نهمین سمینار دوسالانه

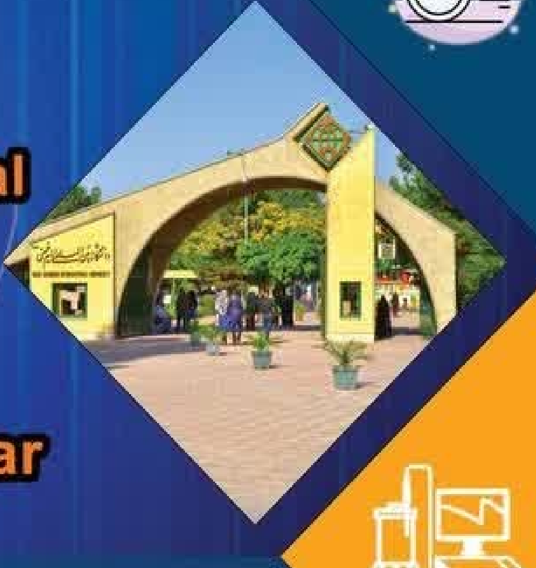
۹ کمومتریکس

انجمن شیمی ایران

9 th Iranian Chemical Society Biennial

Chemometrics

Seminar



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دانشگاه بین المللی امام خمینی
IMAM KHOMEINI
INTERNATIONAL UNIVERSITY

Program book proceeding of the 9th Iranian Chemical Society Biennial Chemometrics Seminar

Oct. 18, 19-2023
Imam Khomeini International University

* * *

In the name of God

* * *

WELCOME Message from the Seminar Chairman

Dear friends and colleagues

We are pleased to welcome all dear guests, professors, researchers, participants and dear friends to the 9th Biennial Iranian Chemistry Seminar. This prestigious event will be held on October 18-19, 2023 at Imam Khomeini International University, Qazvin, Iran.

The organizing and executive committees are happy to host researchers and scientists of chemistry in Iran. This biennial seminar serves as a platform to showcase and discuss the latest developments in all areas of chemometrics.

The seminar program includes public and invited speakers as well as engaging poster sessions covering a wide range of topics. We strongly believe that these special sessions will shed light on current focal points and trends in chemometrics research and foster collaboration for the advancement of the entire field. We sincerely thank the respected Iranian scientists who will share their expertise in this seminar, as well as the keynote speakers of famous foreign scientists, Prof. Roman Tauler Ferrer (University of Barcelona, Spain), Prof. David Balabio (University of Milan). -Bicocca, Italy), and I appreciate the kindness of Prof. Marcel Mader (Newcastle University, Australia).

Also, from the cooperation of the Iranian Chemical Society, Islamic World Science Reference Base (ISC), Chemometrics Committee, Scientific and Referee Committee, Executive Committee, Honorable President and Honorable Officials of Imam Khomeini International University. Also, we sincerely thank the dedicated efforts of the organizing committee, students and all the university staff who played a unique role in organizing this exceptional event.

As we look forward to the seminar, we are thrilled to have each and every one of you with us and envision an engaging and fruitful gathering. Let's join forces and create an unforgettable experience together!

Warm regards,
Mohammad Reza Khanmohammadi Khorrami
Seminar Chairman

The Brief History of Iranian Biennial Chemometrics Seminars

No.	City	Year	*Chairman*	Organizer
1st	Arak	2006	*Dr. Gholam Hassan Azimi*	Arak University
2nd	Urmia	2009	*Prof. Morteza Bahram*	Urmia University
3rd	Tabriz	2011	*Dr. Abdolhossein Naseri*	Tabriz University
4th	Shiraz	2013	*Prof. Bahram Hemmateenejad*	Shiraz University
5th	Tehran	2015	*Prof. Jahanbakhsh Ghasemi*	Tehran University
6th	Babolsar	2017	*Prof. Mohammad Hossein Fatemi*	University of Mazandaran
7th	Shahrood	2019	*Prof. Nasser Goudarzi*	Shahrood University of Technology
8th	Tehran	2021	*Dr. Ahmad Mani-Varnosfaderani*	Tarbiat Modares University
9th	Qazvin	2023	*Prof. Mohammadreza Khanmohammadi Khorrami*	Imam Khomeini International University

Scientific Committee

Prof. Hamid Abdollahi

Institute for Advanced Studies in Basic Sciences, Zanjan

Prof. Mohammad Reza Khanmohammadi Khorrami

Imam Khomeini International University

Prof. Jahanbakhsh Ghasemi

Tehran University

Prof. Bahram Hemmateenejad

Shiraz University

Dr. Ahmad Mani-Varnosfaderani

Tarbiat Modares University

Prof. Mohammad Hossein Fatemi

Mazandaran University

Dr. Abdolhossein Naseri

Tabriz University

Dr. Hadi Parastar

Sharif University of Technology

Dr. Maryam Khoshkam

University of Mohaghegh Ardabili

Dr. Soodabe Seifi

Technical and Vocational University (TVU)

Executive Committee

Prof. Mohammad Reza Khanmohammadi Khorrami *(Scientific-executive head of the seminar)*

Prof. Majid Soleimani *(Executive head of the seminar)*

Dr. Ali Reyhani *(Dean of the faculty)*

Dr. Mahsa Mohammadi *(PhD at IKIU)*

Dr. Mina Sadrara *(Postdoctorl researcher at IKIU)*

Mr. Ali Ramshini (*Master of management information system****)***

Ms. Zahra S. Hajiseyedrazi *(Master of science)*

Ms. Mozhgan Zarnegar *(Master of science)*

Ms. Fatemeh Khoban *(Undergraduate student at IKIU)*

Mr. Mead Hashemizadeh *(PhD student at IKIU)*

Ms. Asra Modares Asgari *(PhD student at IKIU)*

Ms. Farzaneh Khalaj *(Master student at IKIU)*

Ms. Arefeh Zarei *(Master student at IKIU)*

Invited Speakers

Prof. Bahram Hemmateenejad
Speech Topic: *Robust Spectral Scatter correction*

Prof. Hamid Abdollahi
Speech Topic: *Analytical Quality by Design Approach in Development and Application of Chemometric Methods*

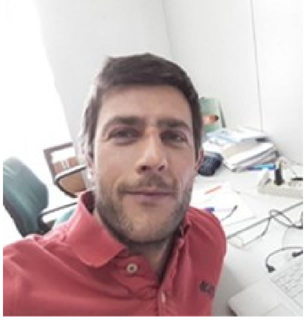
Prof. Roma Tauler
Speech Topic: *Recent advances in the analysis of MS analytical data using the Regions of Interest Multivariate Curve Resolution (ROIMCR) method*

Dr. Hadi Parastar
Speech Topic: *How can chemometrics enhance the utility of miniaturized spectroscopy and hyperspectral imaging in the analysis of complex samples?*

Dr. Ahmad Mani
Speech Topic: *Breath volatilome analysis: A novel tool for diagnosing fatal diseases and following the response to the treatment.*

Prof. Mansour Arab
Speech Topic: *Use of penalized regression methods in QSAR studies.*

Prof. davide ballabio
Speech Topic: *Multitask modelling for QSAR and analytical applications.*



Conference Topics

- ***Multivariate Calibration***
- ***Clustering and Classification Methods***
- ***Chemometrics applications in industries***
- ***Experimental Design***
- ***Curve Resolution***
- ***Drug/Molecule Design and Quantitative Structure–Activity Relationship (QSAR) Study***
- ***Bioinformatic***

9th Iranian Biennial Chemometrics Seminar Timetable

Wednesday, October 18, 2023	
First section	
Title	**Time**
🔔**Recite the holy Quran, National Anthem, schedule announcement**	**08:00 – 08:10**
📢**Academic-executive head of the seminar presentation**	**08:10 – 08:20**
Imam Khomeini International University introduction clip 🎬	**08:20 – 08:30**
Speech: Prof. Khayamian	**08:30 – 08:40**

Wednesday, October 18, 2023		
Second section "scientific speeches"		
Title	**Presenter**	**Time**
Chair: Prof. Khayamian, Dr. Parastar		
Robust Spectral Scatter correction	***Prof. Hemmateenejad***	**08:40-09:20**
Analytical Quality by Design Approach in Development and Application of Chemometric Methods	***Prof. Hamid Abdollahi***	**09:20-10:00**
Enhanced Data Point Importance for Variable Selection Multivariate Calibration Models	***Dr. Valizadeh***	**10:00-10:30**
Chair: Prof. Abdollahi, Dr. Mani		
Recent advances in the analysis of MS analytical data using the Regions of Interest Multivariate Curve Resolution (ROIMCR) method	***Prof. Roma Tauler***	**11:00 – 11:40**
How can chemometrics enhance the utility of miniaturized spectroscopy and hyperspectral imaging in the analysis of complex samples?	***Dr. Parastar***	**11:40-12:20**

Wednesday, October 18, 2023

Third section “scientific speeches”

Title	Presenter	Time
Chair: Prof. Abdollahi, Dr. Naseri		
Breath volatilome analysis: A novel tool for diagnosing fatal diseases and following the response to the treatment	***Dr. Mani***	**14:00-14:40**
Use of penalized regression methods in QSAR studies	***Prof. Arab***	**14:40-15:20**
Advanced Chemometrics-Driven Screening Approach for Orange Juice Authentication Using Dual Handheld NIR Spectrometers	***Ms. Ehsani***	**15:20-15:45**
Chemometrics in Food Authentication	***Dr. Esteki***	**15:45-16:05**
Chair: Prof. Hemmateenejad, Dr. Parastar		
Multitask modelling for QSAR and analytical applications	***Prof. Davide Ballabio***	**16:30-17:10**
Multivariate Curve Resolution as a Pretreatment Step in Multivariate Analysis of Variance	***Ms. Najafloo***	**17:10-17:35**
Sourcoe indentification in crude oil samples by a couple of colorimetric paper- based E-nose and chemometrics data analysis techniques	***Ms. Chaharlangai***	**17:35-18:00**

Thursday, October 19, 2023

First section “scientific speeches”

Title	Presenter	Time
Chair: Prof. Khayamian, Prof. Hemmateenejad		
Slice-based Multivariate Calibration Strategy for Quantification of Polycyclic Aromatic Hydrocarbons in Oil Fractions by Means of GC×GC-TOFMS	*Ms. Piltan Eraghi*	**08:00-08:25**
Development of Colorimetric Sensor Array Based on Metal Ion Complexes for Discrimination and Adulteration Detection of Lime Juice Samples	*Ms. Esmaeili*	**08:25-08:50**
Rapid authentication and classification of grape seed oil using fluorescence spectroscopy combined with sparse classification and regression methods	*Ms. Rahmani*	**08:50-09:15**
Chair: Dr. Naseri, Dr. Mani		
General structure-activity relationship patterns for the ligands of cyclin-dependent kinases as tools for virtual screening of PubChem database	*Ms. Kaveh*	**11:00-11:25**
Enhanced Data Point Importance for Efficient Data Splitting in Classification Models: Application to Olive Oil Authentication	*Ms. Zare*	**11:25-11:50**

Oral presentation

Poster presentation

Experimental Design

Curve Resolution

Enhanced Data Point Importance for Variable Selection Multivariate Calibration Models

Somaye Vali Zade[a], *Hamid Abdollahi*[b*]
[a] *Halal Research Center of IRI, Food and Drug Administration, Ministry of Health and Medical Education, Tehran, Iran*
[b] *Faculty of Chemistry, Institute for Advanced Studies in Basic Sciences, 45195-1159, Zanjan, Iran*

ABSTRACT

Variable selection techniques are a critical step to obtaining a good prediction performance and explaining the underlying phenomena in multivariate calibration methods. We introduced a novel utilization of Data Point Importance (DPI), specifically designed for variable selection in the context of multiblock data (PLS). As previously stated, [1], within the DPI framework, author's focus revolved around establishing and arranging the significance of individual data points to preserve the underlying data microstructure. This involved organizing the sequence of more crucial variables in a manner where the foremost variable exerts the greatest influence on preserving the data microstructure. Furthermore, a novel adaptation of the DPI has been developed and implemented here for variable selection. In this modified approach, termed Enhanced DPI, not only have the Essential Points been prioritized systematically, but the concept of DPI has been extended to encompass all data points. The data points are positioned based on the data structure across different layers, where the significance of these layers also influences the sequencing of data point importance. In this proposed work, our suggestion involves carrying out the identification of DPI and their subsequent arrangement, contingent upon changes in the inner polygon's relative area, within the realm of the PLS space. The latent variables in PLS are formed through linear combinations of observed variables, yet the principle guiding weight selection is rooted in maximizing the covariance between the latent variable(s) representing the X data and the y data (including distinct attributes like concentrations of an active compound). This selection criterion aligns with the method's overarching objective: modeling y as a function of X. Consequently, PLS involves defining basis vectors within the row and column spaces, with the rows and columns representing points distributed within their respective spaces. PLS loadings serve to delineate the inner polygon of these row and column spaces, facilitating the arrangement and sorting of data rows and columns based on the PLS space. The proposed method has been used to sort the importance and selection of the variables in spectroscopic multivariate PLS calibration method for a three-component simulated and real data. The proposed procedure was compared to a variable importance in projection (VIP) method as a well-known variable selection method.

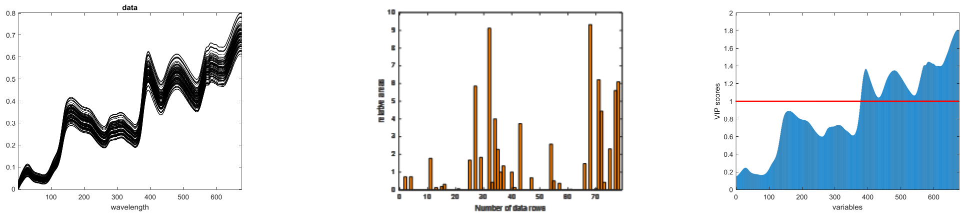


Figure (1); The data set (left panel) the selected variables in column (middle panel) space with our procedure. VIP scores for each variables using the PLS model (right panel).

References: [1] S. Vali Zade, K. Neymeyr, M. Sawall, H. Abdollahi, Journal of Chemometrics, (2022).

Advanced Chemometrics-Driven Screening Approach for Orange Juice Authentication Using Dual Handheld NIR Spectrometers

Samaneh Ehsani[a], *Hassan Yazdanpanah*[b], *Hadi Parastar*[a] *

[a]*Department of Chemistry, Sharif University of Technology, Tehran, Iran*
[b]*Food Safety Research Center, Shahid Beheshti University of Medical Sciences, Tehran, Iran*
E-mail addresses (Corresponding author): h.parastar@sharif.edu

ABSTRSCT

Citrus fruits, particularly oranges, are widely consumed globally due to their appealing sensory properties and nutritional value [1]. However, their popularity has made citrus juices, and orange juice in particular, a prime target for adulteration and fraud. Adulteration of orange juice typically involves dilution with water or pulp wash, addition of organic acids such as citric, tartaric, malic, and citrate acids, sugars, other additives, and even juice-to-juice adulteration. The "sugar to acid ratio" or "Brix to acid ratio" is commonly used to describe the taste or tartness of fruit juices. Higher Brix or Brix to acid ratios indicate a higher sugar content, resulting in a sweeter and less tart juice. In the juice industry, this ratio is often manipulated by adding pulp-wash to adulterate the juice with the aim of achieving lower tartness levels [2, 3].

Given the significance of this issue, this study investigated the feasibility of using two handheld NIR spectrometers as rapid screening techniques, in combination with class modelling (DD-SIMCA and soft-PLS-DA) and discrimination strategies (Ensemble learning and hard-PLS-DA), for the first time, to authenticate orange juice samples and identify levels of Brix to citric acid ratio in pulp-wash as adulterants. Both NIR spectrometers coupled with DD-SIMCA demonstrated 100% sensitivity and specificity in calibration and prediction sets. Furthermore, ensemble learning approaches such as Gradient Boosting Tree (GBT) and Adaptive Boosting (Adaboost) coupled with the NIR Tellspec spectrometer were able to perfectly predict the levels of adulterants with a limit of detection (LOD) of 2% and 5% for Brix to citric acid ratio and pulp-wash, respectively. This outperformed hard-PLS-DA, which is the most commonly used technique in food control studies.

Keywords: Orange juice, Adulteration, Handheld NIR spectrometers, Ensemble learning, Class modelling, Partial Least Squares-Discriminant Analysis.

References:

[1] F. Shahidi, “Handbook of functional beverages and human health”, CRC press, (2016), 423-424.

[2] W. W. Widmer, F. P. Cancalon, S. Nagy, “Methods for determining the adulteration of citrus juices”, Trends in Food Science & Technology, 3, (1992), 278-285.

[3] E. A. Wistaff, S. Beller, A. Schmid, J. J. Neville, T. Nietner, “Chemometric analysis of amino acid profiles for detection of fruit juice Adulterations-Application to verify authenticity of blood orange juice”, Food Chemistry, 343, (2021), 128452.

Chemometrics in Food Authentication

*M. Esteki**

University of Zanjan
E-mail address (corresponding author): m.esteki@znu.ac.ir

ABSTRACT

The guarantee of food safety and quality along the food chain is demanding great attention from the food industry and consumers. Regulatory authorities, retailers, food producers, and processors are all actively interested in ensuring that food quality matches by the claims they are posing. Fraud and adulteration detection, so-called food authentication, is a process that verifies food compliance with its label description [1]. This may include the geographical origin, production method, processing technologies, and food composition. Various types of food fraud, including substitution, dilution, tampering, misrepresentation, and mislabeling, are often used to derive financial profits by reducing manufacturing costs or extending shelf lives. Authenticating foodstuffs that hold a certificate of specific character (CSC), protected designation of origin (PDO), or protected geographical indication (PGI) is essential with agro-food products [2]. Food adulteration is a growing challenge for food manufacturers and analysts because most adulterants are unknown and difficult to recognize using the typical targeted screening methods. This industry urgently needs non-targeted screening methods for food samples to provide proof of origin and prevent deliberate or accidental undeclared additions to those samples. Nowadays, the rapid growth of the capabilities of modern analytical instruments provides a large amount of data involving a wide range of factors (features) that need chemometrics for the extraction of meaningful information. Chemometrics provides powerful tools in calibration and classification analysis, applied in targeted and non-targeted approaches to identify various food fraud situations or verify of their geographic or biological origin. The most common multivariate methods and principles for food authentication can be classified into three categories: exploratory data analysis; data description and visualization, discrimination, and classification; and regression and prediction. Classification methods based on multivariate data analysis could be supervised or unsupervised. In unsupervised methods, the purpose is to identify clusters or relationships between samples without prior knowledge of classes or groups. In contrast, supervised methods require information on class membership and a training stage to build a proper mathematical model.

Classification techniques are of either of two main types. One is known as “discriminant analysis” or “hard modeling” and partitions the data space into isolated regions (classes); the other, known as “class modeling” or “soft modeling”, models each category or class separately [3].

Keywords: food Authentication, classification, exploratory data analysis

References

[1] M. Esteki, J. Simal-Gandarab, Y. Vander Heyden, “A review on the application of chromatographic methods, coupled to chemometrics, for food authentication”, Food Control, 93, (2018), 165- 182.

[2] M. Esteki, J. Regueiro, and J. Simal-G´andara, “Tackling Fraudsters with Global Strategies to Expose Fraud in the Food Chain”, Comprehensive Reviews in Food Science and Food Safety, 18, (2019), 425- 440.

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Multivariate Curve Resolution as a Pretreatment Step in Multivariate Analysis of Variance

Maedeh Najafloo[1], Jmileh Mohammad Jafari[1], Mahsa Akbari Lakeh[2], Paul J. Gemperline[3], Hamid Abdollahi[1]*

[1]*Faculty of chemistry, Institute for Advanced Studies in Basic Sciences, Zanjan, Iran*
[2]*Radboud University, Nijmegen, the Netherlands*
[3]*East Carolina University, Greenville, NC, United States*
E-mail address (corresponding author): abd@iasbs.ac.ir

ABSTRACT

In analytical chemistry, it is common to study the effect of changes in one or more factors (like temperature or type of catalyst) on a measured response for several possible purposes (like optimizing the yield of a reaction). Usually, in such studies, data is collected on the basis of an experimental design to guarantee that it will contain the information targeted by the study. Analysis of variance (ANOVA) is a statistical model that aims to decompose the total response variation to test the significance of each factor effect. ANOVA is utilized to determine the effect of the studied factors, as well as, to quantify the effect of different levels of each factor [1]. With the advancement of technology, it is possible to study the effect of the desired factors on multiple responses. As a result, ANOVA, due to its univariate nature, is not applicable to these datasets. ANOVA simultaneous component analysis (ASCA), which is an extension of ANOVA, is applicable in such cases [2]. In a dataset coming from an experimentally designed study, various chemical components can be influenced by the factors under investigation. ANOVA based methods decompose the dataset into matrices that represent the effects of each factor and their potential interactions, allowing for the examination of the effect of factors. However, in this decomposition, the effects of factors on the chemical components cannot be examined separately. Since the studied factors may have different effects on chemical components, investigating the effects of each factor on the chemical components can be crucial in various studies like metabolomics or food industry. MCR-ASCA approach has been proposed in this work to achieve the above-mentioned goal. In this approach, data is decomposed into the contributions of chemical components, and then the contribution of each component is decomposed with ASCA model for obtaining further information about the desired components. Several simulated and experimental data sets are applied for illustrating the advantages of applying this approach.

Keywords: ANOVA, ASCA, MCR-ASCA

References:

[1] Fisher R. Ronald Fisher. Darwinism.337.
[2] Smilde AK, Jansen JJ, Hoefsloot HC, Lamers R-JA, Van Der Greef J, “Timmerman ME. ANOVA-simultaneous component analysis (ASCA): a new tool for analyzing designed metabolomics data. Bioinformatics”, (2005), 21(13):3043-8.

