-Propanol-Methanol-Ethansolfunic acid 90:5:5:0.2). Fortunately enantiomers ratio could be follow with UV detector in 310nm without the need for CD spectra. Contrary to what was initially suspected elution orders of enantiomers were different so that S-enantiomer on OC and R-enantiomer on OD were first eluted in reverse orders. This study shows adding 3,5-dimethyl to phenyl in OD CSP not only create more π-π interactions but also completely changes chiral orientation of indoxacarb during the interactions because in every enantioselectivity there are three interactive point that at least changing of two point is needed to be inverted. So different between the stationary phases of substituted celluloses can be much more complex than previously thought and substitutions as edge of CSP have most roll in chiral separations.

Keywords: Chiral, Cellulose, HPLC, Indoxacarb

References:

[1] Y. Zhang, K. Zhang, B. Song, H. Ling, Z. Li, M. Li, D. Hu, Biomed. Chromatogr. 28, (2014) 1371.

[2] Y. Zhang, K. Zhang, D. Hu, H. Ling, L. Zhong, A. Huang, K. Zhang, B. Song, J. Agric. Food Chem. 17 (2014) 9066.

Iranian Rice Bran Amino Acids Extractiori n and Identification using Trimethylsilyl Derivative and GC-Mass Spectrometry

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Rice bran is a source of proteins, amino acids, oil and nutrient. The oil in rice bran is generally extracted and used as high quality cooking oil, while the deoiled bran, however contains high level of protein and amino acids, has not been utilized to its full potential. In this study, in order to identify the amino acids found in rice bran, initially rice bran was deoiled by using soxhlet system and n-hexane as solvent. Then deoiled rice bran was suspended in distilled water (1 gr in 5 ml of water) and alkaline hydrolysis was carried out by sodium hydroxide in pH=11 at 30℃. After 45 minutes the pH of the suspension was adjusted to 7 with hydrochloric acids solution. The residue bran was separated from suspension by centrifuging, then the remaining solution was dried in oven at 65℃. The amino acids content of the matter was derived into trimethylsilyl by using Bis (Trimethyl silyltrifluoro) acetamide (BSTFA) prior to identification with GC-Mass. According to the results, among of existing amino acids, L-Homoserine was identified.

Keywords: amino acids, rice bran, trimethylsilyl, GC-Mass Spectrometry

References:

[1] I. Sereewatthanawut et al. / Bioresource Technology 99 (2008) 555–561.
[2] Hand Book of Analytical Derivatization Reaction by Daniel R Knapp ISBN ISBN: 978-0-471-03469-8, November 1979.

Calculation of thermodynamic parameters of solute using invers gas chromatography with naphthalenic imidazolium- based dicationic ionic liquids as new stationary phase

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Ionic liquids (ILs) possess high-thermal stabilities, negligible vapor pressure and are highly tunable making them attractive solvent systems. GC employing ILs stationary phases has proven to be a powerful tool for the determination of important thermodynamic properties involving mixtures of ILs and organic solvents. There are three methods to determine multiple solvation interactions between the ILs and the solute molecules. These methods include Rohrschneider–McReynolds classification system, solvation 39 parameter model, and measurement of thermodynamic parameters of the ILs such as activity coefficients at infinite dilution.

In this work, novel ionic liquids imidazolium based and NTf_2^- anion which is germinal dicationic with naphthalene groups was synthesized. Column packings, containing (5, 10, 15 and 18)% stationary phase (ILs) on Chromosorb W/AW (mesh 60/80), were prepared using dichloromethane as the solvent.

The activity coefficient at infinite dilution has been determined for 26 solutes by inverse gas chromatography technique (IGC) at four different temperatures (313,323,333 and 343˚K). Solvation interaction between solvent and 43 solute molecules have been measured at 313,343 and 373˚K using Abraham solvation parameters.

The final results showed that the thermal stability of imidazolium based dications ILs is considerably higher than their monocationic analogreues. Moover; synthesized ILs exhibit high selectivity for separation of polyaromatic compounds.

Keywords: Abraham solvation parameters, activity coefficient at infinite dilution, Gas chromatography; Ionic liquid,

References:

[1] C. Poole, N. Lenca, *chromatography*, **2014**, 1357, 87-109

[2] K. Tabar Heydar, H.G. Gharavi, M. Nazifi, M. Mirzaei, A. Sharifi, *Fluid phase Equilib*, 2013, 353, 93-100

[3] J. Yuan, D. Mecerreyes, M. Antonietti, *Progress in Polymer Science, **2013***, 38, 1009-1036

Application of synthesized room temperature ionic liquid for separation/preconcentration of Naproxen by in situ solvent formation microextraction

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Naproxen is a nonsteroidal anti-inflammatory drug (NSAID). It works by reducing hormones that cause inflammation and pain in the body. It acts by reducing the levels of prostaglandins, chemicals that are responsible for pain, fever and inflammation. Determination and preconcentration of naproxen to reduce its toxicity in biological fluids is important and therefore sensitive analytical teqnique is required for its detection. Several microextraction methods, such as liquid-phase microextraction (LPME), dispersive liquid–liquid microextraction (DLLME) have been developed to miniaturize the LLE procedure and to reduce the amount of organic solvent as well. Ionic liquids (ILs) are being recently considered as replacement solvents in sample preparations, due to their unique chemical and physical properties. This work is aimed at developing a microextraction technique against very high content of salts, and a new mode of homogeneous liquid-liquid microextraction (HLLME) based on ILs, termed in situ solvent formation microextraction (ISFME) is reported.

This work is based on the use of 1-Butyl-3-methylimidazolium Bromide ionic liquid as extraction solvent. To 1 mL sample solution containing Naproxen added 100 mg of the IL. The mixture was transferred into a conical centrifuge tube, shaken the mixture and 1 mL counter ion NTf2$^-$ was added, upon which a cloudy solution was appeared. The resulted solution was then centrifuged for 6 min at 5000 rpm, the two phases were separated and the organic phase was analyzed for Naproxen content by spectrophotometric detection at 232 nm.

The parameters like sample pH, amount of IL, amount of counter ion and effect of centrifuge conditions were investigated to find the effective ones, and optimized as 3, 100mg, 0.05 mol L^{-1} and 6 min at rate of 5000 rpm respectively. The IL, [Bmim]$^+$[Br]$^-$ as extraction solvent and NTf2$^-$ as ion-pairing agent could efficiently phase transfer the Naproxen.

Keywords: Ionic liquid; ISFME; Naproxen; Spectrophotometry

Removal of food dyes from aqueous solution by chitosan/clay nanocomposite films

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Chitosan is a polysaccharide composed by polymers of glucosamine and N-acetyl glucosamine. Due to the advantages, coupled with its biocompatibility and biodegradability, chitosan has been capture of dissolved dyes from aqueous solutions [1-3].In this work, blends of chitosan and clay micro/nanoparticles were prepared by dispersion of the clay particles in the film matrix and chitosan/clay nanocomposite films were applied to remove acid red 18 and FD&C blue no. 2 dyes from aqueous solutions. Batch adsorption equilibrium experiments were carried out at different temperatures (298–328 K). Freundlich, Langmuir and Redlich–Peterson models were fitted to the experimental data. The adsorption capacities of chitosan/clay nanocomposite films were 273.8 mg g^{-1} and 205.3 mg g^{-1} for the acid red 18 and FD&C blue no. 2, respectively, obtained at 298 K. It was found that the adsorption of acid red 18 onto chitosan/clay nanocomposite films was a relatively fast process, reaching about 86% of saturation in 82 min. The strong electrostatic interaction between the $^{-}$NH^{+3} of chitosan and food dye can be used to explain the high adsorption capacity of food dyes onto chemically cross-linked chitosan/clay nanocomposite films. These results suggested that the chitosan/clay nanocomposite films were strongly colored during the adsorption of acid red 18 and FD&C blue no. 2, confirming the high affinity between films and food dyes. The chitosan/clay nanocomposite films maintained its structure and were easily separated from the liquid phase after the adsorption process.

Keywords: Adsorption; Chitosan; Clay; Food dyes; Nanocomposite

References:

[1] W.S. Wan Ngah, L.C. Teong, M.A.K.M. Hanafiah, , Carbohydr. Polym. 83 (2011) 14461456.
[2] G. Crini, P.M. Badot, Sci. 33 (2008) 399–447.
[3] J.S. Piccin, G.L. Dotto, M.L.G. Vieira, L.A.A. Pinto, J. Chem. Eng. Data 56 (2011) 3759 3765.

Electrically stimulated liquid phase microextraction combined with differential pulse voltammetry: A new and efficient design for in-situ determination of clozapine from complicated matrices

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In this work, for the first time, a new, simple, low-cost and efficient design was presented that combined electromembrane extraction (EME) with differential pulse voltammetry (DPV) for in-situ determination of extracted clozapine (CLZ) from human plasma samples. Charged target analyte was extracted by applying a 200 V d.c. electrical potential from an acidic sample solution, through the supported liquid membrane (SLM) into an acidic acceptor solution, which was located into the lumen of a porous hollow fiber. 2-Nitrophenyl octyl ether (NPOE) was impregnated into the pores of the hollow fiber and used as SLM. Three microelectrodes, an Ag/AgCl, a platinum wire, and a graphite pencil lead as the reference, counter and working electrodes, respectively, were fixed by passing through a septum and located into a pipette tip connecting to the end of hollow fiber for electrochemical analysis of CLZ. Central composite design and response surface methodology were used to optimize the main parameters influencing the extraction efficiency and analytical response (current) including pHs of donor and acceptor phases, extraction time and electrical potential difference. Under the optimize conditions, the proposed method showed a wide linear range of 3-1500 ng mL^{-1} with determination coefficient higher than 0.993. Extraction recovery of 42% was achieved which corresponded to a preconcentration factor of 114. Limits of detection and quantification of 0.9 ng mL^{-1} and 3.0 ng mL^{-1} were obtained, respectively. The intra- and inter-day precisions (RSD%, n = 3) were less than 3.5% and 6.7%, respectively. Finally, the proposed method was successfully applied for determination of CLZ from some human plasma samples.

Keywords*:* Electromembrane extraction; Differential pulse voltammetry; Clozapine; In-situ determination; Plasma sample.

Biodiagnose by inferared spectrometry: PCOs via blood serum analysis

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Poly Cystic Ovarian syndrome (PCOs) is an extremely common endocrine system disorder, which enlarges ovaries with thickened sclerotic capsules and abnormal high number of follicles. The initial screening tests for diagnosis of PCOs include determinations of blood serum levels of different hormone such as TSH, FSH, LH, AMH, and PLR.

In this work, the outcome of Eliza kit assey and qualitative diagnosis of PCOs disorder in adult women blood serum samples based on infrared (IR) spectroscopy in 800 – 3000 cm^{-1} spectral region were compared. An approach to find spectral features with in dataset includes multivariate analysis methods such as (PCA) and (PLS-DA) which have been compared to discriminate between normal and PCOs sample, where spectral characteristic features contributing most to difference or separation are identified for further analysis.

Spectral features due to amino acids such as arginine, lysine, proline, glutamate and Histidine, organic acids like citrate and potentially lipids (CH2–CH2–C=C) with significant decreases noted in the levels of citrulline, lipid (CH2–CH2–C=C, arginine, lysine, ornithine, proline, glutamate, acetone, citrate and histidine where the most important characteristics to discriminate blood serum samples for PCOs diagnosis.

Keywords: Diagnosis; Chemometrics

A Simple Method for Simultaneous Determination of Brilliant Blue FCF and Sunset Yellow in Food Samples Based on Cloud Point Extraction and Spectrophotometric Detection

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In this study, a simple and low-cost method was developed for extraction and pre-concentration of brilliant blue FCF and sunset yellow in food samples using cloud point extraction (CPE) prior to spectrophotometric determination. The effects of main factors such as solution pH, surfactant and salt concentrations, incubation time and temperature on the cloud point extraction of both dyes were investigated and optimized. Linear range of calibration graphs were obtained in the range of 16–1300 ng mL^{-1} for brilliant blue FCF and 25–1300 ng mL^{-1} for sunset yellow under the optimum conditions. Limi of detection values for brilliant blue FCF and sunset yellow were 3 and 6 ng mL^{-1}, respectively. The relative standard deviation (RSD) values of both dyes for repeated measurments (n=6) were less than 4.57 %. The obtained results demonstrate the proposed method can be applied satisfactory to determine these dyes in different food samples.

Keywords: Brilliant blue FCF, Sunset yellow, Triton X-100, Cloud point extraction, Spectrophotometric, Food samples

References:

[1] R. Heydari, M. Hosseini, S. Zarabi, Spectrochim. Acta A 150, (2015) 786.
[2] N. Pourreza, M. Ghomi, Talanta 84, (2011) 240.
[3] S.M. Ghoreishi, M. Behpour, M. Golestaneh, Food Chem. 132, (2012) 637.

Efficient adsorption of Eu(III) and Th(IV) ions from aqueous solutions by a Schiff base functionalized mesoporous silica SBA-15 sorbent

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Radionuclides are important industrially and environmentally. With the rapid development of the nuclear industries, the contamination of these elements, such as thorium and europium, in wastewater is a major environmental concern. Therefore, several separation strategies have been developed [1]. Sorption is considered to be one of the most effective and convenient technique because of its simplicity, selectivity, high capacity, eases of handling and environmental safety [2]. Recently, mesoporous materials have attracted much attention due to their high surface areas, large and uniform pore sizes, excellent mechanical and thermal stability, and high sorption capacities. These characteristics make these materials to be considered as potential candidates for removal of radionuclides from aqueous solutions [1,3].

In this work, SBA-15 mesoporous silicas was synthesized, and then was functionalized with *N*-propylsalicylaldimine and characterized using XRD, SEM and TEM techiques. The adsorption of Eu(III) and Th(IV) were performed as a function of aqueous phase pH, contact time, adsorbent dose, temperature, initial ions concentrations, volume and ionic strength. ICP-OES was used for measuring the concentration of metal ions. By using 0.04 g of the adsorbent in contact with 20 mL of the aqueous solution (10 mg/L of each ions) adjusted at pH 4 and after 5 h, a quantitative removal of the ions (> 95%) was achieved. It was also indicated that stripping of the adsorbed ions can be achieved by using dilute nitric acid solutions. This allowed using the proposed method for a preconcentration process of the studied metal ions, and also the possibility to reuse the adsorbent. The adsorbents were successfully used for removing of the target ions from various real water samples. The adsorption isotherms and the kinetics of the processes were described well with Langmuir and pseudo second order models, respectively. Thermodynamic investigations show that adsorption processes are endothermic and spontaneous.

Keywords: Adsorption, Eu(III), SBA-15, Schiff base, Th(IV)

References:

[1].Y. Liu *et al.*, Appl. Surf. Sci. 285 (2013) 258-266.
[2].L. Zuo *et al.*, J. Radioanal. Nucl. Chem. 288 (2011) 379–387.
[3] Y. Liu *et al.*, J. Radioanal. Nucl. Chem. 292 (2012) 803-810.

A Sol-gel Preconcentration Method for Sensitive and Selective Spectrofluorimetric Determination of Silver

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Silver is an important element in industry. Silver compounds and alloys are extensively used in photographic film or papers, jewelry, mirrors and other electrical and electronic applications. Due to antibacterial properties of silver colloids, silver compounds and alloys have been widely used to disinfect the water used for drinking and recreational purposes, in dental and pharmaceutical preparation, and in implanted prosthesis. Various uses of silver discharge human to mining and production of silver. The human activities cause leakage of silver as different compounds to the environment. This may cause the aquatic and terrestrial organisms to be exposed to silver [1].

A selective sol-gel based preconcentration-spectrofluorimetric method has been developed for silver ion determination. Silver ion was reduced to silver nanoparticles by using hydrazine, and then the nanoparticles were extracted by acidifying the solution containing sodium alginate. The formed dispersed alginic acid, extracted silver nanoparticles. After accumulating the gel phase, a low volume of sodium hydroxide was used to dissolve the gel phase. The solution was injected into an aqueous stream for spectrofluorimetric detection. The excitation and emission wavelengths were 380 and 558 nm, respectively. The limit of detection of the method was 0.02 μmol L^{-1} and a wide linear response for Ag(I) in the range of 0.1-25.0 μmol L^{-1} was obtained. The relative standard deviations and recoveries, for entire of the working range, were in the range of 1.5-2.4 and 96.0-98.8%, respectively. The effects of various chemicals as foreign species on the determination of silver were investigated; the method showed high selectivity on the determination of silver. The analytical method was applied for the determination of silver in water, jewels and antibacterial samples, successfully.

Keywords Silver nanoparticles; Sol-gel preconcentration method; Spectrofluorimetry

References:

[1] G. H. Rounaghi, I. Razavipanah, M. H. Vakili-Zarch, M. Ghanei-Motlagh, M. R. Salavati, *Journal of Molecular Liquids* 211 (2015) 210.

Highly selective colorimetric detection of cadmium(II) using silver nanoparticles modified with tetra ethylene glycol bis (8-quinolyl) ether

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Colorimetric methods have received significant attention in Analytical Chemistry in that they minimize or eliminate the necessity of using expensive and complicated instruments. Colorimetric method is fast, selective and sensitive. In this work, AgNPs functionalized with tetra ethylene glycol bis (8-quinolyl) ether (TEG). This method was developed for the determination of Cd^{2+}. It is based on the finding that cadmium ion causes the aggregation of silver nanoparticles capped with TEG, while other cations do not exert an effect. The surface plasmon resonance band of the modified AgNPs provides the quantification of cadmium at very low concentrations. As a result, the color of the solution changes from yellow to red which can be detected visually or by spectrophotometry. Parameters affecting the recovery, including pH, the concentration of TEG, Effect of reaction time on TEG-AgNPs aggregation induced by Cd^{2+}were examined. The aggregation of the AgNPs was confirmed by UV–vis and TEM. Limit of detection was found 0.16 µM for Cd^{2+}. The ratio A595 / A395 nm is linearly correlated to the concentration of cadmium ion in the 0.5 to 6.0 µM range. The method was successfully applied to the determination of Cd^{2+} in (spiked) real water and urine samples and gave recoveries that ranged from 92.7 to 98.6 %.

Keywords Silver nanoparticle; Colorimetric detection; Cadmium ions; tetra ethylene glycol bis (8-quinolyl) ether

References:

[1] S. Chen, Y. Xu, B. Xu, and M. Guo, Journal of Neurochemistry, **2011,** 119, 1108–1118.

[2] Jan Knápek, Josef Komárek, Pavel Krásenský, Spectrochimica Acta Part B, **2005,** 60, 393-398.

[3] Fei Zheng, Bin Hu, Talanta, 85, **2011**, 1166-1173.

Biosynthesis and stabilization of Ag nanoparticles using orange blossom extract and their characterization

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Biosynthesis of nanoparticles has received considerable attention due to the growing need to develop environmentally benign technologies in material synthesis [1]. Currently, silver nanoparticles is one of widely used particles in the field of nanoparticles after of carbon nanotubes. So that, nano silver is a wonderfully scientific achievement in nanotechnology of various fields of medicine, industry, agriculture, animal husbandry, packaging, household appliances, cosmetics, health, military, and so on [2-4]. In recent years a number of biomimetic processes have been used for the synthesis of silver nanoparticles[5-6]. Indeed, over the past several years, plants, algade, fungi, bacteria, and viruses have been used for low-cost, energy-efficient, and nontoxic production of metallic nanoparticles[6]. But so far there is no report on the development of silver nanoparticles by utilizing orange blossom. In this paper we have reported the green synthesis of silver nanoparticles (AgNPs) by reduction of silver nitrat, using orange blossom extract. Orange blossom extract as reducing and stabilizing agents. The process for the synthesis of AgNPs is rapid, novel, economic and ecofriendly. Nanoparticles were characterized with the help of Transmission Electron Microscope(TEM), X-ray diffraction(XRD) and UV–Vis absorption spectroscopy. Formation of the AgNPs were confirmed by surface Plasmon spectra using UV-Vis spectrophotometer and absorbance peaks at 413/4 nm. The morphology of the particles was studied using TEM which confirmed the formation of spherical particles with size 5-50 nm. XRD study shows that particles are crystalline in nature with face centered cubic (fcc).

Keywords: Green synthesis; Silver nanoparticles; orange blossom extract; SPR; UV-Vis spectra.

Reference:

[1] D. Mandal, M.E. Bolander, D. Mukhopadhyay, G. Sankar, P. Mukherjee, Appl. Microbiol. Biotechnol. 69 (2006) 485-492.

Selective adsorption of uranium ions on tosulfamic acid functionalized SBA-15; isotherm and kinetics investigations

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Uranium as a nuclear fuel, is an important element industrially and energetically. However, because of the high toxicity and radioactivity, U(VI) is considered as one of the most hazardous speciescausing progressive renal injury, kidney failure and death [1]. Thus, the recovery and the removal of uranium is a principal environmentally and industrially.To these aims, a varietyof techniques including chemical precipitation, solvent extraction, membrane processes and adsorption havebeen developed. Among these, adsorption is promising with many advantages such as higherenrichment factors, lower consumption of chemical reagents and flexibility [2]. SBA-15 is a mesoporous silica material with a narrow pore size distribution, great pore volumes, and mechanical and thermal stability. These adsorbents have been shown to be efficient for removal of various chemical species from water samples[1,2].In the present communication, asulfamicacid functionalizedSBA-15has been synthesized and characterized by XRD, SEMandTEM techniques.The removal of uranium(VI) ions from aqueous solutions (10mgL^{-1}) by the synthesized SBA-15 has been studied and the parameters affecting this process were optimized. Under optimized conditions; 0.01g adsorbent, 20 mL sample solution containing 10 mg/L of U(VI), pH=5, contact time 120 min , the sorption amounts were about 63%.This removal percentage was augmented to 100% by repeating two times the adsorption process. A quantitative stripping of the adsorbed ions was achieved by using dilute nitric acid, which allows to use the method for a preconcentration process of U(VI) ions. It was found thatthis adsorbent could remove selectively uranium(VI) ions with respect to some other associated ions.The adsorption isotherms and kinetic were well described by Langmuir and pseudo second order models, respectively. Thermodynamicstudy shows that adsorption process is endothermic and spontaneous. The method was used successfully for selective removal of uranium ions from various water samples.

Keywords: Adsorption; functionalizedSBA-15; Uranium.

References:

[1]Y.Liu *et al.*, Journal of Radioanalytical and Nuclear Chemistry,292 (2012) 803–810.
[2]X. Wang*et al.*, Annals of Nuclear Energy,56 (2013) 151–157.

Application of UVC and ZnO nanoparticles for photocatalytic degradation of ciprofloxacin drug

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Ciprofloxacin (CIP) is a famous synthetic chemotherapeutic antibiotic. It is widely found either in water or wastewater. In this study ciprofloxacin was photo-catalytically degraded using synthetic zinc oxide (ZnO) under UVC light and examined the effect of pH, ZnO concentration, antibiotic concentration, presence of different anions, stirring and purging the solution on the efficiency of UVC/ZnO process.

A 100 mL of the CIP aqueous solution was mixed with required amount of ZnO and were placed in tubular glass reactor. A 9 W low-pressure mercury UV lamp was placed in a quartz sleeve and was longitudinally inserted at the axial center of reactor. The mixture was stirred in dark for 20 min by a magnetic stirrer to attain adsorption/desorption equilibrium of CIP on photo-catalyst surface. After that, UV lamp which is emitted radiation at 254 nm and was placed in the sleeve, switched on to start the photo-degradation process. After 10 minutes irradiation times, 3.0 mL of solution were sampled using a syringe and then centrifuged to separate the photo-catalyst for determination of CIP concentration by UV/Vis spectrophotometer at 273 nm.

The optimum operating conditions for complete degradation (100%) of antibiotic in an aqueous solution containing 10 mg L^{-1} CIP were: pH 5.0, 0.15 g L^{-1} ZnO, stirring speed of 600 rpm, without purging and irradiation time of 180 min. From kinetic studies, photo-catalytic reactions under optimum conditions followed a pseudo-first order kinetics with rate constant (k) of 0.017 min^{-1}. Since performance of the CIP degradation may be affected by anions in the water, estimated amounts of the different anions (Cl^-, HCO_3^-, SO_4^{2-}, NO_3^-, and HPO_4^{2-}) were studied and there was no noticeable interfere. This method was successfully applied for degradation of CIP in tap water as a real sample.

Keywords: Ciprofloxacin; Photocatalytic degradation; UVC/ZnO.

Study on the Interaction of Sunset Yellow with DNA using UV-Visible Spectrophotometry, Spectrofluorimetry and Viscometery Techniques

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The use of food dyes is at least controversial due to their essential role. Synthetic color food additives uses frequently in food industry. Moreover many of food colors have been related to health problems mainly in children that are considered the most vulnerable group [1]. The purpose of this work is to present spectrophotometric, spectrofluorometry and viscometery techniques to study the interaction of calf thymus DNA (ct-DNA) with Sunset Yellow (SY) at physiological pH (Phosphate buffer, pH 7.4). The maximum absorbances for SY at wavelengths 312.5 nm and 480 nm are significantly decreased by increasing of ct-DNA in solution. The binding constants for DNA-SY adduct was calculated through the plot of A_0 / (A-A_0) versus 1 / [DNA], as 4.56 $\times 10^3$ and 1.15$\times 10^3$ L.mol^{-1} in the two wavelengths of 312.5 and 480 nm respectively. In the spectrofluorometry study, the florescence spectra were recorded in the range of 450-700 nm at excitation wavelength of 430 nm. The fluorescence intensity for SY at 480 nm was enhanced by increasing ct-DNA concentration due to the increasing of the planarity in the structure of SY-DNA and decreasing of the collision frequency of solvent molecules with SY, usually leads to the emission enhancement [2-3]. The effect of ionic strength was also studied in the interaction of SY with ds-DNA for understanding the mode of interaction. Moreover, the viscosity of SY was increased by titration with ds-DNA showing association of SY with ct-DNA. Intercalative binding increases the length of DNA and viscosity increases significantly, whereas groove binding typically has a smaller effect on viscosity [4].

Keywords: UV-Vis Spectrophotometry; Spectrofluorometry; Viscometery; ct-DNA; Sunset Yellow.

References:

[1] S. Kashanian, S.H. Zeidali, K. Omidfar, N. Shahabadi. Mol. Biol. Rep (2012) 39: 10045-10051

[2] Y. Ni, S. Du, S. Kokot, S. Anal. Chim. Acta 2008, 584, 19.

[3] A.A. Ensafi, R. Hajian, S. Ebrahimi, J. Braz. Chem. Soc. 2009, 20, 266.

[4] D.T. Breslin, J.E. Coury, J.R. Anderson, L. McFail-Isom, Z.Y. Kan, L.D. Williams, L.A. Bottomley, G.B. Schuster. J. Am. Chem. Soc. 1997, 119, 5043.

Photocatalytic degradation of 2,4,6-trichlorophenol with nano CdS synthesized by microwave-assisted and auto combustion sol–gel methods

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Presence of choloro phenols in the environment is very common, this is because it is an important industrial chemicals. 2,4,6-trichlorophenol (2,4,6-TCP) is one of derivation of chloro phenols that has been used as a fungicide, glue preservative, insecticide. Nano Photocatalyst is a suitable way for the removal of this toxic material from water due to its easy, reliable, nontoxic and cost effective operation. CdS is one of the most promising nano photocatalyst with better properties like band gap, fine optical transmittance, and appropriate band potentials under different thermodynamic conditions for photocatalytic redox reactions.

In the present work, CdS nanoparticles were synthesized by microwave assisted and auto combustion sol-gel methods. Nanoparticles were characterized by XRD , FTIR, and FESEM. Their photodegradation evaluated on 2,4,6-TCP in aqueous solution under UV-C (low-pressure mercury vapor lamp with power of 30 W) irradiation. At set time, 5 ml of solution was withdrawn and the remain concentration of 2,4,6-TCP was evaluated by UV–vis spectrophotometer. The influences of catalyst loading, initial concentration of 2,4,6- TCP and pH of the solution were investigated. The results show that after 4 hours, the degradation of 2,4,6-TCP by nanoparticles synthesized by microwave-assisted sol-gel method (88%) was successfully better than auto combustion sol-gel method (43%). Short reaction time, small particle size, narrow particle size distribution, and high purity were the advantage of CdS synthesis by microwave-assisted sol-gel method.

Keywords: Microwave-assisted; 2,4,6-Trichlorophenol; Photocatalyst; CdS

References:

[1] Y. Hu, Y. Liu, H. Qian, Z. Li, J. Chen, Langmuir 26 (2010) 18570.
[2] U. I. Gaya, A. H. Abdullah, M. Z. Hussein, Z. Zainal, Desalination 263 (2010) 176.

Spectrophotometric Method for Determination of Aluminum in Water Samples by Using chromeazurol S and a Water Soluble Ionic Liquid

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The present study describes a simple and sensitive spectrophotometric method for the determination of aluminum in real water samples. The method is based on the effect of an ionic liquid namely, 1-methyl-3-hexadecyl-imidazolium bromide (C_{16}mimBr), on aluminum ion and chrome azurol S (CAS) complex. It is well known that the addition of surfactant substances improves the selectivity and sensitivity of the methods developed for determination of metal complexes due to their batho and hyperchromic effects. Alkylimidazolium salts are one of the most important classes of ionic liquids (IL); as they are easy to handle, stable against water, and having high ionic conductivity. Similar to traditional surfactants, these organic salts display pronounced hydrophilic and hydrophobic molecular fragments. Due to their inherent amphiphilicity, they exhibit a surfactant-like behavior when carbon number of alkyl chain is higher than 8 and they form micellar aggregates in aqueous solutions The ternary complex of Al–CAS–C_{18}mimBr displays a distinct absorption peak with excellent analytical characteristics and offers the advantages of simplicity for the determination of Al (III) ions, without any need for a solvent extraction step. The limit of detection (LOD) and linear range of the method were obtained 0.14 ng mL^{-}1 and 0.3-30 ng mL^{-1} respectively. The method was validated and applied successfully to the determination of Al(III) ions in real water samples.

Keywords Aluminum (III), spectrophotometry, chrome azurol S, 1-methyl-3-hexadecyl-imidazolium bromide

Halloysite nanotubes as a new adsorbent for solid phase extraction and spectrophotometric determination of iron

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This paper reports the use of halloysite nanotubes (HNTs) as a new solid phase extraction adsorbent for preconcentration of iron (II) from water and food samples. Halloysite nanotubes with molecular formula of $Al_2Si_2O_5(OH)_4 \cdot nH_2O$ have been used for adsorption of some metal ions via ion exchange process and by formation of inner-sphere and outer-sphere complexes through $Si\text{-}O^-$ and Al-O- groups. In this work, unmodified HNTs were used for preconcentration of iron (II) as a cationic complex of iron (II)-2, 2-bipyridine. Adsorption efficiency of this cationic complex on solid sorbent is much better than that of bare metal ion and moreover, the complex is colored which enables spectrophotometric determination of iron after elution by a proper eluent. The metal complex is effectively adsorbed on the sorbent in the pH range of 3.5 - 6.0 from 50 mL of aqueous solution of Fe(II) with a preconcentration factor of 50. The retained complex is eluted by trichloroacetic acid and its absorbance is measured spectrophotometrically at 520 nm. Under the optimum conditions, the calibration graph is linear in the 5.0 - 500 μg L^{-1} concentration range, with a detection limit of 1.3 μg L^{-1}. The method was applied for the determination of trace iron in various water and food samples and the accuracy was assessed through the recovery experiments and analysis of a certified reference material (NIST 1643e).

Keywords Iron, spectrophotometry, halloysite nanotubes, solid phase extraction

Determination of atorvastatin by using the cupric oxide nanoparticles–HCO_3^- –H_2O_2 chemiluminescence reaction

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Eliciting electromagnetic radiation from a chemical reaction without using any external excitation source, such as light sound, heating or even mechanical force, is called chemiluminescence (CL) [1]. This phenomenon can be catalyzed by several substances such as metal ions, enzymes and nanomartials, among others. In this study, we report that CuO NPs are capable of catalyzing week CL reaction of HCO_3^-–H_2O_2. The CuO NPs were prepared by using quick precipitation technique [2]. The synthesized CuO NPs were characterized by exploiting X-ray diffraction (XRD), transmission electron microscopy (TEM), scanning electron microscopy (SEM) and dynamic light scattering (DLS) analysis. Furthermore, it was found that atorvastatin has inhibitory effect on the HCO_3^-–H_2O_2 – CuO NPs CL system. Atorvastatin is in a group of drugs called HMG CoA reductase inhibitors, or "statins." It is interesting atorvastatin reduces levels of "bad" cholesterol (low-density lipoprotein, or LDL) and triglycerides in the blood, while increasing levels of "good" cholesterol (high-density lipoprotein, or HDL). Atorvastatin is used to treat high cholesterol, and to lower the risk of stroke, heart attack, or other heart complications in people with type 2 diabetes, coronary heart disease, or other risk factors. Based on the inhibitory effect on this drug, a new approach were suggested for determination of atorvastatin. To this sense, the CL reaction of $HCO3^-$– H_2O_2 – CuO NPs was optimized to achieve highest CL intensity. Then, under the optimum conditions, the calibration plot for atorvastatin was plotted in the concentration range from 1.3×10^{-7} to 1.0×10^{-4} mol/L. The limit of detection of the CL method was 1.3×10^{-8} mol/L and the relative standard deviation (RSD) for 11 replicate determination of 10^{-5} mol/L atorvastatin was 4.0 %. The study of the effect of foreign species on the CL system revealed that the CL system possessed good selectivity. In addition, the applicability of the CL method for real samples was demonstrated by the CL determination of atorvastatin in pharmaceutical formulations and environmental and tap waters.

Keywords: Chemiluminescence; cupric oxide nanoparticles; hydrogen peroxide; sodium bicarbonate; Atorvastatin

References:

[1] Sorouraddin MH, Iranifam M, Imani-Nabiyyi A.. J Fluoresce 2009; 19:575–81.
[2] Chen W, Hong L, Liu AL, Liu JQ, Lin XH, Xia XH.. Talanta 2012;99:643–8.

Speciations Effect of Manganese Ions ($MnSO_4$, Mn-EDTA , MnO nanoparticles)on Growth of Two Beens Varieties Using Atomic Absorption Spectrophotometer

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This study consisted of two experiments and was designed based on completely randomized block design with 3 replications. In the first experiment aimed to assess effect of different Mn fertilizers on the seed germination and seedling growth of two pinto beans cultivars. In the second experiment, we evaluated effects of different Mn fertilizers and their application method on vegetative and reproductive traits of 191 and 193 pinto bean cultivars. Treatments were nano particles of MnO(%0.05, %0.1, %0.15) ,$MnSO_4$(%0.3), Mn-EDTA (%0.1 . %0.3 . %0.5) , nano MnO(%0.1) + Mn-EDTA(%0.3) and control. The results of first experiment showed that the interaction of cultivar × fertilizer treatments on seed germination and seedling vigor index (SVI) was not significant, but the main effects of each factor were significant. So that, the highest percentage of seed germination and seedling vigor index related to MnO nanoparticles treatment and had significant different from other treatments. The second experiment was designed under greenhouse conditions and by three ways (1-one spraying before and after flowering, 2-twice spraying before and after flowering, 3- seed treatment). Compared to control treatment, Manganese fertilizers improved vegetative characteristics(such as plant height, root and shoot dry weight)and quality(Manganese content in seed) of both pinto bean cultivars. Among the Manganese fertilize treatments, %0.1 of MnO nanoparticles was the best as a superior treatment. Generally, based on the results twice foliar application of %0.1 of MnO nanoparticles can be best treatment to achieve maximum growth and yield of to pinto bean cultivars. Between vartieties, 191 had more mean traits as compared with 193.

Keywords: Foliar spray ; Mangane chelate; Nano manganese oxide particles ; Pinto bean ; Seed application.

References

[1]Seifi Nadergoli , M., Yarnia, M. and Rahimzade Khoei, F. " Meddle-East Journal of Scientific Research. 2011.**Vol. 8** , pp. 859-865.

Evaluation of nanophoto catalytic degradation of diazinone and malathion pesticides using ultraviolet light in the presence of magnetic nano-composite of TiO_2

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Organophosphorus is one of the widely used pesticides over the world. Organophosphorus pesticides (OPPs) are hazardous to human because of their persistence, stability and toxicity. Advanced oxidation processes (AOPs) such as UV/H_2O_2, UV/O_3, UV/ZnO, UV/TiO_2 and UV/Fenton processes have been commonly used for the removal of toxic compounds. Fe_3O_4 and TiO_2 have been widely used due to their easy availability and nontoxicity.

Therefore, in the present study, applicability of Fe_3O_4–TiO_2 nanocomposite as an efficient photocatalyst for the degradation of diazinon and malathion was evaluated. In this study, the treatment conditions included the presence of UV and aeration, pH, agitation, amount of nano-TiO_2, initial diazinon and malathion concentrations and the contact time were studied and optimized. After mixing the solution and absorbent at the designated time, absorbent in the solution without filtration and only with the use of an external magnetic field are collected and uptake of diazinon and malathion in the samples were analyzed by UV-Vis. The prepared Fe_3O_4–TiO_2 composite was characterized by of SEM, EDX, XRD and FT-IR. UV/Fe_3O_4–TiO_2 composite showed the greatest photocatalytic activity compared with other processes. The results showed that by providing optimal conditions the removal of these pesticides is possible. The proposed method was applied to natural and environmental water samples, which showed good agreement with reference method results.

Keywords: Photocatalysis; Magnetic nanocomposite of TiO_2, Diazinon; Malathion; Environmental water samples.

Determination of Doxorubicin drug using platinum coated magnetic nano particles: Resonance light scattering studies.

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Doxorubicin (DOX) also known as hydroxydaunorubicin, is an anthracycline antibiotic and a drug used in cancer chemotherapy. It works by intercalating DNA and could cause some adverse effects such as life-threatening heart. Therefore, the development of sensitive and reliable analytical methods for the determination of DOX is a basic requirement for the study of this analyte in different types of samples with complex matrices [1].

Resonance light scattering (RLS) has emerged as a powerful optical technique based on elastic light-scattering. Due to the advantages of high sensitivity, rapidness, simplicity and convenience. In the past few years, nano composite materials have been subjected to extensive research as the combination of different nano scale functionalities are capable of endowing the substrate with enhanced properties and thus have great application potentials in various fields. The core/shell nanostructure is an ideal composite system that combines the advantages of core and shell and has shown enhanced physical and chemical properties. In this study magnetic Fe_3O_4 nanoparticles (MNPs) were synthesized by the Solvothermal method and then modified with APTES [2]. Amino groups coated magnetic Fe_3O_4 nanoparticles were covered with platinum. Physical characteristics of Pt@ Fe_3O_4were studied using SEM and XRD measurements. The magnitude of RLS intensity of the Pt@Fe_3O_4 obtained by the synchronous scanning at $\lambda_{ex}=\lambda_{em}$ ($\Delta\lambda$=0 nm) under optimum condition: ultra-sonication time: 30 min, pH 5, nanoparticle concentration : 10 mg L^{-1} . The linear dynamic range was established from 0.05 -7 mg L^{-1} of Doxorubicine and the limit of detection was found to be 0.0028 mg L^{-1} using proposed method.

Keywords : Determination, Doxorubicin ,Nanocomposite , Resonance light scattering.

References:

[1] M. Ahmadi, T. Madrakian , A. Afkhami , *New J.Chem* , **2015,** 39 , 163-171.

[2] A. El-Toni .M. Ibrahim , J. Labis, A. Khan ,M .Alhoshan , *Mol . Sci* , **2013 ,**14, 11496-11509.

Adsorption behavior of Samarium (III) and Gadolinium (III) ions using D2EHPA/ TBP impregnated resin

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Extractant Impregnated Resin (EIR) is a good alternative to solvent extraction and ion exchange techniques for separation and recovery of metal ions. EIR has been widely used in the nuclear methods because of its simplicity, fast and cheap compared to the other techniques [1-3]. In this work, a method was developed for the separation of Sm (III) and Gd (III) ions using extraction chromatography resin made by impregnating Amberlite XAD-4 with a mixture of TBP and D2EHPA. For studying the uptake of Sm(III) and Gd(III) from nitric acid media, a series of batch adsorption method were carried out. The parameters affecting the extraction process such as nitric acid concentration, D2EHPA/TBP ratio, extraction time and temperature were investigated. The results showed that 0.1M nitric acid was desirable region and with increasing of acid concentration, a sharp decline was observed in the uptake of two metal ions. The optimal value for D2EHPA/ TBP ratio was obtained to be 1:1 that attributed to the higher uptake of Gd(III) as compared with Sm(III). The uptake of Sm(III) and Gd(III) were determined as a function of time (range from 10 – 360 min) in 0.1 M nitric acid medium. Accordingly, the adsorption kinetics of Sm(III) was relatively slower than Gd(III). The results of temperature effect showed that increasing the temperature from 10 to 25◦C leads to increase in the adsorption of Gd(III) as compared to Sm(III). Under optimal conditions, separation factor (S.F) of Gd and Sm was obtained to be 4.6. This satisfactory result can be practically used in the separation of Sm(III) and Gd(III) by chromatography column.

Keywords: Adsorption; Gadolinium; impregnated resin; Samarium

References:

[1] H. Matsunaga, , Ismail, A.A., Wakui, Y, & Yokoyama, T. 2001. React. Func. Polym. 49: 189–195.

[2] P. K. Mohapatra, S. Sriram, V. K. Manchanda, L. P. Badheka, *J. Sep. Sci. Technol.* 2000, 35, 39.

A novel fluorescent sensor based on dithiazole-pyridine having a different recognition between transition metal ions and proton

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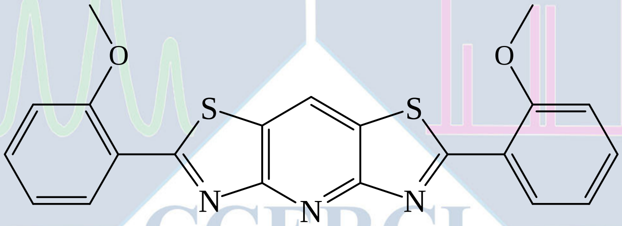
Among the methods available for chemical sensors, the fluorescence technique has become a powerful tool due to its simplicity and high sensitivity. The fluorophore 2,6-bis(2-methoxyphenyl)dithiazolo[4,5-b:5',4'-e]pyridine) **1**, with a planar structure, was synthesized in a one-pot Willgerodt–Kindler reaction.[1]



1

The calculated Φ_F in various solvents is in the region 0.06–0.46. The fluorescence were carried out by the addition of metal ions to **1** in MeOH solutions. Except Cu^{2+} which gave non-fluorescent 'off-mode' **1**•Cu^{2+} complex, no noticeable changes were observed with other transition metals. The detection limits of **1** for Cu^{2+} was found out to be 8.78 mg litre^{-1}.

Keywords: Copper detection; fluorescent chemosensors

References:

[1] H. R. Darabi, M. Kargar, R. Hajipoor, N. Abouali, K. Aghapoor, Kh. Jadidi, B. Notash, H. Sayahi, *Tetrahedron Lett.*, **2016**, *57*, 256-259.

Determination of dobutamine by using graphene oxide- enhanced luminol chemiluminescence

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Chemiluminescence (CL) reactions are chemical reactions in which the energy of reaction is released in the form of light. In recent decades, CL- based analytical methods have received extensive attention due to their advantages such as high sensitivity,wide liner range, simplicity and inexpensive equipment [1]. Graphene oxide (GO) is a material in the form of sheet with atom thickness that can disperse in water [2]. GO can intensify the light emission from the CL reaction of luminol - oxygen. This phenomenon is due to the ability of GO in production of reactive oxygen species [3]. Dobutamine prescribed for heart disease treatment and its measurement in the pharmaceutical industry is very important from the quality of manufactured drugs point of view. In this work, a new, simple and inexpensive method was developed to measure dobutamine. The method was based on inhibitory effect of dobutamine on the GO-luminol- O_2 CL reaction. GO was synthesized by improved Hummers method. The synthesized GO was characterized by transmission electron microscopy (TEM), X-ray diffraction (XRD), ultra violet absorption (UV-Vis) and fourier transform infrared spectrometry (FTIR).. The effect of concentrations of GO, NaOH and luminol were on CL intensity was investigate and optimized. Under the optimum conditions, a liner relationship was obtained between CL intensity and concentration of dobutamine in the range of 3×10^{-7}-5×10^{-6}mol L^{-1}. The detection limit of this method 2.4×10^{-7} mol L^{-1} and its relative standard deviation (RSD) for nine replicate determinations of 2×10^{-6} mol L^{-1} dobutamine was 1.2%.

Keywords Chemiluminescence; Dobutamine; Luminol; Graphene oxide.

References:

[1] M. Iranifam, Luminescence 28 (2013) 798-820.
[2] D.R. Dreyer, A.D. Todd, C.W. Bielawski, Chem. Soc. Rev 43 (2014) 5288-5301.
[3] M. Hao, N. Liu, Z. Ma, Analyst 138 (2013) 4393-4397.

Spectrophotometric determination of explosive tetranitrocarbazole with dispersive liquid- liquid microextraction

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Tetranitrocarbazole (TNC) is a particulartype of polynitroaromatic compounds that is commonlyapplied in the preparation of landmines for military and terroristactivities, so its determination is an important task. In this method, a fast, simple and reliable method for the sensitive determination of trace amounts of TNC as an explosive reagent was developed by combination of dispersive liquid-liquid microextraction (DLLME) and microvolume UV–vis spectrophotometry. In this method, TNCwas converted to anion form in basic medium and extracted to carbon tetrachloride as an ion pair by Aliquat 336, which also acts as a disperser agent. The effect of important parameters, such as the pH in the sample solution, the amount of Aliquat 336 and the type and volume of extraction solvent were investigated and optimized. Under the selected conditions, the linear calibration graph was obtained in the range of 50-800 ng mL^{-1} of TNC**,** with the correlation coefficient of 0.999.The detection limit of this method was 16 ng mL^{-1}ofTNC. The method was successfully applied to the determination of tetranitrocarbazole in water samples.

Keywords: Tetranitricarbazole; Spectrophotometry; Dispersive liquid-liquid microextraction.

References:

[1] A. Larki, M. Rahimi Nasrabadi, N. Pourreza, Forensic Sci. Int. 251 (2015) 77.
[2] N. Pourreza, S. Rastegarzadeh, A. Larki, Talanta, 134 (2015) 24.
[3] P. Poormoghadam, A. Larki, S. Rastegarzadeh, Anal. Methods, 7 (2015) 8655.

Analytical application of graphene oxide-sensitized luminol chemiluminescence reaction for determination of paracetamol

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Generally, analytical Chemiluminescence (CL) technique is based on the measurement of the electromagnetic radiation (usually visible/near-infrared radiation) emitted by a chemical reaction [1]. On the other hand, in recent years, nanomaterials with the unique physical and chemical properties can amplify the CL signal and improved the sensitivity the various CL detection systems [2]. In this work, we synthesized graphene oxide (GO) by using improved hummer method. Then, 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 spectroscopy, fourier transform infrared (FTIR). This study revealed that GO were well separated from each other and dispersed in solution. These GO were used for enhancing of luminol– O_2 CL reaction. Then, we found that paracetamol were capable of altering CL emission of GO enhanced luminol –O_2. Based on this finding, a new 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 7×10^{-6}–5×10^{-5} M with a detection limit of 8×10^{-7} M. The relative standard deviation for 5 determinations of 2×10^{-5} M paracetamol was 3.39%. The method was successfully applied to the determination of paracetamol in pharmaceutical formulations.

Keywords: Chemiluminescence; Graphene Oxide; Luminol; Paracetamol.

References:

[1] J.A. Ocaña-González, M. Ramos-Payán, R. Fernández-Torres, M.V Navarro, M.A Bello-López, Talanta 122(2014)216.
[2] B.A. Gorman, P.S. Francis, D.E. Dunstanb, N.W.Barnett, Anal. Chem 395(2007)397.

Ionic liquid assisted synthesis of a new grapheme quantum dot as a nanosensor: Application to the fluorescence detection of isoniazid

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Graphene quantum dots (GQDs), as defined, are a kind of 0D material which can be regarded as incredibly small pieces of grapheme. The GQDs exhibit new phenomena due to quantum confinement and edge effects, which are similar to CDs. Compared with organic dyes and semiconductive quantum dots (QDs), GQDs are superior in terms of their excellent properties, such as high photostability against photobleaching and blinking, biocompatibility, and low toxicity. Therefore, GQDs have attracted significant attention from researchers. Generally, the PL behaviors of GQDs are related to their sizes, morphologies, and compositions which are decided by both the starting materials and the fabrication methods. The preparation methods of GQDs can be classified into two categories: top–down(cut down large carbon structures) and bottom–up(small moleculesas a starting) methods .

These methods always involve complex synthetic procedures, and the special organic precursors may be difficult to be obtained. In the past few years, increasing efforts have been paid to the advanced synthesis of GQDs via simple routs [2].

In this study, a button-up method was used for synthesis of graphene quantum dots. The new graphene quantum dots were synthesized by an organic precursor in the presence of an ionic liquid. It showed a good fluorescence depend on the pH and also showed a high quantum yield. The most fluorescence intensity was achieved at pH=12 and it showed the most quenching efficiency at the presence of isoniazid. Effect of buffer type, ionic strength, and quantum dots concentration was investigated and optimized. This system with high quantum yield was used for fast and simple determination of isoniazid in tablet sample. This nano sensor showed the linear response for isoniazid in the range of 7.6×10^{-7} to 6.8×10^{-3}.

Keywords: graphene quantum dots, isoniazid, ionic liquid, fluorescence detection

References:

[1].Sun, H.; Wu, L.; Wei,W.; Qu, X. Mater. Today 2013, 16, 11, 433-442.

[2]. Pan, D. Y.; Guo, L.; Zhang, J. C.; Xi, C.; Xue, Huang, Q. H.; Li, J. H.; Zhang, Z. W.; Yu, W. J.; Chen, Z. W.; Li, Z.; Wu, M. H. J. Mater. Chem. 2012, 22, 3314.

[3].G.K. Mcevory, AHFS Drug Information, American Society of Hospital Pharmacists, Bethesda, MD, 1990, pp. 344–348.

A sensitive colorimetric probe for determination of cimetidine based on anti-aggregation of gold nanoparticles in the presence of chitosan

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Cimetidine (*N''*-cyano-*N*-methyl-*N'*[2-[(5-methyl-1H-imidazole-4-y1)methyl]thio]ethyl]-guanidine is a potent H_2-receptor antagonist which inhibits gastric acid secretion in humans and has been proven to be highly effective in the treatment of duodenal ulcer. Therefore, the detection of this drug in biological and pharmaceutical matrices is highly demanded [1-2].

In this work a simple and sensitive method was introduced for the detection of trace amounts of cimetidine based on anti-aggregation of gold nanoparticles (AuNPs) as a probe. The AuNPs was synthesized by ascorbic acid as reducing agent and chitosan as stabilizer. It is found that cimetidine induces the anti-aggregation of the Au-NPs, leading to a color change from blue to red. This change can be seen with bare eyes, and monitored by UV–vis spectroscopy which represents a simple and reliable colorimetric assay for the determination of cimetidine. Effect of some parameters including stabilizer and reducer concentration on the surface plasmon band of Au NPs was studied and optimum conditions were obtained. The colorimetric assay exhibited high sensitivity with a low detection limit of 3.1 ng ml^{-1} of cimetidine. The presented method is capable of determining cimetidine over a range of 4–80 ng ml^{-1}. The relative standard deviation for eight replicate measurements of 60 ng ml^{-1} cimetidine was 4 %. This probe was applied for the rapid determination of cimetidine in real samples.

Keywords: Cimetidine; Anti-aggregation; Chitosan; Gold nanoparticles

References:

[1] M. Shamsipur, F. Jalali, S. Haghgoo, J. Pharm. Biomed. Anal. 27 (2002) 867–872.
[2] M. Soledad Garcia, M. Isabel Albero, C. Sa´nchez-Pedren˜o, M.S. Abuherba, J. Pharm. Biomed. Anal. 32 (2003) 1003_ 1010.

Assessment of a novel and green chemistry colorimetric system for analysis of inorganic arsenic (III) by hydride generation and utilizing a optimized compact digital camera as the sensor with image processing

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Arsenic (III) is a very toxic element that sometimes found in ground or waste waters which has harmful effect on human health. This research explained a novel, simple and green method for colorimetric determination of As (III) using a digital camera as the detector. It is based on chemical hydride generation of arsine(AsH_3) from acidic solution of As (III) by $NaBH_4$ [1] and sequential reaction of arsine with Fe (III)- 1,10-Phenanthroline solution that produces red complex of Fe(II)- 1,10-Phenanthroline. The intensity of the red color is related to concentration of arsenic (III) and extracted by image processing -Image J- software. For achievement to the best results, we investigate the changes of (RGB) value in terms of red color intensity of the complex. Blue was the best that it showed the highest sensitivity. Therefore we used a blue LED as source of light in subsequent measurements. We also optimized some factors that are influencing in the proposed method, such as acidity of the sample, concentration of $NaBH_4$ and time of reaction. The calibration curve will be linear about the range of 5-50 µg ml^{-1} for As (III) and detection limit about 1 µg ml^{-1}. This method has two main advantages, the first is using a cheap and available detector (digital compact camera) compared with expensive and professional device such as UV–Vis spectrophotometer [2], AAS [3] and AFS [4]. The second and main benefit is utilizing of non-toxic indicator based on Fe^{3+}/Fe^{2+} redox system in aqueous solution, compared with common indicator such as silverdiethyldithiocarbamate in organic solvent like morpholine- chloroform [4]. Our system can use as a portable kit to measure high range concentration of As (III) in industrial and wastewaters without need for any sample preparation.

Keywords As(III); Hydride generation; Fe(II)-1,10-Phenanthroline; Digital image processing .

References:

[1] M. Hashemi, P. Modasser, Talanta, 73 (2007)166-171.

[2] M.H. Arbab-Zavar, M. Chamsaz, T. Heidari, Analytical Science, 26(2010)107-110.

[3] A. Caiminagua, L. Fernández, H. Romero, B. Lapo, J. Alvarado, Analytical Chemistry Research, 3 (2015) 82–88.

[4] Z. Zou, S. Wang, J. Jia, F. Xu, Z. Long, X. Hou, Microchemical Journal, 124(2016)578-583.

Carbon nanodots originated from chitin nanofiber as chemoprobe for fluorescence sensing of D-Penicillamine in biological fluids

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Carbon quantum dots (CQDs) or fluorescent carbon nanoparticles have received increasing interest as potential competitors to conventional semiconductor quantum dots owing to their environmental friendliness, low toxicity, simple, low cost synthetic methods and fascinating optical properties [1]. Penicillamine or cuprimine is an anti-rheumatic drug used to treat patients with active rheumatoid arthritis. Penicillamine is also utilized as a copper chelating agent to remove excess copper associated with Wilson's disease [2]. Herein, we report for the first time the preparation of CQDs via one-pot hydrothermal oxidation route with chitin nanofibers (CNFs) as carbon source and their application for a turn-on photoluminescent sensor for D-Penicillamine. The CNFs as biodegradable nanomaterials have fine nanofiber networks with a typical width 10-20 nm [3]. The fabricated CDs were characterized by TEM, PSA, FT-IR. The photoluminescence of as-prepared CQDs can be effectively quenched by Cu^{2+} owing to the binding of Cu^{2+} to the surface of the CQDs and the electron transfer from the photo-excited CQDs to Cu^{2+}. In the presence of D-Penicillamine, Cu^{2+}preferred to bind with D-Penicillamine owing to its high affinity toward D-Penicillamine and subsequently the photoluminescence of CQDs is recovered. The recovered photoluminescence intensity of CQDs was linearly proportional to the concentration of D-Penicillamine in the range of 1–50 µg mL^{-1} with a detection limit of 0.4 µg mL^{-1}. The proposed sensor was successfully applied to the determination of D-Penicillamine in biological fluids with satisfactory results.

Keywords: Carbon quantum dot; Penicillamine; Chitin nanofiber; Fluorescence sensing

References

[1] Sh.Y.Lim, W. Shen, Zh. Gao, *Chem. Soc. Rev.*, 44 (2015) 362-381.
[2] M.R. Hormozi-Nezhad,, M. Azargun, N. Fahimi-Kashani, J IRAN CHEM SOC, 11 (2014) 1249-1255.
[3] S. Ifuku, H. Saimoto, Nanoscale 4 (2012)3308-3318.

Simple and portable chemoprobe for fluorescence sensing of 2-mercaptobenzothiazol by using CdTe-Quantum dots in “Lab on paper” method

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“Lab on paper” or paper-based analytical devices (PADs) have been developed for providing low-cost, portable and disposable platforms for monitoring the various biological and chemical analytes [1]. Luminescent semiconductor nanocrystals, or quantum dots (QDs) have worldwide attracted more and more attention for biochemical sensing and imaging applications due to fascinating properties such as high luminescence efficiency, good photostability and size-dependent emission wavelengths [2]. 2-mercaptobenzothiazole (MBT) is widely used as a corrosion inhibitor in various industrial processes [3]. We report herein the development of a simple fluorometric method for monitoring of 2-mercaptobenzothiazole (MBT) by using CdTe quantum dots (CdTe-QD) in PADs. The ability of CdTe-QD for fluorometric sensing of MBT was first examined in the solution by spectrofluorophotometer. The fluorescence of loaded paper with CdTe-QD under UV radiation faded away upon addition of MBT due to its fluorescence quenching. The image of the PADs was taken by a digital camera and the picture was processed and analyzed using Adobe Photo shop software. The increase in the mean color intensity of the PADs test zones upon addition of MBT was used as an analytical signal for monitoring of MBT. The parameters affecting the paper MBT probe were optimized to enhance the selectivity and sensitivity of the method. Under optimum conditions, the mean color intensity was linearly proportional to the concentration of MBTin the range of 1–50 µg mL^{-1} with a detection limit of 0.5 µg mL^{-1}. The relative standard deviation of ten replicate measurements of 20 µg mL^{-1} of MBT was 1.27%. The proposed sensor was successfully applied to the determination of MBTin different water samples with satisfactory results.

Keywords: Lab on paper; paper-based analytical devices; 2-mercaptobenzothiazole; Quantum dots

References:

[1] N. Pourreza, H. Golmohammadi, Talanta 131 (2015) 136–141.
[2] M.F. Frasco, N. Chaniotakis, Sensor 9 (2009) 7266-7286.
[3] N. Pourreza, H. Golmohammadi, T. Naghdi, and H. Yousefi, *Biosens. Bioelectron.* 74 (2015) 353–359.

Sensitive colorimetric detection of explosive 2,6-bis(picrylamino)pyridine after preconcentration by dispersive liquid- liquid microextraction

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Explosives are used mainly in military purposes, industries, mining and agricultural activities. Due to the increased attention on homeland security, human health and environment issues, the investigation and detection of nitroaromatic explosives residues and explosive-like compounds is an issue of major importance in countering terrorist threats and contamination of soil and groundwater. In this paper, an experimental investigation for sensitive spectrophotometric detection of explosive, 2,6-bis(picrylamino)pyridine (BPAP) has been carried out, using dispersive liquid- liquid microextraction. Based on this procedure, which is a dispersive-solvent-free technique, the extractant is dispersed in the aqueous sample solution using Aliquat 336 (acted as disperser agent and carrier to extraction solvent) and monitored with microvolume UV-Vis spectrophotometer. The effect of different variables such as pH, concentration of sodium hydroxide, type and volume of extraction solvent, concentration of Aliquat 336 solution and coexisting substances were systematically investigated and optimized. The proposed method is capable of determining BPAP over a range of 2.0-150.0 ng mL^{-1} with a limit of detection 1.0 ng mL^{-1}. Relative standard deviations (RSD) for 20.0 and 80.0 ng mL^{-1} of BPAP were 3.3 and 1.2 % (n= 10), respectively. This colorimetric method has been successfully applied to determine BPAP in different water and soil samples.

Keywords: 2,6-bis(picrylamino)pyridine, Aliquat 336, Dispersive liquid-liquid microextraction.

References:

[1] A. Larki, M. Rahimi Nasrabadi, N. Pourreza, *Forensic Sci. Int.* **2015,** 251, 77-82.
[2] N. Pourreza, S. Rastegarzadeh, A. Larki, *Talanta*, **2015**, 134, 24- 29.

Spectrophotometric and Potentiometric Determination of Acidity Constant of Aurin in Water-organic Solvent Mixtures

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In this study, the acidity constants of Aurin in binary mixtures of methanol-water at 25 °C and an ionic strength of 0.1 M have been determined by spectrophotometric and potentiometric methods. The spectra of Aurin in binary solvent mixtures at various pH values in 380-580 nm intervals were recorded (Figure 1).

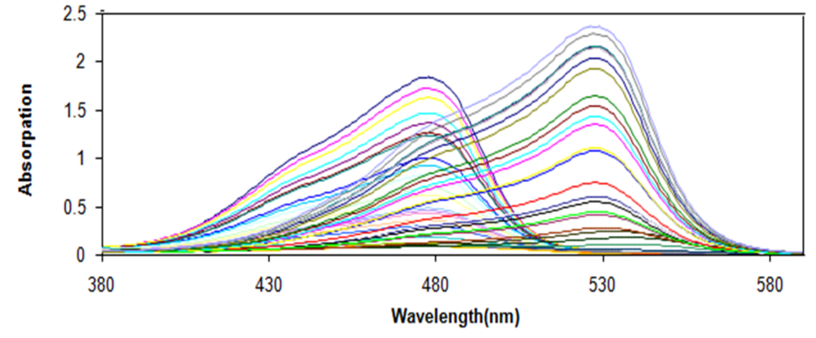

Figure 1. Absorption spectra of Rosolic acid in pure water at different pH values

As the percent of organic solvent increases in solvent mixtures the *pKa* constants increased as well. It has been shown that the solvating ability and dielectric constant of the solvent play a fundamental role in dissociation reactions. Water is a solvent of high solvating ability, (i.e. donor number DN = 33, and dielectric constant ε = 78) which can dissociate the acid and stabilize the produced anion and hydrogen ion. Thus, it is expected that addition of methanol with lower donor number and dielectric constant (DN = 19, ε = 32.7) to water decreases the extent of interaction between the acid anion and proton with solvent, and this increases pKa_1 constants of 1.57 to 2.05 and pKa_2 of 10.26 to 10.56 with spectrophotometric and amount 1.64 to 2.07 for pKa_1 and 10.29 to 10.58 for pKa_2 with potentiometric methods. DATAN and BEST were programs applied for determination of acidity constants [1-2].

Keywords: Potentiometric; Rosolic acid; Spectrophotometric

Refrences:

[1] A. Niazi, M. Ghalie, A. Yazdanipour, J. Ghasemi, **Spectrochim. Acta Part A 64** (2006) 660.

[2] A. Niazi, A. Yazdanipour, J. Ghasemi, Spectrochim. Acta Part A 65 (2006) 73.

A novel dual mode "on and off" fluorescence probe based on embedded label free silver nanoparticles in Poly vinyl alcohol-borax hydrogel for Fe (III) and thiosulfate determination

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In this research, a novel on-off fluorescence probe has been developed based on polyvinyl alcohol-borax (PB) hydrogel for the first time. The label free silver nanoparticles were synthesized in situ and embedded into (PB) hydrogel without any reducing agent. The maximum wavelength for label free silver nanoparticles in hydrogel is 441.6 nm. After preparing this new probe, the effect of Fe (III) and thiosulfate was investigated. The size- depending of label free silver nanoparticles is responsible to enhance and quench of fluorescence as well as obvious color changing. Effect of some parameter such as silver concentration, polyvinyl alcohol and borax concentration, pH variation and etc. was investigated. Under the approved condition, the linear detection range was validated over the concentration of 1.4×10^{-8}-2.7×10^{-6} M and 1×10^{-7}-1×10^{-6} M for Fe (III) and thiosulfate, respectively. A Limit of detection of 0.09 µg mL^{-1} was obtained for Fe (III). The relative standard deviation 0.269 µM of Fe (III) was 1.39 % (ten replicate measurements). This cost-effective dual mode probe has been satisfactory used to the Fe (III) detection in some real samples such as rice flour, dates, apricots, walnuts and yogurt with acceptable result and good fluorescence recovery. While the proposed method has simple and remarkable design, the great potential of it has been proven.

Keywords: Poly vinyl alcohol-borax hydrogel; silver nanoparticles; thiosulfate, leaching

References:

[1] Wen-Fei Meng, Mei-Pan Yang, Bo Li, Zhao Cheng, Bing-Qin Yang, Tetrahedron. **2014**, 70, 8577-8581

[2] Xiao-Hung Zhang, Chuan-Fang Zhao, Yue Li, Xiu-Ming Liu, Ao Yu, Wen-Juan Ruan, Xian-He Du. Talanta **2014**, 119, 632-638

Silica-based Carbon dot-Fe(II)-$K_2S_2O_8$ as a new chemiluminescence system and its application for determination of norfloxacin

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A simple and sensitive chemiluminescence (CL) method based on Silica-based Carbon dot-Fe (II)-$K_2S_2O_8$ system, is designed for the determination of norfloxacin. Carbon dots (Cdots) are a fascinating class of luminescent nanomaterials that comprise discrete, quasispherical carbon nanoparticles with sizes below 10 nm. They typically display high quantum yield fluorescence with interesting size- and excitation wavelength-dependent behavior. Recently Silica-based Cdots (Si-Cdots), as a new kind of Cdots, have been introduced and attracted considerable interest in various areas. In this work, Si-Cdots were prepared by a hydrothermal method and characterized by fluorescence spectra and transmission electron microscopy. The very weak CL of the Fe(II)-$K_2S_2O_8$ system is enhanced by a factor of ~100 in the presence of Si-Cdots. Possible mechanisms that lead to the effect were elucidated by recording fluorescence and CL spectra. Furthermore, we found that norfloxacin has an increasing effect on the CL system. Based on this phenomenon, a new analytical method was developed for the determination of norfloxacin in the concentration range of 2.5 to 200 µg L^{-1}, with a limit of detection (3s) of 1 µg L^{-1}. The developed method was applied to the determination of norfloxacin in humen serum samples with satisfactory results.

Keywords Chemiluminescence; Si-Cdots; Norfloxacin

Application of molecularly imprinted polymer- sol-gel deposited on glass slides for optical identification and determination of nalidixic acid

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This paper illustrate the preparation and usage of molecularly imprinted polymer- sol-gel (MIP sol-gel) for specific recognition of antibiotic nalidixic acid. In this research work, an appropriate and transparent glass slide that passed a light in a proposed wavelength range was used as a support and then the MIP sol-gel was deposited on it.This support was cheap and have a ability to connect to sol-gel easily.The nalidixic acid MIP sol-gel was prepared using nalidixic acid as a template and acrylamideandN,N'-methylendiacrylamid as a functional monomer and cross linker, respectively.Because of the radical polymerization process, Azobisisobutyronitrile (AIBN) was applied as an initiator. The non-imprinted sol-gel was synthesized in the same way without addition of nalidixic acid. The influence of certain variables including the sample pH, amount of cross linker, amount of functional monomer, temperature and elution time on the extraction efficiency of the antibiotic was assessed. Selectivity was also demonstrated for template over two of its similar substances. Under the optimum condition, detection limit was achieved less than 10 mg L^{-1}. In addition real sample analysis has been performed on plasma samples containingnalidixic acid and showing specific recognition. From the results, it is appear that MIP Sol-gels based glass slides can be a promising toolfor current, emerging and future medical applications.

Keywords molecularly imprinted polymer, sol-gel, nalidixic acid, glass slide

References:

[1] M. M. Moein, M. Javanbakht, M. Karimi, B. Akbari-aderganic, M. Abdel-Rehim, *Analyst*, **2015**, 140, 1939-1946.

[2]S. Güney, F. Ç. Cebeci, *Sens. Actuators, B*, **2015**,208, 307-314.

[3]I. Bakas, A. Hayat, S. Piletsky, E. Piletska, M. M. Chehimi, T. Noguer, R.Rouillon, *Talanta,* **2014**, 130, 294-298.

Gold Nanoparticle immobilized on a silanized glass slide Surface as Sensor for butane thiol vapor detection

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We demonstrate that gold nanoparticles (GNPs) immobilized on silanized glass acts as an optical sensor that quantify butane thiol vapor. GNPs are the most popular material due to their optical properties in the visible region that are dominated by the surface plasmon resonance (SPR). Butane thiol, also known as butyl mercaptan is a low molecular weight thiol, volatile, clear to yellowish liquid with a fetid odor, highly flammable and it is found in kerosene and gasoline. High affinity between butane thiol and GNPs through Au-s bond leads to aggregation of GNPs that immobilized on silanized glass and cause decreasing of absorption at 542 nm in SPR spectrum of GNPs and can be used as an optical sensor for quantitative detection. In this research glass slide surface activated by Aminopropyltriethoxysilane(APTES). Spherical GNPs synthesized by sodium citrate reduction, immobilized on silanized glass by silanization agent. This method represents advantages of metal gold nanoparticles and solid substrate stability in one package. The effect of some parameters such as temperature, time, pH and concentration of gold nanoparticles were evaluated. The sensor has minimal technological requirements and can be detected with UV-visible spectrophotometer. This method with low cost and time consuming can be useful in the petrochemical, Pharmaceutical industries and detection of rotten food. Under the selected conditions, linear calibration graphs were obtained in the range of 200-800×10^{-6} molL^{-1} (R^2=0.9836) with 7.8% relative standard deviations (rsd).

Keywords butan thiol, gold nanoparticle, optical sensor, silanized glass slide, surface plasmon resonance

References:

[1] N.Nath, A.chilkoti, *Anal. chem*, (2002), *74,504*-509.
[2] N.Hajdukova, M.prochazka, J.stepanek, M.spirkova, *Colloids and surfaces A*, (2007), 301,264-270.
[3] j.zhang, *optical properties and spectroscopy of nanomaterials*,(2009),world scientific publishing, singapor, 205-217.

Multi-way analysis of excitation emission fluorescence data from separated whey proteins using ultrafiltration combined with ion exchange chromatography

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The protein fractions, α-lactalbumin (α-La) and β-lactoglobulin (β-Lg) represent almost 70% of the protein concentration in whey. The interest in isolating both fractions is based on their individual nutritive and physiological properties.

UV-absorbance based detection and two-dimensional fluorescence spectroscopy is not informative enough to monitor protein content in whey complex environment. To overcome this limitation, multi-dimensional fluorescence spectroscopy and multi-way analysis techniques are considered to bemore informative to investigate protein content in whey [1]. So the current work, proposes separation of α-La and β-Lg and a new approach for monitoring the fractionation of proteins by making use of excitation-emission fluorescence spectroscopic data analyzed by chemometrics techniques. To achieve this goal a method based on ultrafiltration (UF), in combination with anion exchange chromatography (AIEX) [2], was applied to separate α-Laand β-Lg. In the next step three-way data array were recorded by measuring excitation-emission fluorescence of each steps in chromatography. Then PARAFAC [3] was performed to analyze the resulting data.It was observed that two species eluted at 0.1 M ionic strength. The concentration of one of them was initially increasing, exhibit a maximum, and then decreasing, but the concentration of other species was initially high and then decreasing. Electrophoresis reports these two species can be α-La and bovine serum albumin (BSA) respectively. Also two species having same emission spectral profiles eluted at 0.25 M ionic strength. The concentration profiles of one of them was increasing and then decreasing but, for the other one concentration was constant in primary steps and then decreasing. Electrophoresis reports these two species can be Lactoferrin (LF) and β-Lg respectively.

Multi-way analysis techniques has practical applications as it could offer the opportunity for monitoring of separation processes.

Keywords: Fluorescence; Ion exchange chromatography; Multi-way analysis; Ultrafiltration; Whey proteins

Spectroscopic Study On The Interaction Between 5,10,15,20-Tetrakis(4-N-Heptyl- Pyridyl)Porphyrin Copper(II) And ct-DNA Using Multivariate Curve Resolution-Alternating Least Squares

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Deoxyribonucleic acid (DNA) is an important genetic substance in the organism, which plays a key role in cell proliferation, syn-thesis of proteins and transcription of genetic information in living cells [1]. The interactions of cationic porphyrins with nucleic acids have received considerable attention [2]. Several have clinical potential as anticancer agents in photodynamic therapy [3], probably as a consequence of their ability to selectively accumulate on the surface of tumor cells, become internalized, bind to genomic DNA, and then induce DNA strand cleavage.

In this study, interaction of 5, 10, 15, 20-tetrakis (4-N-heptyl-pyridyl) porphyrin Copper (II) (CuTHPyP) with calf-thymus DNA was studied in tris buffer and low ionic strength at 27 °C by spectroscopic method. The binding constant K and the stoichiometric coefficient of CuTHPyP with DNA were evaluated. Multivariate curve resolution-alternating least squares (MCR-ALS) chemometrics method was applied to resolve the combined spectroscopic data matrix, which was obtained by the UV–vis method. Pure spectra of CuTHPyP and CuTHPyP–DNA complex, and their concentration profiles were then successfully obtained.

Keywords: Multivariate curve resolutions; calf thymus DNA (ct-DNA); tetra-cationic porphyrin; UV-visible spectroscopie method; DNA-porphyrin interaction

References:

[1] S. Kashanian, Z. Shariati, H. Roshanfekr, S. Ghobadi, DNA and Cell biology 31 (7) (2012) 1341-1348.

[2] R. J. Fiel, J. Biomol. Struct. Dyn. 6(6) (1989) 1259-1274.

[3] A. Villanueva, L. Caggiari, G. Jori, C. Milanesi, J. Photochem. Photobiol., B 23(1) (1994) 49-56.

Spectroscopic Study on the Interaction between 5, 10, 15, 20-Tetrakis (4-N-Heptyl- Pyridyl) Porphyrin Tetrachloride and DNA Using Multivariate Curve Resolution-Alternating Least Squares

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Double-stranded deoxyribonucleic acid (dsDNA) consists of two molecular chains, where one chain is tightly bound to the other by numerous hydrogen bonds to form a double helix. DNA is a molecule that stores genetic information and is therefore the most important biological molecule [1]. Porphyrins are well studied compounds, and their chemical and photochemical properties have been widely used in medicine and biology. The application of porphyrins in photodynamic therapy due to the quality of accumulation in tumor cells highlights the importance of comprehension of porphyrin–DNA interactions [2, 3].

In this study, interaction of 5, 10, 15, 20-tetrakis (4-N-heptyl-pyridyl)porphyrin tetrachloride (THPyPCl$_4$) with calf-thymus DNA was studied in tris buffer and low ionic strength at 27°C by spectroscopic method. The binding constant K and the stoichiometric coefficient of THPyPCl4 with DNA were evaluated. Multivariate curve resolution-alternating least squares (MCR-ALS) chemometrics method was applied to resolve the combined spectroscopic data matrix, which was obtained by the UV–vis method. Pure spectra of THPyPCl$_4$ and THPyPCl$_4$–DNA complex, and their concentration profiles were then successfully obtained.

Keywords: Multivariate curve resolutions; calf thymus DNA (ct-DNA); tetra-cationic porphyrin; UV-visible spectroscopie method; DNA-porphyrin interaction

References:

[1] B. Armitage, Chemical Reviews 98(3) (1998) 1171-1200.
[2] L. G. Marzilli, New Journal of Chemistry 14(6-7) (1990) 409- 420.
[3] M. G. Vicente, Current Medicinal Chemistry-Anti-Cancer Agents 1(2) (2001) 175-194.

Simultaneous determination of cysteine and homocysteine by using their effects on the absorption spectrum of silver nanoparticles

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In this work a sensitive colorimetric method based on the shift in the position of plasmon peak of pvp-stabilized-AgNPs. was used to measure Cysteine and homocysteine in blood plasma. The reaction involves electrostatic interactions between the thiol molecules attached to the surface of the silver nanoparticles. The co-action between particles leads to a decrease in the plasmonic peak at 398 nm and rise of a new peak at 520 nm, resulting a color change from yellow to pink. Effective parameters including nanoparticle concentration, ionic strength, pH of solution and time were studied. Concentrations of these amino acids can be identified and measured by controlling the reaction conditions and the pH of the solution. Cysteine was measured at pH =4.0 and homocysteine measurment was made at pH = 7.5.

Calibration curve obtained by this method at 520 nm has a linear range of 1.0-8.0 µM (R=0.9972) with 0.6 µM detectoin limit for Cysteine and linear range of 1.5-11 µM (R=0.9966) with 0.9 µM detectoin limit for Homocysteine.

The possible interferences in the measurement process due to the presence of other species present in real samples were studied and it was found that the proposed procedures are free from interferences of most common interfering compounds.

Keywords Cysteine, Homocysteine, Polyvinyl pyrrolidone, Silver nanoparticles

Detection and quantification of peanut adulteration in almond powder using inductively coupled plasma optical emission spectrometry combined with chemometrics

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Food adulteration has been practiced since a long time ago and becomes increasingly in the last years more sophisticated. Food adulteration tends to be economically motivated and is achieved through the addition, substitution or removal of food ingredients. To guarantee food safety and quality, most analytical strategies are based on the knowledge of the contaminants. There is increasing demand for the development of fast, easy to use and low-cost analytical methods to test for adulteration. Almond (Prunus amygdalus) is classified as a drupe in which the edible seed or kernel is the commercial product. Its seeds are typically used as snack foods and its powder as ingredients in a variety of processed foods, notably bakery and confectionery products. The most frequent adulteration in almond powder is carried out with peanut because of its lower price. Trace metal profiling can be used to characterize a food products and it is also expected that adulteration could change the element profile of a particular food sample, such as nuts. In this work, the trace element profile of almond and peanut has been demonstrated by means of inductively coupled plasma optical emission measurement in combination with different chemometric approaches. The ability of multivariate analysis methods; such as principal component analysis (PCA), and linear discriminant analysis (LDA) to achieve discrimination of adulterated and pure almond samples from their elemental content have been investigated. The calculations were performed using 23 variables (contents of Al, B, Ba, Be, Bi, Ca, Cd, Co, Cr, Cu, Fe, Ga, K, Li, Mg, Mn, Na, Ni, Pb, Se, Sr, Te, Ti and Zn at $\mu g.g^{-1}$ level determined by ICP-OES). Additionally, the levels of peanut used to adulterate almond powder were successfully quantified using partial least squares. The predictive ability of the LDA and PLS models were evaluated by statistical parameters of the prediction set (98.0% classification accuracy of LDA and RMSEP of 2.18 for PLS model).