Source identification in crude oil samples by a couple of colorimetric paper-based E-nose and chemometrics data analysis techniques

Mahsa Chaharlangai [1], *Javad Tashkhourian* [1], *Masoud Riazi* [2], *Mehdi Escrochi* [2], *Bahram Hemmateenejad* * [1]
[1]*Chemistry Department, Shiraz University, Shiraz, Iran*
[2] *IOR-EOR Research Institute, School of Chemical and Petroleum Engineering, Shiraz University*
E-mail address (corresponding author): hemmatb@shirazu.ac.ir

ABSTRACT

Crude oil source identification is crucial in discussing oil pollution or oil spills [1]. The chemical composition of crude oil is not identical, and depending on its source and origin, it has a wide range of compositions. Many studies have been conducted to identify the differences in crude oils and define unique markers to make distinguishments. In recent years, special efforts have been made to develop simple and inexpensive sensing methods to analyze the chemical composition of crude oil and use these results in crude oil source identification [2]. An E-Nose is one of these sensing devices that can sense and recognize odors and flavors using an electronic chemical sensor array system. This sensor array comprises a series of sensors, each exhibiting different characteristics when exposed to the volatiles emitted by the analyte [3]. The combination of this system with appropriate pattern recognition methods is fascinating in the analysis of crude oil [4]. In this research, the colorimetric paper-based E-nose is instructed by pH indicators. These prepared E-noses are used for the discrimination of crude oil samples based on their source and origin. Crude oil samples were collected from several oil wells belonging to the Mansouri oil field and with two geological formations, Ilam and Saruk. The National Iranian South Oil Company provided these samples. The colorimetric sensor arrays were made by spotting the pH and redox indicators on the silica-gel plates; the fabricated sensor was stacked to the petri dish cap and exposed to vapors of the VOC of crude oil samples. The petri dish should be transferred into an oven with a certain temperature for a specified period. For the colorimetric part of this sensor, the image of the sensors was recorded by a scanner before and after its exposure to the vapors of the analyte, and RGB values were analyzed with ImageJ software. Pattern recognition methods such as PCA and HCA were used to investigate the discrimination ability of the developed sensor array systems in the discrimination of crude oils. The crude oil samples were clustered in two classes in 3-dimentional PC space based on PCA results. The total variance of data for three first PCs was 98 %. Based on PCA results, discrimination of crude oils based on the type of geological formations was successful. HCA dendrogram represented excellent discrimination without misclassification among all types of crude oil samples.

Keywords: Source identification, crude oil, colorimetric E-nose, sensor array, chemometrics, pattern recognition.

References:

[1] J. R. Radović, "Chemometrics-assisted effect-directed analysis of crude and refined oil using comprehensive two-dimensional gas chromatography–time-of-flight mass spectrometry". Environmental science & technology, (2014), 48(5).

[2] S. F. Hashemi-Nasab, and H. Parastar, "Pattern recognition analysis of gas chromatographic and infrared spectroscopic fingerprints of crude oil for source identification". Microchemical Journal, (2020), 153.

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Slice-based Multivariate Calibration Strategy for Quantification of Polycyclic Aromatic Hydrocarbons in Oil Fractions by Means of GC×GC-TOFMS

Mahsa Piltan Eraghi, *Hadi Parastar* *

Department of Chemistry, Sharif University of Technology, Tehran, Iran
E-mail address (corresponding author): h.parastar@sharif.edu

ABSTRACT

Combining GC×GC with mass spectrometry (MS) enhances the power of the instrumentation beyond conventional chromatography methods. The GC×GC–TOFMS method offers several practical advantages, including higher peak capacity, greater separation power, high sensitivity, and improved selectivity [1]. Nevertheless, the complexity of multidimensional chromatography presents a significant challenge in handling and interpreting the vast amount of data generated [2]. In this study, the focus was on quantitation of a mixture of polycyclic aromatic hydrocarbons (PAHs) including dibenzoanthracene, fluorene, dibenzothiophene, naphthalene, 1-methylnaphthalene, 3,6-dimethylnaphthalene, pyrene, 1-methylphenanthrene, phenanthrene, and anthracene. To address these issues, a novel slice-based multivariate calibration strategy was introduced, utilizing the total ion chromatogram (TIC). The data related to distinct segments of the target analytes injected from the first column into the second chromatography column were organized, creating a new matrix. The concentration of each segment was then determined based on the ratio of the total concentration of that analyte in the first column. Subsequently, multivariate calibration techniques of partial least squares regression (PLSR), support vector machine (SVM) and radial basis function-artificial neural network (RBF-ANN) method, were employed to construct appropriate models, and analytical figures of merit (AFOMs) were obtained for each method. The PLSR model outperformed the other ones according to the two criteria: R^2 (0.991-0.999) and RMSE (0.02-0.07). Compared to the conventional approach of using the entire chromatogram in the form of pixels and applying data volume reduction methods, the advantage of this approach lies in its reliance on the concept of two-dimensional chromatography itself, eliminating the need for pre-processing methods to reduce data volume. This leads to a more efficient analysis of complex samples with less loss of important information [3]. For example, the values of sensitivity, analytical sensitivity and LOQ_{min} obtained for analytes in the PLSR method are in the range of 2.64×10^5-2.41×10^6, 7.18-102.88 and 0.43-2.42, respectively. Finally, to prove the potential of the proposed strategy in real samples, quantification of PAHs in the heavy oil sample was successfully performed.

Keywords: Two-dimensional gas chromatography, Machine learning, Chemometrics, PAHs.

References:

[1] S. Squara, A. Caratti, A. Fina, E. Liberto, N. Spigolon, G. Genova, G. Castello, I. Cincera, C. Bicchi, C. Cordero, “Artificial Intelligence decision-making tools based on comprehensive two-dimensional gas chromatography data: the challenge of quantitative volatilomics in food quality assessment”, J. Chromatogr. A. 1700 (2023) 464041.
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Development of Colorimetric Sensor Array Based on Metal Ion Complexes for Discrimination and Adulteration Detection of Lime Juice Samples

Nazanin Esmaeili, Bahram Hemmateenejad, Mohammad Mahdi Bordbar*

E-mail address (corresponding author): hemmatb@shirazu.ac.ir

ABSTRACT

The Quality assurance of beverages are important growing need of both industry and consumers. Lime, is one of the most important citrus species cultivated. Lime fruits are rich in nutrients such as vitamins, fiber, minerals, carotenoids, phenolic compounds, flavanones, hesperidin and eriocitrin [1]. Thus, lime juice quality control is importance because of synthetic product effects consumers' health. Until now, several analytical methods have been used to find a method to detect adulteration in lime, lemon and other Citrus juice. Gas chromatography–mass spectrometry (GC-MS), Liquid chromatography–mass spectrometry (LC-MS), high performance liquid chromatography (HPLC), solid-phase microextraction followed by GC-MS (SPME-GCMS), HPLC coupled with diode-array detection, electrospray ionization tandem mass spectrometry (HPLC-DAD-MS/MS), Near-infrared spectroscopy (NIR) and Fourier-transform infrared spectroscopy (FTIR) are common methods for detection of adulteration. However, they are expensive, time consuming, destructive, need professional operator, and don't have point-ofneed capabilities [2-3].

In this work a simple colorimetric sensor array made of 32 metal ion complexes including 4 chemical responsive dyes and 4 metal ions in 2 buffered and non-buffered environments, was prepared by dropping the solutions of metal ion complexes on a hydrophobic paper. The colorimetric sensor array responses to volatile organic compounds (VOCs) in the head-space of 11 hand-made lime juice samples, 12 commercial samples of different brands and 15 adulterated samples, were evaluated using sensor images recorded by an ordinary flatbed scanner. The developed sensor array produced color difference map patterns as a unique fingerprint, for different types of the lime juice samples. Multivariate RGB responses of the designed sensor were analyzed with statistical unsupervised pattern recognition methods including principal component analysis (PCA) and hierarchical clustering analysis (HCA) without any preprocessing. The sensor array was provided an acceptable discrimination between commercial, natural and adulterated lime juice samples. Besides, analysis of the sensor array data by discriminant analysis method resulted in correct identification of the commercial sample brands. In addition, the array could discriminate natural lime juices prepared in three consecutive years. This sensor array can be used up to 1 month after production with a small deviation of 5.25% with fresh sensor responses and provide reproducible responses.

Keywords: Colorimetric sensor array, metal ion complex, lime juice, discrimination, adulteration, pattern recognition.

References:

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Rapid authentication and classification of grape seed oil using fluorescence spectroscopy combined with sparse classification and regression methods

Niloofar Rahmani, *Ahmad Mani-Varnosfaderani**

Department of Chemistry, Tarbiat Modares University, Tehran, Iran
E-mail address (corresponding author): a.mani@modares.ac.ir

ABSTRACT

Authentication and classification of grape seed oil (GSO) varieties have attracted much attention in food industry, in recent years [1]. In the present work, excitation-emission fluorescence spectroscopy and sparse chemometric methods were used to classify different varieties of GSO taken from different grape genotypes. Moreover, GSO adulteration with sunflower oil (SFO) was successfully assessed using sparse regression methods. Fluorescence spectra were obtained in the wavelength regions of λ_{ex}= 200-500 nm and λ_{em}= 200-800 nm. More than 200 samples from five different GSO genotypes were used to build multivariate models. The sparse version of N-way partial least squares discriminant analysis (sNPLS-DA) [2] was used to develop interpretable classification models. The capabilities of the sNPLS-DA model provide a valuable insight about the important wavelengths in fluorescence spectra to distinguish between GSOs. Furthermore, adulterant levels in GSO samples were quantified using sparse regression techniques [3], including the least absolute shrinkage and selection operator (Lasso), Ridge, and Elastic net, and the results were compared with those obtained using the VIP-PLS method. The overall accuracy for sNPLS-DA was 1.00 and the coefficient of multiple determination (R^2) for Lasso model was 0.914, for the test sets. The results in this work revealed that sparse classification and regression models, including sNPLS-DA and Lasso, coupled with excitation-emission fluorescence spectroscopy can be effectively used to assess the quality of oil samples in the food industry.

Keywords: Grape seed oil, Excitation-emission fluorescence spectroscopy, Sparse methods, Adulteration detection.

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General structure-activity relationship patterns for the ligands of cyclin-dependent kinases as tools for virtual screening of PubChem database

Sara Kaveh[1], *Ahmad Mani-Varnosfaderani*[1]*, *Marzieh Sadat Neiband*[2]
[1] *Department of Chemistry, Tarbiat Modares University, Tehran, Iran*
[2] *Department of Chemistry, Payame Noor University (PNU), Tehran, Iran,*
E-mail address (corresponding author): a.mani@modares.ac.ir

ABSTRACT

Cyclin-dependent kinases (CDKs) are a multifunctional family of enzymes, which can modify different protein substrates involved in the cell cycle progression (1). The identification of selective CDK inhibitors is very important for developing anticancer drugs. The main aim of this study is to find general structure-selectivity relationship patterns for CDKs molecules and applying such rules for virtual screening purposes. We collected 12704 active and inactive ligands of CDK1, CDK2, CDK4, CDK5, and CDK9 from the Binding DB to achieve this goal. For every molecule, a broad range of molecular descriptors was computed, encompassing topological, constitutional, and both 2D and 3D descriptors by using DRAGON 5.5 software (5) and we used the variable importance in projection (VIP) approach for selecting discriminative molecular features (6). Certain key factors, including the hydrophobicity, the number of secondary amides (aliphatic), and C-043, have been identified as significant parameters in characterizing the inhibitory effects of CDK inhibitors. The C-043 is a common molecular descriptor between three active/inactive classification groups for CDK1, CDK4, and CDK9. This descriptor represents the number of X--CR..X fragments in a molecule and it is placed in the block of atom-centered descriptors. We used two machine learning methods for the classification of ligands using their activities including counter propagation artificial neural networks (CPANN) and supervised Kohonen networks (SKN). We downloaded two million random molecules from the PubChem database to evaluate multivariate classifiers for ligand-based virtual screening (7). The average values of the enrichment factor (EF10%) for the CPANN and SKN were 5.22% and 7.41%, respectively. In addition, the average values of the area under the receiver operating characteristic (ROC) curves were greater than 0.78 and 0.87 for the CPANN and SKN models, respectively. The study has found that it is possible to define and distinguish specific subspaces within chemical space that are relevant to CDK ligands. These subspaces have their own diagnostic boundaries encompassing all molecules and chemical compounds closely associated with CDK ligands. This knowledge can help guide the development of new CDK ligands with enhanced efficacy and selectivity.

Keywords: Binding DB, Cyclin-dependent kinase, Chemical space, Selective drug design, SAR, Virtual screening.

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Enhanced Data Point Importance for Efficient Data Splitting in Classification Models: Application to Olive Oil Authentication

Zahra Zare[1], *Somaye Vali Zade*[2], *Hamid Abdollahi*[1]*

[1]*Institute for Advanced Studies in Basic Sciences (IASBS), Zanjan, Iran*

[2]*Halal Research Center of IRI, Food and Drug Administration, Ministry of Health and Medical Education, Tehran, Iran*

E-mail address (corresponding author): abd@iasbs.ac.ir

ABSTRACT

In the realm of data science, classification models are vital for predicting or identifying classes within datasets. The success of creating a classification model hinges on accurately selecting samples for both the training and testing datasets. Proper data splitting during data preprocessing directly influences the effectiveness and efficiency of the final classification model. In PCA space, data points can be categorized into essential and non-essential points. Essential points (EP) represent convex hull vertices built from data points in a normalized space, forming a representative set of data. On the other hand, non-essential points are located inside the convex hull. Recently, an algorithm called Data Point Importance (DPI) has been introduced [1] to determine the order of importance of EPs, enabling the sorting of information and selection of samples within the dataset. DPI provides an easily calculable value that reflects the impact of each data point on preserving the data structure's pattern. This research extends the concept of DPI to non-essential points, establishing the sequence of importance for all data points and sorting information for each of them. The study evaluates the idea of Enhanced DPI (EDPI) and its application in selecting important points that affect the efficiency of class modeling. In the proposed algorithm, data points are examined in the form of layered convex hulls, and their order of importance is evaluated. EDPI is used to rank all data points (samples) in the row space of the training set of the target class based on their significance in preserving the data structure. The approach is applied in class modeling (DD-SIMCA) for authenticating extra virgin olive oil samples. The research also compares the results obtained from sample selection using the EDPI strategy with the Kennard-Stone method (KS). The study utilizes Raman spectra of pure samples and samples adulterated with various oils to develop one-class models for evaluating the authenticity and adulteration of extra virgin olive oil. Figure 1 illustrates the ranking results of data points (samples) based on the Enhanced DPI strategy, demonstrating that the proposed method for data splitting outperforms the KS method in many cases [1].

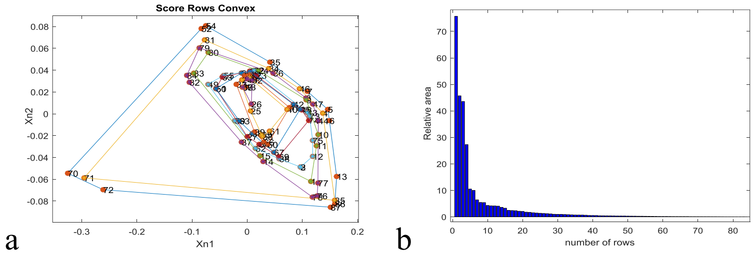

Figure1. Convex polygon of data points (Row space) (a). Bar plot DPI data points (Row space) (b).

Keywords: Essential points (EP), Data Point Importance (DPI), Enhanced DPI (EDPI).

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Comparison between Univariate and multivariate methods in Regression analysis of Sensor arrays

Zahra Shojaeifard, Bahram Hemmateenejad*,*
Chemistry Department, Shiraz University, Shiraz, Iran.
E-mail addresses (Corresponding author): shojaeifard.z@gmail.com; hemmatb@shirazu.ac.ir

ABSTRACT

Array-based sensor platforms are inspired by the mammalian olfactory system. Multiple sensor elements in these devices selectively interact with target analytes, producing a distinct pattern of response and enabling analyte identification. It provides a multidimensional data set that needs to be processed by multivariate analysis methods. In quantitative analyses, the relation of sensor array responses and different concentration of analyte can be obtained by univariate and multivariate regression methods. In the univariate approach, response vector of each concentration convert to a value by calculating the Euclidean norm. While in multivariate regression methods, the relationship is built between the sensor array responses and analyte concentration. Many times these two methods used interchangeably in analyzing the sensor arrays data [1]. However, it is a challenge that univariate and multivariate methods can quantifying the species in complex mixture the same or not. To compare two univariate and multivariate method in analysis the sensor arrays, the operation of a sensor array based strip in four different real matrix (cell culture, milk, , Orange juice and tap water) were considered to evaluate the dependency of color values (R, G and B) on the concentration (pH values) [2]. Since the studied real samples may be complex, the standard addition method was applied for pH determination. To do so, for each real sample solution, the response of the strip was measured by dipping it in the sample solution. The Euclidean norm and PLS calibration models were built for each real sample systems. To evaluate the ability of the methods, the correlation coefficient (R^2) between predicted and the actual pHs calculated for multivariate methods and between the Euclidian norm and pHs for univariate method was compared. Also, the models were used to predict the pH of unknown sample and compare by the obtained pH of unknown samples calculated by Euclidean norm method. However, the R^2 obtained from PLS model and Euclidean norm methods are so close to each other, (cell culture: 0.97, 0.99; milk: 0.94, 0.96; Orange juice: 0.97, 0.98; and tap water: 0.97, 0.97, related to PLS model and Euclidean norm, respectively.), but their ability in prediction the pH of unknown sample are significantly different (Recovery for cell culture: 0.98.9, 103.5; milk: 90.5, 80.93; Orange juice: 91.8, 31.8; and tap water: 104.4, 81.2, related to PLS model and Euclidean norm, respectively). It can be concluded that chemometrics method can be a better candidate for prediction the unknown concentration in sensor arrays data.

Keywords: Regression method, Sensor array, chemometrics.

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Alternating Conditional Expectation (ACE) Algorithm for robust regression analysis of simulated dataset in the presence of homoscedastic and heteroscedastic noise

*Mohammadreza Khanmohammadi Khorrami *, Mahsa Mohammadi, Zahra S. Hajiseyedrazi*
Department of Chemistry, Faculty of Science, Imam Khomeini International University, Qazvin, Iran
E-mail address (corresponding author): m.khanmohammadi@sci.ikiu.ac.ir

ABSTRACT

Regression analysis, aimed at efficiently predicting outcomes by examining the relationships between variables, is acknowledged as a crucial research area in the field of chemometrics. The relationship among variables and the nature of noise are two important components of information in regression modeling. When these parts are known, the regression is carried out easily. But what about the unknown data? This means data without any prior information about the relationships between variables and patterns of noise. The aim of this study is to answer this challenging question. Actually, classical regression procedures may encounter problems in this situation because these methods are based solely on constant and normally distributed residuals [1, 2]. Therefore, an alternative solution must be provided.

This solution utilizes robust methods. In this work, the performance of several regression methods including simple least squares (SLS) as a classical regression technique, weighted least squares (WLS) method, and Alternating Conditional Expectation (ACE) as a robust method were evaluated for univariate regression analysis of a simulated dataset with 100 data points. These data points were mathematically simulated according to a nonlinear equation: $y = 2.1 + 0.4\,x^2$. The study was conducted in four steps. In the first step, the data produced without noise were analyzed using regression approaches. Then, homoscedastic (constant) noise with values of 0.1 and 10 were added to raw data, and these noisy datasets were utilized as inputs for regression models in second and third steps, respectively. In the last step, heteroscedastic (non-constant) noise was added to raw data for further analysis.

The statistical parameters such as R^2 of 1.000, R^2_{adj} of 1.000, sum of squares of residuals (SSE) of 3.65E-05, the variance inflation factor (VIF) of 2714149.979, and the Bayes Information Criterion (BIC) of -1473.126508 were the results of ACE for heteroscedastic data. The results demonstrate that ACE has the most efficient performance compared to other methods. This superiority stems from transformation-based nature of this approach. ACE suggests the best transformation function with the highest correlation between response and descriptor variables. Variable transformation makes the error variance stable and normalizes its distribution. Therefore, highly satisfying outputs are obtained without needing to consider the relationship among the variables and the noise pattern [3, 4].

Keywords: ACE, transformation, robust regression analysis, SLS, WLS, homoscedastic noise, heteroscedastic noise.

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Alternating Conditional Expectation (ACE) Algorithm for robust regression analysis of simulated dataset in the presence of Outliers

*Mohammadreza Khanmohammadi Khorrami *, Mahsa Mohammadi, Zahra S. Hajiseyedrazi*

Department of Chemistry, Faculty of Science, Imam Khomeini International University, Qazvin, Iran
E-mail address (corresponding author): m.khanmohammadi@sci.ikiu.ac.ir

ABSTRACT

The purpose of the univariate regression model is to discover the relationship between response and descriptor variables, which means accurately calculating the regression coefficients. The presence of random noise and outlier data is recognized as important sources of uncertainty in regression models. Outliers are data points with high residual values compared to other points, leading to abnormalities in the regression process. This issue becomes more challenging when the dataset becomes smaller. Two strategies have been taken into account to deal with data contaminated with outliers. Firstly, using outlier detection procedures (such as Dixon's test, Grubb's test, Cook's squared distance, squared Mahalanobis distance, etc.), and secondly, utilizing robust methods (median-based techniques, Jacobian matrix method, Additivity and Variance Stabilization (AVAS), and Alternating Conditional Expectation (ACE)) [1-3].

This study investigated the effect of outlier data on the performance of various regression models, such as simple least squares (SLS), median-based methods like Single Median (SM), Repeated Median (RM), and Least Median of Squares (LMS) methods, as well as the Jacobian matrix technique, AVAS, and ACE. Six pairs of data points were defined as raw data, and the presence of an outlier in the response variable was investigated.