Keywords: Adulteration; Almond; ICP-OES; Chemometrics

Development of a Spectrophotometric Method for Determination of Sulfamethoxazole Based on Supermagnetic Solid Phase Extraction

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Sulfamethoxazole (SMX) has been employed as an antibacterial and antibiotic drug. It is used commonly in combination with trimethoprim [1, 2]. In this work, an efficient selective method is developed for the determination of SMX based on the combination of extraction with super magnetic Fe_3O_4 nanoparticles and analysis via ultraviolet spectrophotometry.

Iron oxide magnetic nanoparticles were prepared by co-precipitation method. The Fe_3O_4 nanoparticles enwrapped by the SiO_2 and further by polyaminoimide polymer. The magnetic molecularly polymer nanoparticles were characterized by Fourier transform infrared spectroscopy (FT-IR), scanning electron microscopy (SEM).

The prepared magnetic adsorbent is well dispersed in water and can be easily separated magnetically from the medium after loading with the adsorbate. Parameters affecting the extraction efficiency including extraction times, adsorbent dosage and pH, sample and solvent value have been investigated. The extracted SMX could be easily desorbed with ethanol and determined spectrometrically at 265 nm.

Under the optimum condition,a good linearity ($R^2 = 0.9997$) in calibration range of 0.05-50.0 mg L^{-} SMX were achieved. The relative standard deviation for triplicate runs ranged between 3 and 7%. This method was successfully applied to the analysis of trace levels of SMX in real samples as well as pharmaceutical samples.

Keywords sulfamethoxazole; Spectrophotometry; Supermagnetic micro extraction; Nanoparticles

References:

[1] K. Kargosha; S. H. Ahmadi; Analytical Letters, **1999**, 32,1613-1626.

[2] Ivana Cesarino; Vivian Cesarino; Marcos R.V. Lanza; Sensors and Actuators B, **2013**, 188, 1293–1299.

Simultaneous determination of resorcinol and hydroquinone in their binary mixture by novel spectrophotometric methods

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The simultaneous determination of isomers by spectrophotometric methods is not easy because of the existence of overlapping spectra. In this work, two spectrophotometric methods were developed for the simultaneous determination of resorcinol (RES)and hydroquinone (H_2Q), namely, the extended ratio subtraction method (EXRSM) and the simultaneous ratio subtraction method (SRSM). The simultaneous determination of the H_2Q and RES levels is of great necessity due to their co-existence in the environmental samples as environmental pollutants with high toxicity. RES and H_2Q are widely used in cosmetics, tanning, pesticides, flavoring agents, medicines, anti-oxidants, dyes, and photography chemicals.

Lotfy et al. have introduced the extended ratio subtraction method (EXRSM) and the simultaneous ratio subtraction method (SRSM). These methods were used in this work.

The effects of different parameters such as the pH and concentration of the divisor were investigated for both isomers in the two methods. For both methods, the linear concentration ranges for RES and H_2Q were 1-15 and 1-12 μg mL^{-1}, respectively. The developed methods were effectively used for analysis of various spiked water samples with different RES to H_2Q ratios. These methods are simple, sensitive, precise, and selective for the analysis of binary mixtures with overlapping spectra. They do not require a special program.

Keywords Hydroquinone, Resorcinol, Extended ratio subtraction, Simultaneous ratio subtraction

A New Colorimetric Turn on Method for Highly Selective Sensing of Silver Ion using Gold Nanoparticles

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Development of rapid and efficient methodologies for detection of heavy metal ions in environmental samples has been an important issue. Among them, Ag^+ is highly toxic for aquatic organisms. It can deactivate sulphydryl enzymes and accumulate in human body [1]. Traditional detection methods, such as atomic absorption spectroscopy and inductively coupled plasma-atomic emission spectroscopy, have been used to detect trace amounts of heavy metal ions. But these methods are time-consuming, require expensive instruments and complex procedures [2]. Therefore, it is essential to develop portable sensors that are easy to prepare, convenient to use and have high selectivity and sensitivity.

In recent years, much efforts have been made to prepare various kinds of heavy metal ion sensors, such as fluorescence based sensors, colorimetric sensors and ion selective electrodes [2]. Colorimetric measurements are particularly promising since they are simple and powerful methods enabling naked eye detection of the hazardous ion. However, a challenge is the fact that some of these probes have poor selectivity and are active in organic solvent. Therefore, it is important to develop a highly selective and sensitive colorimetric Ag^+ sensor.

Gold nanoparticles (AuNPs) have been widely used in the development of colorimetric probes for detecting metal ions, anions and biomolecules because of their unique optical properties. In this work, a sensitive and selective turn on colorimetric probe has been designed for Ag^+ detection based on using AuNPs. An aggregation of Au NPs caused by tris buffer in pH 7.5 was successfully prevented in the presence of Ag^+ ions. In fact, higher concentrations of Ag^+ ions keep Au NPs dispersed and the color of solution remains red. By decreasing the amount of Ag ions, the extent of complexation reaction between tris and Ag decreases. As a result, tris induces the Au NPs aggregation and the color of solution changes to blue. A linear range of 1-9 µM was obtained through UV-Vis measurements. As a distinct advantage, this sensor showed high selectivity and applicability for determination of silver ion in waste water samples.

Keywords: Colorimetric sensors, Gold nanoparticles; Silver ion

References:

[1] C.-G. Yang, M. Zhang, and Z.-R. Xu, Anal. Methods, 7 (2015) 1110.
[2] X. Xing, H. Yang, M. Tao, and W. Zhang, J. Hazard. Mater., 297(2015) 207.

Multivariate thermometry by nucleic acid-based fluorescent nano-probes

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Immobilization of molecular beacons (MBs) with different stabilities and fluorophores on gold nanoparticles (AuNPs), results in biocompatible nano-assemblies as promising sensors for wide range low resolution thermometry. Univariate calibration melting curves, as other single wavelength fluorescence readouts, could strongly be affected by noise and other difficult to control variations in complex environments like biological systems and microdevices. In this paper, by the aid of improving the performance the proposed nano-thermometers in terms of accuracy and precision, multivariate data sets were employed to obtain melting curves. Two-way and three-way data sets were acquired by recording emission spectra and excitation-emission landscapes, respectively. Nonnegative matrix factorization (NMF) and parallel factor analysis (PARAFAC) were the employed multivariate techniques to achieve melting curves. To find the best descriptive calibration equations for temperature prediction, polynomial equations were fitted to the derived melting curves. The prediction errors for multivariate thermometry are considerably lower than those of univariate thermometry. In addition to higher accuracy, the superior repeatability and reproducibility of multivariate results, particularly for PARAFAC, is a sign of the improved robustness and precision of regarding melting curves. The obtained results recommend the employment of multivariate data and techniques to enhance the performance of similar fluorescent nano-probes.

Keywords: nano-thermometers; multivariate thermometry; univariate thermometry; multiway techniques; fluorescence spectroscopy

References:

[1] S. Ebrahimi, Y. Akhlaghi, M. Kompany-Zareh, A. Rinnan, ACS nano 8 (2014) 10372.

[2] C. Kang, H. L. Wu, S. X. Xiang, L. X. Xie, Y. J. Liu, Y. J. Yu, R. Q. Yu, Analytical Methods 6 (2014) 6358.

Determination of sodium dodecyl sulfate by using chemiluminescence reaction of graphene quantum dots

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Chemiluminescence (CL) is the emission of electromagnetic radiation (usually visible and near-infrared region) from a chemical reaction which is usually exothermic [1]. Generally, the analytical methods based on CL reactions can be used for determination of various substances such as pharmaceuticals, metal cations and environmental pollutants, among others. In this study, we report the application of CL reaction of graphene quantum dots (GQDs) for measurement of sodium dodecyl sulfate (SDS).To this aim, GQDs were simply synthesized by pyrolysis of glucose [2]. Then, the prepared GQDs were characterized by ultraviolet and visible (UV-VIS) spectroscopy, fourier transform infrared (FTIR) spectroscopy, X-ray diffraction (XRD) and also transmission electron microscopy (TEM). It was found that GQDs in the presence of cetyltrimethylammonium bromide (CTMAB) and in alkaline medium led to emission of light. In order to obtain highest light emission, the concentrations of reactants involved in the CL reaction were optimized. After optimization, our preliminary tests revealed that SDS could inhibit the CL reaction of GQDs. The inhibitory effect of SDS was linearly proportional with concentration of SDS in the range of $3.5 \times 10^{-3} – 5.2 \times 10^{-2}$ mol/L. The limit of detection of CL method and its relative standard deviation were 1.1×10^{-3} mol/L and 2% (n=5), respectively. The method possessed acceptable selectivity and can be exploited for determination of SDS in various water samples beside to detergent samples.

Keywords: Chemiluminescence; Graphene quantum dots; Sodium dodecyl sulfate; Carbon nanostructures.

References:

[1] M. Iranifam, M.A. Segundo, J.L. M. Santos, J.L. F. C. Limab, M.H. Sorouraddin, Luminescence 25(2010) 409.
[2] T.Hallaj, M.Amjadi, J.L. Manzoori, R.Shokri, Micro Chim. Acta 182(2014)789.

Lysozyme adsorption from aqueous solution using new magnetitenano-bio-adsorbent Fe_3O_4@Isinglass

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The efficient adsorption and purification of proteins has become essential for recentadvancements in biomedical and pharmaceutical research.Knowledge of single protein adsorption is helpful fordeveloping suitable adsorbents for protein separation incomplicated natural systems.In this study, lysozyme due to its physiologicalandpharmaceuticalfunctions, such as, antibacterial and antiviruswas selected as model proteininto investigate its adsorptionontomagnetite/isinglass (Fe_3O_4/IG) composite. For this purpose, a magnetite/isinglass (Fe_3O_4/IG) composite was synthesized and characterized by Fourier transform infrared spectrometer (FTIR), transmission electron microscopy (TEM), scanningelectronic microscope (SEM),vibrating- sample magnetometer (VSM) and Brunauer-Emmett-Teller (BET) analysis. Then, the composite was used as a magnetic adsorbent for lysozyme adsorption from aqueous solutionsby UV-Visible spectroscopy at 280 nm. The effect of pH, ionic strength, adsorptiontime, initial lysozyme concentration and adsorbent dosage on the adsorption of lysozyme from aqueous solutions using batch adsorption process was investigated. The optimal conditions were equilibrium time=90 min, pH=5.8, initial concentration of lysozyme=0.5 mg/ml, adsorbent dosage=15 mg and ionicstrength=0. Themaximum binding capacity of lysozyme was about 137 mg/g Fe_3O_4/IG.Pseudo-second-order kinetic model was found to be the best fit.The relative standard deviation (RSD %) value with three replicates under optimized conditions was 4.95 %. Finally, the mixture of lysozyme and bovine serum albumin (BSA) was used as model proteins to investigate the selectivity of the lysozyme adsorption. TheSodiumdodecyl sulfate polyacrylamide gel electrophoresis (SDS–PAGE) analysis showed that adsorption of lysozyme from protein mixture is selective.

Keywords: Lysozyme adsorption, protein separation, magnetite/isinglass nanoparticles

Preparation, characterization and evaluation of water-soluble L-cysteine-capped-ZnS quantum dots as fluorescence probe for detection of butachlor as popular agricultural chloroacetanilide herbicide

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Quantum dots (QDs) are colloidal nanocrystalline semiconductors possessing unique properties due to quantum confinement effects. In recent years, QDs with water solubility and good photoluminescence stability become a new class of fluorescent probes for many biological applications. It possesses several qualities that make them very attractive for fluorescent tagging: broad excitation spectrum, narrow emission spectrum, precise tenability of their emission peak, longer fluorescence lifetime than organic fluorophores and negligible photobleaching.

In this work water-soluble L-cysteine-capped-ZnS nanoparticles were prepared in aqueous solution at room temperature through a straightforward one-pot process by using safe and low cost inorganic salts as precursors, and characterized by TEM, XRD, spectrofluorometry and UV-Visible spectrophotometry. The prepared L-cysteine-capped ZnS Quantum dots was used as a novel fluorescent sensor for herbicide butachlor recognition. Preliminarily studies showed that fluorescence enhancement of the L-cysteine-capped-ZnS nanoparticles depends on the concentration of butachlor solution and any change in fluorescence intensity was directly proportional to the concentration of butachlor. Fluorescence enhancement was observed at pH 4.4 with the excitation and emission wavelengths of 265 nm and 359 nm, respectively. Under optimum conditions, the linear range for the detection of butachlor was 1.07×10^{-6} to 3.35×10^{-3} ppm with a detection limit of 1.36×10^{-7} ppm. Enhancement of its fluorescence due to butachlor at 3.5×10^{-6} ppm level was unaffected by the presence of excesses amounts of other common agricultural pesticides. The proposed fluorescent sensor was successfully used for determination of butachlor in natural water and soil samples.

Keywords: Butachlor, Fluorescence probe, Nanoparticles, Quantum dots

A green off-on fluorescent probe based on one-pot synthesis of carbon quantum dots for specific detection of mercury (II) ions

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Mercury (II) ions is one of the most prevalent toxic heavy metal which lead to environmental pollution, bio organism damaging and etc. so development of analytical protocols to detect Mercury (II) ions is highly desired. In this research, a facile and novel fluorescent probe has been designed based on carbon quantum dots prepared by carbonization of the Prosopis juliflora leaves as a precursor source. The unmodified carbon quantum dots exhibits a blue luminescence with a 5% quantum yield. The synthesis protocol was easily performed with one pot rapid process. The off fluorescent is observed in the presence of mercury (II) which is specifically recovered with the addition of a Succimer drug. The gradually recovered fluorescence is due to the high affinity of chelating property of Succimer drug towards mercury (II) with a good restoration. The effective parameters such as pH, buffer and reagents concentration on the fluorescence signal were tested. Subsequently two linear calibration graph were obtained over a wide range of 10-500 ng mL^{-1} (LOD= 5.43 ng mL^{-1}) for mercury (II) under optimal condition. The relative standard deviation for mercury (II) determination according to this reliable method were less than 3% (n=10). Our proposed green probe has been successfully applied for trace mercury detection in environmental samples.

Keywords: Carbon quantum dots; Succimer; mercury (II); off-on fluorescence

References:

[1] X. Cui, L. Zhu, J. Wu, Y. Hou, biosensor and bioelectronics, **2015,** 63, 506–512.
[2] J. Hou, F. Zhang, X. Yan, L. Wang, J. Yan, H. Ding. Anal. Chem. Acta. **2015**, 859, 72-78.
[3] A. Konwar, N. Gogoi, G. Majumdar, D. Chowdhury. Carbohydrate Polymers. **2015**, 115,238-245

A novel determination of rare earth element (Dy) in water samples using ICP-MS after flotation-assisted homogeneous liquid-liquid microextraction

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In this study, a method based on floatation assistance of homogeneous liquid-liquid microextraction (FA-HLLME) combined with inductively coupled plasma-mass spectroscopy (ICP-MS) was proposed for determination of trace Dysprosium as rare earth element in water samples [1-3]. As one of the miniaturized separation and extraction techniques, homogenous liquid–liquid microextraction (HLLME) has been widely applied in the field of environmental monitoring and assessment. DMVPA (Di-Methyl phenyl phosphonate) was used as the complexing agent and 1-Octanol and Acetone were selected as extraction and homogeneous solvents, respectively. The factors that influenced the extraction efficiency for Dysprosium determination (including pH, extraction and homogeneous solvents, concentration of DMVPA and NaCl, extraction time) were studied statistically. Under the optimum conditions (pH=7.0, 140 μL 1-Octanol, 1.0 mL Acetone,2.045×10^{-4} mol L^{-1} DMVPA, 2.0 mol L^{-1} NaCl and 60 sec of extraction time), the linear dynamic range for Dysprosium determination was 10.0 - 300.0 ng L^{-1} (R^2=0.9982) with limit of detection (LOD) for Dysprosium was 4.81 ng L^{-1}. The relative standard deviation (R.S.D.) (C=60 ng L^{-1}, n=7) was 1.82%and the enrichment factor of 166 for Dysprosium extraction. The proposed method was successfully applied to determination of Dysprosium in different water samples.

Keywords: Dysprosium; Rare earth element; Determination; FA-HLLME; ICP-MS

References:

[1] S. Veyseh, A. Niazi, Talanta, 147 (2016) 117.
[2] A. Niazi, N. Khorshidi, P. Ghaemmaghamei, Spectrochim. Acta Part A, 135 (2015) 69.
[3] A. Niazi, S. Habibi, M. Ramezani, Arabian J. Chem., 8 (2015) 706.

Geochemometrics classification of soil samples in Behabad region by analysis of uranium and thorium by ICP-MS

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Inductively coupled plasma mass spectrometry was used to determine the uranium and thorium composition of 150 soil samples of Behabad city Region in Iran. The achieve geochemometrics classification of the soils by their elemental composition; cluster analysis (CA) and principal component analysis (PCA) were used for multivariate statistical modeling of the input data [1, 2]. CA displays the object similarity. The search for natural groupings in the samples was one of the main ways to study the structure of the data. PCA was used as a descriptive tool to visualize the data in two dimensions, finding relationship between the variables and honey sample. Prior the geochemometrics processing the data matrix was autoscaled. Mainly supervised pattern recognition techniques, such as LDA and C&RT were performed for the whole data set in order to discriminate and classify soil samples according to their origin and detect corresponding to region. Analyzes revealed an excellent separation between soil samples according to their type with the efficiency of LDA model as 100%. In conclusion, this study achieved satisfactory discrimination among soil samples from Behabad region of Iran by uranium and thorium analysis using ICP-MS. The data obtained and related to concentrations of elements in different soil samples was used for their classification by means of the pattern recognition.

Keywords: Geochemometrics; Classification; Uranium; Thorium; ICP-MS

References:

[1] M. Chudzinska, D. Baralkiewicz, Food Chem. Toxi *49* (2011) 2741-2749.
[2] J.C. Raposo, P. Navarro, A. Sarmeiento, Microchem. J. 116 (2014) 125-134.

Evaluation of FA-HLLME for trace quantitative of Europium rare earth element in water samples by ICP-MS

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This work aims at monitoring the rare earth elements (REE) on water samples based on floatation assistance of homogeneous liquid-liquid microextraction (FA-HLLME) combined with inductively coupled plasma-mass spectroscopy (ICP-MS) was proposed for determination of trace Europium in water samples. As one of the miniaturized separation and extraction techniques, homogenous liquid–liquid microextraction (HLLME) has been widely applied in the field of environmental monitoring and assessment [1, 2]. PAN (1,2-pyridylazo-2-naphthol) was used as the complexing agent and toluene and methanol were selected as extraction and homogeneous solvents, respectively. The factors that influenced the extraction efficiency for Europium determination (including pH, extraction and homogeneous solvents, concentration of PAN and NaCl, extraction time) were studied statistically. Under the optimum conditions (pH=8.0, 170 µL toluene, 0.75 mL methanol, 180 microlitre PAN, 2.5 mol L^{-1} NaCl and 60 sec of extraction time), the linear dynamic range for Europium determination was 2.5-600 µg L^{-1} (R^2=0.9987) with limit of detection (LOD) for Europium was 1.157 ng L^{-1}. The relative standard deviation (R.S.D.) (C=50 ng L^{-1}, n=7) was 2.206% and the enrichment factor of 429 for Europium extraction. The proposed method was successfully applied to determination of Europiumin different water samples.

Keywords: Europium; Determination; RRE; FA-HLLME; ICP-MS; Watersamples

References:

[1] S. Veyseh, A. Niazi, Talanta, 147 (2016) 117-123.
[2] A. Scott, Chemical Geology, 82 (1990) 159.

Thin film pH optical sensor based on phenol red entrapped in sol-gel matrix

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In this study, an optical sensor for pH measurement was designed based on thin film sol–gel process using phenol red as indicator. The sol–gel process is a simple way to produce a silica network through hydrolysis and subsequent condensation of silicon alkoxides at low temperatures. Sol–gel glass is well suited as a support matrix which provides a chemically and physically stable environment with excellent optical clarity, and can be cast into both monoliths and thin films. Pure silica xerogels contain a relatively high concentration of unreacted surface silanol groups that continue to condense long after the gel is dry. This leads to shrinking and cracking of the thin film. One approach to improve shrinkage of films is addition of organo-silane coupling agents. However, analyte diffusion may be hindered as well, resulting in a long response time using mentioned methodologies for improving leaching and shrinkage of sol-gel films. In this study, we evaluated the effect of addition of ionic liquid [C_4mim][Cl] as a drying control chemical additive in the synthesis of silica sol–gel thin films. The behavior of phenol red entrapped in sol-gel matrix was investigated. The thin films were prepared through the sol–gel process by means of hydrolysis and acid catalyzed reaction of tetraethoxysilane and vinyltriethoxysilane with the ionic liquid [C_4mim][Cl]. The analytical performance of the prepared sensor in ionic liquid modified sol-gel matrix was compared with unmodified one. Prepared pH sensor is suitable for wide pH range measurements between 7.0 and 13.0. The obtained sensor is crack free and exhibits great performance for measuring pH in wide linear dynamic range, fast response time, less than 1 min, good reversibility and stability.

Keywords: pH sensor; Sol- gel; Phenol red; Ionic liquid; Thin film.

References:

[1] Á.P. Timbó, P.V. F. Pinto, H.A. Pinho, L.P. de Moura, J. B. Chretien, F.W. Viana, R.G. D. Filho, E. Silva, M.E. da Silva, J.W. M. Menezes, G. de Freitas Guimarães, W.B. Fraga, *Sens. Actuator B-Chem.* 223 (2016) 406-410.
[2] X. Z. Sun, C.B. White, Z.W. Yu, L.M. Zhu, *J. Sol-Gel Sci. Technol.* 74 (2015) 641-649.
[3] Z. Liu, J. Liu, T. Chen, *Sens. Actuator B-Chem.* 107 (2005) 311-316.

Effect of morphine on resonance light scattering properties of Au@Fe_3O_4 nanoparticles: Investigation possibility of morphine determination in the presence of thebaine

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Resonance light scattering (RLS) spectroscopy, is a simple and sensitive analytical tool, which has been extensively used for various (bio)analytical tasks. Since RLS intensity depends on the molar absorptivity as well as the size of the scatter, it is particularly useful in studying the aggregation of chromophores in various chemical and biological systems [1, 2]. Morphine and thebaine are naturally occurring alkaloids in poppy seeds, have long been used as a drug, and is also abused .As drug, morphine is used as an effective analgesic in the treatment of severe pain and codeine is widely used as a cough suppressant and moderate pain reliever too. But excessive or habitual use of these drugs causes toxic symptoms.

In this work, a new method was investigeted for the determination of morphine in presence of thebaine, using Au nanoparticles coated on the surface of Fe_3O_4 (AuNPs@Fe_3O_4) -based resonance light scattering (RLS) technique. Light scattering properties of the synthesized nanoparticles in the presence or absence of drugs have been selected as the detection signal. In this regard, resonance light scattering has been used as the detection method. RLS intensity was obtained by the synchronous scanning at $\lambda_{ex} = \lambda_{em}$ (Δ= 0 nm). The addition of these drugs to nanoparticles solution in acidic medium leads to the aggregation of nanoparticles, which, in turn, causes a marked enhancement in RLS intensity at 400 nm.The effects of important experimental factors such as pH, concentration of nanoparticles and ultrasonic time on RLS signal were investigated and optimized. Under the optimum conditions, the calibration graphs were linear in the range of 0.05 – 5.00 and 0.1 – 8.0 mg L^{-1}, for morphine and thebaine, respectively with corresponding limits of detection of 0.037 mg L^{-1} and 0.12 mg L^{-1}

Keywords: Fe_3O_4 (AuNPs@Fe_3O_4); Light scattering; Morphine; Spectrophotometry; Thebaine

References:

[1] M. Ahmadi, T. Madrakian, A. Afkhami, *Anal. Chim. Acta*, 2014, 852, 250-256
[2] M. Ahmadi, T. Madrakian, A. Afkhami, *Sens. Actuators, B*, 2015, 210, 439–445.

Simultaneous Removal of Binary Mixture of Basic Blue 41(BB) and Toluidinblue O (TO) Using Derivative Spectrophotometric Determination, Multivariate Optimization and Adsorption Characterization of Dyes on Magnetic Nano Particle Modified by Poly Dopamine.

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Novel core–shell Fe_3O_4@poly (dopamine) magnetic nanoparticles were prepared through an in situ self polymerization method [1]. The present study deals with the simultaneous removal of basic blue 41 and toluidinblue O by Fe_3O_4@poly (dopamine) magnetic nanoparticles.

The utilization of magnetic nanoparticles with dopamine as a novel organic coating material and efficient adsorbent is successfully carried out to remove two cationic dyes from aqueous solutions in binary batch systems. A first-order derivative spectrophotometric method is developed for the simultaneous determination of BB and TO in binary solutions[2]. The linear concentration range and limits of detection for the simultaneous determination of BB and TO were found to be: 1–20, 1–15 mg/L, 0.3 and 0.5 mg/L, respectively. The influence of various parameters, such as contact time, initial concentration of dyes and sorbent mass on the dye adsorption is investigated. A response surface methodology achieved through performing the central composite design (CCD) is utilized to optimize the removal of dyes by surfactant-modified nanoparticle alumina through a batch adsorption process [3]. The proposed quadratic model resulting from the CCD approach fitted very well with the experimental data.

Under the selected conditions, two linear calibration graphs of TO and BB were obtained in the range of 100–325 and 100–400 mgL^{-1}, with the correlation coefficients of greater than 0.999 respectively.

Furthermore, XRD, FT-IR analysis, thermodynamic, isotherms and kinetics of adsorption were also explored.

Keywords: Dye removal; magnetic Nanoparticles; Poly Dopamine; Central composite design;

Reference:

[1]M. Mart´ın, P. Salazar, R. Villalonga, S. Campuzano, J.M.Pingarr´on and J. L. Gonz´alez-Mora, J. Mater. Chem. B, (**2014**), 2,739.

[2] J. Zolgharnein, M. Bagtash, T. Shariatmanesh, Molecular and Biomolecular Spectroscopy ,137 ,(**2015**), 1016–1028.

[3] J. Zolgharnein , A.Shahmoradi, J. Chem. Eng. Data,(**2010**), 55, 5040–5049.

Colorimetric Detection of Formaldehyde in Water Samples Using Silver Nano Particles and UV/Vis spectrophotometry

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Plasmon resonance scattering (PRS) is a new, sensitive and simple spectral analytical technique, and applies to determination of trace substances with satisfactory results. It has been reported that some metal nanoparticles (NPs) such as nanosilver exhibited a particular optical and electronic properties, and were utilized to nano-analytical chemistry [1, 2]. Formaldehyde is a common environmental pollutant from industrial activities, incinerators and car exhaust emissions. A PRS method is proposed for determination of Formaldehyde in water samples, based on the aggregation of AgNPs by it. As well known, AgNPs solution exhibit a strong PRS signal at 392nm, we found that a PRS signal quenching happened in the presence of Formaldehyde, and the quenching was proportional to the Formaldehyde concentration. Also the AgNPs solution color change in the range of golden to brown due to the formation of aggregates can be easily observed with the naked eye. A typical analysis was carried out by following steps. 0.5 ml AgNPs solution and 0.5 ml of 0.05 M phosphoric acid-sodium hydroxide buffer (pH 5.5) were diluted to 3.5 ml by doubly distilled water. This solution transferred to a 1 cm path-length cell and its absorption spectra was recorded. Then small volumes of Formaldehyde solution were added to the solution and allowed to react for 40 min at room temperature. Absorption spectra of the reacted solutions were recorded, and the amount of quenching (ΔA) was followed as the analytical signal. Influence of time of interaction and pH on ΔA were evaluated. Under optimized conditions the calibration graph was linear in the range of 0.3-30 $\mu g.l^{-1}$ and the correlation coefficient was 0.995, with a detection limit of 0.18 $\mu g\ l^{-1}$. The recovery of formaldehyde was more than %93.

Keywords: Formaldehyde, Plasmon resonance scattering, Silver nanoparticles

References:

[1] Lin, Y., Chen, C., Wang, C., Pu, F., Ren, J., Qu, X., Chem. Commun., 47 ,pp. 1181–1183,2011.
[2] Kang, C. Y., Xi. D. L., Yuan-Yuan, Chen., Zhi Liang. J., Talanta, pp. 867-870, 2008.

Preparation of molecularly imprinted polymer with carbon nanotubes for selective separation and spectrophotometric determination of L-cysteine

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A new molecularly imprinted polymer coated on carbon nanotubes (MIPs/MWNTs) was synthesized. The L-Cys-MIP are prepared by dissolving s amounts of L-Cys in 35 acetonitrile as a porogen solvent in the presence of ethylene glycol-dimethacrylate (EGDMA) as cross-linking, acrylic acid (AA) as functional monomer, and 2,2-azobisisobutyronitrile (AIBN) as initiator. The synthesized MIPs were characterized by scanning electron microscopy, Xray diffraction, Fourier transform infrared spectroscopy, spectrophotometry and thermal analysis techniques. The application of this sorbent was investigated in preconcentration and determination with a simple and selective spectrophotometric method with charge transfer of DDQ and low concentrations of L-Cys. Furthermore, For achieving optimal preconcentration and reducting non specific interactions, various parameters affecting the extraction efficiency were evaluated. Under the optimized conditions, An excellent linearity was found within the wide range of 3.0–200 ng ml^{-1}with coefficient of determination (r^2) > 0.993 and the limit of detection was found to be 1.5 ng mL^{-1}. Validation of the presented method was performed by analysing several standard reference materials with certified L-Cys concentrations and apple.

Keywords: DDQ; Spectrophotometry; molecularly imprinted polymer; carbon nanotubes.

References:

[1] Y. Lai, A. Ganguly, L. Chen, K. Chen, Biosens. Bioelectron. 26 (2010) 1688–1691.
[2] S. Mitchell, G. Steventon, Drug Metab. Rev. 44 (2012) 129–147.
[3] L. Chang, T. Wu, F. Chen, Microchim. Acta 177 (2012) 295–300.

Application of Modificated Magnetic Nanoparticles in Drug Delivery

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One of the most common types of magnetic nanoparticles and nanomaterials are creating their own unique features specific performance relative to the other nanostructures. These particles are used in various branches. But their role in the environment - particularly in the field of drug delivery medical remarkable that for the inherent magnetism of many things, including its acquisition facilitates the delivery is very important. In this study, beta cyclodextrin grafted magnetic nanoparticles were used for testosterone drug delivery. Magnetic nanoparticles were synthesized by co-precipitation method. Magnetic nanoparticles tend to agglomerate due to their small size and magnetic properties. thus, modification is necessary to avoid agglomeration and increase blood circulation longtitude. Here, magnetic nanoparticles were modified whit aminopropyltrimetoxy silane (APTS) to form silane-iron core-shell and then coupled with beta cyclodextrin. The Synthesized nanoparticles were characterized by Scanning Electron Microscopy (SEM), Nuclear Magnetic Resonance (NMR), Fourier Transform Infra-Red (FT-IR) spectroscopy and Analysis Thermo Gravimetric (TGA) methods.SEM Results showed that the nano particles had mean diameter of 40 nano meter. FT-IR result revealed magnetic nanoparticles formation, APTS modification and β-CD grafting on nanoparticles. The resulting nanoparticles were then employed as carrier for testosterone. The solution absorbance measurements were performed by absorption in UV-Vis spectroscopy and results were studied. The parameters affecting drug loading efficiency including drug concentration, carrier amount and solvent were optimized. Drug release behavior was studied in phosphide buffer 0.01 M, pH 7.4 at (37 ^{o}C) .results indicate that the carrier had sustained release behavior.

Keywords: Cyclodextrin, Drug delivery, Magnetic, testosterone

Reference:

[1]. M. C. Roco, Handbook on Nanosci. & tech. 2 (2007) 3.1_3.26.
[2]. S. K. Sahoo, S. Parveen, J.J Panda, Nanomedicine. 3 (2007) 20_31.
[3]. R. Lillard, J. Exp. Mol. Pathol. 86 (2008) 215_223

A Novel Colorimetric Sensor for Sensitive Determination of R-Citalopram Based on Its Plasmonic Interaction with Silver Nanoparticles

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Chiral recognition is among the important and special modes of molecular recognition [1]. It is highly desirable to develop a simple, rapid, sensitive, and high throughput routine assay for chiral recognition. Recent years have witnessed the development of utilizing AgNPs and AuNPs [1]. The key factor is the chiral molecules adsorbed on the nanoparticles surface. These nanoparticles-based colorimetric methods for chiral recognition need modifying chiral molecules on to nanoparticles and separating the unmodified nanoparticles or surplus chiral molecules. It is known that AuNPs and AgNPs themselves exhibit inherent chirality [2]. May be, the AuNPs or AgNPs without chiral molecules modification can be used for chiral discrimination.

The antidepressant citalopram is a highly selective serotonin reuptake inhibitor that is primarily prescribed for the treatment of depression. In vitro studies in rat brains have shown that the pharmacological effect of citalopram primarily lies on the S-CIT enantiomer, whereas the R-CIT enantiomer is considered to be pharmacologically inactive.

In this study a novel, simple and rapid method has been developed for determination of CIT enantiomers. It is based on the inherent chirality of AgNPs [2] and decreasing of surface plasmon resonance (SPR) band intensity at 390.0 nm and a new absorbance peak at 570.0 nm. The experimental conditions were optimized and the results showed that R-citalopram can be determined in a linear range from 7.6×10^{-9} to 1.7×10^{-4} Mwith correlation coefficients of 0.9952 and LOD3.0×10^{-9} M.

Keywords: Chiral recognition; citalopram enantiomers; silver nanoparticles

Reference:

[1] Y. Kubo, Sy Maeda, S. Tokita, M. Kubo, Nature, 8 (1996) 522.
[2] C. Liu, B. Li, C. Xu, Microchim. Acta, 181 (2014)1407.

A highly sensitive colorimetric sensor for isopernaline detection based on organic molecules-functionalized gold nanoparticles

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In this work, we developed a simple, rapid and sensitive colorimetric method for the determination of isopernaline, based on 2-Amino-5-mercapto-1,3,4-thiadiazol (AMTD) functionalized gold nanoparticles. Isopernaline could induce the aggregation of the AMTD-AuNPs through hydrogen-bonding interactions, which caused the colloidal solution changed from red to blue. This change can be seen with bare eyes, and monitored by UV-vis spectroscopy and transmission electron microscopy. The linearity of the calibration graph was found over the concentration range of 0.2 µM to 180 µM with a correlation coefficient of 0.99. Under the optimum experimental conditions, the detection limit was found to be 60 nM and the relative standard deviation was obtained 1.5% for the determination of 100 µM isopernaline (n=10). The present method was successfully used for the determination of isopernaline in human serum sample.

Keywords: 2-Amino-5-mercapto-1,3,4-thiadiazol, colorimetric detection, isopernaline, gold nanoparticles

References:

[1] Zh. Chen, Y. Hu, Q. Yang, Ch. Wan, Sensors and Actuators B 207 (2015) 277.
[2] J. Feng, H. Guo, Y. Li, Y. Wang, W, Chen, A. Wang, Applied Materials and Interfaces 5 (2013)1226.
[3] S. Shahrokhiana, M. Khafaji, Electrochimica Acta 55 (2010) 9090.

Selective and sensitive speciation analysis of Cr(VI) and Cr(III) in water samples at sub-μg L^{-1} level by electrothermal atomic absorption spectrometry after electromembrane extraction using complexation with 1,5-diphenylcarbazide.

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EME as an alternative to hollow fiber-liquid phase microextraction (HF-LPME) was introduced by Pedersen-Bjergaard in the year 2006 . In this method, the applied electrical potential across the supported liquid membrane (SLM) can be acted as a powerful driving force for migration of charged species toward the electrode of opposite charge in the acceptor phase. In this work the electromembrane extraction followed by electrothermal atomic absorption spectrometry (ET-AAS) for extraction and preconcentration of Cr(VI) and Cr(III) in water samples was studied. In this method, 1,5-diphenylcarbazide (DPC), a selective complexing agent for Cr(VI) was used. The Cr(III) was extracted based on the electrokinetic migration of cationic complex toward the negative electrode within the hollow fiber. On the other hand, Cr(III) ions were determined by this procedure following the oxidation to Cr(VI). Mass transfer of Cr(VI) ions across the SLM was enhanced by complex formation with the1,5-diphenylcarbazide.The effects of extraction parameters including pH, type of organic solvent, chelating agent concentration, stirring rate, time of extraction and applied voltage were investigated. Under the optimized conditions, the analyte was quantified by ET-AAS Spectrometer, with acceptable linearity range from 0.05 to 2 ng mL^{-1}(R^2 value = 0.996), and repeatability (%RSD) between 3.7% and 11.3% (n = 4) for 5.0 and 1.0 ng mL^{-1}Cr(VI) solutions respectively. Also, enrichment factor of 100 that corresponded to recovery 60% was achieved. The estimated detection limit (S/N ratio of 3:1) was 0.02 ng mL^{-1}. Finally, the proposed method was successfully applied to determine Cr(III) and Cr(VI) species in some real water samples.

Keywords: Electromembrane extraction (EME); 1,5-diphenylcarbazide (DPC); electrothermal atomic absorption spectrometry (ET-AAS)

Competitive ^{7}Li NMR study of the stoichiometry, stability and hermodynamic data for the complexation of metal ions with two asymmetrical branched (N_3O) containing pyridine moiety in ionic liquid-acetonitrile mixtures

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Lithium-7 NMR spectroscopy was used to investigate the stoichiometry, stability and thermodynamic data of a Li^+ complex with two asymmetrical branched amines, 2-(2-amino ethyl) pyridine – yl - methyl amino ethanol (A^1) and 2-(2-amino propyl) pyridine – yl - methyl amino ethanol (A^2) in 25-25, 50-50, 75-25 and 100-0 wt% acetonitrile (AN)- [BMIM][PF_6] (ionic liquid) mixture solution at various temperatures. A competitive ^{7}Li NMR method was also employed to probe the complexation of Li^+, Co^{2+}, Ni^{2+}, and Cu^{2+} ions with A^1 and A^2 in the same solvent systems (Scheme 1). The formation constants of the resulting complexes were evaluated from computer fitting of the mole ratio data to an equation that relates the observed chemical shifts to the formation constant. There is an inverse relationship between the complex stability and the amount of ionic liquid in the solvent mixtures [1]. In the all studied solvent mixtures, the stability of the resulting 1:1 complexes was found to vary in the order $Cu^{2+} > Ni^{2+} > Co^{2+} > Li^+$. The resulting complexes with the amines A^1 and A^2 vary in the order of $MA^1 > MA^2$. This is due to the fact that the amines, A^1 and A^2 differ in the size of their central chelate rings so that they can form five and six membered rings, respectively. As it is well documented in the complexes forming a six-membered chelate ring are expected to be less stable than those forming a five-membered chelate ring. The temperature dependence formation constant was used for the evaluation of the enthalpy and entropy values for the complexation reaction. It was concluded that in all complexes, except for lithium ion, the resulting complex enthalpy is stabilized and the ΔH compensates the $T\Delta S$ contribution [2].

Keyword: ^{7}Li NMR; Stability; Metal ions

References:

[1] G. Herlem, P. Tran-Van, P. Marque, S. Fantini, J.F. Penneau, B. Fahys, *J. Power Sources*,2002,**107**,80.
[2] M. Shamsipur, M. Irandoust, K. Alizadeh, V. Lippolis, *J. Incl. Phenom.Macrocycl. Chem.*,2007,**59**,203.