For the dataset with outliers, SLS, as a representative of classical regression methods, had weak results. Also, the efficiency of median-based approaches was not good. The results of the Jacobian method were not desirable, which may stem from not defining the initial equation for this model. The performance of AVAS was broadly satisfying, but ACE was the best procedure. The final statistical results of ACE were an R^2 of 1.000, R^2adj of 1.000, sum of squares (SSE) of 7.32E-30, and the variance inflation factor (VIF) with an infinity value. Selecting the best transformation function with the highest correlation coefficient between the response and descriptor variables and stabilizing the error variance distribution are important advantages of ACE that lead to the best results [4].

Keywords: SLS, SM, RM, LMS, Jacobian, AVAS, ACE.

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Integrating Second-Order Calibration with Analytical Quality by Design (AQbD) for Universal Calibration in Pharmaceutical Analysis

Somaye Vali Zade[a*], *Marzieh Ranjbar*[a], *Sajedeh Alavi*[b], *Hamid Abdollahi*[b*]

[a] *Halal Research Center of IRI, Food and Drug Administration, Ministry of Health and Medical Education, Tehran, Iran*

[b] *Faculty of Chemistry, Institute for Advanced Studies in Basic Sciences, 45195-1159, Zanjan, Iran*

ABSTRACT

The quantitative determination of active pharmaceutical ingredients in complex matrices, such as pharmaceutical tablets from different manufacturers, poses challenges due to potential interference from various molecules, some of which may be unknown [1]. To address this issue, we have developed a novel and powerful approach by integrating second-order calibration with the Analytical Quality by Design (AQbD) framework for pharmaceutical analysis.

Our focus was on drug analysis using second-order data with the AQbD approach, where we leveraged second-order calibration methods such as Rank Annihilation Factor Analysis (RAFA) and Multivariate Curve Resolution-Alternating Least Squares (MCR-ALS) using pH-wavelength data. The goal was to create a universal calibration model for the quantitation of acetylsalicylic acid (ASA, Aspirin) in different commercial formulations. By applying the AQbD approach and second-order calibration strategies, we successfully developed a calibration model with second-order advantages. Second-order data, obtained from spectrophotometric monitoring of complex mixtures of several drug formulations at different pH levels, provided unique insights and enhanced the selectivity, sensitivity, and robustness of the analytical method in the presence of complex interfering matrices.

This research highlights the effectiveness and novelty of integrating second-order calibration within the AQbD framework for pharmaceutical analysis. Our results demonstrate that second-order calibration methods are powerful tools for developing universal calibration models, paving the way for more efficient and reliable [2] drug analysis in the pharmaceutical industry.

Keywords: Analytical Quality by Design (AQbD), Second-Order Calibration, Aspirin, Pharmaceutical Analysis.

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Second-Order Calibration for Quantification of Food Colorants in Complex Samples: An Universal Calibration Approach

Somaye Vali Zade[a], *Mehran Mohseni*[b], *Hamid Abdollahi*[c]

[a] *Halal Research Center of IRI, Food and Drug Administration, Ministry of Health and Medical Education, Tehran, Iran*
[b] *Department of Food and Drug Control, School of Pharmacy, Zanjan University of Medical Sciences, Zanjan, Iran*
[c] *Faculty of Chemistry, Institute for Advanced Studies in Basic Sciences, 45195-1159, Zanjan, Iran*

ABSTRACT

The utilization of colorants in food products is imperative to achieve visually appealing and natural shades that appeal to consumers. However, due to cost and stability considerations, natural colorants are frequently substituted with synthetic alternatives, which may present potential health risks. A variety of analytical methods have been proposed for the detection of food colorants [1, 2], with separation techniques being the most commonly employed. Nevertheless, the establishment of a universal calibration for accurate quantification across diverse real and complex samples remains a challenging endeavor. In order to address this issue, contemporary analytical instruments, when combined with multi-way multivariate calibration methodologies, offer effective solutions for quantification problems, particularly in the presence of unknown interferents. Second-order calibration methods demonstrate promise in developing universal calibration models for determining colorants in food products.

This study introduces a higher-order multivariate chemometric approach to construct a universal calibration for quantifying Sunset Yellow (SY) as a model compound in various food products, even in the presence of non-calibrated interferences. By utilizing second-order pH-spectrophotometric data obtained through hyper-spectral imaging, the MCR-ALS second-order calibration strategy achieves efficient quantitation of SY in different food products, providing a practical and effective approach for food analysis and quality control. The data pertaining to the standard samples and the real sample containing SY at 16 different pH were simultaneously measured using a hyperspectral imaging (HSI). This design enhances the analysis speed by leveraging the capabilities of the HSI device and creates a second order data to achieve the advantage of analyzing samples with non- calibrated components. The proposed method successfully analyzed real samples of colored drinks, jelly, and candy. The proposed method is applicable for the quantitation of all colorants that exhibit sensitivity to pH and function as weak acids or bases.

Keywords: Food Colorants, Second-Order Methods, Universal Calibration, Hyperspectral Imaging

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Enhancing Pesticide Residue Quantification in Honey through Integrated Chemo-physical and Chemometric Separation using LC-MS Spectrometry: Comparison with Multiple Reaction Monitoring

Somaye Vali Zade[a], *Vahideh Mahdavi*[b], *Hasti Gordan*[b], *Hamid Abdollahi*[c]
[a] *Halal Research Center of IRI, Food and Drug Administration, Ministry of Health and Medical Education, Tehran, Iran*
[b] *Iranian Research Institute of Plant Protection, Agricultural Research, Education and Extension*
[c] *Faculty of Chemistry, Institute for Advanced Studies in Basic Sciences, 45195-1159, Zanjan, Iran*

ABSTRACT

Honey, a naturally occurring product generated by bees, holds considerable nutritional and ethnomedical significance. Its constitution, primarily comprising carbohydrates and water, demonstrates variability rooted in the sources of nectar. The widespread consumption of honey on a global scale has precipitated the imperative for rigorous quality control and vigilance against contamination within commercial transactions. The utilization of pesticides in agricultural practices, pivotal for augmenting yields, can engender the presence of pesticide residues in foodstuffs, thereby necessitating the establishment of Maximum Residue Limits (MRLs). The main objective of the present study is to monitor residues of some major pesticides in honey samples collected from important areas of honey production in the country. Divergences in MRLs across different nations have engendered contentious discussions in international trade circles. The comprehensive analysis of pesticide residues within honey demands the application of sophisticated methodologies owing to its intricate matrix [1]. Modern analytical techniques such as GC-MS/MS and UHPLC-MS/MS, coupled with proficient extraction and purification protocols, offer stringent detection thresholds for the analysis of multiple pesticide residues, congruent with established MRLs. Among these methods, LC-MS/MS in Multiple Reaction Monitoring (MRM) mode emerges as a benchmark approach for the analysis of intricate samples [2]. This mode enables the selective isolation of target analytes while excluding background noise, delivering enhanced sensitivity and reproducibility. Alternatively, LC-MS operated in full scan mode, reliant solely on a single-quadrupole mass spectrometer, has the potential to circumvent challenges like peak overlapping. Nevertheless, full scan LC-MS is marked by a lack of selectivity, thereby complicating the resolution and precise quantification of targeted compounds, particularly when compared to MRM. The phenomenon of overlapping peaks and the presence of interfering substances are commonplace in the quantitative analysis of complex samples like biological fluids. To surmount these intricacies, a shrewd approach capitalizing on three-way LC-MS data and second-order calibration was devised. This strategy achieves quantitative precision comparable to MRM, leveraging the concept of "mathematical separation" in lieu of the conventional optimization of physical separations. This innovative strategy bestows amplified selectivity and sensitivity upon the analytical process. Its practicality is underscored by its efficiency, cost-effectiveness, and eco-friendliness, thus emerging as a viable alternative for the precise determination of target analytes within intricate systems. In a specific project context, the analysis of 38 pesticides within honey samples was accomplished through the utilization of LC-MS data and advanced chemometric techniques. The inadequacies of the chromatographic approach in addressing peak separation intricacies were compensated through the employment of chemometrical separation. The integration of fchemometrical and physico-chemical separation techniques led to a discernible augmentation in the selectivity of the analytical methodology.

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Mutual Information Map for Unraveling the Independence of Solutions in the Area of Feasible Solutions for Three-Component Systems

Fatemeh Sadat Hashemi-Nasab[1], *Hamid Abdollahi*[2], *Hadi Parastar**[1]

[1]*Department of Chemistry, Sharif University of technology, P.O. Box 11155-9516, Tehran, Iran*
[2] *Faculty of Chemistry, Institute for Advanced Studies in Basic Sciences, Zanjan, Iran*
E-mail addresses (Corresponding author): h.parastar@sharif.edu, h.parastar@gmail.com

ABSTRACT

Investigating rotational ambiguity in decomposition-based methods is crucial in chemometrics, as it poses significant challenges [1]. The presence of rotational ambiguity gives rise to an area known as the Area of Feasible Solution (AFS) [1]. Hence, this study focuses on exploring the relationship between AFS and the concept of independence, which is the main constraint in Independent Component Analysis (ICA)-based techniques [2]. The investigation involves calculating the independence using mutual information (MI) [3, 4] for feasible solutions. Additionally, a novel concept called the MI map is introduced to enhance our understanding of AFS in this context. To achieve this, we simulated various chromatographic datasets, ranging from simple to complex, for three-component systems, taking noise into account (X_1 to X_5). An experimental chromatographic dataset was also used for validation (X_6). The range of allowable responses was computed using the Facpack algorithm, and multiple responses were obtained for each dataset, with MI calculated for each response. Examination of the findings revealed that the different solutions within the feasible bands are associated with distinct different MI values. As anticipated by the duality concept, spectral profiles exhibit lower MI values, indicating higher independence, while concentration profiles demonstrate higher MI values, suggesting greater dependence. We examined four well-known ICA algorithms (mean-field ICA (MF-ICA), mutual information-based least dependent component analysis (MILCA) and joint approximate diagonalization of eigenmatrices (JADE)) as well as multivariate curve resolution-alternating least squares (MCR-ALS) to understand their solutions and MI values for the simulated and experimental datasets. The MI maps demonstrated that the solutions from MF-ICA and MCR-ALS fell within the AFS, aligning with the expectation that ICA algorithms aim to minimize MI values for signals. In contrast, the solutions from MILCA and JADE were outside the AFS, as they solely focused on maximizing independence. Furthermore, we assessed the alignment of MI values by obtaining MI values with 10 repetitions for the noisy data, confirming the consistency of MI ratios across these repetitions. Additionally, the concept of independence was re-evaluated for triangles with equal areas in AFS using MI calculations. This investigation contributes to a better understanding of permissible responses in three-component systems and sheds light on the implications of using different ICA algorithms in chemometrics. The results support the validity and applicability of our approach and provide insights for further analysis and research.

Keywords: Rotational ambiguity, Independent Component Analysis, Mutual information, Independence.

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Enhanced Data Point Importance for Subset Selection in Partial Least Square Regression: A Comparative Study with Kennard-Stone Method

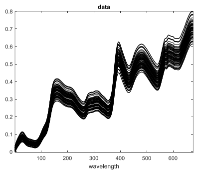
Mahya Vazifeh Solout[a], *Somaye Vali Zade*[b], *Hamid Abdollahi*[c], *Jahan Bakhsh Ghasemi*[a*]

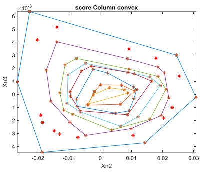
[a] *Chemistry Faculty School of Sciences University of Tehran, Tehran POB 14155-6455, Iran*
[b] *Halal Research Center of IRI, Food and Drug Administration, Ministry of Health and Medical Education, Tehran, Iran*
[c] *Faculty of Chemistry, Institute for Advanced Studies in Basic Sciences, 45195-1159, Zanjan, Iran*

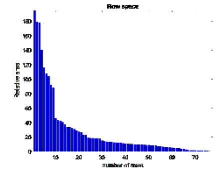
ABSTRACT

Upon the application of multivariate analysis to a dataset, whether involving singular block data (PCA, MCR, SIMCA) or multi-block data (PCR, PLS), the process of choosing a subset of samples from the complete dataset becomes essential. This procedure is referred to as subset selection. A subset refers to a smaller, representative portion of the entire dataset that is used for the purpose of building, refining, or validating the model. The characteristics of the subset chosen within the calibration model depend on the specific goals and requirements of the calibration process. The subset should accurately represent the overall characteristics of the entire dataset. It should capture the various patterns, trends, and variations present in the data. So, the choice of subset within a calibration model is a critical step.

We proposed a new method for subset selection based on data point importance (DPI) in partial least square regression. In PLS space, data points can be categorized into essential and non-essential points. Essential points (EP) represent convex hull vertices built from data points in a normalized space, forming a representative set of data. On the other hand, non-essential points are located inside the convex hull. Recently, an algorithm called Data Point Importance (DPI) has been introduced [1] to determine the order of importance of EPs, enabling the sorting of information and selection of samples within the dataset. DPI provides an easily calculable value that reflects the impact of each data point on preserving the data structure's pattern. This research extends the concept of DPI to non-essential points, establishing the sequence of importance for all data points and sorting information for each of them. The study evaluates the idea of Enhanced DPI (EDPI) and its application in selecting important points to subset selection in PLS regression. The algorithm we present involves analyzing data points through layered convex hulls, assessing their relative importance. The ranking of all data points (samples) in the training is accomplished using EDPI, which determines their relevance in maintaining the integrity of the data structure within the row space. The study also conducts a comparison between the outcomes achieved through sample selection using the EDPI strategy and those obtained via the Kennard-Stone method (KS). Figure 1 depicts the ranking outcomes of data points (samples) utilizing the Enhanced DPI strategy, showcasing the comparable performance of the proposed data splitting method compared to the KS approach for corn data.







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Application of the alternating conditional expectation (ACE) algorithm for the determination of oxygenate compounds in gasoline samples using ATR-FTIR spectroscopy

Mina Sadrara[a*], *Mohammadreza Khanmohammadi Khorrami*[a*]

[a] *Chemistry Department, Faculty of Science, Imam Khomeini International University, 3414896818 Qazvin, Iran*
E-mail addresses (Corresponding author): minasadrara@gmail.com (M. Sadrara)
E-mail addresses (Corresponding author): m.khanmohammadi@sci.ikiu.ac.ir (M. R. Khanmohammadi)

ABSTRACT

This work aims to examine the nonparametric robust principal component analysis-alternating conditional expectation (rPCA-ACE) algorithm combined with FTIR spectroscopy as a rapid and accurate analytical method for predicting the quality of gasoline samples based on oxygenates content (methanol, methyl tert-butyl ether, and isobutanol). The ACE algorithm estimates a set of optimal transformations for independent and dependent variables in multiple regressions which results in a linear correlation between the transformed predictors and the transformed response, minimizing the error [1, 2]. In this study, the ACE algorithm was applied to an empirical gasoline dataset and considered a series of possible transformations of the independent and dependent variables to find the best transformations. Among all possible transformations, the ACE algorithm identified a series of polynomials and a nearly linear transformation as the best transformations for the independent and dependent variables, respectively. The regression statistics for calibration and prediction, including the correlation coefficient (R^2_{cal}=0.9692), root mean square error of calibration (RMSEC=2.8638), and root mean square error of prediction (RMSEP=4.0498) (%v/v) for oxygenates content, were calculated. The ACE model showed improved regression results compared to the linear PLS model (R^2_{cal}=0.9550, RMSEC=3.9052, RMSEP=5.1342) and PCR model (R^2_{cal}=0.9160, RMSEC=6.5330, RMSEP=7.0270). By applying the ACE technique to the synthetic fully non-linear dataset obtained from the equation $y' = \exp(y)$ for the response variable, we demonstrated the power of the ACE algorithm in multivariate analysis and its ability to identify the exact functional relationship between independent and dependent variables to solve fully non-linear problems.

Keywords: Alternating conditional expectation (ACE) algorithm, Non-linear regression, Oxygenates, Gasoline, FTIR Spectroscopy

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A comparative analysis of univariate regression models using the simulated exponential dataset

*Mohammadreza Khanmohammadi Khorrami *, Mahsa Mohammadi*
[a]*Department of Chemistry, Faculty of Science, Imam Khomeini International University, Qazvin, Iran*
E-mail address (corresponding author): m.khanmohammadi@sci.ikiu.ac.ir

ABSTRACT

In this study, we investigated the effectiveness of univariate regression models in evaluating a simulated exponential dataset. Several univariate regression models were used, including Simple Least Squares (SLS), Least Median Squares (LMS), Single Median (SM), Repeated Median (RM), Jacobian Model (JM), Alternating Conditional Expectation (ACE), and Additivity and Variance Stabilization (AVAS). The performance of these regression models was verified through statistical parameters. The study involved simulating exponential data using Eq (1). The variable X contained data ranging from 1 to 100 with an interval of one.

$$X = 1:100, \quad X1 = \sqrt{X}, \quad y = e^{X1} \quad (1)$$

The processing and regression of the exponential simulated dataset were carried out using MATLAB software (V-2009, MathWorks, USA) with programs written by the corresponding author (M. Khanmohammadi Khorrami). An M-file/MATLAB algorithm was implemented, providing comprehensive details of the univariate regression models. The results obtained in this study can also be useful for comparative analysis with different algorithms. The investigation focused on utilizing non-linear data in univariate regression analysis, and it was found that the ACE and AVAS models provided valuable recommendations for future applications. The values obtained for the ACE model, including sum of squares total (SST), sum of squared regression (SSR), sum of squares error (SSE), R^2, and adjusted R^2, were 99, 99, $3.65*10^{-5}$, 1.00, and 1.00, respectively. For the AVAS model, the values were 100, 100, $8.81*10^{-3}$, 0.99, and 0.99, respectively. These results indicate that the ACE and AVAS models successfully explained a significant portion of the total variation in the data (SST) and the variation accounted for by the model (SSR). Additionally, the low SSE value suggests minimal errors in the model's predictions. An R^2 value of 1.000 implies that the model captures all the variability present in the data, indicating a strong fit. The ACE and AVAS models offer several advantages over traditional linear regression models. They are flexible and powerful tools for modeling complex relationships between variables, including the ability to capture nonlinear relationships. This study demonstrates the high potential of the ACE model for regression of exponential simulated datasets, which holds importance in data analysis.

Keywords: Univariate, Regression, SLS, SM, RM, LMS, JM, AVAS, ACE.

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Authentication and classification of black tea from narrow-geographic origins based on the combination of UV-Vis fingerprinting and chemometric methods

*Nahid Mohammadi, Mahnaz Esteki**

University of Zanjan
E-mail address (corresponding author): m.esteki@znu.ac.ir

ABSTRACT

Tea is the second most consumed beverage in the world, and its characteristic flavor is due to the chemical components such as catechins, vitamins, amino acids, caffeine, and volatile aroma components derived from tea leaves. The chemical composition of tea leaves determines their quality characteristics. The geographical features and environmental factors such as slope aspect, altitude, soil characteristics, temperature, rainfall, and sun exposure mainly influence this parameter [1]. The combination of UV-Vis spectrophotometry by multivariate data analysis methods for authentication of food products has been recently proposed as an efficient technique in food science and technology [2]. This study investigates the feasibility of UV-Vis spectroscopy coupled with chemometric methods to authenticate tea samples based on their geographical origins in a narrow longitudinal strip (200 km). Black tea samples were obtained from five geographical areas in the Northern provinces of Iran, including Ramsar, Lahijan, Shaft, Leilakooh, and Oshiyan. Samples of 0.1 g of tea were used to perform the extraction process. 40.0 mL of 20% methanol aqueous solution was added to a 0.1 g tea sample and then heated at 80 °C for 20 min in a sealed beaker. The sample was heated on a hot-plate magnetic stirrer equipped with a thermometer. The spectrum of each sample was immediately recorded using a UV–Vis spectrophotometer. Several preprocessing methods, such as standard normal variate (SNV), auto-scaling, multiplicative scatter correction (MSC), mean centering (MC), first derivative, and their combinations, were applied to eliminate the noninformative information. The partial least squares-linear discriminant analysis (PLS-LDA) model using first derivative spectra represented the following results, including 98.0% of sensitivity, 99.6% specificity, and a mean accuracy of 98.0%. The satisfactory results of the models depicted that the chemical components of tea, such as polyphenols, chlorogenic and fatty acids that absorb UV radiation, are the chemical markers that can discriminate tea samples based on their geographical origin. Therefore, UV-Vis spectral fingerprinting combined with chemometrics could be a practical, feasible, and simple method for classifying tea based on their geographical origins in a narrow longitudinal strip.