Application of Tungsten Alloys as New Cathodic Materials for Detection of Thallium Using Electrochemical Hydride Generation - Graphite Furnace Atomic Absorption Spectrometry

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The choice of a suitable cathode material is of paramount importance in construction of electrochemical hydride generation (ECHG) electrolytic cell. Usually, cathode materials with high hydrogen over-voltage are used for this purpose[1]. In the present research, new cathodic materials based on tungsten alloys are introduced to be used in electrochemical hydride generation (ECHG) coupled to graphite furnace atomic absorption spectrometry (GFAAS) for determination of thallium in tap water. In comparison to other cathodic materials used to date for electrochemical hydride generation of thallium, performance of the tungsten alloys cathodes is substantially better in the following aspects: higher interference tolerance, higher corrosion resistance and longer useful working time. Experimental design as a powerful, practical and useful tool can use for screening and optimization of effective factor in analytical methods[2]. Here, the Plackett–Burman design was applied for screening of effective variables on electrochemical hydride generation of Thallium. Electrolysis time, electric current, carrier gas flow, catholyte concentration, temperature of atomizer were proved to be significant factors. These parameters were optimized by using the central composite optimization design and the response surface equations were derived. Under optimum conditions, the calibration plot was constructed which was linear in the range of 0.05-0.3 ng mL^{-1} for thallium. The limit of detection (LOD) of the method was found to be 0.014 ng mL^{-1}. Also, the relative standard deviation of the method was 1.8% (RSD, n = 7). Finally, the applicability of the method for determination of thallium in spiked tap water has been reported.

Keywords: Thallium; Electrochemical hydride generation; Tungsten alloys; Graphite furnace atomic absorption spectrometry.

References:

[1] M.H. Arbab-Zavar, M. Chamsaz, A. Yousefi, N. Ashraf, Talanta 79 (2009) 302.

[2] F. Kamarei, H. Ebrahimzadeh, Y. Yamini, Talanta 83 (2010) 36.

Determination of triton X 100 by using chemiluminescence reaction of graphene quantum dots

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Graphene quantum dots (GQDs) are small fluorescent nanoparticles with unique properties that make them attractive tools for research in various scientific fields. Graphene has attracted increasing attention among the scientific community ever since it was isolated as a single layer of material from highly oriented pyrolytic graphite (HOPG) in 2004 by Novoselov and Geim using the “Scotch-tape method”. GQDs, as defined, are a kind of 0D material with characteristics derived from both graphene and carbon dots swhich can be regarded as incredibly small pieces of graphene. Suitable analytical techniques are needed for the quality control. Chemiluminescence (CL) detection has become quite a useful tool in the last years due to its simplicity, low cost and high sensitivity. Moreover, no external light source is needed. CL is often described as a dark-field technique: the absence of strong background light level reduces the background signal and leads to improved detection limits. Due to these advantages, CL methods have been widely applied to analysis in recent years. Surfactants are one of the major components (10-18%) of detergent and household cleaning products and are used in high volumes. Several types surfactants of are commonly found in natural waters and consequently, their impact on the environment has been, and continues to be, discussed in the U.S.A., Western Europe and Japan. Then, the prepared GQDs. It was found that GQDs in the presence of cetyltrimethylammonium bromide (CTMAB) and in alkaline medium led to emission of light. In order to obtain highest light emission, the concentrations of reactants involved in the CL reaction were optimized. After optimization, our preliminary tests revealed that Triton X100 could inhibit the CL reaction of GQDs. The inhibitory effect of triton X 100 was linearly proportional with concentration of triton x100 in the range of 1.2×10^{-3} – 1.5×10^{-2} mol/L. The limit of detection of CL method and its relative standard deviation were 6.6×10^{-4} mol/L and 1.4% (n=9), respectively. The method possessed acceptable selectivity and can be exploited for determination of triton x100 in various water samples beside to detergent samples.

Keywords: Chemiluminescence; Graphene quantum dots; Triton X100; Carbon nanostructures.

Determination of cobalt (II) ions by using graphene oxide-hydrazine hydrate chemiluminescence reaction

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Chemiluminescence (CL) is defined as the production of light through a chemical reaction that is accompanied by energy release of >45 kcal mol^{-1}. This phenomenon has been exploited as a powerful and important analysis tool in analytical chemistry. CL-based analytical methods present various advantages such as high sensitivity, rapidity, safety and controllable emission rate [1]. Recently, graphene oxide (GO) has attracted considerable attention of scientists due to its unique structure and extraordinary properties, and hold great promise for potential applications in nanomaterial and nanotechnology scientific fields. For instance, GO has been employed to increase the intensity of some of the CL reactions. In this work, GO was synthesized by using improved Hummer method. At this method used H_2SO_4 to intercalate graphite with the assistance of $NaNO_3$, and $KMnO_4$ to oxidize the acid-intercalated graphite. Hummer`s method has several merits. First, the use of a strong oxidant, $KMnO_4$, ensures the completion of reaction within several hours. Second, no explosive ClO_2^- is formed since the absence of chlorate. Third, the replacement of fuming HNO_3 with $NaNO_3$ eliminates the acid fog. The synthesized GO were characterized by exploiting FT-IR spectroscopy, X-ray diffraction (XRD) and transmission electron microscopy (TEM). In the following, it was found that GO layers were able to increase the intensity of weak CL reaction of hydrazine - sodium carbonate. Furthermore, the study of effect of some metal cations on the GO- hydrazine hydrate - sodium carbonate CL system revealed that cobalt (II) ions can catalyzed the GO - hydrazine hydrate - sodium carbonate CL reaction. After optimization of the concentration of the compounds involved in the CL system to achieve highest light emission, the CL system was used to measure cobalt (II) ions concentration. The developed CL method for cobalt (II) ions possessed the dynamic linear range from 6×10^{-7} to 1×10^{-5} mol/L and its detection limits was 4×10^{-7} mol/L. The method featured acceptable selectivity and thus can be exploited for determination of cobalt in various real samples.

Keywords: Chemiluminescence; Graphene oxide; Hydrazine; Cobalt (II).

References:

[1] M.Liu, Zh.Lin, J-M.Lin, Anal. Chim. Acta 670 (2010) 1-10.

Enhanced luminol-O_2 chemiluminescence reaction by CuO nanoparticles as oxidase mimics and its application for determination of ceftazidime

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Ceftazidime (CFZM) is a semisynthetic third generation cephalosporin antibiotic of high antibacterial activity, used for treating common bacterial infections. Due to insufficient oral bioavailability, CFZM is limited to parenteral administration. It is mainly eliminated from the consumers' body through renal excretion (1, 2). For the first time, this article reports that CuO nanoparticles (CuO NPs) have intrinsic oxidase-like activity and are capable of catalyzing oxidation of luminol by dissolved oxygen (DO) to generate enhanced chemiluminescence (CL) emission. In addition, it was found that ceftazidime (CFZM) has the effective attenuating effect of CFZM on the CuO NPs-catalyzed luminol-O2 CL system in alkaline medium. Based on this finding a simple and sensitive CL method for the determination of CFZM was developed. The linear dynamic range of the method is 1 × 10-7- 4 × 10-6 mol L-1 with correlation coefficient of the calibration line being r2 = 0.9902. The limit of detection (LOD) was equal to 2.5 × 10-8 mol L-1 and relative standard deviation of the method with respect to 2.5 × 10-8 mol L-1 CFZM was equal to 4.5% (n = 4). The applicability of the method was demonstrated on pharmaceutical preparations, and tap and ground water. The CuO NPs were simply synthesized by quick-precipitation method and, then, were characterized by using X-ray diffraction (XRD), transmission electron microscopy (TEM) and scanning electron microscopy (SEM) techniques. In addition, the possible mechanism for the CL reaction was discussed.

Keywords: Oxidase mimics; CuO nanoparticles; Ceftazidime; Luminol; Chemiluminescence

References:

[1] S.R. El-Shaboury, G.A. Saleh, F.A. Mohamed, A.H. Rageh, J. Pharm, Biomed. Anal. 45 (2007)1.
[2] M Zhou, R.E. Notari, J. Phar Sci. 84 (1995)534.

Determination of isoniazid in pharmaceutical formulations and water samples by using of the luminol-graphene oxide chemiluminescence system

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Isoniazid is an antibiotic used to tuberculosis chemotherapy [1]. Due to the pharmacological importance of this antibiotic, several methods for the determination of isoniazid have been reported. In general, chemiluminescence (CL) is the emission of electromagnetic radiation from a chemical reaction which is usually exothermic [2]. Hao et al [3]. reported that graphene oxide (GO) can enhance the intensity of light emission CL reaction luminol – O_2. This catalytic activity was due the fact that the GO can react with the dissolved oxygen and produce $O_2^{-\bullet}$, oxidizing luminol to produce CL emission. In this work, GO were used for enhancing of luminol– O_2 CL reaction. To this aim, we synthesized GO by using improved hummer method. Then, the prepared GO were characterized by ultraviolet and visible (UV-Vis) spectroscopy, fourier transform infrared (FTIR) spectroscopy, X-ray diffraction (XRD), scanning electron microscopy (SEM) and also transmission electron microscopy (TEM). Then, we found that isoniazid drug were capable of enhancement CL emission of GO enhanced luminol – O_2. Based on this finding, experimental conditions such as concentrations of luminol, sodium hydroxide and GO were examined and optimized. The proposed method exhibited good performance and its linear range was from $1 \times 10^{-7} - 1 \times 10^{-4}$ M. Moreover, the relative standard deviation and limit of detection for the method for isoniazid were 3.38% (n = 5) and 7.9×10^{-8} M, respectively. The method was applied to the determination of isoniazid in pharmaceutical formulations and water samples.

Keywords: Chemiluminescence; Graphene Oxide; Isoniazid; Luminol.

References:

[1] Y. Huang, Z. Zhang, D. Zhang, J. Lv, Anal. Chem 368(2000) 429.

[2] M. Iranifam, M.A. Segundo, J.L. M. Santos, J.L. F. C. Limab, M.H. Sorouraddin, Luminescence 25(2010) 409.

[3] M. Hao, N. Liu, Z. Ma, Analyst 138 (2013) 4393.

Production of Poly Hydroxybutyrates from Analyses of Cyanobacteria for the Production of Bioplastics and Polyhydroxyalkanoates Bio-based plastics and their properties

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The increasing effect of non-degradable plastic wastes is a growing concern. As an alternative, researches are being attempted from living resource to produce bio plastics on the basis of their biodegradability. Due to their cost effect nature, now the scientists are searching an alternative resource like photoautotrophic cyanobacteria. In this review the promising importance and growing awareness of using cyanobacteria as PHB resource are being reported. Many publications evidenced that various cyanobacterial species accumulate intracellular poly-β-hydroxybutyrate granules as energy and carbon reserves inside their cells when they are in stress conditions. PHB is biodegradable, environmental friendly and biocompatible thermoplastics. Varying in toughness and flexibility, depending on their formulation, they can be used in various ways similar to many non-biodegradable petrochemical plastics currently in use. Promising strategies involve genetic engineering of microorganisms to introduce production pathways are being investigated for the past two decades. Such kind of researches focusing on the use of alternative substrates, novel extraction methods, genetically enhanced species and mixed cultures with a view to make (CH2)x C R O O_n from cyanobacteria (blue green algae) more commercially attractive are presented and discussed.

Keywords: Bioplastics ; Analytical plastics Spectrophotometry ; Cyanobactery; Biodegradability ; Petrochemical plastics ; Metabolic

References:

[1] Malaysian Polymer Journal (MPJ), Vol 2, No. 2, p 31-57, (2007)
[2] Maskow, T., Babel, W. 2000. J. Biotechnol. 77:247-253
[3] A. Vellore ,VIT University 10.1016/j.algal.2013.03.002.

Application of rank annihilation factor analysis to the analysis of the two-way spectroscopic data of molecular complex formation between chlorpheniramine and iodine analysis

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Chemical kinetics has been widely acknowledged as a fundamental theory in analysis of chemical processes and the corresponding reaction outputs and rates. The study and application of chemical kinetics thus provide a simulation tool to predict many characteristics a chemical process. A simple way to kinetics study is absorbance measurement by wavelengths scanning that creates a two-way data set and analysis of data using proper chemometrics methods. There is a powerful class of methods based on rank annihilation factor analysis (RAFA). RAFA is based on rank analysis for two-way spectral data and can be employed to analyses quantitatively "gray system" with unknown background. In this study the kinetics of the reaction of the chlorpheniramin with iodine in organic solvents has been investigated from the two-way kinetic-spectral data obtained through the charge transfer complex formation. Rate constants in three solvents was measured by RAFA approaches. Variation in the kinetic constants were in complete agreement with the model proposed and the solvent polarities. Also soft modelling exploratory data analysis such as evolving factor analysis (EFA) and multivariate curve resolution-alternating least squares (MCR-ALS) used for getting information about the number of species as well as concentration and spectral profiles of each individual species involved in the multivariate monitored process. The methods were obtained good results.

Keywords: Kinetics, Rank annihilation factor analysis (RAFA), Spectrophotometry

Determination of Oil and Grease in Water with a UV-Visible Spectrometer

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The concentration of dispersed oil and grease (OG) is an important parameter for water quality and safety. OG in water can cause surface films and shoreline deposits leading to environmental degradation, and can induce human health risks when discharged in surface or ground waters. Additionally, OG may interfere with aerobic and anaerobic biological processes and lead to decreased wastewater treatment efficiency. Also oil concentration in organic solvents is important for industry in boilers and so on.

OG in water is commonly determined by extraction into a non-polar, hydrocarbonfree solvent followed by measurement of the infrared absorption spectrum of the extract, but we use Uv-Vis. spectrometer. In this study the analytical behavior of oil and surfactant is evaluated during detection and determination of trace amount of oil in both aqueous and non-aqueous environmental samples. The introduced method shows acceptable linearity and precision, with a detection limit below 0.4 mg L^{-1}. The recoveries are high but show some variability with values ranging from 93 to 98.95%. Some advantages of this method include: simplicity, low cost, very short response time and vast linear range.

Keywords: Oil determination; Water; Uv-Vis. spectrometer.

Selective and sensitive colorimetric detection of Cr^{3+} using 4-amino-5 methyl-4H-1,2,4-triazole-3-thiol functionalized gold nanoparticles

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A rapid, selective and sensitive colorimetric method for detection of Cr^{3+} was developed based on functionalization of the gold nanoparticles [1,2]. The surface of the Au NPs was functionalized using 4-amino-5-methyl-4H-1,2,4-triazole-3-thiol (AMTT). In the presence of Cr^{3+} ions AMTT-Au NPs immediately aggregated and resulted in a visible color change of the Au NPs solution from red to blue. This Cr^{3+} induced aggregation of AMTT-Au NPs can be seen with naked eyes and also monitored by UV-Vis spectroscopy with a detection limit of 0.2 µM (at a signal-to-noise ratio of 3). AMTT-Au NPs showed excellent selectivity toward Cr^{3+} compared to other metal ions K^+, Na^+, Cs^+, Fe^{3+}, Ni^{2+}, Cu^{2+}, Co^{2+}, Zn^{2+}, Ba^{2+}, Ca^{2+}, Mg^{2+}, Cd^{2+}, $Pb^{2+}$and Hg^{2+} ions. The results showed that the absorbance ratio (A_{650}/A_{525}) was linear for Cr^{3+} concentration in the range of 0.6-6µM with R^2=0.999. The best detection of Cr^{3+} was achieved over a pH range of 3-5. Furthermore, the proposed colorimetric method based on AMTT-Au NPs were successfully used for Cr^{3+} ion detection in Tap water.

Keywords: Colorimetric sensor; Cr^{3+}; Gold nanoparticles, ligand functionalized

References

[1] Shu-Hua Lo, Ming-Chun Wu, Parthiban Venkatesan, Shu-Pao Wu, Sens and Actuators B 220 (2015) 772–778.

[2] Y. Sung, S. Wu, Sens Actuators B 197 (2014) 172–176.

Oxygen Reduction by Bimetallic Cobalt Complex at a Liquid−Liquid Interface

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Interface between two immiscible electrolyte solutions (ITIES) is one of the most fundamental physicochemical processes. The catalytic reduction of oxygen in aqueous acidified media is a key step in the development of fuel cells and batteries. Oxygen reduction is the most frequently studied catalytic reaction at soft interfaces [1, 2].

Oxygen reduction catalyzed by a bimetallic cobalt complex at a polarized water/1,2-dichloroethane, (DCE), interface was investigated by using a weak electron donor, namely ferrocene (Fc).Voltammetry measurements at the water/DCE interface were performed in a four-electrode configuration. Two- phase reactions were performed in small glasses under stirring conditions. The oxidation reaction of Fc was monitored by visible absorption spectrophotometry at the maximum absorbance of the Fc^+ band (λ=620 nm). Two-phase shake flask experiments and ion transfer voltammetry results indicate that the catalytic reaction proceeds as a proton-coupled electron transfer reduction of oxygen to mainly water than the hydrogen peroxide. The resultant kinetically limited time profiles of the formation of Fc^+ in the absence and presence of the bimetallic cobalt complex show that the oxidation of the electron donors precedes much faster in the presence of the complex.

Keywords: Bimetallic cobalt complex, Ferrocen, Hydrogen peroxide, ITIES, Oxygen reduction

References:

[1] M. Mendez, R. Partovinia, I. Hatay, B. Su, P. Ge, A. Olaya, Phys. Chem. Chem. Phys. 12 (2010) 15163.

[2] B. Su, I. Hatay, P. Ge, M. Mendez, C. Corminboeuf, Z. Samec, Chem. Commun.46 (2010) 2918.

Fluorescent carbon quantum dots: synthesis, characterization and bioimaging

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Carbon quantum dots (CQDs) are a new class of carbon based nanomaterials that have attracted many researches in the field fluorescent sensors, photocatalysis, drug delivery and bioimaging. The CQDs are synthesized by various methods such as microwave irradiation, hydrothermal, electrochemical carbonization and.

In this study, CQDs were prepared by three facile and cost effective methods including microwave irradiation, hydrothermal and chemical method. Various materials were used as carbon source such as citric acid and ascorbic acid. To gain the best photoluminscence behavior the reaction condition such as time, carbon source concentration and temperature were optimized by Taguchi method. The size of CQDs were analyzed by dynamic light scattering and the surface functional properties were investigated by FT-IR. The fluorescence quantum yield of the synthesized CQDs was determind. The cytotoxicity of synthesized CQDs was evaluated by MTT assay.

The diameter of prepared CQDs was about 2nm. The presence of several functional groups such as O-H, COOH, and N-H was approved. The UV-Vis spectra show an absorption maximum in 290 nm and a strong fluorescent maximum in 460 nm. The results of MTT assay showed that the carbon dots were non-toxic and suitable for bioimaging. The synthesized CQDs with excellent water solubility, non-toxicity and bright fluorescence were used for in vitro imaging.

Keywords Bioimaging, Carbon Quantum Dots, Fluorescent, Quantum Yield

Construction of an optode using carbon quantum dots for potassium determination in human serum

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Potassium ion, which is the most abundant metal ion in cells, is important to every major body function due to play its key roles in biological systems. Carbon dots are as new class of fluorescent materials and have been extensively used as sensing element in sensors. In this study the carbon quantum dots were synthesized by microwave method using citric acid as carbon source and 2, 2'-(Ethylene-dioxy) bis (ethylamine) as the co-reactant. The carbon quantum dots were fixed on transparent bed and used as a potassium ion sensitive optode. The pH range was optimized. Interferences of other alkaline and alkaline earth ions on potassium ion determination were studied. A good linear dynamic range of 1×10^{-5} to 2×10^{-4} mol L^{-1} with the correlation coefficient of about 0.99 was obtained. An excellent selectivity, limit of detection (LOD) and sensitivity were obtained that make it suitable for determination of potassium in human blood serum or water. As a result, the blood potassium levels are determined which were satisfactory and closely comparable with the results given by the diagnosis clinic with ion selective electrode method.

Keywords: Carbon quantum dot, Fluorescence, Optode, Potassium determination

References:

[1] Walz, W., Role of astrocytes in the clearance of excess extracellular potassium. Neurochemistry international, 2000. **36**(4): p. 291-300.

[2] Goncalves, H.M., et al., Layer-by-layer immobilization of carbon dots fluorescent nanomaterials on single optical fiber. Anal Chim Acta, 2012. **735**: p. 90-5.

Application of cellulose based membrane as an optical sensor for identification and determination of 2, 4, 6 Trinitrotoluene (TNT)

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A simple chemical optical sensor based on the ion exchange reaction was used for determination of TNT by spectrophotometric method. The membrane sensor was produced using immobilization of methyltrioctylammonium chloride on the tree ethyl cellulose film. In the basic medium, the TNT reacts with NaOH to give the ‘Meisenheimer anion’ form [1], which it exchanged by chloride counter ion and after adsorption, changed the colorless transparent membrane to pink. The sensor can be regenerated by using diluted nitric acid solution. This optode is stable and could be stored under water for more than 20 day without reagent leaching. The effect of different parameters such as pH, amount of methyltrioctylammonium concentration and contact time was investigated and optimized. The calibration curve was liner in the range of 0.5-16.0 mg L^{-1} of TNT and limit of detection was 0.1 mg L^{-1}. The relative standard deviation for eight replicate measurements of 2 and 12 mg L^{-1} of TNT was 5.8 and 2.6, respectively. The sensor was successfully applied to the determination of water and soil samples.

Keywords: methyltrioctylammonium chloride; Spectrophotometry; optical sensor; Trinitrotoluene.

References:

[1] A. Larki, M. Rahimi Nasrabadi, N. Pourreza, Forensic Sci. Int. 251 (2015) 77.
[2] A.A. Ensafi, A. Katiraei Far, S. Megdadi. *Sens. Actuators B.* 133 (2008) 81.

Femtoliter Scale Detection of Salmon Calcitonin by an Invert Thermal Lens Microscope

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Sensitive detection of nonfluorescent molecules at the femtoliter (fL) scale has been achieved in a micro fluidic cell. Smaller sample volumes and higher sensitivity have been significant targets for using Photothermal lens microscopy as a detection system.

Herein, an invert photothermal lens microscope was utilized for highly sensitive determination of calcitonin as a polypeptide hormone which effectively used for treatment of postmenopausal osteoporosis and hypercalcemia. The absorption band of calcitonin is in UV wavelength region while the excitation with the focused UV laser can decompose analytes by photochemical reactions, resulting in the reduction of the detection sensitivity. To overcome these problems Gold nano particles has been used. 13nm-GNPs was prepared through the classical citrate reduction method.

GNPs exhibit surface plasmon resonance (SPR) absorption at visible wavelengths. The functional molecules on the surface of calcitonin covalently binds to the surface of GNPs and forms the core-shell super assembly, which decrease the thermal conductivity of GNPs. This decrease of thermal conductivity will result the increase of PTLM signal. As a consequence the Photothermal lens signal enhanced. The changes of PTLM signal in the focal volume of 1.6 fL ($f=10^{-15}$) were proportional to the concentration of calcitonin over the range of 400-1000$\times10^{-9}$ molL^{-1}. The limit of detection was estimated to be 248$\times10^{-9}$ molL^{-1}, and the relative standard deviation for seven repeated measurements of 500$\times10^{-9}$ molL^{-1} calcitonin was 0.57%.

Keywords: Calcitonin, Gold nanoparticles, Invert thermal lens microscope.

References:

[1] N. Shokoufi, S. Madarshahian, LAP Lambert Academic Publishing (2012) 43-47.
[2] C. H. Chesnut, M. Azria, S. Silverman, M. Engelhardt, Osteoporosis International 19(4) (2008) 479-491.

Determination of Methimazole by Gold Nanoparticles Using a Flow Injection Photothermal Lens Microscopy

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Sensitivity, thermooptical properties and low sample consumption are major properties that highlighted photo thermal lens microscopy (PTLM) for detection of samples. In this work, a combined flow injection photothermal lens microscopy was utilized for highly sensitive determination of methimazole as an anti-hyperthyroid drug in pharmaceutical samples by using Gold nanoparticles (GNPs).

GNPs exhibit surface plasmon resonance (SPR) absorption at visible wavelengths. Negatively charged GNPs bind thione groups onto the surface of methimazole. Following the addition of methimazole, the color of gold colloid solution gradually changes. The thione portion of methimazole covalently binds to the surface of the GNPs and forms the core-shell super assembly, which decrease the thermal conductivity of GNPs. This decrease of thermal conductivity will result the increase of PTLM signal. As a consequence the Photothermal lens signal enhanced. The changes of PTLM signal in the optical focal volume of 1.6 fL ($f=10^{-15}$) were proportional to the concentration of methimazole over the range of $150\text{-}600\times10^{-9}$ $molL^{-1}$. The detection limit of methimazole through this approach (S/N =3) was 119×10^{-9} $molL^{-1}$, and the relative standard deviation for seven repeated measurements of 300×10^{-9} $molL^{-1}$ methimazole was 0.46%.

Keywords: Flow Injection, Gold nanoparticles, Methimazole, Photothermal lens microscopy, Plasmonic.

References:

[3] N. Shokoufi, S. Madarshahian, Thermal lens spectrometry:Techniques and Instrumentation, LAP Lambert Academic Publishing, (2012) 43-47.

[4] S.Kurbanoglu, C. C.Mayorga-Martinez, M. Medina-Sánchez, L. Rivas, S. A. Ozkan&A.Merkoçi, *Biosensors and Bioelectronics*, 67, (2015) 670-676.

[5] Z. Zhong, S. Patskovskyy, P. Bouvrette, J.H. Luong& A. Gedanken, *J. Phys. Chem. B.*108 (13), (2004) 4046.

Nanoclusters formation study of inclusive and exclusive complexation of macrocyclic ligands in gas phase by using ion mobility spectrometry

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The study of structure and stability of noncovalent host-guest complexes represents a promising strategy to probe the intrinsic properties of these complexes in gas-phase. Macrocyclic ligands such as crown ethers and cryptands have been extensively used as interesting model compounds for the study of molecular recognition in biological systems. In this work, the interaction of the various reactant ions with the macrocyclic ligands was studied in the gas phase using ion mobility spectrometry. The effect of type of donating atom and skeleton rigidity of the ligand on the nature of produced nanoclusters was investigated by comparing the interaction of two-dimensional (18-crown 6, diaza-18-crown-6) and three- dimensional (cryptand 222) cavity of ligands with different reactant ions (H_3O^+, NH_4^+ and $CH_3NH_3^+$) as guest ions in the gas phase. The results obtained indicated that the interaction between the macrocyclic ligands and different reactant ions is influenced by the chemical structure of the ligands and their cavity type. The donor atoms of the ligands also play important roles on the nature of produced inclusive and exclusive nanoclusters complexes.

Keywords : Macrocyclic ligands, Ion mobility spectrometry, Nanocluster.

References:

[1] N. Alizadeh, P. Shahdousti, S. Nabavi, M. Tabrizchi., *Inter. J. Mass Spectrom, 308(2011)18.*
[2] S. Maleknia, J. Brodbelt., *J. Am. Chem. Soc., 115 (1993) 2837.*

Impregnated 4-(2- Pyridylazo) resorcinol sodium into the activated carbon in order to enrichment of Ni^{2+} and Mn^{2+} in vegetable Samples and their measurement by atomic spectrometry

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In this work, a simple, sensitive, environmental compatible and very low cost method was performed for enrichment of Ni^{2+} and Mn^{2+} in water and vegetable samples and determination by atomic spectrometry. The activated carbon was modified by loading 4-(2- Pyridylazo) resorcinol mono sodium salt mono hydrate. Subsequently, this sorbent was used for the enrichment of metal ions such as Mn^{2+} and Ni^{2+} ions. The effective parameters, such as contact time and the amount of 4-(2- Pyridylazo) resorcinol was optimised. The influences of the various analytical parameters such as pH, amount of sorbent, speed and time of agitation, type and volume of eluent on the preconcentration and recovery were investigated. Results indicated that the pH 6, 0.3g of sorbent, speed 900 rpm, time of agitation 45 min. Volume and concentration of eluent (HNO3) 4 mL 3.0 mol L^{-1} respectively. The maximum recovery of Mn^{2+} and Ni^{2+} onto the modified activated carbon were 95.4% and 98.6%, respectively.

In the optimum conditions, linear ranges were obtained 2.0 – 60.0 µg L^{-} and 2.0 – 165.0 µg L^{-1} for Mn^{2+} and Ni^{2+}, with the correlation coefficients of 0.9990 for Mn^{2+} and 0.9978 for Ni^{2+}. The enrichment factor of 312 was obtained for each ion. Limit of detection were 0.15 µg L^{-1} and 0.25 µg L^{-1}, respectively. The concentrations of Mn^{2+} and Ni^{2+} in spring hot water were obtained 12.0 ± 0.7 µg L^{-1} and 8.7 ± 0.5 µg L^{-1}.The concentrations of these ions in cucumber were 14.1 ± 1.5 µg L^{-1} and 3.9 ±0.2 µg L^{-1}, respectively.

Keywords: Enrichment; Flame atomic absorption spectrometry; Modified activated carbon; Vegetable samples

References:

[1] M. Ezoddin, F. Shemirani, Kh. Abdi, M.R. Jamali, Hazard Mater 178 (2010) 900.
[2] T. Dasbasi, S. Sacmaci, A. Ulgen, S. Kartal, Food Chem 197 (2016) 107–113.

Simultaneous Infrared Spectrometric determination of Acetaminophen, Ibuprofen and Caffeine in Pharmaceuticals by Chemometric Method

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In this study, the simultaneous determination of acetaminophen(AC), ibuprofen(IB) and caffeine(CA) in pharmaceuticals by a chemometric approach using IR spectrometry has been reported as a simple alternative to using separate models for each component. Spectra of AC, IB and CA were recorded at several concentrations within their linear ranges and were used to compute the calibration mixture between wavenumbers of 1500 and 1750cm^{-1} at resolution of 1cm^{-1} in acetone. Partial least squares regression (PLS) was used for chemometric analysis of data and the parameters of this procedure were optimized. The analytical performances of this method were characterized by relative prediction errors (<3%) and recoveries (>98%) and were compared with other spectrophotometric methods. Although the components show an important degree of spectral overlap, they have been determined simultaneously and rapidly requiring no separation step. This method was successfully applied to authentic pharmaceutical formulations, Novafen® capsule and Cetofen® tablet, with no interference from excipients as indicated by the recovery study results. The proposed method is simple and rapid and can be easily used in the quality control of drugs as alternative analysis tool.

Keywords: Acetaminophen, Ibuprofen, Caffeine, Infrared Spectrometry, Simultaneous Determination

References:

[1] E. Souri etal, Journal of Analytical Chemistry 70 (2015) 333-338.
[2] M. R. Khoshayand etal, Spectrochimica Acta A 70 (2008) 491-499.
[3] S. H. Ahmadi etal, Iranian Journal of Chemistry & Chemical Engineering in press (2015).

Analytical Chemistry for Cultural Heritages, An Overview to Recent National Studies

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Conservation research is focused on the conservation of material aspects of cultural heritage. It includes scientific studies where historical, conservational and/or chemical, physical and biological methods are used. Thus, it is basically interdisciplinary in its approach. Chemistry was first applied to the conservation field in the 18th century. Today, chemistry and analytical chemistry in particular, plays a crucial role in the characterization of the nature of heritage materials, as well as supporting archaeometric analysis, mechanisms of degradation and evaluating the performance of restoration materials and methods. During last decade, several Iranian research groups have been working with various methodologies for material characterization and analysis of cultural objects using advanced analytical techniques especially nondestructive methods. Different spectrometric analyses using FTIR, Raman, UV-Vis, atomic absorption and emission and molecular fluorescence spectrometers has been reported in the investigation of historical metal and non-metal objects, paintings, monuments, textiles, papers, manuscripts and etc.[1-3] Various X-ray based techniques such as PIXE, XRF and XRD have also been used in analyses of the historical samples.[4,5] Chromatographic separations, as well as, have been applied in the analyses of these samples.

In this paper, a brief review of most important analytical studies of Iranian researchers in recent years, have been presented. Widespread potential of analytical chemistry in areas of cultural heritage, archaeology and art has also introduced to young analytical chemists.

Keywords: Analytical Chemistry, Cultural Heritage, Instrumental Analysis, Conservation

References:

[1]- R. Bahadori, S. H. Ahmadi, CHEMCH 2012, Paper PS1.11, Istanbul, Turkey.
[2] S. H.Ahmadi‹R. Bahadori, 6th Electrochem. Sem. of Iran, 2010, Paper 227, Kish, Iran.
[3] P. Holakooee, SpectroChim Acta A, 20135, 116, pp.49-53.
[4] P. Holakooee, A. H. Karimy, SpectroChim Acta A, 2015, 134, pp.419-427.
[5] R. Bahadori, F. Bahrololoomi, S. H. Ahmadi, ISA 2012, pp.19-23, Leuven, Belgium.

Peanut Agglutinin Lectin: Isolation, Purification and Biological Characterization

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Plant lectins are a family of highly diverse proteins plant origin that recognize and bind to specific carbohydrate structural epitopes. It is now well recognize that carbohydrate-binding proteins containing metals in the active sites, function as central mediators of information transfer in biological systems and perform their duties by interacting with glycoproteins, glycolipids and oligosaccharides without altering their structure. As proteins with legume lectin domains on the one hand have multiple significant biological functions including anti-fungal, anti-viral, and most notably anti-tumor activities, and one the other hand they are probably the most abundant group of lectins, which have given them much attention compared with the other plant lectins, peanut (Arachis hypogaea) was selected and focused in our research project. Peanut agglutinin (PNA), one of the peanut's lectin, by the molecular weight of 110 kDa is a Homotetrameric protein which have sensitive to galactose. More importantly, this lectin is a good marker to determination some cancer's level such as Colon and Breast cancer; for example, when PNA nears the cancer cells binds to the T-antigen that is composed of two galactose. Here in, on the basis of specific affinity of some groups of carbohydrate to PNA, we synthesized a series of carbohydrate conjugated silica beads; galactose as a monosaccharide, lactose as disaccharide and chitosan as polysaccharide were chose and immobilized on silica particles surface. The main aim of this study was evaluation of the ability of these surface engineered beads for purification of PNA in a native form in a mild conditions from the soaked buffered solution of Peanuts. Our results indicated that chitosan functionalized silica beads have the excellent potential adsorption capacity for PNA purification in a complex mixture. Finally by using silica-chitosan bead, PNA with approximately 400 ppm concentration is purified completely. Structure of purified protein were confirmed by LC-MS/MS, SDS-PAGE, circular dichroism (CD) spectra and fluorescence spectra. To provide more information about the structure of purified protein, the biological activity of purified PNA was assessed by a hemagglutination test. Since polysaccharides can provide a chain of affinity moieties, it can facilitate the purification of lectin proteins and perhaps make an ideal strategy to development of smart beads.

Keywords: Peanut Agglutinin Lectin; Affinity beads; Protein purification;

High selective and sensitive determination of tetracycline from biologics samples using molecularly imprinted polymer-coated Magnetic spinel zinc ferrite nanocomposite followed by using charge transfer complex formation and spectrophotometric detection

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In this study, a simple and selective method was successfully developed for the determination and preconcentration of tetracycline in biologics samples using magnetic molecularly imprinted polymer (MMIP) as sorbent. The MMIP has been synthesized by using tetracycline as template molecule, methacrylic acid (MAA) as functional monomer, ethylene glycol dimethacrylate (EGDMA) as crosslinking agent, functionalized $ZnFe_2O_4$ magnetite spinel nanocomposite with vinyl group as magnetic component and 2,2-azobisisobutyronitrile (AIBN) as the initiator. The prepared magnetic molecularly imprinted polymer were characterized and confirmed by Fourier transform infrared spectra (FT-IR), X-ray diffraction spectrometry (XRD), transmission electron microscopy (TEM) and scanning electron microscopy (SEM). The extraction procedure was performed in a single step by blending and stirring the MMIP and the urine sample. The extracted tetracycline easily desorbed with a mixture of acetonitrile/acetic acid and analyzed by spectrophotometric detection based on charge transfer complexation reaction of tetracycline with acceptor 7,7,8,8-tetracyanoquinodimethane (TCNQ) that was measured at 420 nm. For achieving optimal preconcentration and reducing nonspecific interactions, various parameters affecting the extraction efficiency such as pH value, adsorbent amount, eluent concentration and volume and sample volume have been investigated and established. Under the optimal conditions, linear range of calibration curve and enrichment factor of the proposed method for tetracycline was 0.01 to 1.5 mgL^{-1}, 300 respectively. The relative standard deviation (RSD) of the repeated experiments for tetracycline was 2.4.0%. Determination of tetracycline in real samples showed good recovery (99.6-99.9%).

Keywords: tetracycline; determination; magnetic molecularly imprinted polymer; TCNQ; spectrophotometric detection

Measuring tyrosinase activity and protein concentration by spectrophotometric method

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Tyrosinase, an oxidoreductase enzyme, was extracted from common mushrooms (**Agaricus bisporus) purchased from local market.** Tyrosinase extraction was carried out in three simple steps. First, fresh mushrooms (200 gr) were homogenized in 367 mL pre-cold acetone (-22^{o}C) to remove soluble impurities by centrifuging at 7000 rpm, 20 min and 0 ^{o}C. Then, 134 mL phosphate buffer was added to separate all of the proteins from mushroom pulps with centrifuging at 10,000 rpm for 20 min and 0 ^{o}C to collect supernatant as the product. The remaining proteins and negligible amount of the tyrosinase were salted out by adding ammonium sulfate powder to the supernatant to make 30% saturated solution during stirring for 30 min at 0 ^{o}C and centrifuging at 10,000 rpm for 20 min. After that, tyrosinase was similarly separated using the 60% saturated solution. Finally, the collected sediments was dissolved in 13 mL phosphate buffer and stored at -22 ^{o}C as the crude enzyme. Enzyme activity was measured colorimetrically in the buffer using L-tyrosine as substrate. For this purpose, 100 µL of the crude enzyme solution was added to 1 mL L-tyrosine solution and the mixture was homogenized. The changes in absorbance were monitored at 475 nm using a UV-Visible spectrophotometer. The activity was calculated from slope of the linear curve of absorbance increase verse time According to this slope, activity of the crude enzyme was about 4983 unit/ml. The amount of protein in the crude enzyme solution was calculated by using the Bradford protein assay. The protein concentration in the crude enzyme solution was determined colorimetrically at 595 nm with the assay reagent as the standard protein. For this purpose, 0.1 mL crude enzyme solution was added to 5 mL Bradford solution and the mixture was stirred for 5 min, then the absorbance was measured at 595 nm. The protein concentration of 1.8 mg/mL in the crude enzyme solution was measured by using UV-Visible spectrophotometer.

Keywords: Activity; Colorimetry; Enzyme; Tyrosinase; Spectrophotometry

Investigation of thermionic electron emission intensity of tungsten filament using multi-wall nanotube carbon

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Metal valance electrons by accepting required energy, called work function is unique for any metal, can leave the metal surface. Thermionic emission is process that electron-knocked energy source gets thermal energy. In the fluorescent lamp, the desired metal is tungsten filament in the role of cathode. In order to improve electron emission, cathodes are usually treated with chemicals, compounds of metals with a low work function. Carbon nanotube (CNT) is considered as a compound with low work function and good electron field emission.