Keywords: Classification, authentication, tea, geographical origin, UV-Vis spectral fingerprint, linear discriminant analysis

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DD-SIMCA one-class modeling of blue ballpoint pen inks using hyperspectral imaging: forensic analysis of questioned documents

*A Safarnejad[1], M. Reza Hormozi-Nezhad[2],[3] H. Abdollahi [1]**

1. Department of Chemistry, Institute for Advanced Studies in Basic Sciences (IASBS), Zanjan 45137-66731, Iran
2. Department of Chemistry, Sharif University of Technology, Tehran 11155-9516, Iran
3. Institute for Nanoscience and Nanotechnology, Sharif University of Technology, Tehran, Iran
E-mail address (corresponding author): abd@iasbs.ac.ir

ABSTRACT

Alteration and addition of parts of numbers or text on documents is a common type of fraud that forensic document examiners often encounter in their casework. This type of fraud is typically committed to deceive or mislead others, and it can occur on a wide range of documents, from financial records and contracts to wills and deeds. Hyperspectral imaging (HSI) is a powerful tool for forensic analysis of document forgery [1-3]. The aim of this study is to investigate the issue of text addition and the order of crossed ink lines, which are commonly encountered in questioned documents. Twelve blue ink pens from different brands and models were employed to prepare the samples on A4 paper in two different ways: (i) a vertical line of 5 mm in length was drawn using each pen. (ii) A horizontal line was drawn with pen 1 and vertical lines were drawn with all 12 pens onto this line (pen1 under 12 pens). Out of the 144 possible pairwise comparisons between the 12 pens, 7 pair were selected for further analysis based on the criterion of the angle between the mean vectors of the pairs. Reflectance spectra were acquired using a linear scanning hyperspectral camera (HSI-Vis-12bit), manufactured by Parto Afzar Sanat corporation, between 400 - 950 nm with 2 nm step resolution. HSI data was performed on the samples at 5 different times, 1, 2, 30, 40, and 80 days after the lines were written. The image resolution obtained was 272x135 pixels and 536 wavelengths, which represents three-dimensional data. Three regions of each of the vertical lines were manually selected as regions of interest, resulting in a total of 168 pixels for one pen. The preprocessing methods used were conversion to pseudo-absorbance (log (-1/R)), smoothing using the Savitsky-Golay filter with a second-order polynomial and 20 points window, and Standard Normal Variate (SNV) method. The problem at hand is formulated as an authentication problem, and a one-class classifier technique known as data-driven soft independent modeling of class analogy (DD-SIMCA) is employed to classify pairs of blue ballpoint pen ink samples. Classification results from DD-SIMCA yielded 97-100% sensitivity for the training set and 39–100% specificity for different test samples. The results indicate that HSI-Vis combined with DD-SIMCA is suitable for authentication of blue ballpoint pen ink on paper for questioned document examination except when the inks are very similar to each other.

Keywords: Class modeling, Forensic, Hyperspectral imaging, DD-SIMCA, Questioned document.

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Machine learning for characterization of the phytochemical profile of black tea during different infusion time

*A. Zahiri, M. Esteki**

University of Zanjan
E-mail address (corresponding author): m.esteki@znu.ir

ABSTRACT

Tea is the second most consumed drink after water, and black tea is the most abundant type of tea produced worldwide. Green and black tea are the most traditional styles of tea products representing 20–22% and 76–78% of the worldwide production, respectively [1]. Green tea comes from the unfermented, dried leaves, while black tea is a fully fermented product. The interest in tea and the analysis of its chemical compounds has increased significantly due to its nutritional, economic value, and the positive effects of tea on human health [2]. However, few studies have addressed the availability of these compounds associated with the infusion time of the black tea drink. For this purpose, machine learning methods were used in this study to investigate the effect of brewing time on its chemical composition. In this way, the following procedure was used: In a round-bottom glass flask, 1.0 g of black tea and 20.0 mL of methanol were added, and the mixture was refluxed at 60°C for 3 h. Sampling was done four times between 0 and 3 hours (once every hour). The GC-FID technique was employed for analysis of the extracts of 100 samples (25 samples for each time), and the peak areas were used to construct the machine learning models. Various pre-processing methods, such as mean centering (MC), auto-scaling, multiplicative scatter correction (MSC), and standard normal variate (SNV), were used to remove irrelevant variations. Machine learning methods, including principal component analysis-linear discriminant analysis (PCA-LDA), partial least square-discriminant analysis (PLS-DA), and support vector machine (SVM), were employed to characterize the phytochemical composition of the tea samples. The constructed models showed a distinct class separation between the tea samples that were analyzed immediately after adding methanol (0 hour) and the samples corresponding to 3 hours sampling. The samples corresponding to brewing time of 1 and 2 hours appear in one cluster. The obtained results showed that the brewing time may therefore be an important factor affecting the phytochemical composition of black tea.

Keywords: Black Tea, GC, Machine learning.

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Chemotaxonomic survey of fatty acids in littoral algae from the Persian Gulf: Application of machine learning for characterization of algae

E. Dashtaki[1], *M. Esteki*[1]*, *A .Mahdinia*[2]
[1]University of Zanjan,[2] *Oceanography and Atmospheric Science*
E-mail address (corresponding author): m.esteki@znu.ac.ir

ABSTRACT

The ocean covers 70 percent of Earth's surface, and is the natural habitat of many plants, animals, and microorganisms. Algae are some of the most common organisms inhabiting the earth [1]. The algae group is divided into multicellular organisms, “macroalgae” or seaweed, and unicellular organisms, known as “microalgae” (measuring from 1 µm to several cm). Algae are an important source of vitamins, some essential minerals and trace elements, proteins, polyunsaturated fatty acids including omega-3 fatty acids, polysaccharides, polyphenols, sterols, pigments, amino acids, antioxidants, and fiber. Algae have been used in many industries, including chemical, cosmetic, pharmaceutical, environmental cleaning, feed and fertilizer, conventional food, and fermented food. Studies of algae biological activity demonstrated that they possess antioxidant, antibacterial, antiviral, and antifungal properties. Among the various research fields in which macro- and microalgae are appearing, food technology is one of the most important areas. Fatty acids (FA) are widely occurring in natural fats and dietary oils, and they are also critical nutritious substances and metabolites in living organisms. Degenerative diseases related to inappropriate FAs consumption cause two-thirds cases of the population death who are living in affluent, industrialized nations. FAs and lipids are constituents of all algae cells. Lipids represent 1–5% of algal dry matter and exhibit an interesting PUFA composition. Algal FAs are beneficial and act as prophylactic supplements for type-2 diabetes, atherosclerosis, coronary heart diseases, arrhythmias, and cancer [2]. The aim of the present study is to conduct a chemotaxonomic survey of fatty acids in littoral algae from the Persian Gulf. In this way, the fatty acids of littoral algae from the Persian Gulf (green, red, and brown algae) were derivatized into corresponding fatty acid methyl esters (FAMEs) and were analyzed by gas chromatography with flame ionization detector (GC-FID) instrument. Machine learning methods, including linear discriminant analysis (LDA), partial least squares discriminant analysis (PLS-DA), and support vector machine (SVM), were used to construct the models which extract significant variables, visualize discriminations, and classify the studied algae samples based on their fatty acid fingerprints. The results demonstrated that machine learning methods, including LDA, PLS-DA, and SVM, can characterize and classify the macroalgae samples based on their fatty acid composition (the obtained accuracies for the calibration and the test sets were between 98.0% and 100%).

Keywords: Chemotaxonomic, algae, fatty acid, Persian Gulf, gas chromatography.

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An integrated paper-based optical tongue/nose device combined with chemometrics methods for identification of fermentation degree and aerial parts of Iranian tea

*Raziyeh Shahali, Zahra Shojaeifard, Bahram Hemmateenejad**

E-mail address (corresponding author): hemmatb@shirazu.ac.ir

ABSTRACT

In this research, we proposed an integrated paper-based optical tongue-nose colorimetric sensor array for quality evaluation of tea samples using their chemical constituents in both liquid extracts and volatile organic compounds in their aroma. The integrated device combined the electronic tongue (using 5 reagents) and nose (using 8 indicators) on two sides of a paper that embedded in a chamber. For the electronic tongue phase a flower-like design with eight petals (1mm diameters) and for electronic nose phase, circular areas were designed in 1 mm diameter (deposit sensing elements) around a larger circle in 5 mm diameter (deposit real sample). By placing the electronic tongue and nose on top of each other, the volatile and non-volatile compounds were investigated, simultaneously. Similar to previous studies, the images of the both sensing parts were recorded using a flat-bed scanner and then the imaging data for every reagent spots were extracted in RGB format by ImageJ software [1]. For each sample, the response data of the optical tongue and nose parts of the device were collected in row vectors of length of 15 and 24, respectively. The ability of the developed sensor to distinguish between different types of tea samples according to the degree of fermentation and the type of harvest was evaluated utilizing different chemometrics methods such as principal component analysis (PCA) and linear discrimination analysis (LDA). The accuracy of this proposed device to discriminate tea according to the degree of fermentation and type of harvest was reported as 100% and 92%, respectively. In total, the designed device is portable, rapid and requires low volumes of samples that can be considered a good candidate for simultaneous analysis of volatile and non-volatile compounds of tea samples.

Keywords: Colorimetric, Electronic tongue, Electronic nose, Classification, Sensor array.

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Pattern recognition with supervised artificial neural networks coupled with discrete wavelet transforms for opioid discrimination using the colorimetric sensor array

Zartosht Asadzadeh, Morteza Bahram, Mehdi Moghtader*

Department of Analytical Chemistry, Faculty of Chemistry, Urmia University, Urmia, Iran
E-mail address (corresponding author): m.bahram@urmia.ac.ir

ABSTRACT

Colorimetric sensor arrays offer a fast and accurate method for detecting and identifying various chemicals by analyzing changes in color or fluorescence using spectroscopic devices [1]. Colloidal plasmonic nanoparticles, primarily composed of gold and silver, exhibit vibrant colors in the visible spectrum due to local plasmon resonance (LSPR) [2]. Utilizing nanoparticles, colorimetric sensor techniques rely on alterations in optical properties caused by their aggregations and morphological changes [3]. The aim of this study was to use supervised artificial neural networks and discrete wavelet transforms to discriminate between different opioids using a colorimetric sensor array. Silver nanoparticles of varying sizes were employed to differentiate between methadone, morphine, and tramadol based on their reaction kinetics with the nanoparticles. The data obtained from the experiment was preprocessed using discrete wavelet transforms to reduce its complexity. Neural network-based supervised pattern recognition methods, including CPANN, SKN, and XY-Fused networks, were then utilized for discrimination after optimizing the network parameters using genetic algorithms. The best discrimination performance was achieved using the SKN network and the daubechies (db9) mother wavelet. This resulted in an accuracy of 98% when distinguishing between the drugs in real serum samples that were spiked with the analytes.

Keywords: Pattern Recognition, Colorimetric Sensor Array, Discrete Wavelet Transform, Artificial Neural Networks.

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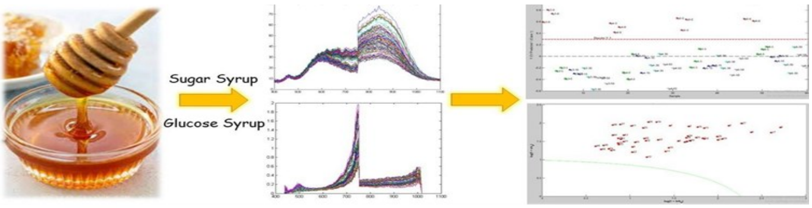
Unveiling the Power of Handheld Vis-NIR Spectroscopy and Chemometrics for Honey Authentication

Zeinab Fallah[1], Hassan Yazdanpanah[2], Ali Aghaei[3], Hadi Parastar[*,1]
[1] *Department of Chemistry, Sharif University of Technology, Tehran, Iran*
[2] *Food Safety Research Center, Shahid Beheshti University of Medical Sciences, Tehran, Iran*
[3] *Noor Research Educational institute (Tavan), Tehran, Iran*
E-mail address (corresponding author): h.parastar@sharif.edu , h.parastar@gmail.com



ABSTRACT

Honey, cherished for its distinctive sensory attributes, nutritional value, and health benefits, is a widely consumed plant-based natural food [1]. However, in recent times, honey has fallen victim to adulteration with cheaper sweeteners. Shockingly, there have been reports of at least 21 different inexpensive sweeteners used for direct adulteration of honey. This adulteration has become so rampant that honey now ranks as the third most adulterated product, globally and within the European Union, trailing only behind milk and olive oil [2]. The objective of this study is to devise an affordable, user-friendly, and time-efficient method for detecting and quantifying two common adulterants in honey using handheld visible-near-infrared (Vis-NIR) spectroscopy, combined with chemometric methods, specifically partial least squares-discriminant analysis (PLS-DA). To achieve this, we prepared four pooled samples from 18 authentic honey samples. These pooled samples were deliberately adulterated with glucose syrup and sugar syrup, and appropriate methods were employed for sample preparation, ensuring homogeneity at three different levels: low, medium, and high adulteration. The Vis-NIR spectra (400 to 1000 nm) of both pure and adulterated samples were recorded in two modes: reflectance and absorbance. The results from these two modes were compared to identify the more effective one. Based on the models generated, we achieved remarkable results in detecting glucose syrup and sugar syrup adulteration in reflectance/absorbance mode, with accuracy rates of 87.5%, 80.95%, 86.3%, and 93.45%, respectively. Additionally, this combined spectroscopic technique and chemometric approach could effectively differentiate between different levels of adulterants in honey samples. Proton nuclear magnetic resonance (H NMR) is a powerful analytical tool which can be used for authenticating honey, at chemical constituent levels. In the last step of present work, we will compare the NIR results with H NMR results as a reference method. This innovative approach holds great promise for ensuring the authenticity and quality of honey products, addressing the pressing issues posed by honey adulteration.

Keywords: Honey, Adulteration, Chemometrics, Handheld spectroscopy, Classification.

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Classification, QSAR analysis and molecular docking of some α-naphthoflavone derivatives as potent CYP1B1 inhibitors

*Samane Mossayebi and Mohammad Asadollahi-Baboli**

Department of Chemistry, Faculty of Science, Babol Noshirvani University of Technology, Babol 47148-71167, Mazandaran, Iran
E-mail address (corresponding author): asadollahi@nit.ac.ir

ABSTRACT

Cytochrome P450 (CYP) enzymes are a group of hemoprotein monooxygenases that participate in the biotransformation of various substances. These enzymes can naturally produce in the body or by external chemicals, such as commonly prescribed medications like docetaxel, tamoxifen, and cisplatin [1]. In the present study, classification and quantitative structure-activity relationship (QSAR) models has been employed to predict inhibitory concentration values and determine active/inactive inhibitors. The models were developed utilizing a dataset consisting of 41 inhibitors of the CYP1B1 enzyme based on α-naphthoflavone derivatives [2]. The dataset was split into the calibration and prediction sets to develop and validate the obtained models, respectively. The active/inactive inhibitors were classified using partial least squares-discriminant analysis (PLS-DA) and k-nearest neighbors (kNN) techniques and molecular descriptors [3]. The specificity, sensitivity and precision of PLS-DA technique are all more than 90% for classification of CYP1B1 inhibitors. The QSAR analysis was performed using stepwise multiple linear regression (stepwise MLR), partial least square (PLS) and support vector machine (SVM). The results of QSAR analysis shows satisfactory results in terms of adjusted R^2 (>0.85) and standard error (<0.5) for all three stepwise MLR, PLS and SVM techniques [4]. Also, Molecular docking studies were used to identify both the important binding sites on the CYP1B1 enzymes and crucial hetero atoms of inhibitors. By utilizing these computational approaches, the current study aimed to assess inhibitory concentrations, interactions and binding patterns of these inhibitors with the CYP1B1 enzyme, eventually providing both predictive and descriptive QSAR analysis.

Keywords: Classification, QSAR, Molecular Docking, CYP1B1 enzyme, α-naphthoflavone derivatives

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A Miniaturized Low-Cost Sniffing Device Based on Chemometrics Analysis an Array of Fluorescent Carbon Quantum Dots and Metallic Nanoclusters for Early Detection of Leukemia in Adults

Shiva Pesaran, Zahra Shojaeifard, Abolfazl Khalafinejad, Vahid Mohammad Karimi, Bahram Hemmateenejad and Javad Tashkhourian**

E-mail address (corresponding author): hemmatb@shirazu.ac.ir ; tashkhourian@shirazu.ac.ir

ABSTRACT

The non-invasive detection of leukemia remains a significant challenge. Blood volatile organic compounds (VOCs) are useful biomarkers [1]. This study demonstrates the potential of an integrated design, consisting of both a sensor array and a sampling vessel, of a paper-based fluorescence sensor array. The paper substrate serves as both a sensing surface and a vessel for samples. To accommodate the paper substrate, a miniature cubic reaction chamber, with dimensions of 330×30×0.02 mm and a tiny opening for blood sample injection, was created using 3D printing technology. Blood samples were taken from 70 new cases of leukemia and 51 healthy individuals as a control group. The sensor array consists of 7 nanoclusters, quantum dots, and carbon dots deposited on hydrophilic regions of a Whatman paper design. 60 µL of the sample that was diluted with heparin was injected through an opening hole in the container cap. An image of the sensor was then captured with a smartphone (irradiated by a 366 nm UV lamp) and compared to the image before the blood vapor was released. The interaction of the sensing element with the volatile blood metabolome caused the fluorescence quenching. The image analysis of sample gave leukemia blood samples specific patterns that differed from healthy samples. A color difference map (CDM) of the sensor array was obtained before and after exposure to blood vapor, which shows that the distinct behavior of the sensor elements in response to exposure of healthy and patient samples results in different color difference maps. A variable selection was performed on the 11 sensor elements, and 7 elements with the highest absolute loading values were chosen to serve as the final indicators. Linear discriminant analysis (LDA) was used to evaluate each multivariate dataset, and the array was able to accurately discriminate between healthy and patient samples with 100% accuracy. In total, the proposed array system provides a non-invasive, portable, fast and cost-effective sensor for early detection of Leukemia in Adults.

Keywords: Leukemia, early detection, Electronic nose, Non-invasive, Sensor array, Discriminant analysis

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Non-Parametric Class Modeling Using Multivariate Curve Resolution Methods

Ali Pahlevan[1 2]*, Somaiyeh Khodadadi Karimvand*[1]*, Federico Marini*[2*] *and Hamid Abdollahi*[1*]
[1]*Department of Chemistry, Institute for Advanced Studies in Basic Sciences, Zanjan, Iran*
[2]*Department of Chemistry, University of Rome “La Sapienza,” Rome, Italy*
E-mail address (corresponding author): abd@iasbs.ac.ir

ABSTRACT

Class modeling in chemometrics uses statistical models to classify samples by chemical properties. This is used in pharmaceuticals, authentication, environmental monitoring, and food quality. Non-normal and non-uniform data require specialized class-modeling methods. Potential Function Methods (PFM) are one of the most efficient probabilistic non-parametric methods [1]. It is a non-parametric method because no assumptions are made about the probability distribution of the samples for a particular class. It is used for discriminant classification and class modeling [2]. The probability distribution for a category is estimated by combining individual contributions from training samples of that class, unlike parametric methods. Multivariate Curve Resolution (MCR) strategies can identify and understand unknown chemical processes and reactions with unknown intermediate species. Recently, MCR-ALS was compared to other methods for distinguishing constituents of two benchmark and two high-dimensional data sets [3]. This work used the efficient data reduction strategy and the MCR method to classify high-dimensional datasets successfully. The efficiency of MCR-DA is comparable to that of tested methods such as PLS-DA [4]. A new MCR-based non-parametric class-modeling strategy is presented here. MCR methods for non-parametric classification were tested on several complex experimental data. The HPLC-CAD dataset of olive and non-olive oils was used. Coupling HPLC to a charged aerosol detector (CAD) produced 120 chromatogram profiles for olive and non-olive oils. These profiles included 71 olive oil samples from extra virgin, virgin, refined, and pomace categories and 44 edible vegetable oils: canola, maize, flaxseed, grape seed, hazelnut, peanut, rapeseed, safflower, sesame, soybean, and sunflower. This study included five olive-non-olive oil mixtures. Olive oil samples were the target, and non-olive and mixed samples were alien. Fatty acids in Triacylglycerides (TAGs) chromatographic profiles differentiated olive and non-olive samples [5]. The results were consistent and reliable compared to non-parametric methods like PFM with PCA compression and other data classification methods.

Target (Olive Oil) $\alpha=0.05$	Sensitivity % (Target Set)	Specificity % (Test Set 1) (Non-Olive)	Specificity % (Test Set 2) (Mix Oil)	Efficiency %
MCR-PFM	94.36	97.72	60	94.12
PCA-PFM	100	100	60	97.93

The proposed MCR approach sometimes results in complex data as good as or even more satisfactory than PCA compression. Like the original data set, MCR profiles and subspaces compress data accurately. MCR profiles are compound-specific and chemically meaningful, unlike PCA representations, and resolving pure component signal weights is beneficial.

Keywords: class modeling, non-parametric, Multivariate Curve Resolution, Potential Function Methods, MCR, PFM

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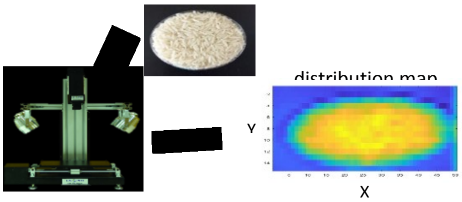
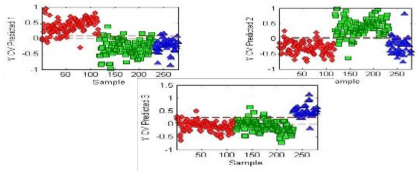
An Innovative Approach for Authentication of White Rice Using Vis-NIR Hyperspectral Imaging Coupled with Multivariate Curve Resolution and Classification Techniques

Maryam Dehbasteh[1], *Nima Naderi*[1], *Hassan Yazdanpanah*[2], *Hadi Parastar**[1]
[1]*Department of Chemistry, Sharif University of Technology, Tehran, Iran*
[2]*Food Safety Research Center, Shahid Beheshti University of Medical Sciences, Tehran, Iran*
E-mail address (corresponding author): h.parastar@sharif.edu





ABSTRACT

Food fraud or food crime is a significant and expanding global problem [1]. Rice, as a staple food for nearly half of the world's population, especially in Asian regions, presents a challenge in terms of rapid, reliable, and user-friendly authentication procedures [2]. The quality of rice is closely linked to its geographical origin, which depends on factors such as cultivation soil, climate conditions, and tillage methods [3]. Besides health concerns, this challenge is also essential for customers considering the cost. In this study, we propose a visible-near infrared hyperspectral imaging (Vis-NIR HSI) system combined with chemometric techniques to distinguish among rice samples from three northern provinces of Iran. We collected a total of 93 rice samples, with 39 from Mazandaran, 38 from Gilan, and 16 from Golestan provinces. Hyperspectral images of the samples in their intact forms were obtained and analyzed using different strategies, including global mean spectra, size reduction of images by binning method and multivariate curve resolution alternating-least squares (MCR-ALS). Among these methods, MCR-ALS allowed us to extract the pure spatial and spectral profiles as well as pure components of rice grains within the specified wavelength range. The identified spectral profile of the selected component was closely associated with rice pigments, carbohydrates, starch, and protein. By employing principal component analysis (PCA) on the resolved spatial profiles (distribution maps), we identified patterns of rice samples. Subsequently, we utilized partial least squares-discriminant analysis (PLS-DA), a supervised classification model, to achieve our objective. By observing the accuracy of 91.2%, 93.3% and 95.15% for each class, the resulting model demonstrated satisfying sensitivity and specificity based on the resolved distribution maps of rice samples, indicating the imaging technique's suitability for analyzing heterogeneous samples. In conclusion, Vis-NIR HSI combined with chemometric methods proves to be a powerful technique for authenticating the geographical origin of rice. This approach offers a promising solution to the challenges posed by rice authentication, providing efficient and reliable results.