In this work, reducing the work function of tungsten filament is took place by coating CNT. Coating is carried out by chemical vapor deposition (CVD). For CVD, filament is put on quartz furnace at 800 ˚C during passing acetylene gas over the filament with 0.5 mL s^{-1}. The coated filament is then used as cathode in fluorescent lamp. Light Intensity was recorded by luxmeter. The results show that treated tungsten have intensity about two times more than untreated one.

Keywords: Thermionic emission; Fluorescent lamp; CNT.

Peak separation property of 18-crown-6 in determination of biogenic amines by head-space solid phase microextraction based on nanostructured polypyrrole fiber coupled to ion mobility spectrometry

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Histamine (His) and cadaverine (Cad) have the same mobilities in pure nitrogen buffer gas and their corresponding peaks are totally overlapped (t_d= 6.7 ms). Peak separation was acquired in the presence of 18-crown-6 vapor as complexation modifier into carrier gas at optimum flow rate. The interaction between 18-crown-6 and the mentioned amines forms nanocluster product ions with different cross section areas (Ω_{His} = 192.65Å^2 and Ω_{Cad} =195.51 Å^2) and ion mobilities ($t_{d(His)}$ = 12.08 ms and $t_{d(Cad)}$=12.38 ms). So, we used 18-crown-6 vapor in cell and head-space solid phase microextraction (HS-SPME) was applied to extraction and determination of biogenic amines by ion mobility spectrometry. The effects of main extraction parameters on the efficiency of HS-SPME were investigated and optimized. The proposed method is much more simple and cheaper than chromatographic methods, with no need of extra organic solvent consumption and derivatization prior to sample introduction.

Keywords: Biogenic amines, Nanoclusters, 18-crown-6, Headspace solid phase microextraction, Ion mobility spectrometry, Peak separation.

References:

[1] C.S. Creaser, J.R. Griffiths, B.M. , Stockton. *Eur. J. Mass Spectrom (2000)6:213-218.*

[2] Z. Li, S. J. Valentine, D. E. Clemmer. *J. Am. Soc. Mass Spectrom (2011) 22:817-827.*

A New Application of RGB Model for Kinetic Determination of Vanadium

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In this study, utilization of a CCD camera (WebCam) as a detector in the chemical reaction with color change is proposed. The measured signal in this study is the RGB based data which is calculated from average of R (red), G (Green) and B (Blue) in each image. Being simple, inexpensive and time saving, the proposed technique in this study can be preferred to spectrophotometric-based methods for following the reaction kinetics. The catalytic effect of vanadium (V) on the oxidation of indigo carmine (IC) by bromate was studied. The optimum experimental conditions were obtained using a one-at-a-time optimization procedure, being pH=2, [IC] = 5.5×10^{-5}M, and [BrO_3^-] =2.3×10^{-3}M. Slope method was applied for determination of vanadium ion. Concentration ranges of 1 – 40 µg ml^{-1} of vanadium (V) were determined. The limit of detection was found to be 0.08 µg.ml^{-1}. The interference effects of various cations and anions on vanadium determination are reported, and the interference of ions is eliminated by a simple procedure. The proposed method was used for the measurement of vanadium (V) in real samples which led to satisfactory results.

Keywords: Indigo carmine, RGB, Spectrophotometric, Vanadium

References:

[1] M. M. Lana, L. M. M. Tijskens, O. Van Kooten, Journal of food Engineering 77 (2006) 871-879.
[2] M. Riccio, E. Resca, L. Bertoni, F. Cavani, P. Sena, M. Ferretti, A. Baldini, C. Palumbo, A. Depol, Optics & Laser Technology (2009).
[3] A. Safavi, N. Maleki, A. Rostamzadeh, S. Maesum, Talanta 71 (2007) 498-501.

Simultaneous Determination of Acetaminophen and Ascorbic acid by Net Analyte Signal-Classical Least Squares Method in Some Pharmaceutical Formulations

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In this work Net Analyte Signal-Classical Least Squares (NAS-CLS) as one of the multivariate calibration methods is presented for the simultaneous spectrophotometic analysis of Acetaminophen (ACE) and Ascorbic acid (AA). Panadol tablet (500 mg ACE/30 mg AA) is a mild analgesic and antipyretic drug and is recommended for the treatment of most painful and febrile conditions including migraine, tension headache and toothache.

The main problem of spectrophotometric multicomponent analysis is the simultaneous determination of two or more compounds in the same mixtures without preliminary separation. Several spectrophotometric determination methods have been used for resolving mixtures of compounds with overlapping spectra such as partial least squares regression (PLSR)[1], principal component regression (PCR)[2] and multi-wavelength linear regression analysis (MLRA)[3]. In this work, NAS-based multivariate calibration method has also been proposed in which the vectors of NAS of mixtures are used as input for other multivariate calibration methods such as classical least squares (NAS/CLS). In this study, all spectra were recorded at pH of 7.0 using Britton–Robinson buffer in the range of 250-310 nm. The total root mean square error (RMSE) for prediction set is 2.0 and 4.5 for ACE and AA respectively showing good accuracy in the range of 0.5 to 90.0 μM. The proposed method was successfully applied for determination of active ingredients (ACE and AA) in Panadol tablets with high accuracy and precision.

Key words: Acetaminophen; Ascorbic acid; Net Analyte Signal -Classical Least Squares method

References

[1] J. Verdu-Andres, F. Bosch-Reig and P. Compins-Falco, *Analyst*, 1995, **120**, 299.

[2] E. Dinc and F. Onur, *Anal. Chim. Acta*, 1998, **356**, 93.

[3] S. Wold, M. Sjostrom and L. Eriksson, *Chem. Intel. Lab. Syst*. 2001, **58**, 109.

Chemometrics-enhanced solid phase nanoextraction combined with gas chromatography for determination of polycyclic aromatic hydrocarbons in environmental samples

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In this study, solid-phase nanoextraction (SPNE) combined with gas chromatography-flame ionization detector (GC-FID) was proposed for determination of thirteen polycyclic aromatic hydrocarbons (PAHs) in environmental samples [1]. The SPNE technique is based on the strong affinity between gold nanoparticles (AuNPs) and PAHs. The AuNPs (~20nm) were prepared by reducing the $HAuCl_4$ by trisodium citrate using Fren's method [2]. Furthermore, characterization of AuNPs was performed by UV-Vis, TEM and DLS techniques. A rotatable central composite design (CCD) combined with multiple linear regression (MLR) was used for designing the SPNE procedure and developing models using the GC peak areas of 13 PAHs [3]. Also, multi-response optimization using Derringer desirability function was utilized to find optimum conditions which were 7.22 min adsorption vortex time, 5 µL of 1,3-propandithiol as desorption solvent, 44 µL methanol, 15 µL n-nonane as acceptor solvent and 9.63 min desorption vortex time. The developed models were finally confirmed by performing the SPNE in optimum conditions which the peak areas of 13 PAHs were in confidence interval of the modeled values. The optimized SPNE-GC-FID method was then used for identification and quantification of target PAHs in standard and real samples using multivariate calibration techniques (e.g., partial least squares (PLS)). In this regard, calibration set was randomly designed in concentration range 5-100 ngmL^{-1}. Then, multivariate analytical figures of merit (AFOM) including sensitivity, selectivity and limit of detection (LOD) were calculated. As an instance the LODs were in range 1-5 ngmL^{-1}. Finally, the proposed strategy was successfully tested for the analysis of real samples (i.e., tap, well and farm waters).

Keywords: Chemometrics; Gas Chromatography; Gold Nanoparticles; PAHs.

References:

[1] W.B. Wilson, U. Hewitt, M. Miller, A.D. Campiglia, J. Chromatogr. A 1345 (2014) 1-8.
[2] S. Basu, S.K. Ghosh, S. Kundu, S. Panigrahi, J. Colloid Interface Sci. 313 (2007) 724-734.
[3] M. Ahmadvand, H. Sereshti, H. Parastar, J. Chromatogr. A 1413 (2015) 117-126.

Application of multivariate image analysis in enantioseparation of racemic 1-(2-Naphthyl)-1-ethanol ester derivatives

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Quantitative structure-retention relationship (QSRR) study has been applied for predicting the retention time of 26 enantiomers of 1-(2-Naphthyl)-1-ethanol esters using multivariate image analysis. The Data set was divided into training set including 20 enantiomers and prediction set including 6 enantiomers according to y-sorting method.

Multivariate image analysis (MIA) descriptors were generated from pixels of two dimensional images and subjected to principal component analysis (PCA) and the most significant principal components (PCs) were extracted. PCs that had highest correlation with the observed retention times were entered into the principal components regression (PCR) model until coefficients of determination larger than a user-defined value ($R^2 \geq 0.70$) were obtained. The most significant PCs then were used for running of partial least squares (PLS).

The coefficient of determination (R^2) for training set and prediction set was 0.730, 0.656 for PCR model and 0.9487, 0.999 for PLS models, respectively. The obtained results indicated that MIA-PLS method may be useful to predict retention times of 1-(2-Naphthyl)-1-ethanol ester derivatives.

Keywords: Multivariate image analysis, Quantitative structure- retention relationship (QSRR), principal component regression (PCR), Partial least squares (PLS).

References:

[1] Z. Garkani-Nejad, M. Poshteh-Shirani, H, Magnetic Resonance in Chemistry 83 (2012) 225-232.

[2] Z. Garkani-Nejad, M. Ahmadvand, Chromatograghia 73 (2011) 733-742.

[3] Z. Garkani-Nejad, M. Poshteh-Shirani, H, Talanta *83* (2010) 225-232.

Synthesis of a robust nano-composite of graphene, CTAB and polyanilineand its application in SPMEfor drug abuse screening

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Tricyclic antidepressants belong to a group of psychoactive medications widely prescribed in the treatment of depressive disorders[1]. These antidepressant drugs are also frequently encountered in drug abuse, forensic medical examinations, and emergency toxicology screening [2].TCAs act mainly as serotonin-norepinephrine reuptake inhibitors (SNRIs) by interfering the reuptake of norepinephrine (as desipramine, nortriptyline, and protriptyline secondary amines) and serotonin (as amitriptyline, imipramine, clomipramine, and doxepine tertiary amines) in the central nervous system. This activity results in an elevation of the synaptic concentrations of these neurotransmitters, and therefore an augmentation of neurotransmission[2].

We report on the direct electrochemical preparation of a nano-composite composed of graphene, cetyltrimethylammonium bromide (CTAB), and polyaniline, and its application to headspace solid-phase microextraction of the tricyclic antidepressant drugs (TCAs) imipramine, desipramine and chlomipramine followed by gas chromatography. The new nanocomposite coating offers good mechanical and thermal stability and high extraction efficiency due to its large specific surface. The SPME conditions were optimized with the aid of Box-Behnken design through response surface methodology. Therefore the optimal values of parameters were calculated as: temperature, 100 ºC; concentration of NaOH, 0.48 M; time, 60 min. The TCAs were thermally desorbed and analyzed by GC. The limits of detections range from 0.10 to 0.35 ng mL^{-1}, and the calibration plots are linear within the 0.30 - 400 ng mL^{-1} concentration range. The method was successfully applied to the extraction and determination of TCAs in plasma, urine, milk and hair samples.

Keywords: SPME; Chemometrics; Nano composite coating, tricyclic antidepressant (TCA) drugs, Multivariate optimization

References:

[1] Carson VB (2013) Mental Health Nursing: The Nurse-Patient Journey. Saunders.
[2] Dart RC (2014) Medical Toxicology. third edn. Lippincott, Williams & Wilkins, Philadelphia

A rapid screening method of drugs in complicated matrices based on electromembrane-surrounded solid-phase microextractionfollowed by ion mobility spectrometry

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Non-steroidal anti-inflammatory drugs (NSAIDs) are among the most commonly prescribed agents worldwide to treat a variety of pain-related conditions, including rheumatic diseases. They work by inhibiting the prostaglandin synthesis involved in the aforementioned diseases.

A new robust method of electromembrane surrounded solid phase micro extraction (EM-SPME) coupled to ion mobility mass spectrometry was applied for non-steroidal anti-inflammatory drugs determination in complex matrices. Moreover, it's the first time that a graphene/polyaniline composite coating is applied in EM-SPME method. The synthesis of graphene/polyaniline composite is investigated as high electrical conductivity and thermal stability.The CTAB doped graphene/polyaniline composite coating has a high electrical conductivity and thermal stability as well as a great surface area which make it a suitable choice as an electrode/sorbent in EM-SPME method coupled to IMS.The experimental results indicate that 1-octanol gave the highest extraction efficiency. The variables affecting EM-SPME, were optimized through central composite design and response surface methodology. The optimum values for each variable in EM-SPME method were obtained: extraction time, 24 min; voltage, 80V and pH of 7.5. Under the optimized conditions, limits of detection of 0.04 and 0.05 ng mL^{-1} were obtained for mefenamic acid and ibuprofen, respectively. The feasibility of the EM-SPME followed by ion mobility mass spectrometry was successfully confirmed by the extraction and determination of sub levels of ibuprofen and mefenamic acid in human urine and plasma samples and satisfactory results were obtained. This study clearly demonstrates the advantages of electromembrane surrounded solid phase microextraction as an excellent method in extraction of less volatile compounds from complicated matrices in a short time as well.

Keyword: Chemometrics; EM-SPME; Graphene/polyaniline nanocomposite; IMS; NSAIDs.

Simultaneous Determination of Sulfadiazine and Trimethoprim in Dairy Products using Net Analyte Signal-Classical Least Squares

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Sulphonamides and dihydrofolate reductase inhibitors such as trimethoprim (TMP) belong to a family of broad-spectrum synthetic bacteriostatic antibiotics that are widely used in veterinary medicine feed additives in most countries[1]. Sulphadiazine (SDZ) belongs to a group of antibiotics called the sulphonamides [2]. Trimethoprim plus sulphadiazine and trimethoprim plus sulphamethoxazole are the most often-used combinations in veterinary medicine [3]. The UV-Vis spectra of TMP and SDZ have serious overlapping with maximum wavelengths at 275 and 260 nm respectively. Due to the overlapping concern, direct spectrophotometric determination of trimethoprim and sulphadiazine is impossible. In this work Net Analyte Signal-Classical Least Squares (NAS-CLS) as one of the multivariate calibration methods is presented for the simultaneous spectrophotometic analysis of TMP and SDZ as important antibiotic compounds. The absorbances at maximum wavelengths depend on the pH of the solution in the range of 2-10, and also the selectivity between maximum wavelengths increased at pH≤6.0. Therefore, pH 5.0 of phosphate buffer was chosen as the optimum solvent to determine both compounds. The best wavelength range for determination of sulphadiazine and trimethoprim in some synthetic mixtures was 255-340 nm, with lower root mean square errors (RMSEs). The proposed method (NAS-CLS) was able to determine trimethoprim and sulfadiazine in the mole ratio of 1:12 showing high selectivity due to the application of NAS vectors in the calibration set. Finally, this method was successfully applied for simultaneous determination of antibiotic residues (trimethoprim and sulfadiazine) in some synthetic samples and milk and yogurt samples.

Keywords: Trimethoprim; Sulfadiazine; NAS-CLS; Simultaneous determination; Milk; Yogurt

References:

[1] J. Raich-Montiu; J. Folch; R. Compano; M. Granados; & M. D. Prat; *Journal of Chromatography A,1172 (2007) 186-193.*

[2] W. Hela; M. Brandtner; R. Widek; & R.Schuh; *Food Chemistry, 83 (2003) 601-608.*

[3] *A.V. Pereira*; & Q. B. Cass; *Journal of Chromatography A*, 826 (2005) 139-146.

Aptamer based TFME Combined with Flow Injection Analysisusing Column-lessHPLCfor Determination of PSA in Biological Fluid

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Inthepresentstudy,a new thin-film based on a DNA aptamer immobilized on cellulose nanofibers was investigated for the determination of Prostate Specific Antigen (PSA) in biological samples. A column-less HPLC-UV system was applied for quantification of PSA in extracted samples. Reaction of amino-modified anti PSA aptamer with the oxidized cellulose nanofibers was performed according to the procedure described by Khayamian et al. with some minor changes. Then a chemometrics approach was applied for the optimization of the extraction parameters such as the composition of desorption solution and volume, pH, extraction time, stirring rate and extraction temperature.

Under optimized conditions, an enrichment factor of 194 was achieved, and the relative standard deviation is 2.9% (n=7).The calibration curve covers the 7–250 ngmL^{-1} range with reasonable linearity (r^2>0.9978). Limit of detections were between 3.1 and 4.8 ngmL^{-1} and relative standard deviations were less than 5.8% under the optimized condition. Relative recoveries were found to be between 86.9 and 95.3%.

Furthermore, the urine samples were analyzed with a standard PSA kit. The comparison of the results shows no significant difference in analyte concentration obtained by the proposed method as an alternative method for the analysis of PSA in urine samples.

Based on our knowledge, for the first time in this work, the specific, effective and derivatization free biochemically modified cellulose nanofibers were combined with the simplicity, speed, and inexpensiveness of spectrophotometric detection. In addition, the proposed method has a wide dynamic range with a compatible limit of quantitation in comparison with the reported methods.

Keywords: Aptamer, Cellulose Nanofibers, Flow injection analysis, Prostate Specific Antigen, Thin Film Microextraction.

Detecting and quantifying apricot kernel adulteration in almond powder by multi-element analysis combined with chemometrics

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Making fraudulent profit from misrepresentation of food has been a feature of society from historical times. The analysis of food products is an area of active research in modern food science and there is increasing demand for the development of fast, easy to use and low-cost analytical methods to test for adulteration. Almond (Prunus amygdalus) is classified as a drupe in which the edible seed or kernel is the commercial product. Its seeds are typically used as snack foods and its powder as ingredients in a variety of processed foods, notably bakery and confectionery products. Due to its high cost, almond can be adulterated by the addition of other nuts. The most frequent adulteration in almond powder is carried out with apricot kernel because of its low price. Thus, it is necessary to establish efficient and feasible methods for the identification and quantification of adulteration in almond powder. In this regard, multi-element analysis has become one of the most powerful systemic approaches to determining authenticity and adulteration. In this work, the multivariate data analysis were performed using 23 variables (contents of Al, B, Ba, Be, Bi, Ca, Cd, Co, Cr, Cu, Fe, Ga, K, Li, Mg, Mn, Na, Ni, Pb, Se, Sr, Te, Ti and Zn at $\mu g.g^{-1}$ level determined by ICP-OES). Principal component analysis (PCA) and linear discriminant analysis (LDA) were used to discriminating adulterated and pure almond samples from their multi-element content. Partial least squares (PLS) regression models were also developed to relate the elemental profiles with the adulteration levels of the tested samples. In this way, almond powder samples were adulterated with apricot kernel in the range 0–90% (w/w) at approximately 5% intervals. The predictive ability of the LDA and PLS models were evaluated by statistical parameters of the prediction set (97.5% classification accuracy of LDA and RMSEP of 2.54 for PLS model). The results clearly ascertain that elemental profile coupled with multivariate analysis methods can be used to detect and quantify the amount of apricot kernel adulterant added to the almond powder.

Keywords: Adulteration; Apricot kernel; ICP-OES; Chemometrics

Application of Chemometric Techniques in the Assessment of Seasonal Variation of Water Quality of Kaptazh Well/Reservoirs Around Zayanderood River (Isfahan)

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Multivariate statistical or chemometric techniques, such as discriminant analysis (DA), cluster analysis (CA), and factor analysis (FA)/principal component analysis (PCA), analysis of variance (ANOVA) and regression analysis (RA) were applied for the evaluation of temporal variation of water quality, and for the interpretation of water quality data for the Kaptazh well/reservoirs around Zayanderood river during the years 1393-1394 by measuring 17 water quality parameters (WQPs) at ten different times. The DA and CA classified ten temporal observations into three groups, reflecting varying water quality levels including moderate hardness, high hardness, and very high hardness under the similarity of water quality parameters, and 17 water quality parameters into three clusters. RA was used to identify correlation between various parameters. The obtained correlation values of regression analysis suggest a significant linear relationship between various WQPs. FA/PCA was applied to the chemical parameters of well/reservoirs with the aim of classification and data summation as well as segmentation of large heterogeneous data sets into smaller homogeneous subsets. Four principle components explained about 76.6 % of the total variance of the water data sets from eigenvalue > 1. This work successfully illustrates that chemometric methods provide useful information for further monitoring strategies.

Keywords: Cluster Analysis; Chemometric Techniques; Temporal Variations; Water Quality;

References:

[1] H. Razmkhah, A. Abrishamchi, A. Torkian J. Environ. Manage. 91 (2010) 852-860.
[2] J.E. Jackson, A Users Guide to Principal Components, Wiley, New York, 1991.

Simultaneous determination of Phosalone and Teflubenzuron by principal component analysis-artificial neural network method in some pesticides formulation and biological fluids

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Simultaneous determination of components in multicomponents formulations could be a difficult task, especially when the absorption spectra of these components have strong overlapping, which prevents UV-Vis spectrometric determination of these components [1, 2]. In This study, multicomponent analysis method based on Principal Component Analysis-Artificial Neural Network method (PCA-ANN) is proposed for the simultaneous determination of Phosalone and Teflubenzuron and resolving of overlabing spectra corresponding of these pesticides. For finding the optimum condition ،the effect of pH values on the spectrum of each compound at a constsnt concentration of pesticides from pH 2 to 11 (40 µmol/lit of Phosalone and 40 µmol/lit of Teflubenzuron) was studies separately. After reducing the number of kinetic data using principal component analysis, an ANN consisting of three layers of nodes was trained by applying a back-propagation learning rule. In this method the pH of 9 was considered as an effective optimum pH from selectivity and sensitivity point of view. The determination coefficient for Phosalone and Teflubenzuron 0.9889, 0.9904 and detection limit for these pectisides 0.551, 0.729 µmol/lit was obtained, respectively. The results confirmed that the PCA-ANN method is suitable for the simultaneous determination of Phosalone and Teflubenzuron in aqueous solutions. The method was successfully applied for simultaneous determination of Phosalone and Teflubenzuron in some synthetic mixtures and pesticide formulation and biological fluide samples.

Keywords Phosalone; Teflubenzuron; Principal Component Analysis-Artificial Neural Network; Biological fluide

References:

[1] Y. Ni, C. Huang, S. Kokot, Anal. Chim. Acta **2007**, 599, 209-218.

[2] D.D. Wu, D.L. Olson, Technol. Forecast. Soc. Change. **2010**, 77, 837-839.

Classification of Iranian pistachios by ICP-OES elemental analysis and chemometrics

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Fruit quality is highly dependent on its geographical origin. Soil, water and climate situation in different cultivations regions, would severely affect the quality of harvested fruits. [5] Iranian pistachio is the best quality of this fruit all around the world. [1] In order to distinguish pistachio samples from different origins and to propose an analytical approach for their discrimination to compete in the global market, 16 varieties of Iranian pistachio were evaluated. A total of 16 cultivars consisting of 4 cultivars from Qazvin and 12 cultivars from Kerman were analyzed. [2] & [4] 11 Elements B Cu Fe Mn Ni Sr Zn Ca K Mg Na Along with the mean value and standard value by optical spectroscopy Inductively Coupled Plasma (ICP-OES) was measured in terms of concentration mg/kg. Multi elemental analysis was conducted by inductive coupled plasma – optical emission spectroscopy (ICP-OES) Several chemometric approaches e.g. SIMCA, LDA, PCA and LS-SVM were modeled to classify the analyzed samples according to their origin. [3] Comparing the results, it was concluded that LS-SVM method can be used to identify the samples with high accuracy and it could be proposed as a reliable model for detection of adulteration in pistachios. Calibration and prediction error for the model were 3.7% and 5% respectively.

Keyword: chemometrics, geographical origin, ICP-OES, Pistachio,

Reference:

[1] Y. Yucel, Pınar Sultanoglu, Turkey, (2013) 231–237.
[2] M. Khanmohammadi, F. Karami, A. Mir-Marqués, A. Bagheri Garmarudi, S. Garrigues, M. de la Guardia, IRAN & SPAIN, (2014) 17–22.
[3] J.B. Ghasemi, E. Zolfonoun, R. Khosrokhavar, Iran 24(1) (2013) 15-22.

Simultaneous determination of benzene, toluene and xylenes (BTX) in gasoline mixtures by ATR-FTIR spectrometry using prediction weighted partial least square (PWPLS) algorithm

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Determination of benzene, toluene and xylenes (BTX) in gasoline mixtures is of great importance. The chromatographic methods for determination of BTX in gasoline samples are expensive and time consuming requiring many preparational steps. A fast, cheap and reliable analytical procedure has been developed for the simultaneous quantitative determination of benzene, toluene and xylenes (BTX) in gasoline mixtures.

The data obtained by the attenuated total reflectance fourier transform infrared (ATR-FTIR) spectrometric method in the wavenumber range of 630–1000 cm-1. The spectroscopic data were treated by prediction weighted partial least square (PWPLS) algorithm. Absorbance spectra were employed for measurement using 29 standard synthetic gasoline mixtures of benzene, toluene and xylenes in iso-octane. 24 samples of this mixture set were chosen as standard and the 5 other were used as predicted samples. The concentration of benzene, toluene and xylenes were varied between 0.08–4.24, 10.30–14.00 and 11.46–15.39 (% v/v), respectively. The method was successfully applied for prediction of BTX in gasoline mixtures with PRESS values in the range of 0.55-1.00.

Keywords gasoline; Spectrometry; chemometrics; ATR-FTIR; PWPLS

References:

[1] E. Lopez – Anreus, S. Garrigues, and M. de la Guardia, Anal. Chim. Acta, 333, 157, 1996.

[2] G.S. Frysinger, R.B. Gaines, E.B. Ledford, J. High. Resol. Chromatogr., 22, 195, 1999.

[3] G.S. Frysinger and R.B. Gaines, J. High. Resol. Chromatogr. 22, 251, 1999.

Calculation of feasible solution in ITTFA

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Soft modeling methods is one of the most important methods of the chemometrics which decompose the data matrix to two concentration and spectral matrices. Mathematical decomposition of the data matrix with soft modeling methods has rotational and intensity ambiguity. These two kinds of ambiguity lead to many concentration and spectral matrices which could reconstruct the data matrix as well as the real component of the system.

The other method of soft modeling analysis is Iterative Target Transformation Factor Analysis (ITTFA). In this method at first we choose an initial guess then we project it in the corresponding space and implement the constraint on the projected profile. At the last section calculate the sum of square between the projected profile and initial guess. If the sum of square in the range of noise the algorithm stops and if it has a meaningful value the projected profile gets as a new initial guess and the algorithm to be continued. ITTFA like the other soft modeling methods is deal with the ambiguity. In this work we are trying to prove that the rotational ambiguity in ITTFA is more than the other soft modeling methods like RFA.

Because of this fact that the rotational ambiguity in ITTFA is more than the other soft modeling methods, this article has the awareness of rotational ambiguity based on the initial guess for ITTFA. SIMPILISMA and OPA are the methods that their solution as an initial guess for ITTFA would be wrong.

Keywords: Chemometrics, MCR,RFA,OPA,SIMPILISMA,ITTFA, rotational ambiguity,

Chemometric-assisted Spectrophotometric Method for the Simultaneous Preconcentration and Determination of Food Dyes in Different Foodstuffs

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Synthetic or natural food colorants are usually added to foodstuffs to improve appearance, taste, and color in order to make them more attractive to consumers. Sunset yellow and Quinoline yellow are two of these synthetic colorants, widely used as additives in foodstuffs and pharmaceuticals [1]. Due to the low concentration of synthetic dyes in food samples and the complexity of the different matrices, an efficient extraction and preconcentration step is usually necessary prior to determination of trace amounts of colorants. In this study, a simple ion pair based surfactant assisted microextraction has been developed for preconcentration of trace amounts of Sunset yellow and Quinoline yellow using spectrophotometric determination. The effective factors on the extraction efficiency were optimized. The calibration graphs were linear in the range of 2.0–60.0 ng mL^{-1} with detection limits of 0.044 and 0.042 ng mL^{-1} for Sunset yellow and Quinoline yellow, respectively. Partial least squares method was applied to resolving overlapped absorption spectra of mixtures of dyes and orthogonal signal correction was used as a preprocessing method. Orthogonal signal correction (OSC) is a preprocessing and filtering method to remove unrelated variation from the response matrix [2]. The root mean squares error of prediction for Sunset yellow and Quinoline yellow with and without orthogonal signal correction was 0.56, 1.62 and 0.80, 1.70, respectively. The proposed method was successfully used to determination of synthetic colorants in various food samples with the recoveries of 95.0–104.6%.

Keywords Ion pair microextraction; Partial least squares; Quinoline yellow; Sunset yellow

References:

[1] R.S. Razmara, A. Daneshfar, R. Sahrai, *J. Ind. Eng. Chem*, **2011**, 17, 533-536.
[2] J. Ghasemi, A. Niazi, *talanta*, **2005**, 65, 1168-1173.

Salting-out assisted Liquid–liquid Microextraction with the Aid of Experimental Design for Determination of Palladium

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The importance of the palladium (Pd) metal has grown many folds in recent years due to the increasing applications for the production of dental and medicinal devices, fine chemicals, pharmaceutical drugs, fuel cells and catalytic converters [1]. Some of palladium compounds have been reported as potential health risks to humans, causing asthma, allergy and other serious health problems [2]. Thus, simple and efficient detection methods for palladium species with high substrate selectivity are in great need. In this study, fast, simple and sensitive salting-out assisted liquid–liquid microextraction procedure has been applied for the preconcentration and determination of palladium in water samples. Response surface methodology (RSM) has been widely used for optimization and modeling of different processes. RSM based on a three-level four-factor Box–Behnken design (BBD) was employed to optimize the extraction conditions (NaCl concentration, amount of extraction solvent, pH and vortex time). Under the optimum conditions, the calibration graph was linear over the range of 5.0–120.0 ng mL^{-1} and relative standard deviation (RSD%, n = 7) 1.63% was obtained. This procedure allows the determination of palladium synthesis and real samples such as waste water with good reliability of the determination.

Keywords Box–Behnken design; Palladium; Salting-out assisted microextraction

References:

[1] J.Y. Lee, B. Raju, B.N. Kumar, J.R. Kumar, H.K. Park, B.R. Reddy, Sep. Purif. Technol 73 (2010) 213-218.
[2] K. Ravindra, L. Bencs, R. Van Grieken, Sci. Total Environ 318 (2004) 1-43.

Comprehensive analysis of stevia essential oil using multivariate curve resolution techniques

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Gas chromatography–mass spectrometry (GC–MS) combined with Chemometric resolution techniques were proposed as a method for the analysis of volatile components of Stevia oil. The essential oil of Stevia was extracted using hydrodistillation method and analyzed with GC–MS in optimized conditions. A total of 70 components were identified using similarity searches between mass spectra and MS database. This number was extended to 95 components with concentrations higher than 0.01% accounting for 94.75% of the total relative content using Chemometric techniques. For the first time in this work, an approach based upon subspace comparison is used for determination of the chemical rank of GC–MS data. The peak clusters were resolved using multivariate curve resolution-alternating least square (MCR-ALS). It is concluded that a thorough analysis of the complex mixtures such as stevia requires sophisticated GC–MS coupled with the Chemometric techniques. In EO of stevia; carvacrol, caryophyllene, caryophyllene oxide, spathulenol, cardinol, a-pinene, limonene, isopinocarveol and ibuprofen were identified as major compounds. These results show EO and extracts possess high antioxidant, anti-inflammation and antimicrobial properties.

Keywords: Gas chromatography; Chemometric; stevia; essential oil

References:

[1] M. Asadollahi-Baboli, A. Aghakhani, J. Sep. Sci. 37 (2014) 990.
[2] M. Jalali-Heravi, H. Parastar, Talanta 85 (2011) 835.
[3] M. Jalali-Heravi, H. Parastar, Chemometr. Intell. Lab. 104 (2010) 155.

Removal of synthetic dyes by kaolin /magnetic Fe_3O_4 nanocomposites and optimization of effective parameters by multivariate chemometrics methods

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Disposing dye wastes into environment is a major concern due to malign effects to the ecosystem. In textile, printing and dying, cosmetic, petroleum and leather industries, a massive amount of dyes could be discharged to the environment mostly due to improper processing, which are highly toxic even at very low concentrations. Clays are an ultimate choice owing to their adsorption properties, low cost, high availability, and environmentally friendly material which could be used either in their natural form or modified with some chemical agents, depending on the target pollutants [1,2].

In this work, a brilliant green (BG) dye in an aqueous solution has been removed using the developed Fe_3O_4/kaolin magnetic nanocomposites. Effective parameters on the efficiency of BG dye adsorption, such as pH, temperature of the solution, equilibrium time of adsorption, agitation speed, initial concentration of the dye and adsorbent dosage, were investigated by central composite design in order to identify the most important parameters and their interactions. Under optimum condition, it has been observed that the developed nanocomposites exhibit excellent adsorption capacity (Q_0 = 209.205 $mg.g^{-1}$), which is considerably high. In addition, isotherm and thermodynamic studies have been conducted to better understand the involved mechanism [3].

Keyword: Brilliant green; Kaolin; Magnetic sorbent; Multivariate optimization

References:

[1] B.Steenari, K. Fedje, Fuel 89 (2010) 2026–2032.

[2] M.T. Yagub, T.K. Sen, S.Afroze, H.M. Ang, Advances in Colloid and Interface Science 209 (2014) 172-184.

[3] R. Khani, J.B. Ghasemi, F. Shemirani, Spectrochim. Acta, Part A., Mol. Biomol. Spectrosc. 122 (2014) 295–303.

A New Thermo-analytical and Thermal-Safety Software for Determination of Kinetic Parameters Using Thermal Analysis Experiments

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Thermal analysis is a useful method for investigation about thermal event which occur in materials. Kinetic parameters such as reaction progress, reaction rate, pre-exponential factor and activation energy are important parameters which play an important role in safety calculation. These parameters could be obtained by thermal analysis calculations. Thermal safety parameters are always an important concern and many attentions are paid for evaluation hazard risk during production, storage and usage period. Calculations are divided in two main categories: 1-Model fitting and 2-Model free. Calculations always are hard and very complex and also need exact solution of differential equations.

We introduce new software in MATLAB for calculation of kinetic parameters based on model free method. By using kinetic parameters which obtained from this software, thermal safety parameters such as Self Accelerating Decomposition Temperature (SADT) are calculated. SADT for a kind of energetic material is calculated about 168.3 ^{0}C. From Differential Scanning Calorimetry (DSC) results, SADT is determined about 169 ^{0}C. Difference between experimental and calculated result by our software is very low and about 0.7 ^{0}C. For 50 kinds of energetic materials SADT is measured and also calculated by our new software. The maximum difference between calculated and experimental SADT is about 3% and the minimum difference is about 0.4 ^{0}C.

Keywords Thermal Analysis; Kinetic; safety; Software

References:

[1] Q.L. Yan, S. Zeman, S. Jimenez , F Zhao, L. Maqueda, J. Malek, J. Hazard. Mater, 271 (2014) 185.
[2] C. Popescu, W.P.C. de Klerk, L. LaHaye, J. Therm. Anal. Calorim, 80 (2005) 511.

A New Kinetic Software for Prediction of Life time and Kinetic Parameters Based on Stabilizer Consumption in Energetic Materials

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Some kind of energetic materials are thermodynamically unstable and only from kinetic aspect are stable and could be kept. In this kind of material, stabilizers are added which cause safe storage and avoid autocatalytic reactions during storage. Stabilizers are consumed during storage period of energetic materials. Calculation of time when stabilizer is consumed in natural aging of energetic material in ambient temperature during storage is very hard and needs sampling in long time intervals and may long many years. For solving this problem accelerated aging is used. This method is shortened time. Aging is done in higher temperatures and short times. By sampling during aging and extraction of stabilizer, the amount of stabilizer is determined by High Performance Liquid Chromatography (HPLC). The important issue is relating results from accelerating aging to natural aging results.

Some kind of calculation method is existed like Arrhenius kinetic order. We use NATO standard AOP-48 based on sequential method. This method is based on a least-square fitting procedure of all ageing data (stabilizer depletion for all temperatures) in order to determine the optimum reaction order (n) value, followed by calculation of the corresponding activation energy (E) and pre exponential factor (A) values. Starting value for n is -0.99999 and increasing step value is 0.001. The end value for n is 2.00001. In optimum value of n, the calculated standard deviation is minimum value. We introduce a new software in MATLAB for all above calculations and predication of life time based on 50% consumption of stabilizer. For a kind of energetic material, Calculated results are: optimum value for n is 0.382, E= 135.262 kJ/mol, A= 2.295E+14 s^{-1}, life time for 50% consumption of stabilizer in 25^{0}C= 70.569 years and Standard Deviation percent is 5.6%.

Keywords Energetic material; Kinetic; Stabilizer; Software; least-square

References:

[1] AOP-48, Ed. 2, Nitrocellulose Based Propellants–Stability Test Procedures and Requirements Using Stabilizer Depletion, NATOAC/326 SG 1, CNG Draft 12, 2006.

Composition Optimization of Modified Multiwalled Carbon Nanotube/Ionic Liquid Paste Electrode by Using a D-Optimal Mixture Design in Design-Expert Software for Analytical Purposes

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The D-optimal mixture design in Design-Expert Software has been used for composition optimization of a modified multiwalled carbon nanotube/ionic liquid paste electrode. In this regard, the percentage of graphite powder, tetraalkylammonium/I_3^- (TAA/I_3^-), multiwalled carbon nanotube (MWCNT) and ionic liquid (IL) in the modified carbon paste electrode (CPE) were optimized. The percentage ranges for the “mixture variables” were as follows: 30-60% graphite, 10-25% TAA/I_3^-, 0.0-20% MWCNT and 10-50% IL. The “constraints” were: 40% ≤ graphite + MWCNT ≤ 60%, 10% ≤ TAA/I_3^- + IL ≤ 50% while graphite + MWCNT + TAA/I_3^- + IL=100%. According to “percentage ranges” and “constraints”, the model designed 21 different CPEs with various component percentages. These CPEs were prepared and their corresponding cyclic voltammograms (CVs) were taken in phosphate buffer solution. Electrochemical results revealed that the optimized compositions were 45% graphite, 15% TAA/I_3^- *(as the new modifier),* 10 % MWCNT and 30% IL. The optimal modified CPE showed good electrochemical properties that were well matched with the model prediction parameters. The resulting electrode provided well-separated oxidation and reduction peaks for I^-/I_3^- redox couple in structure of electrode. The method was successfully applied to the determination of some biomolecules.

Keywords: Carbon multiwalled nanotube, Ionic liquid paste electrode; D-optimal mixture design

References:

[1] A. Afraz, A.A. Rafati, M. Najafi, Materials Science and Engineering C 44 (2014) 58–68.
[2] A. Nezhadali, S. Sadeghzadeh, Sensors and Actuators B: Chemical In Press Accepted Manuscript (2016).

Simultaneous analysis of Brilliant green and Crystal violet by Direct Orthogonal Signal Correction-Partial Least Squares Regression and Studying Adsorption of these Textile Dyes onto Activated Walnut Shell

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In the present work, the simultaneous determination of the brilliant green (BG) and crystal violet (CV) dyes with overlapped absorption spectra in binary mixture solutions was carried out using the partial least squares (PLS) and direct orthogonal signal correction-partial least squares (DOSC-PLS) techniques. The results obtained show that by applying DOSC on the calibration and prediction data for each analyte, the prediction error was minimized (especially for BG) to a large extent. Therefore, for the subsequent experiments, the DOSC-PLS method was used to determine the BG and CV concentrations in the binary mixtures. Then activated walnut shell (AWNS) was used as an economical, efficient, and accessible sorbent for the removal of the cited dyes in a batch experimental set-up. The effects of the experimental parameters such as initial pH, adsorbent dosage, initial dye concentration, contact time, and temperature on the adsorption efficiency of AWNS in a single solution and binary mixture were investigated. The prepared AWNS with a high surface area (296.92 m^2/g, according to Brunauer-Emmett-Teller method) was efficiently applied for the removal of these dyes with a minimum amount of adsorbent (0.8 gL^{-1}) at room temperature and at pH 7.0 (corresponding to the pH value for natural aqueous solutions), and at a considerably short contact time (13 min). These advantages make it appropriate for dye removal. Different isotherms were used to model the equilibrium data obtained for BG and CV dyes in single and binary systems using the non-linear regression in the Matlab software. The analysis data showed that the sip isotherm could satisfactorily explain the equilibrium data.The adsorption kinetic was successfully simulated using the pseudo-second-order kinetic model with the cooperation of the intra-particle diffusion model.

Keywords: Partial least squares regression; Removal; Signal correction; walnut shell.

Fabrication of TiO_2–Polymerized Graphene Composite nanofibers with optimum morphology using CCD method

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In this research, TiO2 nanofibers were synthesized using polymerized grapheme oxide (GO-g-PCA) and poly vinyl pyrolidone (PVP)/ Titanium tetra isopropoxide (Ti(Oipr)$_4$ as precursors with electrospinning technique. In this work, the advances in photocatalysis based on the combination of titania (TTIP) and graphene oxide-graft-poly citric acid is presented. At first Graphene oxide (GO) was prepared and then polymerization process was performed. The effective parameters on fiber diameter such as the PVP wt.%,TTIP wt.%, distance between needle and collector, applied voltage, polymerized GO content and pH were optimized using Central Composite Design method (CCD) by statistical software package Minitab ver.16. It can be seen that, the PVP wt.% was the most important parameter in the fiber diameter of electrospun TiO2-GO-graft-PCA nanofibers. and moreover, prepared GO and GO-g-PCA were characterized using UV, FTIR and SEM analysis. TiO2 nanofibers were prepared in optimum conditions with best morphology (minimum diameter and without bead). Finally nanofibers were checked out via various analysis, including Scanning Electron Microscope (SEM), Thermal Gravimetric Analysis (TGA/DTA) and XRD. The results show that the fibers fabricated successfully.

Keywords: TiO2-polymerized grapheme, TiO2 composite nanofiber. central composite design (CCD), graphene oxide.

References:

[1] S. Ray, J.A. Lalman, Using the Box–Benkhen design (BBD) to minimize the diameter of electrospun titanium dioxide nanofibers, *Chem. Eng. J.* 169 (**2011**) 116–125.
[2] R. Ostermann, D. Li, Y. Yin, J.T. McCann, Y. Xia, V2O5 Nanorods on TiO2 nanofibers: a new class of hierarchical nanostructures enabled by electrospinning and calcination, *Nano Lett*. 6 (**2006**) 1297–1302.

First-order multivariate calibration with pretreated voltammetric data for quantitative purposes in interfering media: A comparative study

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An analytical methodology based on differential pulse voltammetry (DPV) at a glassy carbon electrode (GCE) assisted by two chemometric approaches including back propagation-artificial neural network (BP-ANN) and partial least squares-1 (PLS-1) was developed and validated for the simultaneous determination of Ascorbic acid, Uric acid, Acetaminophen, and Noradrenaline to identify which approach offers the best predictions. The baselines of the DPV signals were corrected by asymmetric least square spline regression (AsLSSR) algorithm. Before applying the PLS-1, lack of bi-linearity was tackled by potential shift correction using correlation optimised warping (COW) algorithm. The multivariate calibration (MVC) model was developed as a quaternary calibration model in a blank human serum sample (drug-free) provided by a healthy volunteer to regard the presence of a strong matrix effect which may be caused by the possible interferents present in the serum, and it was validated and tested with two independent sets of analytes mixtures in the blank and actual human serum samples, respectively. Finally, PLS-1 shows better results than BP-ANN for simultaneous determination of AA, UA, AC, and NA in both blank and actual human serum samples.

Keywords: Multivariate calibration; Ascorbic acid; Uric acid; Acetaminophen; Noradrenaline.

References:

[1] Y. Andreu, S.D. Marcos, J.R. Castillo, J. Galbán, Talanta 65 (2005) 1045–1051.
[2] P. Janda, J. Weber, L. Dunsch, A.B.P. Lever, Anal. Chem. 68 (1996) 960–965.
[3] D. Wen, S.J. Guo, S.J. Dong, E.K. Wang, Biosens Bioelectron. 26 (2010) 1056–1061.

SiO_2 nanoparticles for Adsorptive Removal of Toliudine Blue as a Clinical dye from aqueous Wastes via Multivariate Optimization and Adsorption Characterization

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Toluidine blue is an acidophilic metachromatic dye that selectively stains acidic tissue components [1]. In this study, SiO_2 nanoparticles were used to remove Toluidine blue dye in a batch system. In order to reach a maximum removal efficiency (R%), optimum conditions were explored by means of experimental design approach. The experimental factors were considered such as: pH, contact time, sorbent dosage (m) and dye concentration (C_d) in the solution. Response surface methodology (RSM) including faced central composite design (FCCD) was employed to optimize the removal conditions and to propose an appropriate regression model along with related surface plots. The optimum conditions obtained for 99% removal of dye : pH=6, m= 0.06 g and C_d= 850 mg/L. Langmuir Isotherm fitted well than other Isotherms with equilibrium experimental data and yield the maximum monolayer adsorption of 55.25 mg/g. Second-order kinetic model described well the dynamic behavior of the current adsorption process. The desorption efficiencies with HCl, HNO_3, CH_3COOH and NaOH were low. Also it was found that presence of Na^+, K^+,Ca^{2+} and Mg^{2+} ion have no significant interference on adsorption efficiency. FT-IR analysis identified that the functional groups of sorbent were involved in the adsorption process.

Keywords: Adsorption; Faced central composite design (FCCD); Removal; SiO_2 nanoparticles ; Toliudine Blue

References:

[1] A. Anderson, B. Binsley, H. Mahta-Kashmir, *Talanta*, **2014,**106, 265–271.
[2] J. Zolghrnein , Zh. Adhami, A. Shahmoradi, S.N.Mousavi, Anal.Sci.26(2010), 111-116.
[3] [6] J. Zolgharnein, N. Asanjrani, M. Bagtash, G. Azimi, Spectrochim. Acta Part A 126 (2014) 291–300

QSPR study for retention factor of pesticides in Biopartitioning micellar chromatography using Bee algorithm

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Biopartitioning micellar chromatography (BMC) is a simple and reproducible approach in emulating the partitioning of chemicals in biomembranes [1]. In this paper, Bee algorithm (BA) was used to select the best descriptors, that relates retention factor (log *k*) of pesticides to their structures. Bee algorithm is a new population-based optimization algorithm, which is derived from the observation of real Bees behavior and proposed to feature selection [2].

In this study retention factor (log *k*) in the BMC of 79 heterogeneous pesticides was derived from previous report [1]. These molecules were drawn and optimized in Hyperchem software and descriptors were calculated using Dragon software. The Bee algorithm was performed in MATLAB software.

The data matrix 79×1704 (the zero and same descriptors were deleted) was introduced to the Bee algorithm and seven descriptors were selected. Then the multiple linear regression (MLR) was used for model development. The correlation of coefficient and mean square error were obtained as 0.9054 and 0.0297 respectively.

The main aim of the present work was the development of a quantitative structure-property relationships (QSPR) method using BA methodology for descriptor selection. It is shown in this work that BA is a tool as feature selection method which generates predictive descriptors. The generated model was applied for prediction of retention factor of BMC. MLR was also applied for descriptor selection and the results showed that BA methodology has very good prediction power for this purpose in comparison with MLR.

Keywords: Bee algorithm; Biopartitioning micellar chromatography; QSPR

References:

[1] W. Ma, F. Luan, H. Zhang, J. Chromatogr. A 1113 (2006) 140.
[2] K. Zarei, M. Atabati, S. Moghaddary, J. Chemometr. Intell. Lab 128 (2013) 37.

Application of Linear and Non-linear Methods for Modeling Removal Efficiency of Rhodamine dye from aqueous solutions using Magnetic Fe_3O_4 loaded onto Walnut hull

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The magnetite Fe_3O_4 loaded onto walnut hull was prepared via a simple method [1], and was subsequently characterized using the scanning electron microscopy and FT-IR spectroscopy. Then the applicability of the synthesized adsorbent for removing of Rhodamine (as a textile dye) from aqueous solutions was examined. The effects of the experimental variables such as initial pH, adsorbent dosage, dye concentration, and contact time were studied to optimize the sorption conditions of the dye. Then these variables were used as the inputs to generate the multiple linear regression and artificial neural network (as non-linear model) in order to predict the removal efficiency of this textile dye at different experimental conditions. The validation studies of the linear and non-linear models were performed using the test set (108 experimental data). The results obtained for prediction of the test set by the linear and non-linear models showed the squared correlation coefficients of 0.889 and 0.994, respectively. According to the result obtained, the artificial neural network was more appropriate to describe the behavior of the sorption process under different conditions and can be applied to the development of an automated dye wastewater removal plant. The results obtained for this model also indicated that the dye concentration and solution pH had the highest effects on the dye sorption.

Keywords: Artificial neural network ; Dye; Multiple linear regression; Sorption

References:

[1]. T. Madrakian, A. Afkhami, M. Ahmadi, *SpectrochimicaActa Part A: Molecular and Biomolecular Spectroscopy* 99 (2012) 102.

Untargeted metabolomic profiling of seminal plasma of non-obstructive azoospermia men using gas chromatography- mass spectrometry and advanced chemometric techniques

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This work presents the untargeted metabolomic profiling of the seminal plasma of non-obstructive azoospermia (NOA) men using gas chromatography-mass spectrometry (GC-MS). To this end, the seminal plasma of a total of 30 samples including 11 NOA men with TESE-negative (AZN), 9 NOA men with TESE-positive (AZP) and 10 fertile (F) healthy men (as control group) were collected. Each sample was analyzed triplicate. Advanced chemometrics methods have been used for analyzing the data. Quadratic discriminate analysis (QDA) technique was implemented on data for identification of discriminatory retention times in total ion chromatograms (TICs). The results revealed that the developed classification models in this work were able to predict the groups of samples using only their TIC data. After recognition of discriminatory retention times, asymmetric penalized least square, evolving factor analysis, correlation optimized warping and alternating least squares strategies have been used for preprocessing and deconvolution of the overlapped chromatographic peaks. Finally, thirty six discriminatory metabolites have been identified. These metabolites are discriminatory biomarkers for different groups studied in the current work.

Keywords: Male infertility; untargeted metabolomic profiling; GC-MS; Multivariate curve resolution; Discriminant analysis; Classification

References:

[1] H. Parastar, M. Jalali-Heravi, H. Sereshti, A. Mani-Varnosfaderani, J. Chromatogr. A., 2012, 1251, 176-187.

Simultaneous Determination of Diphenylamine Derivatives Using UV-Vis Spectroscopy and Chemometrics Techniques

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A novel and simple method is presented for the simultaneous determination of diphenylamine and its nitro derivatives in real samples. The analysis of first-order UV-Vis spectra was performed using principle component regression (PCR), partial least square (PLS) and bayesian regularized artificial neural networks (BRANN) techniques. The obtained statistical parameters in terms of regression coefficient (R) and root mean square error (RMSE) were satisfactory for the calibration and validation sets. The results revealed the great impact of the variable selection techniques on the performance of the algorithms for simultaneous calibration of the analytes. In this work a combination of genetic algorithm and BRANN technique (i.e. BRGNN) was proposed for the first time for simultaneous determination of diphenylamine derivatives. The results revealed the superiority of the BRGNN method over weighted and un-weighted PLS techniques. The coefficients of determination for the five derivatives of diphenylamine were 0.94, 0.92, 0.97, 0.91 and 0.93, respectively. Regarding the obtained results in this project, it can be concluded that the combination of multivariate calibration methods with suitable variable selection techniques can improve the identification and quantification ability of UV-Vis spectroscopy for the simultaneous determination of target compounds in different sample matrices.

Keywords: diphenylamine, multivariate calibration, UV-Vis spectroscopy

References:

[1] O. Drzyzga, Chemosphere 8 (2003) 809-818.
[2] B. Hemmateenejad, M. Akhond, F. Samari, Spect. Chim. Acta, Part A 67 (2007) 958–965.
[3] E. Dinc, D. Baleanu G. Ioele, M. D. Luca, G. Ragnob, J. Pharm. Biomed. Anal. 48 (2008) 1471- 1475.

Investigating the formation process of titanium dioxide nanostructures by infrared spectroscopy and chemometrics

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TiO_2 nanostructures have been employed in wide-range of applications such as environmental protection, solar cells, photo catalysts, gas sensors, photo electrodes and electronic devices. Many applications of TiO_2 nano crystalline could be improved by changing the particle size, shape and morphology. Therefore, studying the mechanism of fabrication evolution is critical for size and shape controlled synthesis of nanocrystaline TiO_2. In this work titanium dioxide nanostructures i.e. particles, rods and belts have been prepared by sol-gel method via hydrolysis of TTIP in diluted 2-propanol with water binary solvent. By controlling experimental conditions such as pH and water content of process during hydrolysis of TTIP, TiO_2 nanostructures were fabricated. The prepared samples were characterized by scanning electron microscopy (SEM) for morphological studies and crystalline size analysis. FTIR spectroscopy was employed to monitor the evolution process of the formation of TiO_2 nanostructures utilizing chemometric approaches for process analytics. The evolutionary FTIR absorbance data of TiO_2 nanostructures through structures formation via sol gel methods in various solution conditions were analyzed using factor analysis, evolving factor analysis, and multivariate curve resolution alternating least-squares (MCR-ALS) . Depending on chemical routs, 4، 3and 3 chemical factors were detected being attributed to the TiO_2 nanoparticles ،nano rods and nano belts while the concentration profiles and pure spectra of the structures were resolved.

Keywords: Growth mechanis; Infrared spectroscopy; Multivariate curve resolution–alternating least squares (MCR–ALS); TiO_2 nanostructure.

References:

[1] M. H. Imanieh, Y.Vahidshad, P. Nour Pour Shakesi, S.Shakesi, K. Shabani, World Scientific (2010) 279–285.
[2] Y. Kolenko, K. Kovnir, A. Gavrilov, A. Garshev, V. Frantti, American Chemical Society 110 (2016) 4030-4038.
[3] H. Liu, D. Yang, Z. Zheng, X. Ke, E. Waclawik, H. Zhu, R. Frost, Raman Spectroscopy (2010).

Chemometrics optimization of separation and simultaneous determination of some herbicides by sub-micellar liquid chromatography

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The herbicides are chemical compounds, used to kill weeds and other unwanted plants. The analysis of herbicides residues in various matrices is necessary [1]. High performance liquid chromatography (HPLC) as a sensitive and efficient analytical method has been developed for determination of herbicides at trace levels in different samples [1], but there is no report on separation of them using high submicellar liquid chromatography (HSMLC). HSMLC is a mode of HPLC in which the mobile phase contains high concentrations of both surfactant and organic modifier (OM) [2]. In present work, response surface methodology was applied to optimization of HSMLC separation of six herbicides including Atrazine, Propazine, Simazine, Monuron, Diuron and Propanil. Firstly, effect of type of OM was studied. Then optimization of the parameters affecting the separation including concentration of the OM and of surfactant, pH and temperature was performed simultaneously using central composite design and the multi-criteria decision making method. The optimum condition was a mobile phase consists of, 25.72 mM SDS, %32.16 EtOH, 0.01 M phosphate buffer of pH 4.16 and column temperature of 31.1°C. Under the optimum conditions, the method shows a good linearity (1-10 mg/L), limits of detection (<0.311 mg/L), accuracy (recoveries>86.00) and precision (RSD<5.02). Finally, the proposed method was used to analysis of herbicide residues in an agricultural water sample.

Keywords: Submicellar liquid chromatography, herbicides, response surface methodology

References:

[1] J. L. Tadeo, C. Sánchez-Brunete, L. González, Analysis of Pesticides in Food and Environmental Samples, ed. J. L. Tadeo, CRC Press, Boca Raton, FL, 2008, ch. 1, pp. 1-35.
[2] M.J. Ruiz-Ángel, S. Carda-Broch, M.C. García-Álvarez-Coque, Sep. Purification Rev., 43, (2014) 124.

Removal of Iron from Raffinate Solution of Sarcheshmeh Copper Complex by Magnetic-precipitate Formation Method.

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Iron is usually present in leach solutions and its elimination is a major operational problem in hydrometallurgic extraction of copper [1]. In the present work a simple and inexpensive method is proposed for iron ions removal from raffinate solution of Sarcheshmeh Copper Complex. Raffinate solution usually contains near to 12000 ppm iron inos in the form of Fe^{2+} and Fe^{3+}. Spectrophotometric method was used to measure the concentration of each ion at 515 nm by converting the ions to 1-10 orthophenantrolin complex of iron (II). The magnetic precipitate of iron (iron oxide) was formed by addition of NaOH to the solution at optimum conditions. Then the precipitate was separated from the mixture by a magnet. The central composite design (CCD) method was used to attain the optimum condition of experiment [2]. To do this, temperature, NaOH volume and stirring time of the mixture were evaluated as effective factors. The time required to separate the precipitate and the concentration of iron in the solution (residual iron) were considered as responses. Design Expert software was implemented to derive the response surface model. The suggested optimum condition was tested experimentally and there were good agreement between theoretical and experimental results. In this method complete removal of iron is certified.

Keywords: Hydrometallurgy; Spectrophotometry; Raffinate solution; Removal of iron**;** Central Composite Design.

References:

[1]B. Mckevit, D. Dreisinger, Hydrometallurgy 98 (2009), 122-127.
[2] E.D. Morgan, Chemometrics Exprimental Design, 238-245.

Multivariate Data Analyses Intertwined with Electrochemical Hydride Generation Connected μ-Dynamic Extraction to Investigate Simultaneous Spectrophotometric Trace Assessment of As(III) and Sb(III)

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As (III) is one of the most important toxic trace elements, which can cause serious health problems owing to its carcinogenic effects. On the other hand Sb (III) is in-group of non-essential elements and its toxicity is comparable in behavior to arsenic. In the present research, a selective and sensitive method for simultaneous quantification of As (III) and Sb (III) is proposed. An automated dynamic headspace liquid phase micro extraction technique has been used in combination with electrochemical hydride generation to determine As (III) and Sb (III) -in binary mixture- by UV–Vis spectrophotometry. This method is based on electrochemical reduction of As to Arsine (AsH_3) and Sb to Stibine (SbH_3) in acidic media and on the subsequent reaction of AsH_3 and SbH_3 with silver diethyl dithiocarbamate (AgDDC) to give red complexes that their absorption spectra are so closely overlapping. The effects of various parameters affecting the electrochemical hydride generation and extraction efficiency were studied using a central composite design (CCD) under response surface methodology (RSM). Various linear and non-linear multivariate calibration methods, including multiple linear regression(MLR), Inverse classical least squares(ILS), factor analysis regressions (FARs) and optimized artificial neural networks were compared and evaluated for quantification of binary mixtures of As(III) and Sb(III). As a result, this study showed, electrochemical hydride generation connected with μ-Dynamic extraction is a very successful technique for selective and green chemical sampling of trace amount of As(III) and Sb(III). Chemometrics strategies allow to design a few experiments for concurrent optimizing intently and exactly multi-factor and multi-response (recoveries of As and Sb). Utilizing first order calibration methods assisted with signal processing fulfills conveniently simultaneous UV-Vis spectrophotometric determination of As(III) and Sb(III) (with complete and severe overlapping spectra) without any pre-separation, however in routine analysis it is done with the aid of atomic spectroscopy.

Keywords: Antimony; Arsenic; Chemometrics; μ-Dynamic Headspace extraction; Electrochemical Hydride Generation

Application of experimental design for preconentration of rivsatigmine by magnetic iron oxide nanoparticles modified with Cetyltrimethylammonium Bromide

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Rivastigmine is a parasympathomimetic or cholinergic agent for the treatment of mild to moderatedementia of the Alzheimer's type and dementia due to Parkinson's disease. A novel and fast extraction procedure using magnetic Fe_3O_4 nanoparticles (NPs) modified with Cetyltrimethylammonium Bromide (CTAB), as an efficient solid phase, was developed for preconcentration and spectrophotometric determination of trace amounts of rivastigmine in human urine and industrial waste water. The pure and modified Fe_3O_4 nanoparticles were physicochemically and morphologically characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM). The dependency of extraction percentages to variables such as pH, amount of elution solvent, adsorbent dosage and extraction time were studied by central composite design (CCD) coupled with response surface methodology (RSM) by considering the desirability function (DF). The detection limit of this method for rivastigmine was 0.05 µg/mL and the R.S.D. was 2.73% (n=8). The recovery in human urine and industrial waste waters were investigated and values of 70% to 81% were obtained. The experimental results showed that the proposed method was a simple, sensitive fast and feasible for the analysis of rivsatigmine in environmental and biological samples.

Keywords Central composite design; Iron oxide nanoparticles; Rivastigmine

References:

[1] Leun D., SenGupta A. K., *Environmental science & technology*, **2000,** *34* (15), 3276.

Simultaneous spectroscopic determination of Allura red and Carmoisine using wavelet orthogonal signal correction-partial least squares method after their pre-concentration by cloud point extraction

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This study is a simple, safe, cheap, modified and efficient cloud point extraction for the simultaneous pre-concentration and determination of allura red and carmoisine in the matrix of food samples. Wavelet orthogonal signal correction (WOSC) was used to denoise the spectrophotometric data and hybrid with partial least squares (PLS) regression method was used to determine the simultaneous of each compound after cloud point extraction. The effects of different variables on the extraction process of both dye, were investigated and optimized. Linear range of calibration graphs was determined in the range of 0.06 to 2 µg ml^{-1} for allura red and 0.05 to 1.5 µg ml^{-1} for carmoisine under the optimum conditions. Limit of detection values for allura red and carmoisine were 0.016 and 0.015 µg ml^{-1}, respectively. The root mean square error of prediction (RMSEP) for allure red and carmoisine was 0.0137 and 0.0237 µg ml^{-1}, respectively. Finally, the developed model was successfully applied to the simultaneous analysis of allura red and carmoisine in various food samples.

Keywords: Allura red, Carmoisine, Wavelet orthogonal signal correction; Spectroscopic; Cloud point extraction;

References:

[1] R. khani, J. B. Ghasemi and F. shemirani, *Spectrochim. Acta A*, **122**, (2014) 295.
[2] N. Pourreza and M. Ghomi, *Talanta*, **84**, (2011) 240.
[3] A. Niazi, J. B. Ghasemi and A. Yazdanipour, *Spectrochim. Acta A*, **68**, (2007) 523.

Multivariate Curve Resolution-Alternating Least Squares with Sparsity Constraint

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Multivariate curve resolution – alternating least square (MCR-ALS) was introduced by Tauler et. al [1] and is a well-known method among soft-modeling algorithms with broad range of applications in different fields of science. However, the main drawback of all MCR methods is the presence of rotational ambiguity. Different constraints such as non-negativity, local rank, selectivity, unimodality and hard modeling were applied to MCR-ALS in order to decrease the degree of ambiguity. In this paper, we implemented sparsity constraint as a new constraint for the first time for MCR-ALS algorithm (MCR-ALS-S). The sparsity constraint has been proposed by researches in different field of science. Sparsity is defined as a measure of non-continuity observed in a data as a vector array. It is important to note that mass spectrometry data is almost sparse. Undoubtedly, hyphenated chromatography-mass spectrometry (GC-MS) has been used in analytical chemistry for the detection, identification and quantification of complex samples, such as natural metabolites, drugs and foods. In the present contribution the sparsity constraint has been applied to MCR-ALS algorithm by confining the L-$_{\text{Zero}}$ norm of the mass spectra in each iteration of the algorithm. The results of MCR-ALS with new sparsity constraint were superior over MCR-ALS for resolving two, three, four and five component simulated GC-MS data. The band boundaries of feasible solution for the simulated data were calculated using MCR-BANDS algorithm. The lengths of the bands were astonishingly reduced by implementation of the sparsity constraint on MCR-ALS algorithm. Moreover, the resolved concentration profiles were more accurate when compared with real profiles. In many circumstances, the values of lack of fit calculated using MCR-ALS-S were better that those of MCR-ALS algorithm.

Keywords: Gas Chromatography, Multivariate Curve Resolution-Alternating Least Square, Sparsity Constraint.

References:

[1] Tauler, R.,1995. Multivariate curve resolution applied to second ordrd data. *J. Chemom. Intell. Lab. Syst,* 30, 133-146

Optimization of Alkaline treatment of high-silica ZSM-5 zeolite for selective production of propylene from methanol using Taguchi method

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Methanol to propylene (MTP) process is regarded as a promising alternative route for the high yield production of propylene. Currently, high-silica ZSM-5 zeolite is one of the most promising catalysts for the MTP reaction. However, due sole presence of relatively small micropores in the ZSM-5 zeolites, their catalytic applicability is restricted by diffusional limitations, which induce fast catalyst deactivation [1-2]. To alleviate such limitations, desilication of ZSM-5 in the alkaline solutions has been developed as one of the most efficient methods to design mesoporous zeolites [2, 3]. In this paper, significant parameters associated with the alkaline treatment, such as concentration of NaOH/TPAOH solution (0.1, 0.2 and 0.5 M), TPAOH/(TPAOH+NaOH) molar ratio (0.2, 0.4 and 0.6), temperature (50, 65 and 80) and time (30, 60 and 90), were optimized by L_9 Taguchi orthogonal design to obtain high propylene yield in the MTP reaction over the desilicated zeolites. The performance test runs of the desilicated samples were evaluated in a fixed-bed reactor under atmospheric pressure, 460 °C and methanol WHSV = 0.9 h^{-1} with methanol to water weight ratio of unity in the feed. The results revealed that, alkaline treatment in a 0.2 M mixture of NaOH/TPAOH solution with TPAOH/(NaOH+TPAOH) = 0.4 at 65 ^{o}C for 30 min ensures the formation of narrow and uniform intracrystalline mesoporosity without severely damaging the crystal structure and intrinsic acidity of the zeolite leading to representing the best catalytic performance, including highest propylene selectivity (47.21) and longest catalyst lifetime (80 h).

Keywords: High-silica ZSM-5, Methanol-to-propylene, Desilication, Taguchi optimization

References:

[1] M. Firoozi, M. Baghalha, M. Asadi, Catal. Commun. 10 (2009) 1582.
[2] J. Ahmadpour, M Taghizadeh, C. R. Chimie 18 (2015) 834.
[3] D. Verboekend, J. Javier Pérez-Ramírez, Chem.– Eur. J. 17 (2011) 1137.

Urinary monitoring of non-steroidal anti-inflammatory drugs with the aid of poly (2-aminobenzothiazole)-coated graphen oxide/magnetite nanoparticles composite as a novel sorbent

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Sample preparation is a fundamental and essential step in almost all chemical analyses; particularly for the analysis of complicated sample such as biological, food and environmental samples [1]. In this study, for the first time, 2-aminobenzothiazole monomer was polymerized on Fe_3O_4 NPs, graphen oxide/Fe_3O_4 (GO/Fe_3O_4) and graphen/Fe_3O_4 (G/Fe_3O_4) nanocomposites. The synthesized magnetic nanosorbents were characterized by various techniques. The extraction ability of these nanosorbents including Fe_3O_4, GO/Fe_3O_4, G/Fe_3O_4, Fe_3O_4@poly (2-aminobenzothiazole) (Fe_3O_4@PABT), GO/Fe_3O_4@PABT and G/Fe_3O_4@PABT were compared for dispersive-micro-solid phase extraction of three non-steroidal anti-inflammatory drugs. The results revealed that GO/Fe_3O_4@PABT nanocomposite has higher extraction efficiency for naproxen, diclofenac and ibuprofen as selected model analytes. Following the sorption and elution steps, the model analytes were quantified by high performance liquid chromatography-photo diode array detection. Afterwards, a central composite design methodology combined with desirability function approach was applied to find out the optimal experimental conditions. These optimized values were: pH of the sample, 3.1; sorbent amount, 16 mg; sorption time, 16.5 min; salt concentration, 19% w/v; type and volume of the eluent, 120 µL 40% acetic acid in acetonitrile; elution time; 1 min. The limits of detection and linear dynamic ranges were achieved in the range of 0.07-0.3 µg L^{-1} and 0.25-2000 µg L^{-1}, respectively. The percent of extraction recovery and relative standard deviations (n = 5) were in the range of 85.5-90.5 and 5.4-7.2, respectively. Ultimately, this method was employed for urinary monitoring of the target analytes and satisfactory results were obtained.

Keywords: Dispersive micro-solid phase extraction; Graphen oxide/Fe_3O_4@poly (2-aminobenzothiazole); Non-steroidal anti-inflammatory drugs; Urinary monitoring.

References:

[1] J. He, M. Huang, D. Wang, Z. Zhang, G. Li, *J. Pharm. Biomed. Anal.*, 101, **2014**, 84.

Synthesis, Characterization and Adsorptive Properties of MIL-68(Al) in Aqueous Media; Optimized Experimental Design

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A metal–organic framework material, MIL-68(Al), was solvothermally prepared under reflux condition and characterized by FTIR, BET, SEM, XRD and TG analysis. MIL-68(Al) was then applied as an adsorbent for removal of Malachite Green (MG) as one of the most hazardous dyes in wastewaters, from aqueous solution. The effect of variables such as adsorbent dosage, sonication time, pH and initial concentration of MG on removal percentages of the dye were investigated by central composite design (CCD) under response surface methodology (RSM). The adsorption kinetics, adsorption mechanism, and adsorption isotherm were studied in detail. According to our data, the adsorption of MG follows the pseudo-second order equation, while Langmuir model interprets the equilibrium results. Dye loaded adsorbent can be generated by methanol and reused at least in three adsorption/desorption cycles with high efficiency.

It is worth to note that the optimum adsorption of MG occurred at pH 9, initial dye concentration 58 ppm, 0.0029 g of adsorbent and ultrasonic contact time 5.45 min which indicated the proposed MOF is a good candidate for removal of huge amount of MG in short time by consumption of small amounts of this adsorbent.

Keywords: Metal-Organic framework, Removal, Malachite Green, Response surface methodology

References:

[1]. M. Ghaedi, E. Nazari, R. Sahraie and M.K. Purkait, *Desalin. Water Treat.*, 2014, **52**, 5504.
[2]. D. Kavak , *J. Hazard. Mater.*, 2009, **163**, 308.

Modeling of Competitive Removal of Cationic Dyes by Metal Organic Frameworks; Kinetics and Equilibrium Studies

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The work was devoted to the study of a metal organic framework, MIL-68(Al), for removal of Methylene Blue and Rhodamine B hazardous dyes in wastewaters, from aqueous solution. This nanopore material was characterized using different techniques such as FTIR, TG, SEM, XRD and BET analysis. Central composite design (CCD) was used for the optimization of significant factors including pH, adsorbent dosage, Methylene Blue concentration, Rhodamine B concentration and ultrasonic contact time using response surface methodology (RSM) and the optimized values for these parameters in binary solutions were found to be 6.45, 0.014 g, 60 mg L^{-1}, 15 mg L^{-1} and 9.9 min, respectively. Fitting the equilibrium data to conventional isotherm models (Langmuir, Freundlich, and Tempkin) according to correlation coefficient confirmed the priority of the Langmuir model for data analysis. The maximum sorption capacity of 227 and 29 mg g^{-1} was obtained from Langmuir isotherm for Methylene Blue and Rhodamine B in binary solutions, respectively. The rate of dyes removal by MIL-68(Al) was fitted to traditional models like, pseudo-first, second-order and Elovich models in which pseudo-second order equation was the best model for explanation the adsorption process. The favorable adsorption data together with the good regenerability of the proposed MOF only by using methanol suggest its suitability for the fast and economic simultaneous dyes uptake even under mild conditions (neutral pH, small amount of adsorbent and short operating time).

Keywords: Metal-Organic framework, Dye removal, Isotherm, kinetics

References:

[1] M. Ghaedi, E. Nazari, R. Sahraie and M.K. Purkait, *Desalin. Water Treat.*, 2014, **52**, 5504.

Aerobic Oxidation of Aldehydes to Carboxylic Acids by Highly Efficient Recyclable $LaNiMgO_4$ Nano Catalysts without Solvent

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Our environment, which is endowed by nature, needs to be protected from ever-increasing chemical pollution. Large scale production of pesticides, pharmaceuticals and petrochemicals responsible for causing chemical pollution leads to the development of the concept of ‘‘green chemistry’’. Among the various techniques of green chemistry, microwave-assisted reaction under solvent-free condition emerges as a powerful approach for the synthesis of biologically active molecules in a very fast, efficient and time saving manner without the isolation of any intermediates resulting in atom economy and high selectivity [1,2]. Current applications of lanthanum as a pure element or in associations with other compounds are in super alloys, catalysts, special ceramics, and in organic synthesis [3]. In this paper, lanthanum nickelate substituted with magnesium (LaNiMgO4), nano catalysts have been successfully synthesized in a green co-precipitation method assisted by microwave. The obtained products characterized by XRD, SEM, and FT-IR techniques. Then, these nano catalysts used for oxidation of aldehydes to carboxylic acids in solvent-free condition. Also in this work, recyclability of nano catalyst has been studied and It was found that these nano catalysts could be reused for five cycles with negligible loss of their activity.

Keywords: *Solvent-Free Conditions; Recyclable Nano Catalysts; Microwave-assisted Method*

References:

[1] M. A. Amrollahi, B.B.F. Mirjalili and H. Emtiazi, J. Chem. Sci, 2013, 125, 561–566.
[2] V. Borhade, B.K. Uphade, D.R. Dope, Res. Chem. Intermed, 2014,14, 211–223.
[3] M.C. Palmieri, B. Volesky, O. Garcia, Hydrometallurgy 113 (2002) 31-36.

Evaluation of removal efficiency of heavy metals (Lead and Cadmium) from water samples using magnetic nano-adsorbent modified with mercaptopropyl trimethoxysilane agent

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Today one of the most important subjects is water pollution with heavy metals such as cadmium, lead which can be removed from water by using different methods and sorbents. It is known that over exposure to lead and its compounds can result in damage of nerve, kidneys, liver, brain, cardiovascular, and endocrine system; in serious cases it can cause death. Cadmium is a heavy metal with high toxicity and is best known as a carcinogen element. The release of heavy metal ions into our environment poses a threat to human health as well as to the ecosystem. Owing to their severe toxic effects on living organisms, it is necessary to find ways for their removal, especially that from aqueous systems.

This study aimed to investigate the removal of heavy metals such as Pb and Cd from the environmental water samples using thiol-functionalized mesoporous silica-coated magnetite nanoparticles (TF-SCMNPs). The synthesis of TF-SCMNPs occurred with simple co-precipitation methods. FT-IR, X-ray diffraction, SEM, energy dispersive X-ray, and VSM techniques were used for characterization of the prepared adsorbent. The factors affecting the extraction of the target metal ions such as pH, sample volume, stirring rate, time and amount of adsorbent were studied and optimized. The equilibrium adsorption data of Pb and Cd by TF-SCMNPs were analyzed by isotherm models. Also, adsorption kinetic and capacity of sorbent were investigated. The proposed method showed some advantages to the former methods such as easy preparation of adsorbents, selectivity, precision, short times of pretreatment and high extraction yields, especially for lead. The proposed method was applied to natural and environmental water samples, which showed good agreement with reference method results.

Keywords: TF-SCMNPs nanoparticle; Cadmium; Lead; Environmental water samples.

Investigation of adsorption strontium ion on modified nano-crystalline natural zeolite by using complexing agent N2O2

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The management of wastes in nuclear fuel industries is important and complex. Otherwise, the consequence of the presence of such waste in the environment generates damaging effects on human societies and the earth’s environment. 90Sr with biological half-life of approximately 30 years for the disposal is one of the most radioactive dangerous products. Zeolites are compounds that including the unique properties including molecular sieves, ion exchange, and catalytic behavior and advantages such as natural and low cost are being widely use. In this study, at first was prepared and determined the structure of the natural zeolite of the Sabzevar region (The XRD and SEM images of these particles show the zeolite has nano structure, ≈29.5nm) and to investigate the adsorption properties of this adsorbent towards Sr2+ ion from aqueous solution, effect pH parameter were examined. According to the results, to improve the efficiency of the adsorbent to complete remove Sr2+ ions, capsulated Schiff base ligand (2-hydroxy benzaldehyde)1and2-di-aminoethane (N2O2) into the cavities of zeolite and then effect of various parameters such as pH, contact time, amount of adsorbent, metal concentration and temperature on the process was investigated. Results showed that the adsorption efficiencies depends on pH and with use Schiff base ligand in the structure of the zeolite significantly metal ion uptake has increase. So a quantitative removal of Sr2+ ions in the optimum conditions (pH=6, 30 min. by 0.05 g of the adsorbent) from 20 ml of aqueous sample containing 20 mgl-1 of metal ions was achieved. The investigation of experimental data with kinetic models has shown a good agreement with second order equation and Langmuir isotherm model match to experimental data for studied ions.

Keywords: Adsorption; Natural Zeolite; Schiff base; Strontium

Removal of Sr2+ ion from wastewater using modified nanoparticles with a complexing agent

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The removal of toxic heavy metal pollutants from industrial wastewaters has become a considerable problem for developing industrial activities. Radiostrontium, when accumulated in human bones, is considered one of the most hazardous pollutants because of the chemical and biochemical similarities with calcium. Therefore, methods of processing of strontium-containing wastewaters have attracted much attention of technologists. Nanometer materials play a substantial role in metal ion separation studies owing to their special physical and chemical properties. In this study we report on the application of nanoparticles silica as sorbent for removing Sr2+ ions from aqueous solution. The studied nanoparticle was shown to be a weak adsorbent towards strontium ions but the adsorptive properties of nanoparticles can be improved by modification of the nanoparticle's surface with a Schiff base named salicylaldiminepropyltriethoxysilane. The results show a significant increase in the adsorption values for strontium ions beyond the pH values of 6 and in addition such modification causes pHs of the quantitative adsorption of studied metal ion shifts to the lower pH values. The effect of various parameters such as contact time, metal concentration and amount of adsorbent on the process was investigated. A quantitative removal of the studied metal was achieved by 0.05 g of the modified adsorbent disperse in 20 ml of the sample containing the metal ions with concentration 20 mgl-1 after 60 min of magnetically stirring. Kinetics of the adsorption process was studied by considering a pseudo second-order model. This model predicted chemisorption as the adsorption mechanism of the process. Langmuir, Freundlich and Temkin models were tested for describing the equilibrium data. It was found that Langmuir model was suitable for adsorption of Sr2+.

Keywords: Adsorption; Nano Silica; Modification; Schiff base; Strontium

Evaluation of nanophoto catalytic degradation of diazinone and malathion pesticides using ultraviolet light in the presence of magnetic nano-composite of TiO_2

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Organophosphorus is one of the widely used pesticides over the world. Organophosphorus pesticides (OPPs) are hazardous to human because of their persistence, stability and toxicity. Advanced oxidation processes (AOPs) such as UV/H_2O_2, UV/O_3, UV/ZnO, UV/TiO_2 and UV/ Fenton processes have been commonly used for the removal of toxic compounds. Fe_3O_4 and TiO_2 have been widely used due to their easy availability and nontoxicity.