Keywords: Rice Authentication, Hyperspectral Imaging, Multivariate Curve Resolution

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Harnessing Self-Organizing Maps Algorithm: Classification of Nuclear Magnetic Resonance Spectra for Untargeted Metabolomics of Breast Cancer

Maryam Kashi, *Hadi Parastar**

Department of Chemistry, Sharif University of Technology, Tehran, Iran
E-mail address (corresponding author): h.parastar@sharif.edu

ABSTRACT

Metabolomics has emerged as a promising tool for identifying disease biomarkers, and Nuclear Magnetic Resonance (NMR) spectroscopy enables the simultaneous detection of a wide range of metabolites [1]. However, due to the complex interactions in metabolic networks, metabolites often exhibit high correlation and collinearity. Principal Component Analysis (PCA) and Partial Least Squares-Discriminant Analysis (PLS-DA) have been commonly used in metabolomic studies [2]. Nevertheless, to extract meaningful information and ensure accurate biological interpretation, raw NMR spectral data requires preprocessing, which may introduce its own set of challenges. Self-Organizing Maps (SOMs), a learning method that utilizes artificial neural networks (ANNs) to visualize different patterns in data, offering a powerful alternative to PCA, especially for nonlinear data [3]. Kohonen Maps are self-organizing systems applied to unsupervised problems. In addition, counter-propagation artificial neural network (CP-ANN) are very similar to the Kohonen Maps and are essentially based on the Kohonen approach, but combine characteristics from both supervised and unsupervised learning. In this article, the Kohonen map and CP-ANN algorithms were employed to visualize the relationships between metabolites in control and breast cancer (BC) patient samples to identify potential biomarkers. Metabolites were extracted from blood serum samples of the control group (n=42) and BC patients (n=18) using methanol and chloroform as solvents. The acquired ^{1}HNMR spectra were analyzed using Mestrenova software and subsequently underwent phase and baseline corrections, and regions related to the solvent and those without informative data were excluded. By analyzing the obtained topological map, several important variables, including *lactic acid*, *cysteine*, *glucose*, *serine*, and *tagatose* were identified as influential factors in differentiating between healthy and BC patient classes. Also, the use of CP-ANN algorithm was able to successfully differentiate the two classes with accuracy and sensitivity of 91% and 90% for the control group and patients, respectively. These findings shed light on potential biomarkers for BC diagnosis, and the application of the SOMs algorithm proves to be a valuable approach to exploring complex metabolomic data.

Keywords: Kohonen map, CP-ANN, Chemometrics, Untargeted metabolomics, Breast cancer, Biomarker.

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A New Optical Sensor Array Platform Based on Nanozyme: Classification and Determination of Purine Bases

Mahsa Dezhbakhsh, Morteza Akhond, Bahram Hemmateenejad**

E-mail address (corresponding author): hemmatb@shirazu.ac.ir

ABSTRACT

In the last few decades, nanozymes (synthetic enzymes) have attracted the attention of researchers. Compared to natural enzymes, nanozymes have more advantages such as easy production, high stability, cost-effectiveness. Due to their unique properties, peroxidase-mimicking nanozymes can be considered a potential substitute for peroxidase enzymes in the measurement and analysis of biological compounds. In this research, we proposed an optical tongue colorimetric sensor array based on 8 pseudo-peroxidation nanozymes for quantitative Classification and measurement of purine bases [1]. After the interaction between the nanozymes and analyte and substrate, absorbance at 405 nm wavelength was read by the microplate reader. Then the obtained data were analyzed using chemometrics statistical methods to quantitatively measure and determinate the target purines. In this study, the detection limit for uric acid and adenine analytes was 2.52 µM and 3.63 µM, respectively. The designed nanozyme colorimetric sensor array was able to distinguish purine bases (adenine, guanine, caffeine, xanthine, uric acid, guanosine) well with 100% accuracy using PCA, LDA, HCA pattern recognition chemometrics statistical methods. The diagnostic system based on peroxidation nanograms can be a suitable candidate for the development of multifunctional sensors.

Keywords: Colorimetric, Electronic tongue, Nanozyme, Classification, Determination; Sensor array.

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Partial least squares-discriminant analysis (PLS-DA) for classification of crude oil samples based on sulfur content using ATR-FTIR spectroscopy

Mahsa Mohammadi *, *Mohammadreza Khanmohammadi Khorrami*

Department of Chemistry, Faculty of Science, Imam Khomeini International University, Qazvin, Iran
E-mail address (corresponding author): m.mohammadi70.ac@gmail.com

ABSTRACT

Crude oil is a mixture of hydrocarbons, predominantly hydrogen and carbon, with varying amounts of nitrogen, sulfur, and oxygen. Sulfur, one of the main contaminants in crude oil, is determined for several reasons. Importantly, sulfur compounds are present in different types of chemical structures, such as thiophenes, sulfides, benzo thiophenes, and dibenzothiophene. Crude oils are classified based on sulfur content into sweet and sour oil. In this study, a new and simple approach for classifying the sulfur content present in crude oils is proposed, using attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopy associated with chemometric methods. The feasibility of ATR-FTIR spectroscopy associated with chemometric models was evaluated for sulfur classification in crude oil samples. The sulfur content was determined using X-Ray spectroscopy in the crude oil samples, and the resulting values were used as input data to model the ATR-FTIR spectroscopy. Additionally, for classifying crude oil samples into "sweet" and "sour" categories based on sulfur content, the application of ATR-FTIR spectroscopy in combination with the Partial Least Squares-Discriminant Analysis (PLS-DA) and Support Vector Machine-Discriminant Analysis (SVM-DA) algorithms was successfully performed. Two sets of samples, 70 and 30, were considered for the calibration and prediction sets, respectively, in the classification models. The samples were classified into two classes, sweet and sour crude oil, according to sulfur content. The classification results showed an accuracy of 96% and a classification error of 0.0384 for the prediction set in the PLS-DA algorithm. These results indicate that ATR-FTIR spectroscopy associated with classification models is a rapid and reliable approach for quantifying the sulfur content in crude oils. The interest in classifying sulfur content in crude oil could serve as a model for the development of crude oil analysis in the oil industry.

Keywords: Crude oil, Sulfur,ATR-FTIR, PLS-DA, SVM-DA.

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A comparative study of the phytochemical profile of green tea during various brewing times using machine learning methods

*N. Hosseini, M. Esteki**

E-mail address (corresponding author): m.esteki@znu.ac.ir

ABSTRACT

Camellia sinensis is an evergreen shrub that produces the plant materials used to prepare tea. East Asia constitutes the largest tea-producing area represented by China, which accounts for 38% of world tea production, followed by South Asian countries, India and Sri Lanka. Nowadays, green tea has received increasing attention for its potential health benefits. The health benefits of green tea are mainly due to its polyphenol content; around 60–80% of polyphenols are flavan-3-ols, commonly known as catechins [1]. Catechins are major constituents of the tea leaf (approximately 30% of the dry weight of green tea and 9% of the dry weight of black tea) and of considerable importance because of these compounds are responsible for astringency in the tea infusion [2].

The phytochemical composition, sensory qualities, and antioxidant activity of green tea infusion are significantly affected by brewing conditions [3]. This study aimed to investigate the effect of brewing time on the phytochemical composition of green tea infusion using machine-learning methods.

For this purpose, the following procedure was used: In a round-bottom glass flask, 1.0 g of tea and 20.0 mL of methanol were added, and the mixture was refluxed at 80°C for 3 h. Sampling was accomplished at different time intervals including, 0 (immediately after addition of methanol), 1, 2, and 3 hours. The resultant was injected into GC-FID, the chromatograms were obtained, and the peak areas were used for model construction. Several pre-processing methods, such as mean centering (MC), auto-scaling, multiplicative scatter correction (MSC), standard normal variate (SNV), and their combinations, were employed to improve the quality of the data. Machine learning methods including, principal component analysis-linear discriminant analysis (PCA-LDA), partial least square-discriminant analysis (PLS-DA), and support vector machine (SVM), were employed to characterize the phytochemical composition of the tea samples. The constructed models showed a distinct class separation between the tea samples that were analyzed immediately after adding methanol (0 hour) and the other samples (1, 2, and 3 hours). The results showed that the brewing time after 1 hour did not significantly affect the phytochemical composition of green tea.

Keywords: Green tea, GC, Machine Learning.

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Untargeted metabolic profiling of volatile compounds of grape seed oil using gas chromatography coupled with mass spectrometry

*Niloofar Rahmani, Ahmad Mani-Varnosfaderani**

Department of Chemistry, Tarbiat Modares University, Tehran, Iran
E-mail address (corresponding author): a.mani@modares.ac.ir

ABSTRACT

Grape seed oil (GSO) is one of the most nutritious food products worldwide, which has attracted a lot of attention in the food industry [1]. In the present work, untargeted metabolomic profiling was performed using gas chromatography coupled with mass spectrometry (GC-MS) for pan-metabolome profiling of different varieties of GSO obtained from different grape genotypes. We investigated the metabolome profiles of 20 samples from five different GSO genotypes, and putatively identified 175 volatile compounds (VCs), mostly including fatty acid alkyl esters (27%), aldehydes (10%), alcohols (6%), esters (3%), and ketones (2%), which we termed as the pan-metabolome of GSO. Of the 175 molecules, 20 were present in all the GSO samples (core molecules), and 155 were present in ≥10% but <100% of the samples (accessory molecules). The Boruta feature selection method [2] was used to identify core molecules related to the differentiation of GSO samples. Of the 20 core molecules, ten molecules were consistently ranked as more important than shadow features across 70 iterations. The Kruskal–Wallis test was employed to assess the significant differences between the selected core molecules in different groups of samples. Linear discriminant analysis (LDA), partial least squares discriminant analysis (PLS-DA), support vector machine (SVM), and k-nearest neighbor (KNN) methods were used to classify different GSO genotypes using 10 selected core molecules as predictors. Classification accuracies for all models for the calibration and test sets were 1.00. The results revealed that different GSO genotypes contain metabolites that can be used as markers to predict quality and distinguish genotypes. The results of this study showed that metabolomic profiling can efficiently analyze variations in GSO metabolites and detect differences in metabolic pathways among GSO genotypes.

Keywords: Grape seed oil, Volatile compounds, Metabolomic profiling, GC-MS.

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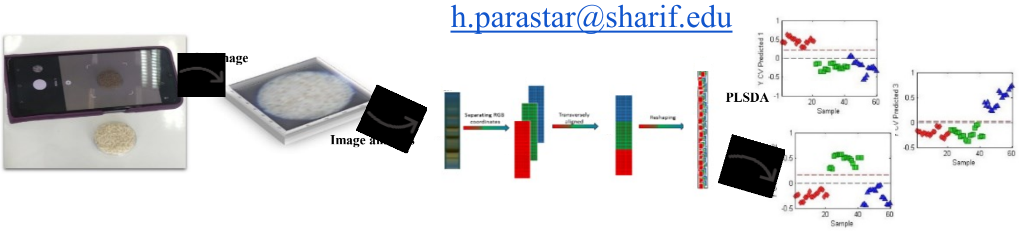
Smartphone Magic: Classifying Rice Samples with RGB Images and Chemometrics

*Nima Naderi, Maryam Dehbasteh, Hadi Parastar**

Department of Chemistry, Sharif University of Technology, Tehran, Iran

h.parastar@sharif.edu



ABSTRACT

Due to the high global demand for rice as a staple food, especially in Asian countries, there has been a significant increase in rice adulteration. As a result, authenticating rice samples and detecting fraud has become a major concern in the food industry. To address this issue, it is crucial to utilize suitable instruments for data acquisition. In recent years, portable instruments have gained popularity over conventional analytical systems due to their reliability, feasibility, cost-effectiveness, and rapid response. Among handheld devices, smartphones are widely employed due to their RGB imaging capabilities, where color is decomposed and quantified into red, green, and blue components [1]. However, raw RGB images often have low resolution, negatively impacting signal throughput during image analysis. Therefore, chemometric tools are required for qualitative and quantitative analysis to improve signal quality, enhance signal-to-noise ratio (SNR), and handle imperfect and variable input data. In this study, 93 rice samples were provided from three provinces in Iran (Mazandaran, Gilan, and Golestan) and recorded their RGB images using a smartphone. After image processing (extracting the RGB spectrum of each image and reshaping the data), Partial Least Squares-Discriminant Analysis (PLS-DA) was used as a supervised classification method to analyze the obtained data. This algorithm works by maximizing the correlation (or covariance) between **X** matrices (instrumental response, i.e. spectra) and **Y** matrix, which includes continuous or absolute values [2]. The proposed approach successfully discriminated rice samples from three different provinces (Mazandaran, Gilan, and Golestan) based on their geographical origins, yielding promising results of high accuracy, sensitivity, and specificity (100%) for both calibration and cross-validation sets. This study demonstrated that smartphones, in combination with chemometrics, are a reliable method for discriminating rice samples, with significant implications in terms of food safety and quality control. This approach can provide fast, accurate, and cost-effective results, helping to ensure the authenticity and quality of rice products.

Keywords: Chemometrics, Rice, Smartphones, RGB images, PLS-DA.

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Discrimination of Bottled Mineral Waters using Dip-Type Colorimetric Paper-based Sensor array and Pattern Recognition Methods

*Yaser Hatameifar, Zahra Shojaeifard, Bahram Hemmateenejad**

E-mail address (corresponding author): hemmatb@shirazu.ac.ir

ABSTRACT

Mineral water is natural water that originated from an underground water table, a well, or a natural spring and is microbiologically intact [1]. In this sense, Bottled mineral water has a specific and consistent chemical composition that is determined by the local geology and hydrology [2].moreover, the revenue of the bottled mineral water industry will be USD 342.40 billion in 2023, and it is expected to grow at a compound annual growth rate (CAGR) of 5.24% [3]. Consequently, the discrimination of original bottled mineral water from adulteration (filled with Tap water) is an important issue.

In this work, we have developed a Dip-Type colorimetric paper-based sensor array with three organic dyes (Bromothymol Blue, Bromophenol Blue, and Methyl Red) using chemometrics' pattern recognition methods (PCA and LDA) for discrimination of original bottled mineral waters from adulterated ones based on differences in ion variety and ion quantity. Almost 40 brands of mineral water and 26 Tap water from different regions of Shiraz and other cities were analyzed by this sensor. Moreover, these experiments were performed in two steps to check the period effect on water. This sensor array was able to discriminate these two water types from each other with an accuracy of > 92 %.

Keywords: Bottled mineral water, Dip-Type Colorimetric sensor array, Pattern recognition.

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Comparative study of random forest and Decision Trees in the modeling of methylene blue adsorption

Mohammad Hassan Omidi[1], *Bahram Ghalami-Choobar*[1], *Mohammad Hossein Ahmadi Azqhandi*[*2]

[1] *Department of Chemistry, Faculty of Science, University of Guilan, P.O. Box: 19141, Rasht, Iran*
[2] *Applied Chemistry Department, Faculty of Gas and Petroleum (Gachsaran), Yasouj University, Gachsaran 75813-56001, Iran*

E-mail address (corresponding author): mhahmadia58@gmail.com , m.ahmadi@yu.ac.ir

ABSTRACT

Globally, there is an increasing issue of freshwater shortage due to population growth and industrial activities [1]. This problem is worsened by the release of contaminated water into water bodies by various industries. To tackle this challenge, it is important to effectively treat and reuse polluted water [2]. Adsorption is a promising method for wastewater treatment because it is simple and operates under mild conditions. However, the success of this process relies on the performance of the adsorbents used, technically and economically [3]. In this study, we have developed and applied a new adsorbent for the removal of methylene blue (MB) from contaminated water samples. The adsorption data collected were analyzed, and Decision Trees (DT) and Random Forest (RF) models were used to simulate and predict the efficiency of the adsorption process. In conclusion, this study highlights the potential of the synthesized chitosan-graphene oxide-clay adsorbent for removing MB from contaminated water samples. The developed DT and RF models provide reliable tools for simulating and predicting the adsorption process, facilitating the optimization and cost-effective implementation of this treatment method. Further research in this field will continue to advance our understanding and application of adsorption processes, ultimately leading to a cleaner and more accessible water supply for everyone.

Keywords: Decision Trees, Random Forest, chitosan, graphene oxide, methylene blue.

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Prediction of the soil organic carbon to water distribution coefficients parameter for some neutral organic compounds from the theoretical derived molecular descriptors and QSPR modeling

Zahra pahlavanyali, Mohammad Hossein Fatemi, Maedeh Hosseinnia*
Chemometric Laboratory, Faculty of Chemistry, University of Mazandaran, Babolsar, Iran
E-mail address (corresponding author): zpahlevanyali@yahoo.com

ABSTRACT

The term of sorption is used frequently in environmental studies to denote uptake of a solute by a solid without referring to specific mechanism. Sorption play an important role in determining environmental fate and impact of organic chemicals. Soil organic carbon to water distribution coefficient, quantitatively describe extent to which an organic chemical is distributed between an environmental solid and an aqueous phase. The soil organic carbon to water distribution coefficients of 57 neutral organic compounds consist of aliphatic and aromatic hydrocarbons, heterocyclic compounds and benzene derivatives were taken from Ref. [1]. The structures of molecules were drawn with HyperChem 4.5 package [2] and exported in a file format suitable for MOPAC 6.0 program [3] for geometry optimization semi-mpirical quantum method AM1. Then, theoretical molecular descriptors were derived for prediction of soil organic carbon to water distribution coefficients of compounds calculated by Dragon 6.0 package. For QSPR modeling, an ANN program was written in FORTRAN 77 in our laboratory. This network was feed-forward fully connected that has three layers with sigmoid transfer function. Descriptors appearing in multiple linear regression (MLR) model were used as inputs of network and signal of output node represent distribution coefficient of interested compound. Thus, this network has five nodes in input layer and one node in output layer. The value of each input was divided into its maximum value to bring them into dynamic range of sigmoid transfer function of network. The initial values of weights were randomly selected from a uniform distribution that ranged between -0.3 and +0.3. The initial values of biases were set to be one. These values were optimized during network training. Before training, network's parameters would be optimized. These parameters are; number of nodes in hidden layer, weights and biases learning rates, and momentum values. Then optimized network was trained using 37 compounds introduced as training set for adjustment of weights and biases values. For evaluate prediction power of network during its training, after each 1000 training cycle, network was used to calculate distribution coefficient of molecules included in test set contains 10 compounds. The standard errors of obtained ANN model are 0.16, 0.19 and 0.27 for training, test and calibration sets respectively. Comparison between statistical results calculated from MLR and ANN models reveals that all statistics have been improved considerably in case of ANN model.

Keywords: Soil-water distribution coefficient, Artificial neural network, Multiple linear regressions, Quantitative structure-property relationship, Molecular descriptors.

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Carbon-based nano fluids; a theoretical study using Quantitative Structure-Property Relationships

Eliye Hamidi *, *Mohammad Hossein Fatemi, Kimia Jafari*

E-mail address (corresponding author): eliye.hamidi@yahoo.com

ABSTRACT

Heat transfer processes consume much of the total energy consumption, so increasing their efficiency is essential. In this area, nanofluids have attracted increasing attention to achieve this goal. on the other hand, considering repeated experimental studies can be toxic, time-consuming, and costly, it is necessary to focus on theoretical developments. The project used the quantitative structure-property relationship (QSPR) method to predict carbon nanofluids' thermal conductivity. were checked, on the factors of temperature, concentration, and specific surface area on enhancing the thermal conductivity of carbon nanofluids. Our dataset contains 72 data points. Data on graphene nanoplatelets (GNP) dispersed in distilled water were collected and modeled using the Monte Carlo method in a software called CORAL and defined the structure using quasi-SMILES. This method was used to calculate the optimal descriptors. The specifications of the proposed models were fully calculated, and the results indicate that the developed model is statistically significant for predicting the thermal conductivity ratio of carbon nanofluids. R^2_m all splits more than 0.5 and ΔR^2_m less than 0.2. The best model is related to split 2 with $R^2_m=0.9290$ and $\Delta R^2_m=0.0301$The best model is related to Split 2 with $R^2_m=0.9290$ and $\Delta R^2_m=0.0301$, while the weakest statistical performance was observed in Split 4 with $R^2_m=0.6509$ and $\Delta R^2_m=0.1890$. The application domain of the created models was clearly defined and correlation weights were calculated for all splits. The results showed that high concentrations, high temperatures, and high surface areas have a positive effect on the thermal conductivity ratio, while low temperatures have a negative effect on the target properties. The statistical performance of the models was satisfactory.

Keywords: Nanofluid, Thermal conductivity, Carbon-based, QSPR, CORAL.