Therefore, in the present study, applicability of Fe_3O_4–TiO_2 nanocomposite as an efficient photocatalyst for the degradation of diazinon and malathion was evaluated. In this study, the treatment conditions included the presence of UV and aeration, pH, agitation, amount of nano-TiO_2, initial diazinon and malathion concentrations and the contact time were studied and optimized. After mixing the solution and absorbent at the designated time, absorbent in the solution without filtration and only with the use of an external magnetic field are collected and uptake of diazinon and malathion in the samples were analyzed by UV-Vis. The prepared Fe_3O_4–TiO_2 composite was characterized by of SEM, EDX, XRD and FT-IR. UV/Fe_3O_4–TiO_2 composite showed the greatest photocatalytic activity compared with other processes. The results showed that by providing optimal conditions the removal of these pesticides is possible. The proposed method was applied to natural and environmental water samples, which showed good agreement with reference method results.

Keywords: Photocatalysis; Magnetic nanocomposite of TiO_2, Diazinon; Malathion; Environmental water samples.

Chemical synthesis of nanostructured polydiphenylamine

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Conducting polymers (CPs) receive extensive research attention owing to their intriguing properties and high application potentials in diversified areas. Various nanostructured forms of CPs have been used in the fabrication of chemical sensors and biosensors [1].

A facile synthesis of nanostructured polydiphenylamine (PDPA) has been developed by chemical techniques. Chemical polymerization was performed by oxidation with ammonium persulfate (APS) of 0.15 M DPA solution in 5.0 M H_2SO_4 and 15% (v/v) acetone to increase the solubility of DPA. The highest yields were obtained with a 1.5:1 molar ratio of APS to DPA. The product was subsequently washed with acetone to dissolved side-products and low-mass oligomers (a 15% weight loss) and dried at 40 °C to reach the high yield of 85.5%.The polymer was characterized by FTIR, SEM, XRD, NMR and GPC analysis. The polymer is oxidizing irreversibly form the yellow (feuco) to the green form (emeraldine) and finally to the blue (pernigraniline) form in two steps with increasing chain length the stability of the emeraldine form of PDPA also increases. DPA undergoes para C-C coupling to oligomers, attaining high degree of polymerization [2, 3].

Keywords: Conducting polymers, High yield polymerization, Nanostructured Polydiphenylamine

References:

[1] T.-H. Tsai, et al., Electroanalysis, (2014) **26**,399-408.
[2] López-López, M., et al. Talanta(2013)**103**, 214-220.
[3]Orlov, A. V., et al. Polymer Science Series B(2006)**48**, 5-10.

Thermolysis and evaluation the effect of diaminoglyoxime on the thermal behaviors, non-isothermal reaction kinetics of energetic compositions

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This paper reports thermolysis of diaminoglyoxime (DAG) as a ballistic modifier, and its effects on the thermal behaviors, non-isothermal decomposition reaction kinetics, and burning rates of the double base propellant formulations. Thermal analysis studies were performed by thermogravimetric analysis and differential thermogravimetry (TG-DTG) and differential scanning calorimetry (DSC) techniques. According to the resulted data, it was found that DAG could change the thermal decomposition mechanism function, thermokinetic parameters and kinetic equation of the propellants. Evaluation of DAG as a ballistic modifier indouble base propellant formulations indicated that it brings down the pressure index to 0.068 compared to 0.24 for the control composition in the pressure range 5–7 Mpa. The results showed that the main exothermal decomposition reaction of the propellant sample in the absence of DAG has the mechanism function of $f(\alpha) = \frac{3}{2}(1-\alpha)^{4/3}[(1-\alpha)^{-1/3}-1]^{-1}$ and the kinetic equation of $d\alpha/dt = 1.60 \times 10^{17}(1-\alpha)^{4/3}[(1-\alpha)^{-1/3}-1]^{-1}e^{-2.21\times10^4/T}$, while modified propellant with DAG has a different function mechanism andkinetic equationas following:
$f(\alpha) = \frac{5}{2}(1-\alpha)[-\ln(1-\alpha)]^{\frac{3}{5}}$ and
$d\alpha/dt = 9.28 \times 10^{40}\,(1-\alpha)\,[-\ln(1-\alpha)]^{3/5}e^{-4.66\times10^4/T}$respectively.

Keywords: Diaminoglyoxime (DAG); Thermal behaviors; Nonisothermal kinetics; Propellant

References:

[1] J.H. Yi, F.Q. Zhao, W.L. Hong, S.Y. Xu, R.Z. Hu, Z.Q. Chen, L.Y. Zhang, J Hazard Mater. 176 (2010) 257.

A New Method for Measurement Density of Hexogen as a Main Ingredient in Propellants and Explosives

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Hexogen is known as a compound with stable chemical and thermal properties, which has been used as one of the main constituent of propellants and explosives since the World War-II . The unique properties of the explosives with micronized particle size and quite spherical have resulted to the increase in their applications in different explosive compounds.

The measurement of density of crystalline explosives such as hexogen is very importance since this parameter directly affects the burning rate, explosion pressure, and sensitivity of the explosive compositions. During production of micronized hexogen, some crystal defects such as dislocated places void and inclusion in crystalline hexogen happens. These cavities affect on ballistic parameters of hexogen. The density of micronized hexogen has been investigated using the flotation method. The advantage of this method is 1- precise measurement of density 2- testing with simple and inexpensive equipment 3- recycling standard solution, and 4- less toxic than organic standard. Standard solution for this purpose is Zinc bromide. Important parameters on the determination of density are temperature, concentration of standard solution and sample weight. Under the optimum conditions, determination of density is done and the value of density is obtained 1.6948 g/cm3.

Keywords: Density of Hexogen; Flotation Method; Zinc Bromide; Micronized Particle Size.

References:

[1] F. Shen, An. F. Z. Hongxiang, X.Xiong, Progress in Nuclear Science and Technology, 1 (2011) 98-101.

Investigation on the effect of diaminoglyoxime on thermal decomposition kinetics of energetic compositions

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The effect of diaminoglyoxime as a ballistic modifier compound on the thermal decomposition of energetic formulations composed of nitrocellulose (NC) and triethylene glycol dinitrate (TEGDN) has been investigated by thermal analysis techniques i.e., differential scanning calorimetery (DSC) and thermogravimetery (TG). The results show that diaminoglyoxime could significantly change thermal behavior of the energetic compositions. Moreover, addition of different amounts of diaminoglyoxime caused appearing the peak in DSC curves at lower temperature and enhancing the activation energy of the decomposition about 3-50 kj/mol. Diaminoglyoxime improves thermal stability of energetic compositions, which makes them more safe in storage and handling. The kinetic parameters such as activation energy (Ea), frequency factor (A), the critical ignition temperature of thermal explosion, the self-accelerating decomposition temperature (T_{SADT}) and thermodynamic parameters for the studied energetic compositions were calculated from the DSC data resulted by non-isothermal methods proposed by Kissinger, Starink and Ozawa–Flynn–Wall methods.

Keywords: Diaminoglyoxime, Ballistic modifiers, TEGDN, Nitrocellulose, Thermal decomposition, Thermokinetic parameters.

References:

[1] Yi Jian-Hua, Zhao F-Q, Wang Bo-Zhou, Liu Qian, Zhou Cheng, Hu R-Z, Ren Y-H, Xu Si-Yu, Xu Kang-Zhen, Ren Xiao-Ning. Thermal behaviors, nonisothermal decomposition reaction kinetics, thermal safety and burning rates of BTATz-CMDB propellant. J Hazard Mater. (2010);181:432-39.

Microwave enhanced Fenton like degradation by surface modified metal-organic frameworks as a promising method for removal of dye from water

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To decolorize methyl orange (MO) dye from aqueous solutions, sulfated metal organic framework loaded on iron oxide nanoparticles, S-Fe_3O_4@MIL-100(Fe), has been synthesized and utilized as a Fenton-like catalyst in microwave system. The morphology and structure of the catalyst was characterized by X-ray powder diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), and UV-Vis diffuse reflectance spectroscopy (DRS). The effects of various parameters such as microwave irradiation time, initial MO concentration, H_2O_2 concentration, catalyst dosage, and solution pH on MO degradation were investigated. The results indicated the decolourization of the MO with the kinetic data following a pseudo first order removal rate and showed that up to 99.9% of MO could be degraded under microwave irradiation time of 6 minutes. Thus, the microwave induced Fenton like by sulfated metal organic framework loaded on iron oxide nanoparticles is a promising technology for the removal of dye from wastewater.

Keywords Iron oxide nanoparticles; Microwave induced Fenton like degradation; Methyl orange; Metal organic frameworks; Sulfonation

References:

[1] S. Dadfarnia, A.M. Haji Shabani, S.E. Moradi, S. Emami, Applied Surface Science, 330 (2015) 85-93.

The Green Synthesis of Silver Nanoparticle Using Antioxidant Herbs

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There is considerable evidence that the antioxidants contained in plant food play a very important role in the maintenance of health [1-2]. The antioxidant power of medicinal herb Cinamomum Zelanicumis estimated from the generation and growth of silver nanoparticles.In the present study, the role of pH in the green synthesis of silver nanoparticles (AgNPs) was investigated. In this work,we focus on the green synthesis of AgNPs using Cinamomum Zelanicum as a reducing and stabilizing agent.Formation of stable silver nanoparticles at different concentrations of NaOH gives mostly spherical particles with diameter ranging from 5 to 50 nm. Formation and stability of silver nanoparticles in aqueous colloidal solution are confirmed using UV–Vis spectral analysis. The nanometallic dispersions were characterized by surface plasmon absorbance measuring at 420 nm for Ag nanoparticles.The microstructure of Ag NPs was observed by transmission electron micrograph(TEM) image and showed that the adsorbent had a regular surface with an average size less than 50 nm. The formation of metallic silver was confirmed by using XRD analysis.The intensity of the resulting particle plasmon absorption bands correlates well with the redox characteristics of these phenolic acids.

Keywords: Antioxidant Activity;Cinamomum Zelanicum; Medicinal herb;Silver Nanoparticles; Surface Plasmon resonance peak.

References:

[1] S.J. Jadhav, S.S. Nimbalkar, A.D. Kulkarni, D.L. Madhavi, in: Food Antioxidants:Technological, Toxicological and Health Perspectives,D.L.Madhavi, S.S. Deshpande, D.K. Salunkhe (Eds.), Marcel Dekker,New York, 1996, pp. 5–64.

[2] J.H. Weisburger, Tea antioxidants and health, in: E. Cadenas, L.Packer (Eds.), Handbook of Antioxidants,Marcel Dekker, NewYork,1996, pp. 469–486.

Evaluation of the factors affecting on the vanadium recovery from sodium vanadate solution by precipitation method

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Vanadium is one of the important metals which is applied extensively in steel industry due to its unique physical and chemical properties. Among the vanadium separation methods, precipitation has been highlighted because of its simplicity and rapid performance. Ammonium ion is an effective precipitating agent in the quantitative recovery of vanadium from aqueous solutions. Vanadium can be precipitated at two pH region, namely pH=2 and pH=7 in two crystalline form. In acidic region, ammonium polyvanadate is precipitated while under neutral condition, only ammonium metavanadate is formed. Our preliminary experiments showed that at the higher pH, the precipitate is more suitable in terms of recovery and purity. Therefore, this region was chosen for further experiments and effect of NH4Cl concentration as a precipitating agent was investigated. It was found that by increasing the concentration of NH4Cl, Vanadium recovery increases, but the presence of sodium ions increases in the metavanadate crystals. Results also showed that the optimal value for NH4Cl was 12% (w/v) and during this condition the vanadium recovery is more than 97%.

Keywords Ammonium Chloride; Ammonium Vanadate; pH; Precipitation

Synthesis of Cyclopenta[*b*]chromen-1(9*H*)-ones in Aqueous Media by TiO_2/CNTs Nanocomposite Catalyst

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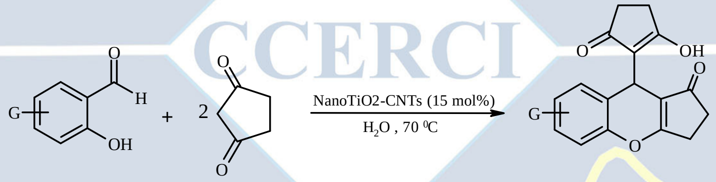
In the last few years, the application of metal oxide nanoparticles catalysts in organic synthesis has been preferably developed. Furthermore, much interest has been shown in chromene derivatives due to their broad spectrum of biological activities such as antioxidant [1], anticancer,antimicrobial, hypotensive, and local anesthetic. One-pot pseudo three-component reaction in a 1:2 mole ratio of salicylaldehydes and 1,3-cyclopentanedione respectively, at 70 ˚C in water and in the presence of TiO_2-CNTs nanocomposite affords 2,3-dihydro-9-(2-hydroxy-5-oxocyclopent-1-enyl)cyclopenta[*b*]chromen-1(9*H*)-ones in high to excellent yields. The present methodology offers several advantageous such as excellent yields, short reaction times, reusability of catalyst, operational simplicity, and mild reaction conditions.



1a-i **2** **3a-i**

1a, 3a G = H
1b, **3b** G= 5-Br
1c, **3c** G= 3,5-Br_2
1d, **3d** G= 5-Cl
1e, **3e** G= 3,5-Cl_2
1f, **3f** G= 4-OH
1g, **3g** G= 5-OMe
1h, **3h** G = 5-Me
1i, **3i** G= 5-NO_2

Scheme 1. Synthesis of 2,3-dihydro-9-(2-hydroxy-5-oxocyclopent-1-enyl)cyclopenta[*b*]chromen-1(9*H*)-one derivatives3

Keywords: Chromene derivatives; TiO_2-CNTs Nanocomposite; Reusability of Catalyst

References:

[1]A L. Alvey, S. Prado, V. Huteau, B. Saint-Joanis, S. Michel, M. Koch, T. Cole, F. Tillequin, and L. Janin,106(2014) 265–271.

Biosorption of Cadmium,Nickel and Lead from aqueous solutions by modified Mespilus germanica leave and determination of thermal isotherms

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Industrial development has caused the release of various pollutants including heavy metals into the environment. These toxic compounds are extremely dangerous to living beings and the environment due to their non-biodegradability, severe toxicity, carcinogenicity, the ability to be accumulated in nature and the ability to contaminate groundwater and surface water. The aim of the present research was to provide an appropriate and cost-effective adsorbent to remove heavy metals from aqueous solutions. The maximum removal efficiency of heavy metals (cadmium,nickel and lead) by modified Mespilus germanica leaves was obtained in pH 6. The optimum amount of adsorbent was 1.0 g, and the optimum contact times were 50 min for cadmium and nickel ions and 90 min for lead ion, respectively. In these optimum conditions the removal efficiencies were 80.25%, 95.73% and 98.11%, respectively.The results obtained showed the highest correlation with Langmuir isotherm model.

Keywords: Biosorption; Heavy metal; Mespilus germanica; Thermal isotherm

References:

[1] Madhu Kumaria, Charles U. Pittman Jr.b, Dinesh Mohana, *Journal of Colloid and Interface Science*,442(2015)120.

[2] Moreno-Piraján JC, Garcia-Cuello VS, Giraldo L., *Adsorption* ,17(2011) 505.

[3] Z. Elouear, J. Bouzid, N. Boujelben, M. Feki, F. Jamoussi and A. Montiel , Hazardous Materials,156(2008) 412-420.

Synthesis of stabilized-bimetallic Ni–Fe nanoparticles with different nickel loading ratios and its application for reduction of the chlorine oxyanions contaminants in aqueous media

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Nanotechnology has multiple and enormous advantages for all application. Among all applications of bimetallic Nanoparticles, the elimination of environmental pollutants such as heavy metals and organic pollutants is attracting considerable attention. In this work, at first, stabilized Ni/Fe bimetallic nanoparticles (S-Ni/Fe) was synthesized using the borohydride reduction method (BRM) in the presence of starch as stabilizing agent and they characterized by field emission scanning electron microscopy (FE-SEM), Energy Dispersive X-ray Spectroscopy (EDS), and X-ray diffraction pattern (XRD). The results show that the synthesized S-Ni/Fe bimetallic nanoparticles are spherical in shape and have nearly uniform distribution with particle size of 20-50 nm. Then, the prepared nanoparticles were used for selective elimination of chlorate impurity in ammonium perchlorate. The main factors controlling the removal of chlorate, such as the initial pH of the solution, dosage of S–Fe/Ni NPs, initial chlorate and perchlorate concentration, the reaction temperature, and reaction time were optimized by using an experimental design based on the Taguchi method. L9 orthogonal array (L9-OA) was used to design experiments with four 4-level factors (3^4). Under optimal conditions, i.e., pH 6.5, dosage of 50 mg S-Ni/Fe NPs and at 30 ºC, chlorate in ammonium perchlorate with a ratio of 1:50 was eliminated with efficiency of nearly 100% without change of perchlorate concentration in solution.

Keywords Bimetallic nanoparticles; Chlorine oxyanions; Co-reductive; Nanoalloys

References:

[1] W. E. Motzer, *Environmental Forensics* 2 (2001) 301-311.

[2] G. W. Huber, J. Shabaker, J. Dumesic, *Science*, 300 (2003) 2075-2077.

Amino-functionalized mesoporous titania as a sorbent for Th(IV) ion

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The striking features of mesoporous titania such as having a very large BET surface area, large pore volume and fast kinetics of sorption attracted many researchers to utilize it as a sorbent and study its sorption behavior towards chemical and radio-toxic metal ions from various waste streams [1, 2].

Amino-functionalized mesoporous titania nanoparticles was prepared using 3-(aminopropyl) triethoxysilane as amine rout and investigated for Th(IV) adsorption in comparision with non-functionalize titania. Prepared sorbents were characterized by transmission electron microscope (TEM), N2 adsorption–desorption isotherms and pore size distribution analyses, differential scanning calorimetry-thermogravimetric analyses (DSC-TGA), Fourier transform infrared (FTIR) spectroscopy and scanning electron microscopy (SEM) equipped with electron dispersive X-ray spectrometry (EDS).

Batch adsorption tests indicated that Amino-functionalized mesoporous titania exhibited higher adsorption efficiency at about ?% toward Th(IV) in comparision to bare titania. In addition, adsorption kinetics, the influence of pH, Time, concentration of Th(IV) ion on the removal efficiency of Amino-functionalized mesoporous titania were studied.

Keywords titania; Th(IV); 3-(aminopropyl) triethoxysilane; sorption behavior

References:

[1] S. Mahdavi, Clean Technologies and Environmental Policy, 2015, Article in press.
[2] M. R. Prairie, L. R. Evans, B. M. Stange, . S. L. Marlinez, Environ. Sci. Technol. 27 (1999) 1776-1782.
[3] A. Nilchi, S. Rasouli Garmarodi, S. Janitabar Darzi, Separation Science and Technology, 45(2010) 801–808.

Experimental studies of atenolol removal from aquatic environments by perlite and diatomite nanoparticles

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In this research, mineral materials consisting of diatomite, perlite and perlite-diatomite composite were used as nano-adsorbents to remove organic compound from aquatic environments. Firstly, diatomite, diatomite/perlite composite and perlite nano-adsorbents were prepared from natural sources. XRD, XRF, BET, SEM and TEM analyses were carried out to investigate the physical and chemical characteristics of sorbents. The nano-adsorbents were used to remove atenolol from synthetic aqueous solutions. The presence of active pharmaceutical ingredients (APIs) in the aquatic environments was reported as early in the 1980s. Among the APIs, b-blockers are an important subclass and among the b-blockers, the toxicity of atenolol (ATL) is the most serious to aquatic organisms and humans, also because of its wide occurrence, relative recalcitrant and resistant to direct photolysis, it was chosen as a model compound in the current investigation.The influence of important parameters including pH, adsorbent dosage, atenolol concentration, temperature and time on adsorption process were investigated. The obtained results show these nano-adsorbents have a suitable efficiency for atenolol removal and their efficiency are sorted as: nano-ditomite > nano-composite > nano-perlite. Furthermore, equilibrium adsorption isotherms and kinetics were investigated. The equilibrium adsorption results are fitted better with the Langmuir isotherm. In addition, the kinetic data follow pseudo-first-order model. Experimental studies show that the adsorption power of nano-diatomite was more efficient than composite and nano-perlite. The atenolol maximum adsorption with efficiency higher than 96% under optimum conditions (atenolol concentration 50 ppm, diatomite dose 0.1 g L^{-1}, natural pH, time 10 min, temperature of 80 ^{0}C) was achieved. Natural nano-adsorbent was effectiveness for atenolol removal from contaminated water to decrease the harmful effects of organic pollutants.

Keywords: Pharmaceutical removal, Nano-adsorbent, Diatomite, Perlite, Atenolol.

Removal chloride from aqueous media by metalloporphyrin coated magnetite nano particles

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Chlorine, commonly employed as a disinfectant in municipal water treatment facilities is highly toxic to many freshwater organisms. Herein we have investigated the application of In (III) TCPP coated Fe_3O_4 nanoparticles for the removal of trace amounts of chloride ions from aqueous solutions. Fe_3O_4 nanoparticles were synthesized by Fe^{2+}/Fe^{3+} co-precipitation in an alkaline solution, surface-modified with APTES and finally functionalized with In (III) TCPP. The morphology and structure of nanoparticles were characterized by XRD, TEM, FT-IR and TGA. The results showed that the adsorption of chloride by Fe_3O_4 /APTES/In (TCPP) nanoparticles was pH-dependant. Under experimental conditions, the Nano sorbent reported here displayed high efficiency for Cl^- uptake (96%). The Main factors affecting the removal of chloride such as solution pH, contact time, reusability and Nano adsorbent dosage were investigated.

Keywords: *nanoparticles; chloride; metalloporphyrin*

References:

[1] G, Salazar, University dissertation from Stockholm: Materialvetenskap, Synthesis, Characterization and Applications of Iron Oxide Nanoparticles, PhD Thesis, Stockholm, Sweden, 2004.

[2] C.M. Allen, W.M. Sharman, J.E. Van Lier, Porphyrins Phthalocyanines, (2001), 5, 161.

[3] Yavuz CT, Mayo JT, Yu WW, Prakash A, Falkner JC, Yean S, Cong L, Shipley HJ, Kan A, Tomson M, Natelson D, Colvin VL, Low-field magnetic separation of monodisperse Fe_3O_4 nanocrystals. Science, (2006), 314, 964.

Competitive ^{7}Li NMR study of the stoichiometry, stability and thermodynamic data for the complexation of metal ions with two asymmetrical branched (N_3O) containing pyridine moiety in ionic liquid-acetonitrile mixtures

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Lithium-7 NMR spectroscopy was used to investigate the stoichiometry, stability and thermodynamic data of a Li^+ complex with two asymmetrical branched amines, 2-(2-amino ethyl) pyridine – yl - methyl amino ethanol (A^1) and 2-(2-amino propyl) pyridine – yl - methyl amino ethanol (A^2) in 25-25, 50-50, 75-25 and 100-0 wt% acetonitrile (AN)- [BMIM][PF_6] (ionic liquid) mixture solution at various temperatures. A competitive ^{7}Li NMR method was also employed to probe the complexation of Li^+, Co^{2+}, Ni^{2+}, and Cu^{2+} ions with A^1 and A^2 in the same solvent systems . The formation constants of the resulting complexes were evaluated from computer fitting of the mole ratio data to an equation that relates the observed chemical shifts to the formation constant. There is an inverse relationship between the complex stability and the amount of ionic liquid in the solvent mixtures [1]. In the all studied solvent mixtures, the stability of the resulting 1:1 complexes was found to vary in the order $Cu^{2+} > Ni^{2+} > Co^{2+} > Li^+$. The resulting complexes with the amines A^1 and A^2 vary in the order of $MA^1 > MA^2$. This is due to the fact that the amines, A^1 and A^2 differ in the size of their central chelate rings so that they can form five and six membered rings, respectively. As it is well documented in the complexes forming a six-membered chelate ring are expected to be less stable than those forming a five-membered chelate ring. The temperature dependence formation constant was used for the evaluation of the enthalpy and entropy values for the complexation reaction. It was concluded that in all complexes, except for lithium ion, the resulting complex enthalpy is stabilized and the ΔH compensates the $T\Delta S$ contribution [2].

Keyword: Li NMR; Stability; Metal ions

References:

[1] G. Herlem, P. Tran-Van, P. Marque, S. Fantini, J.F. Penneau, B. Fahys, J. Power Sources **107** (2002) 80.

[2] M. Shamsipur, M. Irandoust, K. Alizadeh, V. Lippolis, J. Incl. Phenom.Macrocycl. Chem. 59 (2007) 203.

Synthesis of NH_2-functionalized magnetic titanium dioxide nanocomposites for removal of Fuschine acid dye from aqueous solutions

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Major efforts in modern material chemistry are devoted to the design and fabrication of nanostructure systems with tunable physical – chemical properties. In this research, a novel $Fe_3O_4@SiO_2@TiO_2$-NH_2 nanocomposite was synthesized and the potential of magnetic nanocomposites (MNCs) for efficient removal of Fuschine acid as an anionic dye from aqueous solutions was investigated. For this purpose, Fe_3O_4 MNCs were synthesized via chemical precipitation method. The core – shell structured $Fe_3O_4@SiO_2@TiO_2$ MNCs were prepared using Fe_3O_4 as magnetic core, tetra ethylorthosilicate (TEOS) as silica and tetra butyl titanate (TBOT) as titanium sources. The obtained structure was composed of $Fe_3O_4@SiO_2$ core and porous TiO_2 shell. The synthesized MNCs were characterized by FT-IR, XRD, EDX, SEM and BET techniques. The various experimental parameters affecting dye removal efficiency were investigated and optimized using Taguchi fractional factorial design. Results showed that the optimum parameters for adsorption including pH, sorbent weight, ionic strength, stirring time and sample volume were 3.5, 0.05 g, 0, 10 min and 10 ml, respectively. At optimum conditions, the removal efficiency of Fuschine acid was obtained higher than 99% . The kinetic studies showed the fast sorption of dye on the surface of MNCs with pseduo second order kinetic model. Also, the Freundlich and Langmuir isotherms were studied. The results showed very good advantages of synthesized MNCs such as high removal efficiency and fast sorption kinetics as well as the ability to use MNCs several times.

Keywords Fuschine acid, $Fe_3O_4@SiO_2@TiO_2$, Nanocomposite, Adsorption.

Characterization of Golden Pigments Used in Illuminated Quran Manuscripts by Nondestructive Analytical Techniques

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The use of chrysography (golden illumination) for the purpose of book decoration in Iran and surrounding countries is probably traceable to pre-Islamic times. During the Islamic period, some of the oldest specimens of chrysography are those that are found on the folios of fragments of the Quran that have been dated to approximately the beginning of the 2nd century hijri(or 1st half of the 8th century A.D.). In treatises that concern book decoration, not only techniques of preparing dissolved gold, but also way of making paints and inks that seem like gold, have been listed. However, no study of on the compounds used in such paints and inks had ever been undertaken in Iran.

The present study is an investigation of 24 samples of gold colors used in 12 Quran fragments that date from the Safavid and the Qajar periods in order to identify their constituting compounds. The samples were subjected to the two techniques of scanning electron microscopy in combination with energy dispersive X-ray (SEM-EDX)- and the attenuated total reflectance-Fourier transform infrared spectroscopy (ATR-FTIR) in order to determine elemental composition and organic compounds used in them, respectively. According to the results of this study, metallic gold ware used in order to achieve the golden color in twelve samples and some other metal(copper, zinc, and tin) alloys were employed in ten other samples. In two samples the golden color was achieved by combining saffron and tin.

Keywords golden pigment, Quran Manuscripts, SEM-EDX, ATR-FTIR.

References:

[1] E.Pieta, E. Proniewicz, B. Szmelter-Fausek, L. M. Proniewicz, Spectrochim Acta A. 136(2015) 594-600.

[2] Y. Tateishi, H. Einaga, Y. Teraoka, Advanced Materials Research, 48 (2008). 1462-1465.

Determination of Acidity Constants of New Derivatives of Sulfonic Acid Using Titrimetry

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Sulfonic acids are used as catalysts. The simplest examples aremethanesulfonic acid, CH_3SO_2OH and *p*-toluenesulfonic acid, which are regularly used in organic chemistry as acids that are lipophilic (soluble in organic solvents)[1]. Polymeric sulfonic acids are also useful. Dowexresin is sulfonic acid derivatives of polystyrene and is used as catalysts and for ion exchange (water softening). Nafion, a fluorinated polymeric sulfonic acid is a component of proton exchange membranes in fuel cells [2].The acidity of sulfonic acids is the important property relevant to its catalytic activity for acid-catalyzed reactions. Inthis work, the acidity of some new derivatives of sulfonic acidsis determined during titration (titrimetry).In view of the emerging importance of acidity of some derivatives of sulfonic acids, we wish to report an efficient method for the determination of acidityof new derivatives sulfonic acids which are made using alcoholsas raw materials by titrimetry. The results lead us to validate approximation of equilibrium constants. In this experiment, we also used an effective technique to determine the Kafor weak organic acids.

Keywords: Acidity Constant; Titration; Sulfonic acid; Alcohols.

References:

[1] K. Kosswig, “Surfactants” in Ullmann’s Encyclopedia of Industrial Chemistry (2002), Wiley-VCH, Weinheim.
[2] B. Guido,Chem. Rev, 107 (2007) 5366.

Investigation of the catalytic activity of ZSM-5 Zeolite as nanocatalyst in dehydration of glycerol

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Acrolein is a key intermediate that can be used for synthesis of various chemicals such as acrylic acid, and acrylate monomers. Recently, developing cost-effective feedstocks for producing acrolein has attracted growing attention. In this context, catalytic conversion of glycerol as a cost-effective and available raw material has been considered as a promising method. This reaction can take place in the presence of acidic catalyst in liquid or gas phase. ZSM-5 zeolite is a nanosized class of zeolytic catalyst which possesses acidic sites. This catalyst proved its utility I various catalytic conversion. To investigate its catalytic activity in liquid phase conversion of glycerol to acrolein, this reaction performed in the presence of catalytic amounts of ZSM-5 and the reaction variables such as time, temperature and catalyst amount have been studied to optimize the reaction. Furthermore, the structure and acidity of catalyst has been fully characterized. The results indicated that ZSM-5 can catalyze this conversion. However, at low amount of catalyst and temperature, the formation of acetaldehyde is dominant and acrolein can be obtained as minor product. This observation proved that beside the acidity of the catalyst, its structural and textural properties such as pore size and volume can influence the product selectivity.

KeywordsCatalyst, Zeolite, Glycerol dehydration

References:

[1] L. Shen, H. Yin, A. Wang, Y. Feng, Y. Shen, Z. Wu, T. Jiang, *Chem Eng. J.*,(**2012),**180, 277–283.
[2] A. Martin, U. Armbruster, H. Atia, *Eur. J. Lipid Sci. Technol.* (**2012),** 114, 10-23.
[3] T. Hung Kang, H. Choi, Y. Bang, J. Yoo, J. Hwan, S. Wangrae, J. Jun, S. Choi, I. Kyu Song, *J. Mol. Catal. A.* (**2015),** 396, 282-289.

Preparation of amino-functionalized magnetic cellulose nanoparticles for adsorption of platinum(IV) from aqueous solution: Isotherm and experimental design approaches

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The adsorption characteristics of platinum(IV) onto the ethylenediamine-modified magnetic cellulose nanoparticles (MCNGE) have been investigated. The resulting modified magnetic cellulose nanoparticles was characterized by Fourier transform spectroscopy (FT-IR), X-ray diffraction (XRD), Scanning electron microscopy (SEM). A four-factor, central composite design (CCD) combined with response surface modeling (RSM) and optimization was employed for maximizing adsorption of Pt(IV) in aqueous solution by the MCNGE. Four independent variables, viz., Pt(IV) concentration (15-35 mg/l), temperature (34–50 °C), pH of solution (2–5), and particles dose (0.03-0.06 gr) were transformed to coded values and a quadratic model was made to predict the responses. Analysis of variance (ANOVA) perform to test the significance of the independent variables and their interactions for adsorption of Pt(IV) from aqueous solution. The quality of the model was checked by the determination of coefficient (R^2, adjusted-R^2 and adeqate precision). In this case $R^2 = 0.9923$ indicated that only 0.67% of the total variable was not explained by the model. Adjusted-$R^2 = 0.9743$ is also high, showing a high significance of the model. The optimum adsorption conditions were determined as initial pH 2.5, temperature 46°C, adsorbent dosage 0.05 gr and initial platinum(IV) concentration 22mg/l. Langmuir isotherm is found to be the most suitable one compared to Freundlich model tested. The maximum capacity of MCNGE for Pt(IV) was found to be 19.45 mg/g .

Keywords: Adsorption, Magnetic nanoadsorbent, Cellulose, Ethylenediamine, platinum (IV)

References:

[1] G.V. Myasoedova, O.B. Mokhodoeva, I.V. Kubrakova, Anal. Sci. 23 (2007) 1031–1039.
[2] D. Klemm, B. Philipp, T. Heinze , U. Heinze, John Wiley & sons. (1998) 249.
[3] M. Nasef, A.H. EL-Sayed, Poly. Sci. 29 (2004) 499-561

Polyoxometalates as an efficient catalyst for cost-effective synthesis of acrolein

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Currently, acrolein is obtained from oxidation of propylene. Although this process is proved as an industrial procedure, the shortage of propylene capacity provokes new procedures based on cost-effective raw materials. Glycerin can be generated as the by-product of biodiesel production. It can be considered as bio-derived raw material for catalytic synthesis of diverse chemicals such as acrolein.

Polyoxometalates are bi-functional catalysts with both oxidative and acidic properties. They proved their utilities as heterogeneous and recyclable catalysts in various chemical synthesis. There are numerous reports regarding their modification and hybridization. In this study, these catalysts and their supported forms have been exploited for catalytic dehydration of glycerin to acrolein in liquid phase. The optimum reaction condition and the interaction among reaction variables such as time, temperature and catalyst amount were obtained by using Response surface methodology.

Keywords: Catalyst, Polyoxometalate, Acrolein

References:

[1] L. Shen, H. Yin, A. Wang, Y. Feng, Y. Shen, Z. Wu, T. Jiang, *Chem Eng. J.*,**(2012),**180, 277–283.
[2] A. Martin, U. Armbruster, H. Atia, *Eur. J. Lipid Sci. Technol*.(**2012),** 114, 10-23.
[3] T. Hung Kang, H. Choi, Y. Bang, J. Yoo, J. Hwan, S. Wangrae, J. Jun, S. Choi, I. Kyu Song, *J. Mol. Catal. A.* (**2015),** 396, 282-289.

Industry oriented analytical chemistry training program

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It is an undisputed fact that analytical chemistry is of the most fundamental importance not only to all branches of chemistry but also to almost any field of industry. In 2012 (salary survey data), analytical chemistry was the most popular field of work for ACS chemists. Unfortunately in recent years, the position of analytical chemists in industry has been down-graded relative to the other related subjects. These data shows the importance of redefining the curriculum of analytical chemistry in such a way that meets the industry requirements. Feedback from employers suggests that they find it difficult to recruit graduates who have both a strong analytical background and an appreciation of the regulatory aspects of the work, including quality standards like, good laboratory practice (GLP) and ISO/IEC 17025 related subjects such as quality assurance program and proficiency testing. Most of the graduates are actually overqualified in the field of chemistry for the industry but at the same time they are underqualified to work in a professional atmosphere. Some international departments address this problem by assigning industrial supervisors to placement students, and mentors to new graduates. However it seems professional bodies such as Iranian Chemical Society has to encourage the decision maker in higher level education in Iran to start a renaissance in analytical chemistry curriculum. I would suggest students to take an additional module, Further analytical chemistry, or, Quality systems, which focuses on 'professional' aspects such as quality assurance and control, method validation and data handling.

Keywords: Quality assurance, Professional analytical chemistry, GLP, ISO/IEC 17025

References:

[1] Holler, F. James; Skoog, Douglas A.; West, Donald M. (1996). Fundamentals of analytical chemistry. Philadelphia: Saunders College Pub. ISBN 0-03-005938-0.
[2] http://www.rsc.org/education/
[3] M. Valcárcel and A. Ríos, Accred. Qual. Assur., 2 (1997) 98.

Synthesis of Nanopesticides by Encapsulating Pesticide Nanoparticales Using Fanctionalized Graphene

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Nanotechnology has been developed dramatically in various aspects in recent decades such as: medicine, food industries, arm science and etc. In this respect, nanopesticides has been highly influential. Due to their great efficacy, and the decrease in preserving materials of toxins in nature, they are of most importance. In recent years, capsulation of nanopesticides in polymers has been performed [1]. capsulation of pesticides in carbon nonotubes has been done as well[2]. In this work Polymerization of citric acid onto the surface of graphene oxide led to graphene-graft-poly (citric acid) (GO-g-PCA) hybrid materials. Because of the presence of conjugated citric acid branches, synthesized GO-g-PCA hybrid materials were not only soluble in water but also able to trap water-soluble chemical species and metal ions. Trapping of pesticides such as karbendazim and propiconazol in aqueous solution by GO-g-PCA hybrid materials led to encapsulated pesticide (EP) in the polycitric acid shell. Optimum conditions for encapsulation of karbendazim and propiconazol in hyperbranched polycitric acid such as pH, time of stirring, and time of sonic were investigated by the UV−vis spectroscopy method. Encapsulation of pesticides on GO-g-PCA hybrid material was confirmed via TEM analysis. Experiments indicated that the new the GO-g-PCA-EP hybrid material in comparison with bulk pesticide had a superior toxic influence on Rhizoctonia solani fungi. In Agricultural Administration, these materials used to curb pesticides. Due to their economic and biodigestibility use, Toxin Production committee can implement this process.

Keywords: Nanopesticides; Propiconazol; Carbendazim; Rhizoctonia Solani; Graphene oxide

Reference:

[1]N. Memarizadeh, *Ecotoxicology and Environmental Safety*. (**2014).** 107,77–83.
[2]N. Sarlak, A. Taherifar, and F.Salehi, *J. Agric. Food Chem*. (**2014**), 62, 4833−4838

Synthesis and characterization of a novel nanocomposite based on elemental sulfur and graphitic mesoporous carbon

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A novel sulfur nanocomposite was fabricated based on graphitic mesoporous carbon. The graphitic mesoporous carbon was synthesized using sucrose as carbon precursor, nano CaCO3 as hard template and nickel nitrate as graphitization catalyst. The structural properties of the prepared material were characterized using Powder X-ray diffraction (XRD), N2-adsorption/desorption and Scanning Electron Microscopy (SEM) techniques. The mesoporous solid with high surface area of 710 m2/g, average pore size of 2.7 nm and high graphitization degree was applied as nanoreactor for infiltration of molten sulfur at 150 ºC in an inert gas atmosphere. The properties of prepared nanocomposite were investigated by XRD, BET, SEM and cyclic voltammetry methods. The obtained results showed that the desired nanocomposite with enhanced conductivity successfully was synthesized.

Keywords graphitic mesoporous carbon; electrical conductivity; sulfur nanocomposite; hard template; cyclic voltammetry

References:

[1] K. Jin, X. Zhou, L. Zhang, X. Xin, G. Wang, J. Phys. Chem. C, (**2013**), 117, 21112-21119.

[2] W. Ahn, K. B. Kim, K. N. Jung, K. H. Shin, C. S. Jin, J. Power Sources, (**2012**), 202, 394-398.

[3] X S. In, L. Gu, N.H. Zhao, Y.X. Yin, L.J. Zhou, Y.G. Guo, L.J. Wan, J. Am. Chem. Soc, (**2012**), 134, 18510-18513.

Fabrication of $AgBr/Ag/Ag_2CO_3$-mordenite nanocomposite with enhanced visible light photocatalytic activity and stability

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Photocatalytic degradation of organic pollutants by using semiconductor photocatalysts is of growing interests for water purification [1]. It is worth noting that the coupling of various semiconductors with different band gap levels has been widely investigated to enhance the visible-light absorption capability [2].

In this study, the $AgBr/Ag/Ag_2CO_3$-mordenite nanocomposite was synthesized via precipitation method. X-Ray diffraction (XRD), diffuse reflectance spectroscopy (DRS), transmission electron microscopy (TEM) and FTIR, were used for determination of nanocomposites. The photocatalytic activity for degradation of methylene blue (MB) was examined by photocatalysts under visible light irradiation. The results indicated that the $AgBr/Ag/Ag_2CO_3$-mordenite composite exhibited higher photocatalytic activity than Ag_2CO_3 bulk and Ag/Ag_2CO_3-mordenite composite. The best amount of support was 0.2g. The photocatalytic degradation for 100 ml of MB solution ($C_{MB}=10^{-5}M$) by $AgBr/Ag/Ag_2CO_3$-mordenite (20 wt%, 40% wt%, 50% wt%) samples was 80%, 74.24% and 91.5% with 0.07g photocatalyst at 85 min, respectively. The stability of nanocomposite was investigated by cycle experiments. The results exhibited the degradation capacity maintained 77.85% after four cycles, indicating a desirable stability.

Keywords Ag_2CO_3-mordenite; $AgBr/Ag/Ag_2CO_3$-mordenite nanocomposite; Photocatalytic degradation; Plasmonic resonance band

References:

[1] G. Dai, S. Liu, Y. Liang, K. Liu, *RSC. Adv*. **2014**, 4, 34226–34231.
[2] X. Yao, X. Liu, *J. Hazard. Mater.* **2014,** *280*, 260–268.

Bovine Serum Albumin Stabilized Gold Nanoclusters for Chiral Recognition of Naproxen Enantiomers

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Chiral recognition has provided great interest in medical science and pharmaceutics since individual isomers of a drug often differ in their pharmacological bioactivity and undergo different pharmacokinetic and metabolic fates in the biological systems [1]. Naproxen, a chiral compound, is often used as a nonsteroidal anti-inflammatory analgesic drug. The S-naproxen has 28 times higher activity than R-naproxen. Therefore, determination of enantiomer composition of naproxen is important in life science and technology. The recent advances of nanotechnology open new opportunities for the development of sensors for detection of the enantiomeric purities of drugs. Herein, a simple and inexpensive method for discrimination of naproxen enantiomers in aqueous solution using bovine serum albumin-modified gold nanoclusters (BSA-AuNCs) as fluorescence probe has been presented. These nanoclusters have an excitation peak at 480.0 nm with an emission peak at 640.0 nm. A suspension of BSA-AuNCs was introduced into a spectrofluorometric cell followed by injecting S- or R-naproxen; the quenching efficiencies of the nanoclusters at 640.0 nm were probed as the analytical signal. The optimum values for different experimental parameters such as pH, buffer type, buffer concentration, concentrations of the reagents, and temperature were established. The results indicated that S-naproxen had better interaction with BSA-AuNCs than R-naproxen in phosphate buffer solution (pH 7.0) at 37 °C. The method was successfully applied to determination of naproxen enantiomers in pharmaceutical formulations and acceptable results were achieved.

Keywords: Bovine Serum Albumin; Chiral Recognition; Fluorescence Determination; Gold Nanoclusters; Naproxen

References:

[1] L. Zhang, C. Xu, C. Liu, B. Li, Anal. Chim. Acta 809 (2014) 123.

Synthesis of Thoria Nano-Particles Through Water Hydrolysis

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In this research work, a novel, fast, clean, and simple method for preparation of the pure thoria nanocrystalline was developed. The mechanism of $Th(OH)_4$ deposition is the basis of base generation at the electrode surface [1].

The presence of OH^- on the electrode surface causes the local increase of pH and deposition of metal ions as hydroxide/oxide [2].

The thorium hydroxide is converted to thorium oxide through the temperature annealing according to the following reactions:

$Th(OH)_4.H_2O \rightarrow Th(OH)_4 \rightarrow Th(OOH)_4 \rightarrow ThO_2$

XRD pattern shows the as prepared and the thoria based on the ICDD No. 042-1462. The thoria was obtained by heat annealing of the as prepared sample at 600°C.The particle size was obtained by sherrer equation: $D_{hkl} = 0.89\lambda/\beta_{hkl} \cos\theta \quad \beta_{hkl} = \Delta 2\theta\pi/180°$

where D_{hkl} is the average particle size, λ, the incident X-rays wavelength (1.54 Å), θ, the diffraction angle, and β_{hkl}, the full width at half maximum (FWHM) for the highest peak. The particle size was calculated to be about 12 nm.

Keywords: Thoria; Water Hydrolysis; nanoparticles; TEM

References:

[1] T. Yousefi, A.N. Golikand, M.H. Mashhadizadeha, M. Aghazadeh, Curr. Appl. Phys. 12 (2012) 544-549.

[2] T. Yousefi, R. Davarkhah, A.N. Golikand, M.H. Mashhadizadeh, Mat. Sci. Semicon. Proc. 16(2013) 868–876.

Rheum palmatum root extract assisted green synthesis of Ag/ZnO Nanocomposites and investigation of its excellent catalytic activity for reduction of variety of dyes in water

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The presence of toxic dyes and nitroarene compounds in waste waters is of great concern as these are biologically and chemically stable; therefore, it is difficult to remove them by natural degradation [1].

This work reports a facile and green synthesis of Ag/ZnO nanocomposite by extract of Root of Rheum palmatum without any stabilizer or surfactant. The green synthesized Ag/ZnO nanocomposite was characterized by field emission scanning electron microscope (FESEM), energy-dispersive X-ray spectroscopy (EDS), fourier-transform infrared (FT-IR) spectroscopy, X-ray diffraction analysis (XRD) and UV–vis The characterization results confirmed that Ag nanoparticles have been coated on the surface of ZnO nanoparticles. Ag nanoparticles on the surface of ZnO are spherical in shape, ranging between 17 and 22 nm in diameter**.** The Ag/ZnO nanocomposite was found to be effective catalyst for reduction of various dyes, such as 4-nitrophenol (4-NP), Methyl orange (MO) and Methylene blue (MB) in the presence of $NaBH_4$ in water at room temperature. Catalysis reactions were monitored by employing UV–vis spectroscopy. Catalysis reactions followed pseudo-first order rate equation. The catalyst can be recovered and reused several times without significant loss of its catalytic activity.

Keywords: Rheum palmatum root extract; Green synthesis; Ag nanoparticles; ZnO; Reduction degradation

References:

[1] Zhong-YinZhao , Mao-HuaWang , Ting-TingLiu 158 (2015)274–277

[2] Zhen-Zhen Wang, Shang-Ru Zhai, Bin Zhai, and Qing-Da An

Fabrication, design, development and characterization of novel PAN-TiO_2 nanofibers

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Nowadays, production of carbon nanofibers due to the importance and wide applications in space, aircraft, water treatment industry, medicine, agriculture, petrochemical and other industries has become a dynamic competitive, especially the fibers with low precursors consumption, energy and time which produce the highest quality. This paper is an executive, state-of-the-art and innovation of the latest development made in fabrication and application of electrospun PAN-based carbon nanofibers which is exhibited the characterization of high performance PAN-based carbon fibers. We have produced a simple and facile approach to synthesis of nanofibers using electrospinning. In this study, composite nanofibers were electrospun using Polyacrylonitrile (PAN) as a carbon source, Polyvinylpyrrolidone (PVP) and Titanium tetraisopropoxide (TTIP) precursors with optimized parameters. The prepared PAN-TiO_2 fibers were characterized using scanning electron microscopy (SEM), transmission electron microscopy (TEM) and X-ray diffraction (XRD). Thermogravimetric-Differential Thermal Analysis (TG/DTA) used to specify a suitable calcinations temperature and XRD analysis showed the formation of anatase and rutile TiO_2 phases after heat treatment. The characteristic features of carbon fibers are high tensile modulus and high tensile strength combined with low specific gravity. So the mechanical properties of carbon fibers are discussed too. To show this feature, tensile test that is useful for measuring tensile strength was performed which is the best guarantee and excuse to make them.

Keywords: PAN-TiO2 composite, PAN-TiO2 nanofiber, PAN/PVP/TTIP

References:

[1] N. Sarlak, M. Amin Farahmand Nejad, S.Shakhesi, K. Shabani, *Chemical Engineering Journal*, 210 (**2012**) 410–416

[2] W. Kuen Jo, H. Jung Kang, *Ind. Eng. Chem. Res.* **2013**, 52, 4475−4483

[2] F. Huang, Y. Xu, S. Liao, D. Yang, Y. Lo Hsieh, Q. Wei, *Materials* (**2013**), *6*, 969-980

Amino-Functionalized ZnO Thin Films in Photacatalytic Degredation of Dye Pollutants

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In the recent years, the most environmentally friendly pollution-treatment method is the elimination of low-concentration organic pollutants in water by oxidation through air and sunlight. For this purpose, photocatalysts with a high activity should be developed in order to utilize more effectively photocatalytic reactions for elimination of the organic waste. As a well-known photocatalyst, ZnO gained much attention in the degradation of environmental pollutants. Furthermore, ZnO is of special interest, because of the possibilities for modification and control of various ZnO nanostructures. In this paper we demonstrate the successful preparation of thin films of ZnO on glass substrates by the sol–gel method using dip-coating technique. We used zinc acetate and different amino ligands as the structure directing agent. After removal of the amino ligands from the structure, transparent porous ZnO films were obtained. The films structure is characterized by XRD, FTIR, UV-Vis and SEM. The results illustrated that the amino ligands are the good candidates for modification of ZnO thin film nanostructures. Further, the obtained ZnO films are examined by photodegradation of pollutant dyes. The UV-Vis results show that the Congo red exhibits complete degradation in the first hour by using all ZnO thin fims. It may be attributed to the large specific surface area of porous ZnO thin films that are obtained by using amino ligands.

Keywords ZnO Thinfilm; Photodegradation; pollutant dye; pothocatalyst.

References:

[1] K. Sun, W. Wei, Y. Ding, Y. Jing, Z. L. Wang, D. Wang, Chem. Commun.,47 (2011) 7776.
[2] G. Adamopoulos, A. Bashir, W. P. Gillin, S. Georgakopoulos, M. Shkunov, Adv. Funct. Mater. (2010) 1.
[3] L. Znaidi, Mater. Sci. Eng. B, 174 (2010) 18.

Camparison Study the removal of red 195 dye using raw, calcinated and modified marble stone powder: kinetic, thermodynamic and equilibrium studies

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The aim of present study, is investigation of removal of red 195 azo dye using raw, calcinated marble stone powder and marble powder nanocomposite as adsorbents. The effect of various parameters on adsorption such as adsorbent dose, contact time, initial dye concentration, temperature and pH were studied by using the batch technique. The adsorption capacity of adsorbents was increased by dose, contact time and dye concentration. modified adsorbents displayed an improved adsorption capacity due to activated sites in its structures. The equilibrium adsorption data were analyzed by isotherm models of Langmuir, freundlich and temkin. Freundlich adsorption model agree well with experimental data. The maximum adsorption capacity was 198 mg g^{-1}, indicating modified marble stone powder is a good adsorbent for the adsorption of red 195. Mechanism of dye adsorption on powders were determined by applying the experimental data with kinetic models such as pseudo first order, pseudo second order, intraparticle diffusion. The pseudo-second order kinetic was the best kinetic model for the experimental data. Thermodynamics parameters of adsorption process such as ΔG, ΔH, ΔS were also calculated.

Keywords: Marble Stone Powder; Adsorption Capacity; Red 195; Batch Technique, Equilibrium

References:

[1] S.D. Khattr, M.K. Singh, Journal of Hazardous Materials, 167 (2009) 1089-1094.

[2] I.D. Mall, V.C. Srivastava, N.K. Agarwal, Dyes and Pigments, 69 (2006) 210-223.

Physical Properties of Amino acids and their Dependence on Topological Indices

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In this study, physical properties of 10 different types of aminoacids, $C_{3n}O_{n+1}N_nH_{5n+2}$ (n:1-10) such as dipole(D), quadrupole(Q), octapole(O) and hexadecapole(Hex) electric moments are computed by use of the Gaussian 09 program at the Hartree-fock (HF) levels on 6-311G basis set, and also the Randic (X), Harary(H), Schultz (MTI), Wiener (W) and balaban(J) indices are calculated. Then the relationship between the physical properties with mentioned topological indices is studied. Partial Least Squares Regression is performed and the best model is taken as the one presenting the optimal value of prediction coefficient, taking into account the number of descriptors used.

The data is showed that the values of D and Hex moments decrease by increasing number of carbons and increasing the values of the X, H, MTI, W, J indices of the aminoacids. Q and O moments have not good correlation with values of indices. Quantitative structure-property relationships (QSPR) subjects are studied and the results of quantum calculations are compared with the results of linear equations of graph theory calculations and then is defined that the values of the Q and Hex moments have not correlation with above mentioned topological indices, but the values of logQ and logHex have good correlation with H, J,W,MTI, X indices respectively, therefore Harary index is the best index for predicting the values of logQ and logHex. Further, the results of such studies are used to get into the QSPR subjects.

Keywords: Aminoacids, Ab initio Method, Topological Indices

References:

[1] E. Mohammadinasab, M. Goodarzi, Fullerenes, Nanotubes, and Carbon Nanostructures 19 (2011) 550-563.

[2] E. Mohammadinasab, Z. Bayat, World Academy of Science Engineering and Technology,Singapore, August **2009**, 26-28.

[3] H. Wiener, J. Am. Chem. Soc **1947** (1947) 17.

The Application of Graph Theory in Prediction of some Thermodynamic Properties of Aminoacids

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In this study is represented the relationship between some of the thermodynamic properties of aminoacids $C_{3n}O_{n+1}N_nH_{5n+2}$ (n:1-10) in contrast to some topological indices such as Randic (X), Harary(H), Schultz (MTI), Balaban(J) and Wiener (W) and model for designing the quantitative structure-property relationships based on topological indices is presented the (QSPR). Thermodynamic properties such as entropy (ΔS/kJmol^{-1}k^{-1}), thermal energy (ΔE_{th}/kJmol^{-1}) and specific heat capacity at constant volume (C_v/kJmol^{-1} k^{-1}) of aminoacids by use of the Gaussian 09 program at the Hartree-fock (HF) method on 6-311G basis set are computed. Partial Least Squares Regression is performed and the relationship of mentioned thermodynamic properties with above topological indices was studied. Linear diagrams of ΔS, ΔE_{th}, C_v versus the topological indices are drawn and linear equations was defined and is characterized the values of R^2 is acceptable. Quantitative Structure-Property Relationship (QSPR) subjects were studied and the results of quantum calculation for unknown molecules were compared with the results of graph theory calculations and is represented well-related of the values ΔS, with X, H, MTI, J ,w indices respectively, therefore X, MTI are the best indices for predicting the values of ΔS. The values of ΔE_{th} has good correlation first with X, H, MTI, J ,W indices respectively, therefore X is the best index for predicting the values of ΔE_{th}. The values of C_v has good correlation first with X, H, MTI , J ,w indices respectively, therefore X, MTI, H are the best indices for predicting the values of C_v The instructive example is directed to the design of the structure-property model for predicting the thermodynamic properties of the aminoacids which are discussed here

Keywords: Graph Theory, Aminoacids, Thermodynamics properties

References:

[1] **S.** Zhang, H. Zhang, MATCH Commun. Math. Comput. Chem 55 (2006) 427–438.
[2] M. Goodarzi, E. Mohammadinasab. Fullerenes, Nanotubes, and Carbon Nanostructures 21(2) (2013) 102-112.

Fe/ZnO as an effective nanocatalyst for the decolorization of methylene blue under UV light

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Large quantities of dye effluents make environmental pollution problems because they are toxic and carcinogenic substances [1]. Therefore, many methods have been performed for the removal of persistent dye organic chemicals. Among these methods, heterogeneous photocatalytic degradation is an important destructive technology for most of the organic pollutants including organic reactive dyes metal-oxide photocatalysts such as ZnO and TiO_2 have become the center of attention. ZnO has a higher photocatalytic efficiency and lower cost compared to TiO_2 for decolorization [2]. ZnO has excellent physical and chemical properties, such as high melting point (1975 ^{o}C) [3], high thermal and chemical stability, broad range of radiation absorption and high photo stability. ZnO doped with transitional metal ions such as Fe can improve the photocatalytic activities. Dopant ion incorporation is expected to reduce the recombination of electron and hole because the dopant induced shallow donor and acceptor states act as an electron or hole trap, which leads to prolonged carrier diffusion length resulting in better photocatalytic activity. In this study, Fe/ZnO nanoparticles were synthesized by a hydrothermal method. This photocatalyst was synthesized with two different percentage of Iron (3% Fe) and (5% Fe) and used for the degradation of methylene blue under UV light (11 W). The reaction was terminated only after 90 min. Results showed the decolorization with (3% Fe/ZnO) better than the decolorization with (5% Fe/ZnO).

Keywords: Decolorization, hydrothermal, methylene blue, photocatalyst, UV light

Refrences:

[1] A. Reife, H.S. Fremann, Environmental Chemistry of Dyes and Pigments, Wiley, 1996.
[2] S. Chakrabarti, B. Chaudhuri, S. Bhattacharjee, J. Hazard. Mater. 154 (2008) 230–236.
[3] A. Tarlani , M. Fallah , B. Lotfi, A. Khazraei , S. Golsanamlou , J. Muzart , M. Mirza-Aghayan , Biosensors & Bioelectronics. 67 (2015) 601-607.

Preparation and evaluation of chitosan nanoparticles as nasal vaccine delivery of Diphtheria and Tetanus toxoids

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Chitosan nanoparticles (CS NPs) have already been proposed as vehicles for nasal immunization. CS has shown mucoadhesive properties as well as an important drug penetration enhancement capacity across mucosal barriers. It is well established that the mucosal administration of vaccines can provide effective humoral and cellular immune responses, especially if the antigen is adjuvanted using an immunostimulator or a delivery system.

The aim of the present work was to investigate the potential utility of CS in the form of nanoparticles as long-term nasal vaccine delivery vehicles for Diphtheria and Tetanus toxoids.

(DT) -loaded NPs were prepared by ionic gelation method and were characterized by the particle size, zeta potential, loading efficiency, SEM, FT-IR spectroscopy and in vitro release studies.

The resulting nanoparticles had a size, which varied depending on the formulation conditions between 100 and 500 nm. They exhibited a positive electrical charge (approx. +30 mV) and showed and excellent loading capacity (loading efficiency between 50-90% depending on the formulation). The in vitro release profile exhibited sustained release patterns with relatively initial burst release, followed by a subsequent slower release.

Keywords Chitosan; Nanoparticles; Nasal administration; Vaccine carriers

References:

[1] Y. Parajo, I. Angelo, A. Welle, M. Garcia-Fuentes, M. J. Alonso, *Drug Delivery* 17(8) (2010) 596–604.

Removal of lead from industrial Wastewaters with Aluminium Oxide Nanoparticles

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The present paper aims to study the efficiency of Al_2O_3 nanoparticles for removal of lead from industrial wastewaters. The obtained results were predicted by artificial neural networks (ANN). Al_2O_3 nanoparticles were purchased from Lima Co. Nanoparticles size was about 50 nm. The effective factors such as pH, temperature and contact time were also investigated. In addition, absorption studies were performed under the experimental conditions such as pH=1-8, contact time 10-20 minutes, initial concentrations 10-100 mg/L of used heavy metal, and 0.2-2 gr of Al_2O_3 Nano absorbent. A feedforward three layer neural network and Back Propagation Levenberg-Marquardt learning algorithm (BP-LM) were employed in the present study. Data related to temperature, concentration and contact time were considered as input and thermal removal efficiency as target for the neural network. Mean Square Error (MSE) and Coefficient of Determination (R^2) used to evaluate the predicted results were about 0.0001 and 0.999 respectively. This indicated the successful prediction of results by ANN.

Keywords: Al_2O_3 Nanoparticles, Artificial Neural Network, Removal Efficiency, Lead

Reference

[1] Bachmat Y. 1994. Groundwater as part of the water system, In Ground Water Contamination and Control, ed. U. Zoller. Marcel Dekker, Inc, New York, 1438 p.

Removal of Cadmium from Industrial Wastewaters Using Fe_3O_4 Magnetic Nanoparticles

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In the present study, Fe_3O_4 nanoparticles were used to remove cadmium (Cd) from the wastewaters of factories. The wastewater samples containing heavy metal Cd were prepared and studied. The effective factors such as pH, temperature and contact time were also investigated. Nanoparticles size was about 40-50 nm. In addition, absorption studies were performed under the experimental conditions such as pH= 2-10, contact time 5-50 minutes, initial concentrations of 10-100 mg/l of the used heavy metal, and 0.1-0.9 gr of Fe_3O_4 nano absorbent. The obtained results indicated that the absorption percent of Cd is pH-dependent and optimal absorption was observed in pH=5. The other optimal conditions for Cd removal are: 0.9 gr of absorbent and contact time of 50 minutes. Moreover, the experimental equilibrium absorption data was investigated using first- and second order pseudo-kinetic models.

Keywords: Fe_3O_4 nanoparticles, heavy metals, cadmium

Reference

[1] Canter L.W., Knox R.C. 1986. Ground Water Pollution Control, Lewis Publishers, Chelsea, MI, p. 349.

Synthesis and characterization of graphene/$Zn_xCd_{1-x}S$ nanocomposite and its application in photocatalytic degradation of methylene blue under visible light irradiation

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Semiconductor photocatalysts have attracted much attention in the past decade and have been applied for the purification of water and air. In this study, graphene/zinc-cadmium sulfide (RGO/$Zn_xCd_{1-x}S$) nanocomposite has been used as an efficient photocatalyst for the photodegradation of methylene blue under visible light irradiation. Because of high conductivity and high surface to volume ratio, graphene was used as a progressive substrate material in proposed nanocomposite structure. Graphene was synthesized chemically by the oxidation/exfoliation Hummers' method. Then, $Zn_xCd_{1-x}S$ nanoparticles were grown on graphene nanosheets via hydrothermal method in optimal experimental conditions such as reagents ratio, reaction temperature and time. After synthesis, various RGO/$Zn_xCd_{1-x}S$ nanocomposites ($0<x<1$) were characterized by various techniques such as SEM, XRD, XPS, BET, TGA, FT-IR, and UV-Vis-DRS. XRD analysis of RGO/$Zn_xCd_{1-x}S$ nanocomposites showed the crystalline phase of samples converts from hexagonal structure to cubic structure, when the Zn content increases. Methylene blue (MB) as a model compound was photocatalytically degraded in the presence of synthesized photocatalysts under visible light irradiation. The results showed that RGO/$Zn_{0.8}Cd_{0.2}S$ (8.12 Wt% graphene) has maximum photocatalytic activity ($k=0.0094$ min^{-1}) compared with other RGO/$Zn_xCd_{1-x}S$ nanocomposites. The improved photocatalytic activity of RGO/$Zn_{0.8}Cd_{0.2}S$ is attributed to increased migration efficiency of photo-induced electrons via efficient amount of graphene.

Keywords: Graphene; Methylene blue; Photocatalyst; Zinc-cadmium sulfide

References:

[1] X. Wang, H. Tian, W. Zheng, Y. Liu, *Materials Lett.*, 109 (2013) 100–103.
[2] Q. Li, H. Meng, P. Zhou, Y. Zheng, J. Wang, J. Yu, *ACS Catal*., 3 (2013) 882−889.
[3] C. Wang, M. Cao, P. Wang, Y. Ao, *Materials Lett*., 108 (2013) 336–339.

Green synthesis of copper nanoparticles on Clinoptilolite zeolite for removal dyes in aqueous media

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In recent years, there has been great interest in using metal nanoparticles (MNPs) such as Pd, Pt, Au, Ag, Cu and Ru as catalyst in the dye degradation due to their large specific surface area high activity and efficiency [1]. However, due to the instability of small size MNPs such nanoparticles usually need suitable stabilizers. Generally, MNPs are produced by chemical and physical methods [2]. However, many of them require the usage of stabilizers to prevent agglomeration of nanoparticles and hazardous chemicals, which are unacceptable in medicine, pharmaceutical and cosmetics industry, as well as large amounts of energy. Therefore, environmentally benign production methods of MNPs are very desirable. Compared to the chemical and physical methods, biological synthesis does not require the usage of the complicated and expensive apparatus and hazardous chemicals, large amounts of energy, high temperature or pressure. Biological methods do not generate hazardous waste and the products usually do not need purification. The biological methods use the ability of natural reducing agents present in plant extracts for the reduction metal ions. In this work, a clinoptilolite zeolite/copper (cliniptolilite zeolite/Cu) nanocomposite has been successfully synthesized applying a simple in situ reduction method using an aqueous extract of Rheum palmatum root as a reducing and stabilizing agent. The clinoptilolite zeolite/Cu nanocomposite is characterized using Fourier transform infrared spectroscopy (FT-IR), field emission scanning electron microscopy (FESEM) equipped with an energy dispersive X-ray spectroscopy (EDS), X-ray diffraction analysis (XRD) and transmission electron microscopy (TEM). The crystal structure of clinoptilolite zeolite is determined by single-crystal X-ray diffraction analysis. The catalytic activity of the clinoptilolite zeolite/Cu nanocomposite is excellent for organic dye reduction at room temperature and remains the same for several cycles. The present strategy gives a promising way to prepare heterogeneous nanocatalysts composed by metal nanoparticles for broad applications in catalysis and organic transformations.

Keywords: Copper nanoparticles; Zeolite; Rheum palmatum root extract; Green synthesis; Reduction degradation

References:

[1] B. Manu and S. Chaudhari, Bioresour. Technol., 82 (2002) 225.
[2] M. Nasrollahzadeh, S. M. Sajadi, and M. Khalaj, RSC Adv., 4 (2014) 47313.

Synthesis of Highly Ordered Ag/TiO_2/MCM-41 nanocomposite from *Saccharum* via a Mild Hydrothermal Method

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An environmentally friendly, highly ordered MCM-41 was synthesized via a mild hydrothermal method with silica extracted from *Saccharum* as silica source. Amorphoussilica with 86.023 wt. % SiO_2 was extracted from *Saccharum*ash by a suitable alkali solution. The effect of the crystallization time andthe ratio of Na_2O/SiO_2 on the properties of the final product were investigated. The synthesized nano-zeolite was characterized byX-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), energy-dispersive X-ray(EDX), and Brunauer-Emmett-Teller (BET) techniques. Results revealed that the crystallization time and alkalinity havesignificant effects on the structural properties of nano-zeolite which was synthesized via a suitable, mildhydrothermal method at 70 ºC for 7.5 h without any organic additives. It's nitrogen adsorption-desorption isotherm was reversible and showed a type IV one with a desirable specific surface area. X-ray diffraction pattern and TEM image exhibited that MCM-41 has highly ordered structure. The SEM images also revealed that the particle size of the synthesized sample is in nanometer range leading to lower limit of detection and limit of quantification.

Keywords Ag/TiO_2/MCM-41;Saccharum; X-ray diffraction;Scanning electron microscopy

References:

[1] A. Corma, *Chem. Rev.*,(**1997**), 97, 2373-2420.
[2] M. A. Zanjanchi, A. Ebrahimian, Z. Alimohammadi, *Optical Mater.*,(**2007**),29, 794-800.
[3] F. Torney, B. G. Trewyn, V. S. Y. Lin,*Nature Nanotech.*,(**2007**),2, 295-300.

Removing of copper ion (II) from waste water by an N4 cyclic compound

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Adsorption of the ions is attracted many attentions because it has environmental consideration [1]. Macrocyclic compounds have been used for this purpose because they contain hetero atoms which they trap the poisonous metal ions such as Na^+ , Li^+ and K^+ which have been adsorbed into a macrocyclic compound [2-3].In this study, copper ion (II) has been selected for this purpose because it is more toxic than alkali-metal ions. Therefore, a macrocyclic compound of 13 membered N4 type has been synthesized and characterized with different techniques. Then it was applied for adsorbing Cu(II) ions. Results based on TGA diagram showed that the cyclic compound has the capacity adsorption of 90 mg of the toxic ions per 1 gram of the adsorbent compound.

Keywords : Adsorption; Macrocyclic compounds; copper ion (II); N4 cyclic compound

References:

[1] L. Yun.; S. Xing.; X. Qiming.; C. Haidong.; Z. Huixian.; G. Shixiang.; Journal of Hazardous Materials B137 (**2006**) 1149–1155
[2] J. Schulz.**;** G. Warr.; Industrial & Engineering Chemistry Research. (1998), 37, 2807-2811
[3] A. Tarlani.; K.; Narimani. F. Mohammadipanah.; J. Hamedi.; H. Tahermansouri.; M. Amini.; Applied Surface Science 341 (**2015**) 86–91

Congo Red removal by a new nano adsorbent from magnesia

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Natural water pollution is one of the biggest problems created by the industry which hassubstantial effects on our environment. Congo Red as a chemical secondary diazo dye which is water-soluble, yielding a red colloidal solution. It has affinity to cellulose fibers and is widely used in textile industry. Therefore, its waste makes the water sources a deep red color. It is very toxic and may cause cancer in human [1]. Mesoporous materials with porous structure could remove this molecule from the waste. Synthetic mesoporous magnesia has a good potential to be used as an adsorbent of Congo Red compared to the commercial ones because it is highly porous and hydroxyl rich to remove mentioned molecule. The N_2-sorption shows type IV mesoporous diagram. 10 mg of magnesia bleaches the 10 mL (50 ppm) of Congo Red only after 10 seconds. The same process removed the 10 mL of 100 ppm dye after 60 seconds. It could be concluded that new synthetic and highly porous magnesia is a good adsorbent for this toxic pollutant.

Keywords:
Magnesia; mesoporous; Congo Red; Adsorbent

References:

[1] Somasiri, W. Evaluation of the efficacy of upflow anaerobic sludge blanket reactor in removal of colour and reduction of COD in real textile wastewater. **99,** 3692–3699 (2008).

[2] Meshkani, F. & Rezaei, M. Facile synthesis of nanocrystalline magnesium oxide with high surface area. *Powder Technol.***196,** 85–88 (2009).

Efficient decolorization of Congo red by nano Cu/barite

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Azo dyes are consisting of an amine or phenol amine or phenol diazotized amine. Azo dyes are synthetic compounds, and the calculations show that over 51% of all colors which are manufactured per year, contain these compounds [1]. Azo dyes pigments are widely used in the textile industry, printing industry, food, paper and cosmetics [2]. Congo red, which is a carcinogenic azo dye, is used for colorizing the paper products. This dye is found in the waste water and is stable under environmental conditions. Therefore, removing this toxic molecule from waste is very important [3-4].

In this study Congo red was decolorized by Cu/barite that was synthesized by a solvothermal method. Cu/barite was activated at 550 ^{o}C. Then, 30 ppm of Congo red was decolorized only after 10 min under UV-light while the amount of the catalyst was 30 mg. The effect of pH was studied and the acidic medium found to be the best medium for the photocatalytic reaction.

Keywords dyes; decolorization; Congo red

References:

[1] Križanec, B.; Majcen Le Marechal, A. *Croaticachemicaacta*, (**2006**), 79 (2), 177-186.

[2] Bae, J.-S.; Freeman, H. S. *Dyes and pigments*, (**2007**), 73 (1), 81-85.

[3] Ajibola, V.; Rilwanu, R. *Journal of Scientific and Industrial Research*, (**2001**), 60 (9), 735-737.

[4] Rajamohan, N.; Karthikeyan, C. *J Solid Waste TechnolManag*, (**2006**), 1-5.

Removing of Congo red by Copper (II) oxide without using any light source

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Decolorization of the toxic dyes are very important. Because environmental concerns earged the scientist to solve this problem. Many natural and synthetic compounds. Were uses for removing the toxic dyes? Most of catalysts activate by using a uv or visible light source. But structural features of the catalyst makes the possibility to adsorbe the dye.

In a typical synthesis, 0.7gr of CuSO4-5H2O was dissolved in15 mL of distilled water and 10mL Methanol.Reaction mixture was stirred for30 min, followed by the drop-wise addition of aqueous

KOH (1M) under continuous stirring, a blue precipitate was obtained. Reaction mixture was Transferred into a Teflon-lined stainless steel autoclave, and maintained at 150 °c for 24 h. After the reaction, autoclave was cooled to room temperature. The resulting black precipitate was filtered and washed with distilled water,results showed that 0.02gr of copper oxide adsorbe congored molecules(10cc,100ppm)only after 1.5hwith out using any uv or visible light

Keywords: dyes; Removing; Congo red

References:

[1]A. Sadollahkhani,Z.H. Ibupoto,S. Elhag,O. Nur,M. Willander, Ceramics International40(2014)11311–11317.
[2]R.K. Wahi,W.W. Yu,Y. Liu,M.L. Mejia,J.C. Falkner,W. Nolte,V. L. Colvin, Journal of Molecular Catalysis A: Chemical 242 (2005) 48–56.

Identification of Blue pigments used in Objects from Prehistoric Sites in Iran by Analytical Methods

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Blue was a late comer among colors used in art and decoration, as well as language and literature. Reds, blacks, browns, and ochres are found in cave paintings from the upper palethic period, but not blue. Blue was also not used for dying fabric until long after red, ochre, pink and purple. This is probably due to the perennial difficulty of making good blue dyes and pigments. The earliest known blue dyes were made from plants, woad in Europe, indigo in Asia and Africa, while blue pigments were made from minerals, usually either lapis lazuli($Na_{8-10}AlSiOS_{2-4}$) or azurite($2CuCO_3.Cu(OH)_2$. In this study, samples were analyzed by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), Polarizing light microscopy (PLM) and scanning electron microscopy in combination with energy dispersive X-ray microanalysis (SEM-EDX). The blue samples were collected from different prehistoric sites like, Takht-e-Jamshid (550-330 B.C.), in Fars, Jobji Ram Hormoz (585-539 B.C.) in south of Iran, Castle of Yazdgerd Kermanshah (100 B.C.) in west of Iran, Tepe Hesar Damghan (1th millennium B.C.) in central of Iran and Tape Nesfi Gilan (1th millennium B.C.) in north of Iran. The color of samples was blue and green-blue and shape of them was bead, ornaments, shell and blue layer on architectural remains. Results showed that, Egyptian blue and lapis lazuli were used as pigment and raw material for make of objects and ornaments. Lapis lazuli a semiprecious stone of intense blue color, found in a remote area of Afghanistan. Very expensive and difficult to get, lapis lazuli has been prized since the beginning of recorded history, Starting with the rise of civilization around 4500 B.C. and continuing to this day, people have found creative ways to produce blue for artistic expression. Egyptian blue ($CaCuSi_4O_{10}$), the first synthetic form of the rare mineral cuprorivaite (calcium copper tetrasilicate), was widely found in Egypt, Mesopotamia and Rome from second millennium BC. This pigment made by grinding silica, lime, copper and alkali, and heating it to 800 or 900 °C and used on materials like stone, plaster, pottery, wood, papyrus, canvas and wall paintings. In addition to Egyptian blue was used for building of objects such as ornaments, jewelry and decorative objects[3]

Keywords: blue pigment, lapis lazuli, Egyptian blue, prehistoric.

Highly efficient decolorization of spend sulfuric acid remaining after the alkylation process

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The alkylation reaction combines isobutane with light olefins in the presence of a strong acid catalyst. Currently, during this reaction in oil refinery and petrochemical industries, considerably high volumes of black sulfuric acid is remained which considered as a waste material or spend acid. The aim of this study was to find the best method for decolorizing and recycling the spend acid. The results of SEM analysis of the black residue from the spend acid revealed the nano-size structure (38 nm) of this material. In addition, for characterization of the black residues, various spectral analyses such as FT-IR, XRD, ATR, CHNS analysis, and RAMAN were done. In this study, among different tested methods, we found that 18 mL of 30 % (v/v) hydrogen peroxide was highly capable to decolorize about 100 mL of the spend acid within 10 min. The effects of key variables such as reaction temperature, concentration of oxidizing agent, acid to oxidizing agent ratio were carefully studied. The analysis of the produced gases during the process indicated that the black residues were completely oxidized and yielded 20 % (v/v) CO_2. The pale yellow color remained after this process can be related to the dissolved Fe that was composed 0.11 % (w/w) of the spend acid. By simulation experiments in laboratory with pure gas reactants, the origin and causes of the contamination of sulfuric acid during of such important industrial process was clearly identified.

Keywords: Alkylation, Spend sulfuric acid, Black residue, Decolorization, Oxidation.

synthesis of modified multi wall carbon nano tube with diphenyl carbazone coated with anionic surfactant sodium dodecyl sulfate as sorbent and investigate characterization of nanocomposite

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Nano sorbent was synthesized by the reaction of diphenyl carbazone with functionalized multi walled carbon nanotube. Initially, the surface of the multi-walled carbon nanotube oxidized by a mixture of nitric and sulfuric acid and then functionalized using thionyl chloride. The diphenyl carbazone has been attached to the multi-walled carbon nanotubes in a somewhat shorter time and lower temperature than previous reported methods. In order to study and observe the nanoparticles surface, size and shape BET technique and transmission electron microscopy device (TEM) with specification was used. Also the thermogravimetric analysis (TGA) of the nanocomposites was employed to exhibit the stability of nanocomposites and the presence of organic group in the material and elemental analysis technique (CHNSO) is used to identify and determine the amount of elements that are present modified multi wall carbon nano tube with diphenyl carbazone.

Keywords: nanocomposite, diphenyl carbazone and MWCNT.

Application of eggshell waste as a natural sorbent for the removal of azo dyes from aqueous solutions

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Dye compounds is one of the most critical contaminant for natural ecosystems. The scope of this study was to evaluate the feasibility application of eggshell as a sorbent for the removal of Congo red as a typical of azo dyes from aqueous solution. The experiments were carried out in a batch system to optimize operation variables such as adsorbent dosage, Congo red concentration, pH and contact time. The Langmuir, Freundlich, Tempkin and Dubinin–Raduskovich (D–R) adsorption isotherm models were studied and the best results were obtained by Langmuir isotherm model. The maximum adsorption capacity was 5.02 mg g^{-1}, indicating eggshell is a good adsorbent for the adsorption of Congo red. The maximum absorption wave length of this dye (λ_{max}) was determined by spectrophotometer. The adsorption kinetics was studied with the pseudo-first-order, pseudo-second-order, Elovich and intraparticle diffusion models. It was found that the adsorption of Congo red on eggshell followed the pseudo-second order equation which was studied in details. The thermodynamic parameters indicated that the adsorption of Congo red onto eggshell was an exothermic and spontaneous process.

Keywords: Azo dyes; Eggshell; Natural sorbent; Removal