A study on permutation test strategies in ASCA

*F. Maddahi[1], M. Akbari Lakeh[2], J. Mohammad Jafari[1], J. J. Jansen[2], P. J. Gemperline[3], H. Abdollahi[1]**

[1]Institute for Advanced Studies in Basic Sciences (IASBS), Zanjan, Iran
[2]Radboud University, Nijmegen, the Netherlands
[3]East Carolina University, Greenville, NC, United States
E-mail address (corresponding author): abd@iasbs.ac.ir

ABSTRACT

ANOVA Simultaneous Component Analysis (ASCA) examines the significance of the effects of experimental factors and possible interaction between them in chemical data, commonly based on permutation tests [1]. Permutation tests are often used to assess the significance of an observed effect by randomly permuting the data and comparing the observed result to the distribution of permuted results. Several permutation test approaches have been applied in ASCA [2, 3], of which two widely-used methods, restricted permutation, and reduced model, are studied in detail. These significant testing methods differ in terms of which matrix is permuted and which units are exchangeable. Restricted permutation tests involve restricting the permutations to maintain a specific null hypothesis, such as the exchangeability of treatment groups or the independence of observations, while permuting the remaining variables. On the other hand, reduced model permutation tests, involve comparing the observed data to a reduced model in which certain variations or interactions have been removed. Determining the appropriate significance test to employ is a matter of uncertainty. Making the wrong selection could result in erroneous conclusions regarding the significance of the factors at hand. This study delved into multiple simulated datasets, each characterized by varying conditions concerning the significance of factors and interactions. Additionally, an experimental dataset involving feral cabbage plants (Brassica oleracea) was incorporated, focusing on two experimental factors: time and treatment. The study's findings showcased that the restricted permutation test outperforms in assessing the significance of the main factors. Nevertheless, when examining the interaction between these main factors, the reduced model test proves to be more effective. The investigation delves deep into the reasons behind these observed outcomes.

Keywords: Restricted Permutation Tests, Reduced Model Permutation Tests, ASCA

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A brief overview of the application of chemometrics in industry with an emphasis on sensors

*Mohammad Ghaffarzadeh**

Department of chemistry, Faculty of Basic Sciences, Azarbaijan Shahid Madani University, Tabriz, Iran

E-mail address (corresponding author): ghaffarzade.mohammad@email.com

ABSTRACT

The use of chemometrics has been applied as a statistical method merely to produce PCA or PLS regression, without consideration to the main issues, advantages, and disadvantages on the use of these methods. The combination and implementation of chemometrics and sensors relies on gathering data to generate new knowledge. The marriage of these techniques and associated instrumentation for analysis provides a platform to better understand different features of an environmental system. Understanding some of those features can be readily achieved using chemometrics. One of the intrinsic characteristics of these type of analysis is that the analyst should have the required basic knowledge of the processes and the system used to create the sample to complete the multidisciplinary work in environmental monitoring, using sensors, and applying the chemometrics. Ideal sampling systems are those that can be deployed in the environment and have the capacity to continuously monitor/ measure all the desired parameters [1]. When chemical and molecular targets are combined, unknown inferences can be made if the end-user is an expert in designing experiments or using data that proves the original hypothesis the scientist has designed. For example, a study using four contrasting sites were monitored during two consecutive seasons (summer and winter) in order to evaluate the feasibility of differentiating microbial communities from urban, rural, and industrial areas for the two seasons using air as the sample matrix [2]. Fortunately, some of these methods and applications are coming to light into research and development, and their translation into real applications or scenarios have been embraced by the industry, something we hope a galvanized marriage using chemometrics and sensors will achieve only through improved teaching and education.

Keywords: chemometrics, sensors, industry.

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Trace Determination of Vitamins B3 in Food Samples Based on Graphene oxide - cobalt ferrite Nanocomposite and Antibacterial assay

Zahra Khaleghi[a], *Rouhollah Khani*[a]*, *Maryam Moudi*[a]
[a] *Department of Chemistry, Faculty of Sciences, University of Birjand, Birjand, 97179-414, Iran.*
E-mail address (corresponding author): *Rouhollah.khani@birjand.ac.ir*

ABSTRACT

Vitamin B3 (Niacin) is one of the B group vitamins that can be found in two forms, nicotinamide and nicotinic acid, and is essential for living cells. Vitamin B3 is not stored in the body and must be ingested with food. The recommended amount of this vitamin for humans is 12-16 mg day^{-1} [1]. Excessive consumption of vitamin B3 can cause symptoms such as skin itching, headache, stomach ulcer or even liver damage [2]. Therefore, the determination of vitamin B3 in real samples is crucial to control and prevent the symptoms caused by its unauthorized consumption. So, as a result, it is necessary to utilize a sensitive and reliable method to determine vitamin B3. In this work, magnetic cobalt ferrite/graphene oxide ($CoFe_2O_4$/GO) adsorbent was synthesized and characterized by Fourier transform infrared (FT-IR) spectroscopy, vibrating sample magnetometer (VSM), field emission scanning electron microscopy (FE-SEM) and X-Ray diffraction (XRD). Magnetic dispersive micro-solid phase extraction (MD-µSPE) consisting of $CoFe_2O_4$/GO nanocomposite coupled with a green, precise, accurate, and robust spectrofluorometric approach was used for preconcentration, extraction and determination of vitamin B3. Four parameters of pH, adsorbent dose, temperature and sonication time were selected as effective factors on the process and optimized by central composite design (CCD) [3]. Under optimized conditions, the linear range, limit of detection, and the relative standard deviation (R.S.D) were obtained 10–900 ng mL^{-1}, 5.64 ng mL^{-1} and 4.24 % respectively. Finally, the proposed method was successfully applied for preconcentration and determination of vitamin B3 in food samples. In addition, antibacterial activity of the $CoFe_2O_4$/GO nanocomposite was evaluated on *Escherichia coli* and *Staphylococcus aureus* bacteria.

Keywords: Vitamin B3, Central composite design, $CoFe_2O_4$/GO nanocomposite, Food samples, Antibacterial activity

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Synthesis and performance evaluation of zeolitic imidazolate metal-organic framework hybrid nanocomposite based on carbon nanotubes for determination of diclofenac in food and biological samples

Samira Rashidi HematAbadi[a], *Rouhollah Khani*[a*], *Alireza Farrokhi*[a]

[a] *Department of Chemistry, Faculty of Sciences, University of Birjand, Birjand, 97179-414, Iran.*

E-mail address (corresponding author): Rouhollah.khani@birjand.ac.ir

ABSTRACT

Diclofenac is a lipophilic, nonsteroidal anti-inflammatory drug (NSAID) frequently used to treat pain in musculoskeletal injuries, rheumatoid and osteoarthritis [1]. Diclofenac is considered a potent inhibitor of prostaglandin synthetize enzyme and may lead to heart attack and stroke, changes in renal function, agranulocytosis and gastrointestinal disorders[2]. Therefore, it is necessary to utilize a sensitive and reliable method to the determination and quantification of diclofenac in food and biological samples is of particular importance in order to investigate and prevent the side effects of this analyte and the risks caused by its high dose. In this research, dispersive micro-solid phase extraction (Dµ-SPE) method based on zeolite imidazolate framework nanoadsorbent and its hybrid nanocomposite based on carbon nano tubes as an accurate and efficient method for the extraction and preconcentration and determination of diclofenac in biological samples and water was used. In this work, Single Wall Carbon Nanotubes/ zeolite imidazolate framework (SWCNT/ZIF-8) adsorbent was synthesized and characterized by Fourier transform infrared (FT-IR) spectroscopy, Raman spectrophotometry, field emission scanning electron microscopy (FE-SEM) and X-Ray diffraction (XRD). Four parameters of pH, salt addition, adsorbent dose and sonication time were selected as effective factors on the process and optimized by central composite design (CCD) [3]. Under optimal conditions of linear dynamic range, detection limit and the relative standard deviation (R.S.D) were obtained 15-700 ng mL^{-1}, 8.91 ng mL^{-1} and 4.63% respectively. Finally, the proposed method was successfully applied for preconcentration and determination of diclofenac in biological samples of human urine and diclofenac tablets and water samples.

Keywords: Diclofenac, Metal-organic frameworks, Carbon nanotubes, Central composite design, Biological samples.

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Improving the co-removal efficiency of dyes from water by a novel four-component chitosan flexible film containing graphene oxide

Saed Salami [a], *Morteza Bahram* [a, *], *Khalil Farhadi* [a], *Legha Ansari* [b]

E-mail address (corresponding author): m.bahram@urmia.ac.ir

ABSTRACT

One of the major environmental and public problems in the world is water pollution, which has always received significant attention [1]. Industries such as painting, leather, clothing, pulp, paper, textiles, and others use a variety of dyes [2]. In the textile industry, two types of dyes are used to dye fabrics: natural dyes and synthetic dyes. In the present study, a novel four-component flexible film based on α-ketoglutaric acid, chitosan, polyaniline, and graphene oxide (α-CTS-PANI-GO) was synthesized and characterized by Scanning Electron Microscope (SEM), Fourier Transform Infrared Spectroscopy (FT-IR), and Raman spectroscopy. The simultaneous removal properties of α-CTS-PANI-GO were evaluated in the removal of cationic and anionic dyes, Methylene Blue (MB) and Acid Orange 7 (AO7). Using the Central Composite Decomposition (CCD), the effect of different variables such as pH, temperature, adsorbent dose, and time on AO7 and MB removal was studied.

pH 8, temperature 75 °C, adsorbent dose 0.04 g and time 75 minutes were calculated by the experimental design method for maximum absorption. Furthermore, the analysis of variance (ANOVA) was used to determine the adequacy of the model. The complete diversity of the results obtained by ANOVA is divided into two variations: One is related to the model and the other is related to experimental errors and thus determines whether the change is significant from the model or not. It is calculated by the factor *F*-value which is expressed as the square-to-residual error ratio of the mean model. The F-value obtained in the present study was 19.55 and 22.50, which suggested the fitness of the response surface model for MB and AO7, respectively. Also, using the experimental design, the optimal values for maximum removal were obtained. Various isotherm models, such as Langmuir and Freundlich, were investigated, and the processing of experimental equilibrium data confirmed the suitability and application of the Langmuir model. Analysis of experimental adsorption data using various kinetic models, such as quasi-first and second-order models, shows the applicability of the first-order equation. The results showed that in the optimal conditions, the removal percentage was about 95% for AO7 and 80% for MB, which indicates the successful performance of the synthetic film compared to the method.

Keywords: α-ketoglutaric acid, Chitosan film, Polyaniline, Graphene oxide, Cationic dyes, Anionic dyes.

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Multivariate optimization and characterization of removal of Entacapone drug using copper zinc cobalt ferrite nanoparticles modified by cetyltrimethylammonium bromide ($Cu_{0.3}Zn_{0.3}Co_{0.4}Fe_2O_4$@CTAB)

Mostafa Kazemi, Javad Zolgharnein* [1]

E-mail addresses (Corresponding author): kazemichem1@gmail.com

ABSTRACT

Copper zinc cobalt ferrite nanoparticles modified by cetyltrimethylammonium bromide ($Cu_{0.3}Zn_{0.3}Co_{0.4}Fe_2O_4$@CTAB NPs) are used as an efficient adsorbent to remove Entacapone (En) drug from aqueous solutions. The characterization of adsorbent is investigated by field emission scanning electron microscopy (FE-SEM), X-ray diffraction (XRD), Fourier transform infrared (FT-IR) spectroscopy, energy dispersive X-ray spectroscopy (EDX), and the vibrating sample magnetometer (VSM) technique. To optimize the effective factors, response surface methodology (RSM) through using Central Composite design (CCD) is applied. By proper running of the Desirability function option in MINITAB software, the optimum conditions were found as pH 3.0, adsorbent mass (m) 10 mg, and initial dye concentration (C_d) of 77 mg L^{-1}. Isotherm studies of the adsorption process are carried out where the Langmuir isotherm shows the maximum monolayer capacity (q_{max}) is 224 mg g^{-1}. The kinetic studies including pseudo-first-order, pseudo-second-order and intra-particle diffusion models indicate that the pseudo-second-order kinetic model describes better the adsorption kinetic behavior. This study shows that $Cu_{0.3}Zn_{0.3}Co_{0.4}Fe_2O_4$@CTAB NPs have excellent potential for the removal of Entacapone (En) drug from an aqueous solution.

Keywords: Adsorption, Mixed magnetic oxides nanoparticles, Removal, Entacapone, Response surface methodology, Drug.

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Optimizing of the production process of dinitropentamethylenetetramine (DPT) using central composite design (CCD) of experiments

Sajjad Damiri [*], *Seyed Mohsen Mousavi*

Department of Applied Chemistry, Malek-Ashtar University of Technology, Shahin-Shahr, Esfahan, Iran
E-mail address (corresponding author): s_damir@mut-es.ac.ir

ABSTRACT

Dinitropentamethylenetetramine (DPT) is an important intermediate in the production of cyclotetramethylene tetranitramine (HMX) explosive. This substance is usually produced by nitration of the hexamethylenetetramine, or hexamine, by a solution of ammonium nitrate-concentrated nitric acid and acetic anhydride in glacial acetic acid environment [1-3].

In this research, effect of various factors on the production efficiency of DPT high-energy substance have been statistically modelled and optimized by the central composite design of experiments (CCD) using Minitab software, and multivariate linear regression (MLR) method. Also, necessary quantitative and qualitative analyses, including melting point, CHN elemental analysis, Fourier-transform infrared (FT-IR), and carbon-13 /hydrogen nuclear magnetic resonance spectroscopy have been investigated to identify and confirm the quality of the final product. Experimental investigations show that the four main factors affecting the reaction efficiency, i.e., the amount of nitrating agent ammonium nitrate-nitric acid, reaction temperature, nitrating time and retention time, have significant effect on the product production efficiency. Statistical analyzes show a very good agreement between the presented MLR model and the experimental results, enabling the production of DPT with an efficiency of close to 82%.

Keywords: DPT, energetic material, experimental design, modeling, optimization.

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Development and optimization of microwave-assisted extraction of *Satureja bachtiarica* Bunge. essential oil using response surface methodology and its comparison with traditional method

Sayedeh Mansoureh Memarzadeh[a,], Ali Gholami[b], Abdollah Ghasemi Pirbalouti[c], Sayed Ahmad Nourbakhsh[d]*
*[a, *]Food and Drug Deputy, Shahrekord University of Medical Sciences, Shahrekord, I.R. Iran.*
[b] Department of Analytical Chemistry, Faculty of Chemistry, University of Kashan, Kashan, I.R. Iran.
[c] Research Center for Medicinal Plants, Shahr-e-Qods Branch, Islamic Azad University, Fath Highway, P.O. Box 37515-374, Tehran, Iran.
[d]Student and Cultural Deputy, Shahrekord University of Medical Sciences, Shahrekord, I.R. Iran
E-mail address (corresponding author): memarzadeh8291@gmail.com

ABSTRACT

Essential oils are one of the most secondary metabolites in therapeutic herbs, rich in oxygenated compounds [1]. The proficiencies of traditional hydro-distillation (THD) and microwave-assisted steam hydro-diffusion (MSHD) techniques in extraction of Bakhtiari savory oil were evaluated. In order to obtain the golden yield and total phenol (TPC) in MSHD method, three factors were examined at 5 levels by applying central composite design under RSM technique: extraction time (15, 25, 35, 45, 55 min), microwave power (200, 400, 600, 800, 1000 W) and water volume to plant ratio (W/P) (0, 0.5, 1.5, 2.5, 3 ml/g) [2, 3] .The results of RSM in THD method showed, extraction time and (W/P) separately affected on yield and TPC without interaction.The best yield was 1.64 V/W% that collected at conditions [54.16 min, 872.42 W, 2.09 ml/g for extraction time, microwave power and (W/P)]. By using folin-ciocalteu method, the maximum of TPC was 344.07 mgGAE/g that was obtained at points [19.7 min, 1000 W, 3 ml/g for time, power and (W/P)] in MSHD technique. The highest amount of oxygenated fraction (63.24 ± 0.442%) were produced in the microwave method. The MSHD method is the economic technique for green extraction of essential oil from pharmaceutical and fragrant herbs [4,5].

Keywords: Microwave-assisted steam hydro-diffusion; Satureja bachtiarica Bunge; Essential oil; Response surface methodology; GC/MS.

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Optimal Experimental Design for Enhancing Efficiency and Accuracy of Indicator Displacement Assay Sensor Arrays

Kobra Bayat[1]*, Somaye Vali Zade*[2]*, Hamid Abdollahi*[1*]

[1]*Faculty of chemistry, Institute for Advanced Studies in Basic Sciences, Zanjan, Iran*
[2]*Halal Research Center of IRI, Food and Drug Administration, Ministry of Health and Medical Education, Tehran, Iran*
E-mail address (corresponding author): abd@iasbs.ac.ir

ABSTRACT

Chemosensors, specifically, have garnered significant attention and found versatile applications in chemical detection. A crucial category among chemical sensors is based on competitive displacement mechanisms, where the analyte competes for binding with a receptor, usually known as indicator displacement assay (IDA) sensors. The IDA method remains widely employed in sensor applications. In the competitive IDA approach, an indicator initially binds reversibly to a receptor. However, in the presence of a competitive analyte with a higher binding affinity to the receptor, a displacement reaction occurs, leading to the release of the indicator in the system, resulting in a change in the optical signal. It is crucial for the analyte's binding affinity with the receptor to be higher than that of the indicator, based on IDA principles. IDA sensors, despite their lower selectivity, can effectively analyze mixtures and simultaneously determine multiple analytes when designed as sensor arrays. To optimize the design of IDA sensor arrays, we employ the concept of Optimal Experimental Design (OED), a statistical methodology that maximizes the amount of information extracted from data. OED facilitates identifying the most efficient way to collect data, enhancing the accurate and precise fitting of statistical models. In this study, we focus on utilizing OED to design experiments that provide the most efficient sensors for accurate and precise quantitation of mixtures in IDA sensor arrays. The application of OED addresses two fundamental questions in IDA sensor array design and simulations based on hard modeling: 1) How are controllable parameters determined to achieve optimal efficiency? 2) Is the number of sensor elements effective in achieving the first-order advantage? Our findings reveal that OED is highly successful in predicting optimum conditions and answering these critical questions based on simulation data., Also, when only one of the sensor components is active spectroscopically, it's possible to achieve a first-order advantage by designing a suitable sensor array. This advantage can be utilized in quantitative and qualitative analyses based on this active sensor array.

Keywords: Optimal Experimental Design, Indicator Displacement Assay, Sensor Array, First Order Advantage

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Comparative study of response surface methodology and generalized regression artificial neural network in the optimization of Ofloxacin degradation

Bahram Ghalami-Choobar[1], *Mohammad Hossein Ahmadi Azqhandi*[*2], *Mohammad Hassan Omidi*[1]

[1] *Department of Chemistry, Faculty of Science, University of Guilan, P.O. Box: 19141, Rasht, Iran*
[2] *Applied Chemistry Department, Faculty of Gas and Petroleum (Gachsaran), Yasouj University, Gachsaran 75813-56001, Iran*
E-mail address (corresponding author): mhahmadia58@gmail.com , m.ahmadi@yu.ac.ir

ABSTRACT

Ofloxacin (OFX) is considered an emerging pollutant that is commonly found in surface water and wastewater. Due to its potential environmental impact, there is a growing need to develop effective technologies for its removal. One promising approach is the use of advanced oxidation processes, which have shown success in eliminating antibiotics. This study focuses on investigating the application of UV/H_2O_2 and ozonation (O_3) for the degradation of OFX. To obtain meaningful results, experimental designs were implemented, and the data was modeled using RSM and generalized regression neural networks (GRNN) [1]. These modeling techniques allowed for the development of models to accurately describe and predict the degradation of OFX. Additionally, the study aimed to identify the most significant variables that affect the degradation process and to determine the byproducts formed during the treatment [2, 3]. This analysis was performed using high-performance liquid chromatography-mass spectrometry (HPLC-MS). The concentration of the antibiotic and the pH level were identified as the most influential variables affecting the degradation process. In a short span of 30 minutes, a high removal percentage of 90-97% was achieved, with pH being the most significant variable. Utilizing the GRNN analysis, a predictive model was developed, which showed a good fit between the model and experimental data. This indicates the reliability of the model in accurately predicting the degradation of OFX. Furthermore, the study identified the main byproducts formed during the degradation process, with many of them disappearing after 30 minutes of treatment.

Keywords: Ofloxacin, response surface methodology, GRNN, HPLC-MS, Antibiotic.

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Synthesis and characterization of g-CN/rGO photocatalyst for waste water Ciprofloxacin; Generalized Regression Neural Network and Surface Response Methodology study

Mohammad Hossein Ahmadi Azqhandi[*1], *Mohammad Hassan Omidi*[2], *Bahram Ghalami-Choobar*[2]

[1] *Applied Chemistry Department, Faculty of Gas and Petroleum (Gachsaran), Yasouj University, Gachsaran 75813-56001, Iran*
[2] *Department of Chemistry, Faculty of Science, University of Guilan, P.O. Box: 19141, Rasht, Iran*
E-mail address (corresponding author): mhahmadia58@gmail.com , m.ahmadi@yu.ac.ir

ABSTRACT

In this study, a nanocomposite photocatalyst called graphitic carbon nitride-reduced graphene oxide (g-CN/rGO) was synthesized, characterized and applied for the photocatalytic degradation of ciprofloxacin (CP), which serves as a representative contaminant, under visible light illumination [1]. The experiment considered different conditions such as initial CP concentration, irradiation time, photocatalyst dose, and pH [2]. The obtained results were then modeled using response surface methodology (RSM) and generalized regression neural network (GRNN) approaches to provide a more accurate description of the process behavior. To verify the main active species, free radical trapping experiments were conducted. Additionally, the LC-Mass technique was utilized to detect the intermediates formed during the photodegradation process. When comparing the photocatalytic performance of g-CN/rGO with other recently developed counterparts, it becomes evident that it holds promise as an alternative for remediating these types of pollutants in water bodies. The excellent performance of the g-CN/rGO photocatalyst suggests its potential for large-scale photodegradation of persistent organic pollutants in wastewater treatment plants [3].

Keywords: graphitic carbon nitride, reduced graphene oxide, photocatalyst, degradation, RSM.

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BBD Design for optimization of the fabrication a selective nano-electrochemical flexible carbon cloth sensor assembled by AuCDs imprinted by polydopamine to Orlistat accurate repeatable detection

*Neda Zalpour, Mahmoud Roushani**

Department of Chemistry, Faculty of Sciences, Ilam University, Ilam, P. O. BOX. 69315-516, Iran
E-mail address (corresponding author): m.roushani@ilam.ac.ir and mahmoudroushani@yahoo.com

ABSTRACT

One of the cutting-edge emerging approaches being used by researchers in the field of sensors is to go beyond conventional techniques and design flexible, portable, selective sensors that can swiftly and accurately identify trace quantities of target molecules. In this research carbon cloth, as a binder-free 3D flexible material, served as the working electrode. In a single step, hydrothermal approach AuCD nanoparticles were synthetized and used to modify the carbon cloth surface. The molecular imprinting polymer approach using in situ electropolymerization of dopamine monomer in the presence of orlistat as the target molecule utilized to fabricate imprinted sensor [1, 2]. To achieve the most promising results, experimental design used to optimize the variables and instrumental parameters. In comparison to a one-at-a-time experiment, this method requires fewer measurements and can estimate how the elements interact [3]. The statistical significance of a list of the main and interaction effects is assessed using an analysis of variance (ANOVA) table. Utilizing Minitab (Version 21) software, the synergistic effects of the five variables (Electropolymerization pH (A), DA to OST ratio (B), number of CV scan cycles (C), KOH concentration (D), OST elution time (E)) on the DPV response were optimized. One of the most useful optimization techniques, the response surface approach (Box-Behnken model), was utilized to improve crucial experimental factors impacting MIP preparation. In the conditions of pH = 8, dopamine to orlistat ratio = 2.5, electroploymerization cycle number = 30, KOH = 3.5 M, elution time = 20.4 min, and 0.0005 to 1.3 nM linear range with a detection limit of 0.0002 nM, the best response was obtained for the accurate identification of the orlistat by the architected sensor. SEM and ATR-FTIR analysis were used to characterize and survey the correctness of the sensor manufacturing. The stability, selectivity, and performance of the presented sensor were evaluated under optimal conditions. Using blood serum and urine samples, satisfactory outcomes were achieved in real samples. This is the first electrochemical sensor report for orlistat detection to date.

Keywords: Bok-Behnken experimental design, Orlistat, Molecularly imprinted polymer, In situ electropolymerization, Gold carbon quantum dot.

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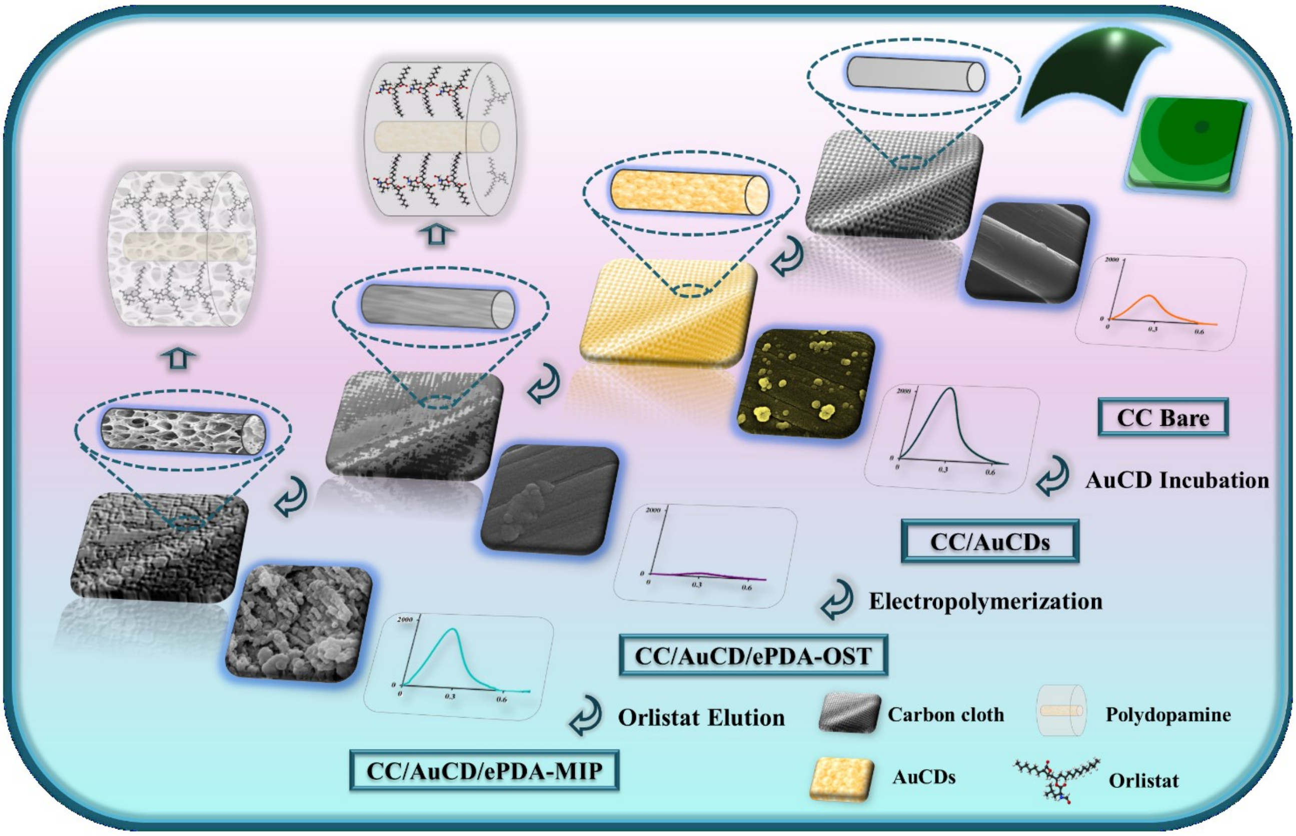
CC Bare
AuCD Incubation
CC/AuCDs
Electropolymerization
CC/AuCD/ePDA-OST
Orlistat Elution
CC/AuCD/ePDA-MIP
Carbon cloth
Polydopamine
AuCDs
Orlistat
2000
0
0.3
0.6

Chemometrics-based GC/MS analysis of black tea volatiles from different regions of Iran

A. Aminianfar, M.H. Fatemi, F. Azimi*

Department of Chemistry, University of Mazandaran, Babolsar, Iran
E-mail address (corresponding author): mhfatemi@umz.ac.ir

ABSTRACT

The current study aimed to obtain an informative chemical signature of the volatile fraction of black tea samples from the main areas of tea cultivation in Iran. Tea is the most popular flavored and functional drink consumed worldwide which has received considerable attention regarding its high consumption and beneficial effects on human health. Tea aroma is one of the most important factors determining this safe drink's quality, origin traceability, and general acceptability. In order to obtain an informative chemical signature of the volatile fraction of black tea samples the chemical consequents and relative content of volatile compounds of Iranian black tea samples from four different typical geographical origins were comprehensively analyzed on the basis of headspace solid-phase microextraction gas chromatography–mass spectrometry (HS–SPME–GC–MS) technology combined with chemometric analysis .A multivariate curve resolution method is applied to resolve and recover the pure response profiles. Multivariate curve resolution-alternative least squares (MCR-ALS) algorithm as an iterative method has been employed combined with this gas chromatographic procedure for resolving the overlapped and embedded peaks and overcoming some challenging fundamental chromatographic problems occurring during GC-MS analysis; an overall volume integration (OVI) technique was also used for the semi-quantitative analysis to obtain the relative concentrations of chemical constituents. GC-MS analysis using chemometric tools resulted in extending the number of identified constituents from 71 to 130 components with concentrations higher than 0.01%. It was found that β-Ionone (7.51%), was the most abundant aroma component, followed by Tridecane (7.44%), Linalool (5.51%), β-Phellandrene (5.48%), Dodecane (5.45%), cis-Geraniol (4.73%), 1,2-Epoxylinalool (4.68%), Linalool oxide (4.45%), and α-Farnesene (4.1%). This is the first report to identify the volatile compounds of Iranian black tea, which improves the identification and authentication of this complex natural product.

Keywords: GC–MS, Multivariate curve resolution, Black tea.

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Studying the kinetic profiles of the simultaneous release of metformin-sitagliptin drugs as a combination drug from the polymer substrate by MCR-ALS method

*Reza Dadashi, Tohid Javandust, Morteza Bahram**

Department of Analytical Chemistry, Faculty of Chemistry, Urmia University, Urmia, Iran
E-mail address (corresponding author): m.bahram@urmia.ac.ir

ABSTRACT

Nowadays, the development of targeted drug delivery systems has reduced the side effects of traditional drug use and also increased the effectiveness of drugs in the body [1]. In order to have a faster effect and cure some diseases, combined drugs are made. It is essential to use fast and reliable analytical techniques to determine the real release profiles of drugs in targeted pharmaceutical systems for combination drugs [2]. Zipmet is a widely used combination drug for the treatment of diabetes, which is made from two drugs, metformin and sitagliptin. In this work, to investigate the release profiles of these two drugs in the presence of each other, first, both drugs were loaded on the Polyacrylic acid-co-2 hydroxyethyl methacrylate cross-linked with EGDMA (PAAHEMA-co-EGDMA) polymer substrate and then the simultaneous release of these two drugs from the polymer substrate in the buffer and plasma environment was investigated by recording spectrophotometric spectra.

The release profile of each drug was extracted from the obtained spectrophotometric data using the MCR-ALS technique. The results showed that the simultaneous release of metformin and sitagliptin drugs from the PAAHEMA-co-EGDMA substrate is faster in acidic pH than in basic and neutral pH. Also, the comparison of the release profiles obtained from the MCR-ALS technique showed that the release rate of the metformin drug is higher than that of sitagliptin from the polymeric substrate. Finally, the results of fitting the obtained profiles showed that Korsmeyer-Pipas and Ritger-Pipas models achieve the best results for metformin and sitagliptin drugs in the presence of each other from the polymer substrate.

Keywords: Drug Delivery, MCR-ALS, Combination drug, Simultaneous release.

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Nano n-TiO_2-P25@ECH@ZrO_2-SO_3H: a novel heterogeneous semiconductor photocatalyst with SO_3H function, effective in removing colored pollutants from aqueous solutions

Farzaneh Khorammanesh, S. Maryam Sajjadi, Ali Amoozadeh, Mehrnoosh Bitaraf*

Faculty of Chemistry, Semnan University, Semnan, Iran, 35131-19111
E-mail address (corresponding author): Sajjadi@semnan.ac.ir

ABSTRACT

In the present work, TiO2 nanoparticles was modified using SO_3H-functionalized heterostructure by simple covalent grafting strategy [1]. The photocatalytic kinetic degradation of violet 16 was investigated using this novel nano-photocatalyst in aqueous solution under two different acidic and basic pHs. The blue LED was used to irradiate the solution at different times over 0-12 h. The reactions were monitored spectrophotometrically and the rank analysis of the data showed there are two spectrophotometrically active components in this system. Multivariate hard modelling approach was applied on the data at basic pH to compute the rate constant of the photo-degradation reaction based on postulated consecutive kinetic model, $A\xrightarrow{k1}B\xrightarrow{k2}C$ [2]. The obtain k1 and k2 were 0.0047 h^{-1} and 0.0127 h^{-1}, respectively. Apart from estimating rate constants, the pure kinetic and spectral profiles of the species involved in the kinetic processes achieved. However, dye's degradation was too slow under acidic pH as no significant changes of signals were observed over time range of 0-12 h.

Keywords: Novel Modified TiO_2, Multivariate Hard Modelling, LED lights, Violet 16.

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Rank annihilation factor analysis method for kinetic-spectrophotometric measurement of morphine in unknown opiate samples mixture

Somayeh Khezri, Morteza Bahram[*]

Department of Analytical Chemistry, Faculty of Chemistry, Urmia University, Urmia, Iran
E-mail address (corresponding author): m.bahram@urmia.ac.ir

ABSTRACT

Measuring the compounds in narcotic drugs, including morphine, is of great importance in medical science and forensic applications [1]. For this purpose, many analytical methods have been developed [2,3]. In chromatographic methods such as LC, GC, TLC, and HPLC, the long procedure is a result of the time-consuming analysis work and the high cost of the device, among the disadvantages of these methods. In this study, a fast, simple, and cheap kinetic-spectrophotometric method was used to investigate and determine the concentration of morphine in the mixture of real drug samples by using the rank annihilation factor analysis (RAFA) method. In the present work, the Marquis reagent was used as a simple and well-known reaction to obtain kinetic-spectrophotometric data of the RAFA method for morphine analyte in the mixture of morphine-heroin-codeine samples. In the first stage, the proposed method was checked with simulated data, and then two-dimensional kinetic-spectrophotometric data were recorded for the standard and mixture of unknown samples. Finally, using the RAFA method, the presence of the mentioned species in the mixture of unknown samples (morphine-heroin-codeine) was detected and its concentration was determined. The results showed that this method as an efficient, effective, and simple technique to determine the concentration of morphine in unknown samples mixture with a linear range of $6\times4\text{-}^{7-}10\times^{5-}10$M has excellent performance. To evaluate and confirm the accuracy of the proposed method, the measurement of morphine in the presence of the ternary mixture of morphine-heroin-codeine in the human urine sample was investigated. The results of this investigation showed that by adding values of 3×10^{-5} and 4×10^{-6} M morphine in the mixture of morphine-heroin-codeine sample, the percentage of recovery was obtained 96.7 and 102.5%, that these results confirm the accuracy of the RAFA method to measure morphine in the mixture of real drug samples.

Keywords: Rank annihilation factor analysis, Kinetic-spectrophotometric, Morphine, Marquis Reagent.

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Hyperspectral Imaging Combined with Multivariate Curve Resolution for Quantitation and Homogeneity Exploration of Active Pharmaceutical Ingredient in Pharmaceutical Products

Zahra Bolhassani[1], *Ali Aghaei*[2], *Hadi Parastar**[1]

[1]*Department of Chemistry, Sharif University of Technology, P.O. Box 11155-9516, Tehran, Iran*
[2] *Noor research educational institute (Tavan), Tehran, Iran*
E-mail addresses (Corresponding author): h.parastar@sharif.edu, aghaei@tavaninstitute.ir

ABSTRACT

In the past decade, the global pharmaceutical market has experienced significant growth, which unfortunately has led to an increase in the prevalence of substandard and falsified medicines. These counterfeit medications may contain insufficient or incorrect amounts of active pharmaceutical ingredients (APIs) [1]. To address this issue, pharmaceutical products now undergo various analytical tests to ensure their quality. Consequently, efforts are being made to develop faster and more intelligent methods [2]. One promising and increasingly utilized technique in pharmaceutical research and industry is Visible-Near-Infrared hyperspectral imaging (Vis-NIR-HSI). This method allows for the acquisition of both spatial and spectral information from an object [3]. Moreover, the multivariate curve resolution-alternating least squares (MCR-ALS) algorithm can be employed to provide distribution maps and pure spectra of all chemical compounds present in complex mixtures [4]. In this study, two sets of samples were prepared: one containing 32.26 to 80.65 %w/w of metformin hydrochloride and the other containing 20 to 80 %w/w of nitroglycerin with 10% lactose as the API. The data from these mixtures were captured using a Vis-NIR HSI device (400–1000 nm). Different unsupervised and supervised multivariate chemometric techniques, including principal component analysis (PCA), MCR-ALS, and partial least squares regression (PLS-R) were used to analyze the HSI images. The direct application of PLS-R on the images did not give satisfactory results for both metformin and nitroglycerin. However, the primary use of MCR-ALS to exploit pure component profiles gave surprising results for metformin (R^2=0.9951) and nitroglycerin (R^2=0.9976). On the other side, the mixing process plays a crucial role in the overall quality of pharmaceuticals, as it can significantly impact the homogeneity of the substances in their dosage form, affecting characteristics such as dissolution and stability. By creating distribution maps of each component by MCR-ALS, we were able to assess the homogeneity of each composition. In conclusion, this technique shows promise in determining the API content and checking its homogeneity in pharmaceutical products. Its potential application in the industry could help ensure the overall quality and efficacy of medicines in the market.

Keywords: Chemometrics, Hyperspectral Imaging, Active pharmaceutical ingredients, PLSR, MCR-ALS.

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Optimized fabrication of chitosan-hydroxy apatite (HAp/CS) nano hybrid for removal of nitrite from water samples

*Mohaddeseh Habibi, Mohammadreza Khanmohammadi Khorrami**

E-mail address (corresponding author): m.khanmohammadi@sci.ikiu.ac.ir

ABSTRACT

Chitosan can be used as an adsorbent to remove pollutants due to the presence of amino and hydroxyl groups, which can serve as the active sites, but typically suffers from low specific gravity and sensitivity to pH [1]. In order to improve chitosan's performance as an adsorbent, cross-linking reagents [2] are widely utilized. In this work. Chitosan/hydroxyapatite (HAp/CS) nanohybrid has been fabricated in an optimized synthesis condition to be employed for the removal of nitrite from water samples. The method was optimized using the design of experiments developing a three-factor, central composite design model. Particle size of the optimum nanohybrid was 17.1 nm. HAp/CS as an adsorbent hybrid was also characterized by X-ray diffraction and Fourier transform infrared spectroscopy to specify its morphology, functionality, and structure. In order to remove nitrite ions by the nanohybrid, cross-linked chitosan-apatite nanohybrid was prepared and the process was monitored by (UV-Vis) spectrophotometry. The UV-Vis spectrum of cross-linked chitosan-apatite nanohybrid suspension was recorded every 5 min to obtain and evaluate the analyte concentration. These spectra were applied as a data matrix while its rows were the time and its columns were wavelengths, to investigate concentration profile of nitrite. PCA revealed that there is one active component in system. After performing of EFA, decomposition is performed by an initial estimation of one of the concentrations or spectral profiles, utilizing a curve resolution method such as evolving factor analysis (EFA), resulted concentration profile was used as initial estimation. The resolved concentration profile obtained from MCR-ALS It is assumed that there is a bilinear relationship between data. Least squares (LS) calculation is error criteria [3].

Keywords: Chitosan/hydroxyapatite (HAp/CS), Nano hybrid- Optimization, MCR-ALS, Nitrite, CCD

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A novel study of pH-dependent optical properties of a water-soluble PNPG-PEG as a conjugated polymer nanoparticle to easy detection of dopamine: Applying MCR-ALS method

Mehri Razavi[1,2], *Mohsen Kompany-Zareh**[1,3], *Rabah Boukherroub*[2], *Maryam Khoshkam*[4]
[1]*Department of Chemistry, Institute for Advanced Studies in Basic Sciences, 45137-66731, Zanjan, Iran*
[2]*Univ. Lille, CNRS, Centrale Lille, Univ. Polytechnique Hauts-de-France, IEMN, Lille, France*
[3]*Department of Chemistry, Dalhousie University, 6274 Coburg Road, Halifax NS B3H 4R2, Canada*
[4]*Department of Chemistry, Faculty of Science, Mohaghegh Ardabili Univerity, Ardabil, Iran*
** Corresponding authors: Prof. Mohsen Kompany-Zareh,*
E-mail addresses (Corresponding author): kompanym@iasbs.ac.ir, mohsenkompany@dal.ca

ABSTRACT

This report is the first study on the coupling of UV-visible and fluorescence spectroscopic data from protein interacted with polyethylene glycol-functionalized poly (N-phenyl glycine) (PNPG-PEG) polymer in different pH values, applying multivariate curve resolution-alternative least-squares (MCR-ALS) algorithm. The obtained nanoparticles (BSA+PNPG-PEG NPs) are useful for sensitive dopamine (DA) detection at optimized pH value. Fabrication of conductive polymer nanoparticle (PNPG), using a two-step polymerization process, was followed by functionalization using PEG. Several characterization methods including XPS, SEM, TGA, FTIR, DLS, UV-vis absorption, and fluorescence spectroscopy confirmed the successful formation of PNPG-PEG NPs [1]. The polymer NPs were then combined with BSA (BSA+PNPG-PEG NPs, (complex I)) to produce a pH-sensitive complex, for presenting an easy, simple, and economical strategy to determine dopamine. Under the various range of pH (2.0, 8.0, and 10.0), in the first step, we applied of DA+ PNPG-PEG (complex II) for directly detect DA in aqua solation, but it does not obviously result. Then we applied of complex I the addition of dopamine to cause the complexed chemical system of DA+BSA+PNPG-PEG (mixture complex III). In pH value of 10.0 compared to the acidic and natural reaction matrix, it was found that the introduction of dopamine solution led to a remarkable increment of the emission intensity in complex III. To benefit from MCR-ALS, rotational ambiguities were reduced using non-negativity, selectivity, and equality constraints. MCR-ALS successfully resolved meaningful pure spectral and concentration profiles [2]. MCR-ALS technique resolved the bilinear data matrix and their resolved spectral and concentration profiles were applied to study DA in complex system (PNPG-PEG+BSA+DA (complex III)) at room temperature. According to the obtained percentage of explained variance (Expl var%) and LOF of the MCR-ALS method, the three meaningful chemical components were obtained for in the complex data (III) from the application of different pH values of 2.0, 8.0, and 10.0 on considered systems of UV-vis and fluorescence spectrum. In other words, the MCR-ALS methodology as an available statical method without any complex separation instruments, the simple, rapid, easy route can provide useful chemical information from overlapping spectrochemical peaks [3, 4].

Keywords: PNPG-PEG; pH; optical sensor; DopamineL MCR-ALS.

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A Comparative Kinetic Study on Electro-chemical Decolorization of some Dyes in Mixtures: Multivariate Hard Modelling Technique

*S. Maryam Sajjadi**

Lamerd Higher Education Centre, Lamerd City, Fars Province, Iran, 74341-67441

Email: Lsmsajjadi@gmail.com

ABSTRACT

In this study, kinetic electro-oxidations of four dyes were simultaneously evaluated on Ti/ ZnO-multi-walled carbon nanotubes anode [1]. The mixture of dyes includes acid red 33 (AR33), reactive orange 7 (RO7), acid yellow 3 (AY3) and malachite green (MG) and the kinetic processes were monitored spectrophotometrically. A time-spectral data was recorded in the time range 0 to 80 min and wavelength range of 220-700nm. The spectra of the analytes were severely overlapped in this wavelength range, a fact which prevents achieving the rate constants of the analytes using common univariate analysis. To overcome this problem, the time-spectral data was resolved by classical least squares method under known pure spectral profiles of the dyes, in turn, the kinetic profiles of the components were analyzed by hard modelling approach [2, 3]. The estimated rate constants of the dyes and their uncertainties were 0.0675((±0.0034), 0.0262 (±0.002), 0.0168 ($\pm 8.94\times 10^{-4}$) and 0.0158 ($\pm 4.95\times 10^{-4}$) for MG, AR33, AY3 and RO7, respectively. Indeed, the results revealed that MG is strongly degradable and the trend of the rate constants is as follows in descending order: MG > AR33 > AY3 > RO7.

Keyword: Signal overlapping, Multivariate analysis, Kinetic Electro-Oxidation Process, Azo dyes

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Comparison of GA-MLR and PSO-ANFIS methods in QSAR study of some derivatives of tricyclic pyridobenzo and *di*-pyrido-*di*-azepinones as HIV-1 inhibitors

Zahra Rostami, Saeid Azimi*

Department of Chemistry, Payame Noor University, 19395-4697, Tehran, Iran
E-mail address (corresponding author): *Rostami@pnu.ac.ir*

ABSTRACT

In this study, the inhibition effect of some derivatives of *tricyclic*-pyridobenzo and *di*-pyrido-*di*-azepinones as HIV-1 inhibitors using Quantitative Structure Activity Relationship (QSAR) is investigated. The study was performed on the extended series of 59 molecules of derivates of *tricyclic*-pyridobenzo and *di*-pyrido-*di*-azepinones as HIV-1 inhibitors. Combination of genetic algorithm- multiple linear regression (GA-MLR) and combination of particle swarm optimization algorithm- adaptive neuro-fuzzy inference system (PSO-ANFIS) was used to create the model as the linear and non-linear methods, respectively. In this study the results indicated that PSO-ANFIS method has the better results for prediction of the biological activity of new and non-synthesized *tricyclic*-pyridobenzo and dipyridodiazepinones derivatives.

Keywords: Tricyclic-pyridobenzo, di-pyrido-di-azepinones derivatives, HIV-1 inhibitors, QSAR, GA-MLR, PSO-ANFIS.

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Design and Evaluation of Novel Small Molecule Activators for AMPK: An In-silico Approach

*Saeid Azimi**, *Zahra Rostami*

Department of Chemistry, Payame Noor University, P. O. BOX 19395-3697, Tehran, Iran
E-mail address (corresponding author): s_azimi@pnu.ac.ir

ABSTRACT

AMP-activated protein kinase (AMPK) plays an important role in regulating energy homeostasis in eukaryotic cells. AMPK is an attractive therapeutic target for managing metabolic diseases such as type 2 diabetes and cancers[1-3]. Nowadays, In Silico study and evaluations are applied through virtual screening tools, such as molecular docking simulations and predictions of ADMET-related properties to investigate new potent activators for target proteins. The molecular docking simulation is performed to achieve the best binding affinity and docking scores. This is done by comparison between the standard recently reported activator and high-scoring selected ligands. Using data servers' libraries as PubChem, some similar compounds selected and simulation molecular docking has occurred. Active site was studied and newly selected ligands were applied to molecular docking simulation in active site and other active cavities in target protein. The results were evaluated and high quantities in binding affinities were selected as candidate ligands. Then prediction of ADMET related properties occurred using ADMETLab 2.0 and prediction results were compared with molecular docking results. Finally, 5-[[6-chloro-5-(3-methyl-1*H*-indol-5-*yl*)-1*H*-benzimidazol-2-*yl*]oxy]-2-methylbenzoic acid and 6-[2-(3-carboxy-4-methylphenoxy)-6-chloro-1*H*-benzimidazol-5-*yl*]-3-methylindole-1-carboxylic acid have best results and must be considerate as potent activator for AMP-activated protein kinase

Keywords: AMP-activated protein kinase, small molecule activator, in-silico design, ADMET, AMPK activator, type 2 diabetes.

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Highly efficient pH-responsive Ag @ Chitosan core shell nano particles for Drug Delivery and anti-human breast cancer properties

S. Esmaeili[*, a], *Y. Tajadod*[a], *Gh. Delpasand*[b]

[a] *Department of Chemistry, Faculty of Science, University of Guilan, Rasht, Iran*
[b] *Department of Biological Science, Rasht Branch, Islamic Azad University, Rasht, Iran*
E-mail address (corresponding author): esmaeili1989@webmail.guilan.ac.ir

ABSTRACT

This study reports developing novel smart drug delivery systems (DDS) that have great importance in anticancer therapeutics. we report the preparation and stabilization of silver nanoparticle as core, and chitosan dihydroxyphenyl acetamide as a shell. The Nano Core- shell was used as a nano carrier for doxorubicin (DOX) as anti-cancer drugs against MCF-7 human breast cancer cells. The nano core shell was designed to be sensitive to pH and it demonstrated a controlled drug release that can be able to distinguish between normal and cancer tissues.
At pH 7.8, the minimum content of drug release was observed for sample fabricated with variable contents of chitosan. At pH 4.3, the effect of chitosan content revealed that the rate of DOX release tends to decrease as its content increased. During two days, 97 % of the loaded DOX released from carriers containing high and low contents of chitosan, respectively. Besides, this Ag@Chitosan nano- core shell carrier shown pH-sensitive drug release. The morphology of the synthesized silver core-chitosan shell nanoparticles was observed by transmission electron microscopy (TEM) and X-ray diffraction (XRD) techniques, and showed a well-defined core-shell structure. [1,2].

Keywords: core shell, drug delivery, nano particle, breast cancer, doxorubicin.

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Modeling quantitative structure-property relationships to predict the environmental properties of some iodinated organic compounds

Zahra Rostami, Shima Ezzati*

Department of Chemistry, Payame Noor University, Hamedan, Iran
E-mail address (corresponding author): rostami@pnu.ac.ir

ABSTRACT

The purpose of this research is modeling and predicting the physicochemical and environmental properties of iodinated organic compounds theoretically and help to design and manufacture new compounds. In this article, an attempt has been made to model and predict the physicochemical properties of 43 iodinated organic compounds using multiple linear regression methods. In this study, more than 255 different topological indices were used and all of them reported in a data matrix. Multiple linear regression techniques were used to obtain a new quantitative structure-property relationship model with high statistical parameters to predict the properties of octanol-water partition coefficient, aqueous solubility, air solubility, vaporization enthalpy, solution enthalpy and normal boiling point of 43 organic iodinated compounds and then a genetic algorithm was applied to select suitable indices. This study shows that the genetic algorithm is very useful in quantitative structure-property relationship analysis and provides a new approach to building better models. The cross-sectional evaluation method of leaving an exit used in this study ensured that the implemented models have acceptable stability and validity. Also, the prediction ability of the model was confirmed by the external evaluation method.

Keywords: Quantitative Structure-Property Relationships (QSPR), environmental properties, iodinated organic compounds, linear regression, genetic algorithm, cross-sectional evaluation method.

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Molecular Docking of the natural phenolic acids with CDK1 in cervical cancer

*Tooba Abdizadeh**

Clinical Biochemistry Research Center, Basic Health Sciences Institute, Shahrekord University of Medical Sciences, Shahrekord, Iran
E-mail address (corresponding author): t.abdizadeh@gmail.com

ABSTRACT

Cervical cancer (CC) is a major cause of cancer death among women worldwide [1]. Cyclin-dependent kinase 1 (CDK1) is a key cell cycle regulator involved in cell cycle maintenance. CDK1 overexpression is associated with cancer and making it a promising target for cancer therapy [2]. In this study, natural phenolic acids including gallic acid, protocatechuic acid, quinic acid, and syringic acid were obtained from PubChem server as 3D structures in SDF files. The 3D structure of CDK1 protein (PDB ID: 6GU6) was retrieved from Protein Data Bank (PDB). Then, molecular docking of these compounds was performed using AutoDock software according to free energy binding (kcal/mol) and ligand interactions with CDK1 protein were showed with UCSF Chimera. The docking results showed that these compounds exhibited the good binding affinity (-9.98 to -10.62 kcal/mol) with CDK1 protein and passed Lipinski's "rule of five". Also, these natural phenolic acids were capable of interacting with Leu83, Asp86, Ile10, Gln132, Lys33, and Lys89 by hydrogen binding and hydrophobic interaction, as critical residues involved in enzyme activity. Therefore, these compounds could be considered as potential inhibitory compound against CDK1 protein in cervical cancer.

Keywords: Phenolic acids, Molecular docking, CDK1.

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Identification of BACE1 inhibitors for Alzheimer's disease using molecular docking method

*Tooba Abdizadeh**

Clinical Biochemistry Research Center, Basic Health Sciences Institute, Shahrekord University of Medical Sciences, Shahrekord, Iran
E-mail address (corresponding author): t.abdizadeh@gmail.com

ABSTRACT

Alzheimer's disease (AD), is a neurodegenerative, progressive, and fatal disorder, is the leading cause of dementia threatening the elderly population [1]. BACE1, a candidate β-secretase enzyme, initiates the pathogenesis of Alzheimer's disease (AD) through the production of amyloid β peptide (Aβ), which serves as a potential therapeutic target [2]. The 3D structure of BACE1, with the PDB ID of 4IVS and resolution of 2.64 Å was retrieved from Protein Data Bank (www.rcsb.org). The natural isoprenylated coumarins including mesuol, and isomesuol were obtained from the PubChem server as 3D structures in SDF files. After validation, these compounds were investigated by docking studies and the compounds with best docking score have been selected. The binding energy and main interactions between the mesuol and isomesuol and BACE1 binding pocket were investigated in detail. The mesuol and isomesuol had a good capability to block the BACE1 with the binding affinity of -10.79 and -10.44 kcal/mol. In addition, these compounds passed Lipinski's "rule of five". These findings suggest that these compounds could be used for BACE1 inhibition in the Alzheimer's disease, after more investigation.

Keywords: Mesuol, Isomesuol, Isoprenylated coumarins, Molecular docking, BACE1

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Three-Dimensional Quantitative Structure Activity Relationship, Molecular Docking and Molecular Dynamics of imidazo[4,5-b] pyridine Derivatives as PDE Inhibitors

Fatemeh Dastafckan[1], Jahan B Ghasemi[2*], Mehdi Jafari[3], Tahereh Momeni Isfahani[3]*

[1] Department of Polymer Science, Iran Polymer and Petrochemical Institute, P.O. Box 14965-115, Tehran, Iran*
[2] Drug Design in Silico Lab, School of Sciences, Chemistry Faculty, University of Tehran, Teheran, Iran*
[3]Department of Chemistry, Arak Branch, Islamic Azad University, Arak, Iran
E-mail address (corresponding author): mahtab7683@gmail.com

ABSTRACT

The Phosphodiesterase (PDE) enzymes adjust the intracellular signaling of cyclic adenosine 3′-5′-monophosphate (cAMP) and cyclic guanosine 3′-5′-monophosphate (cGMP) by cleaving their phosphodiester bonds and converting them to AMP and GMP. Whereas 10 out of 11 PDE isoforms have splice variants in the CNS, it has been postulated that having the means to control the activity of a particular PDE isoform in the CNS could be helpful in a range of neuropsychiatric and neurodegenerative diseases such as psychosis, depression, Alzheimer's disease, Parkinson's disease, etc. [1].

In this work, a three-dimensional quantitative structure-activity relationship(3D-QSAR) was used to establish models of 65 imidazo[4,5-b] pyridine derivatives to explore the quantitative structure-activity relationship as PDE inhibitors [2]. The effect of the docked conformer of each molecule in the enzyme cavity was investigated on the predictive ability and statistical quality of the produced models. Furthermore, a molecular dynamics simulation was applied to recognize end having better insight into the molecule's Hype of molecular interactions. A few key residues (PHE719, GLN 716, SER 667, TRY 683) at the active site of PDE were identified.

Keywords: 3D-QSAR, molecular dynamics simulation, molecular docking, inhibitor, PDE, imidazo[4,5-b] pyridine.

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Molecular docking and receptor-based QSAR studies on inhibitors of PARP-1 as a potential target for cancer therapy

Narjes Najafi[*], *Mohammad Hossein Fatemi*

Faculty of Chemistry, University of Mazandaran, Babolsar, Iran
E-mail address (corresponding author): n.najafi1366@yahoo.com

ABSTRACT

One of the important molecular targets in antitumor drug discovery is Poly ADP-ribose polymerase-1 (PARP-1) enzyme. PARP-1 is one of the key members of DNA repair enzymes that is responsible for the repair of DNA single-strand breaks. Inhibition of PARP-1 has been demonstrated to be a promising strategy to selectively kill tumor cells by targeting DNA repair pathway [1-3]. In the present report, efficient linear and non-linear methods including multiple linear regression (MLR) and support vector machine (SVM) used to develop and establish quantitative structure-activity relationship (QSAR) models capable of predicting half-maximal inhibitory concentration (IC_{50}) values of phthalazinones derivatives as effective PARP-1 enzyme inhibitors. The data set consisted of 77 chemicals that were divided into two subsets of training and test set through Kennard-Stone algorithm.

Forward MLR method was used for reduction of the number of descriptors and feature selection. In this method, the variables are added to MLR model step by step noting the effect on the R value of the model. By applying this method eight descriptors selected and used as input variables in developing of MLR and SVM models. Among these models, SVM model with eight selected molecular descriptors was showed better statistical parameters ($R_{train} = 0.947$, $RMSE_{train} = 0.324$, $Q^2 = 0.728$, $R_{test} = 0.921$, $RMSE_{test} = 0.393$). As a complementary method, molecular docking was used to study the mechanism of interactions between ligands and protein in the active site. Here, all derivatives were docked and the differences in the structures of compounds are exhibited in docking study.

Keywords: Poly ADP-ribose polymerase-1 (PARP-1), QSAR, Support Vector Machine (SVM), Multiple Linear Regressions (MLR), Molecular docking.

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ADME and PASS prediction studies of six different Schiff bases of cinnamaldehyde derivatives

Pardis Roozbahani[1], *Ali Reza Akbarzadeh*[2], *Mehdi Salehi*[1*]

[1]*Department of Chemistry, Iran University of Science and Technology, P.O. Box: 16846-13114, Tehran, Islamic Republic of Iran*
[2]*Department of Chemistry, Faculty of Science, Semnan University, P.O. Box: 35195-363, Semnan, Islamic Republic of Iran*
E-mail address (corresponding author): msalehi@semnan.ac.ir

ABSTRACT

Cinnamaldehyde is an aromatic aldehyde which is one of the most basic compounds in cinnamon oil. A wide range of studies about bioactive properties in cinnamaldehyde have indicated that it possesses several medicinal and biological activities, such as anticancer, antibacterial, antioxidant, anti-inflammatory, antifungal, etc. [1]. During the time-consuming processes of drug discovery and development, a large number of molecular structures are evaluated against a range of parameters. It contributes to effective selection of chemicals for synthesis, testing, and promotion. The ultimate goal such process is to identify the chemicals with the best chance of transformation. Hence, to study the essential pharmacokinetic properties of the compounds, in-silico methods are a valid elective to primary experiments. Therefore, this can be a logical way to decrease labor and related costs [2, 3]. In this study, six different Schiff base cinnamaldehyde compounds derivatives were collected from the corresponding cinnamaldehyde and ADME (absorption, distribution, identification of the metabolism and excretion) properties of the compounds were investigated. For this purpose, the web-based SwissADME has been employed. SwissADME is a validated free web tool to predict and evaluated the pharmacokinetics, drug-likeness and medicinal chemistry friendliness of small molecules. In-silico ADME prediction of compounds represents a potential to develop as good oral drug candidates. A molecule that is probably called an active oral drug candidate should not exhibit more than one violation of the following four Criteria: logP (water-ethanol partition coefficient) ≤ 5, molecular weight ≤ 500, no hydrogen bond acceptors ≤ 10 and number of hydrogen bond donors ≤ 5. These Schiff base compounds follow the criteria of orally active drugs and thus, can be considered as oral drug candidates. Furthermore, the topological polar surface area values of compounds ranges from 35.85 to 81.78 [4-9]. Moreover, some biological activities of the compounds were predicted by PASS (Prediction of Activity Spectra for Substances) online software. This computer program predicts the biological activity of a compound on the basis of its structural formula [10-12]. Two studied compounds represented the maximum probable ($p_a = 0.457$ and 0.432) antineoplastic (multiple myeloma) activity, while two other compounds show the highest probable (p_a=0.499 and 0.567) antihypoxic activities among the other compounds. Furthermore, the last compound demonstrates a high antiprotozoal (amoeba) property (P_a= 0.486) compared to the other compounds. What is more, one of the compounds which has the P_a value equal to 0.529 shows the highest antimycobacterial activity [6-9].

Keywords: Schiff base, Cinnamaldehyde, SwissADME, PASS online.

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Investigating the potential of anti -inflammatory properties of Fluphenazine by using statistical model of molecular docking and its application for drug design

Monir Shalbafan[*1], *Mohamad Hasan Sadeghpour*[2], *Masoumeh Shalbafan*[3]

1. Dept of chemistry, Imam Khomeini International University, Qazvin, Iran
2. Dept of Industrial Management, Branch, Qazvin Islamic Azad University
3. Dept of Materials Engineering, Imam Khomeini International University, Qazvin
E-mail address (corresponding author): m.shalbafan2012@yahoo.com

Abstract

The main cause of inflammation is the protein Cyclooxygenase-2 (COX-2) known as the major prostaglandin synthetase enzyme [1]. Thymoquinone, which is found as a phytochemical compound in Nigella Stiva plants, has an anti-inflammatory property. Fluphenazine is a typical antipsychotic of the phenothiazine class .Its mechanism of action is not entirely clear, but is believed to be related to its ability to block dopamine receptors [2]. In this paper, the molecular docking process was carried out by employing the Autodock 1.5.6 method that was using the Lamarckian genetic algorithm as the score function. The lower the value of ΔG is indicated the better binding affinities between the target and the novel ligand molecule. The results from the molecular docking study showed that Fluphenazine and thymoquinone is bound strongly to the active site region of COX-2 with binding energy of -7.8 and -6.1, respectively. It has been found that Fluphenazine has a more powerful inhibitory effect on COX-2, so it can be used as a potential anti-inflammatory for drug design.

Keywords: Molecular docking, Fluphenazine, binding energy, anti –inflammatory, Cyclooxygenase.

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DFT Study and NBO Analysis on Conformers of 1,3,2-Dithiaphosphane -2-Sulfide derivatives

Nasrin Masnabadi[*]

Department of Chemistry, Roudehen Branch, Islamic Azad University, Roudehen, Iran

E-mail address (corresponding author): masnabadi2009@gmail.com; Masnabadi@riau.ac.ir

ABSTRACT

Stereoelectronic interactions associated with Generalized anomeric effect (*GAE*) and electrostatic effect on the conformational behaviors of 2,5,5-trimethyl-1,3,2-dioxaphosphinane 2-sulfide (**1**), -dithiaphosphinane 2- sulfide (**2**) and -diselenaphosphinane 2- sulfide (**3**) were investigated using DFT (Density Functional Theory) method. These compounds have been analyzed by means of DFT method and natural bond orbital (NBO) interpretation. These compounds were fully optimized with DFT: B3LYP method using 6-311+G** and 6-31G** basis sets. Both basis sets showed that the Gibbs free energy difference values ($\Delta G_{eq\text{-}ax}$) between the axial and equatorial conformers decreases from compounds **1** to **3**. Based on results obtained from the NBO analysis, stereoelectronic effect corresponding to the $n_{ax}X\rightarrow\sigma^*$P-C electron delocalization in the equatorial conformations and $n_{ax}X\rightarrow\sigma^*$P-S in the axial conformations have the highest level of stability energy, where X= [O, S, Se]. Stereoelectronic effect through the $n_{ax}X\rightarrow\sigma^*$P-S interaction is of major relation or impressive to demonstrate conformational preference in the specific X─P(S)Me─X segment. Our results show that the *GAE* is more considerable for the justification of the conformational preferences of compounds than the other factors [1-2].

Keywords: Conformational Preferences, Stereo electronic interactions, Electron delocalization, Stability energy, DFT (Density Functional Theory), Dioxaphosphinane.

References:

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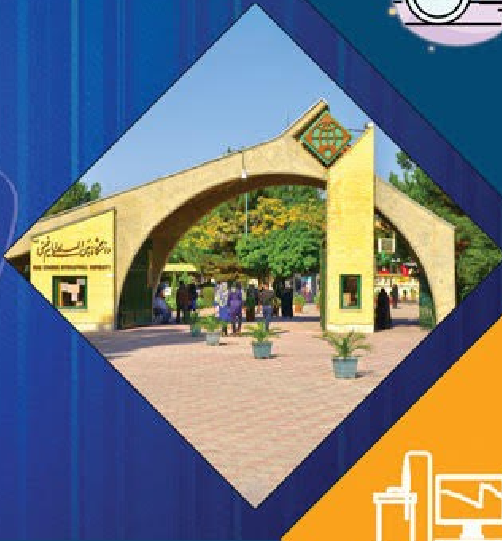
9th Iranian Chemical Society Biennial Chemometrics Seminar

Wednesday, October 18, 2023

Thursday, October 19, 2023



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Faculty of Science

Imam Khomeini International University, Qazvin, Iran

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