In The Name of God

Program Book proceeding of the Sixth Iranian Biannual Chemometrics Seminar

26-27 Oct. 2017 University of Mazandaran Babolsar, Iran

WELCOME MESSAGE FROM THE SEMINAR'S CHAIR

Mohammad Hossein Fatemi
Chair of 6th Iranian Biannual Chemometrics Seminar

It is our pleasure to welcome you to the Sixth Iranian Biannual Chemometrics Seminar (SIBCS) at university of Mazandaran on 26th and 27th October 2017. This seminar, undoubtedly, is the largest gathering of researchers in the field of analytical chemistry in the chemometrics in Iran.

The organization committee is endeavoring to bring together academics in the outstand evolving field of chemometrics from all parts Iran to exchange idea, discover opportunities and future perspectives. The scientific program will feature to plenary talks, 7 invited talks and 13 accepted talks and 72 posters which are distributed in two days.

Your active participation in the intriguily discussions during this major event will be quite valuable and highly appreciated.

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Professor of Analytical chemistry
University of Mazandaran

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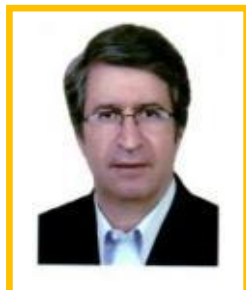
با سلام خدمت اساتید محترم و دانشجویان عزیز

علم کمومتریکس در ایران بسیار پیشرفته و تاثیر گذار در پیشبرد این علم در جهان بوده است .عوامل موثر در این پیشرفت را می توان اساتید برجسته، کارگاههاي آموزشي کمومتریکس دردانشگاه تحصیلات تکمیلی علوم پایه زنجان و دیگر نقاط کشور، همکاري اساتید ایراني با اساتید برجسته بین المللي، سمینارهاي کمومتریکس و وجود دانشجویان علاقه مند به علم و علم کمومتریکس در ایران دانست . اینجانب در موارد فوق نقش چشمگیري نداشته ام و فقط در بین افرادي بوده ام که در شروع کمومتریکس در ایران فعالیت داشته ام و لذا از محبت کمیته کمومتریکس ایران بسیار سپاسگزارم. اینجانب بسیاری از مطالب کمومتریکس را در کارگاههاي آموزشي برگزارشده در دانشگاه تحصیلات تکمیلی علوم پایه زنجان یاد گرفتم . بدون شك همه اساتید محترم و دانشجویان عزیز در نقاط مختلف کشور در پیشبرد این علم موثر بوده اند و وظیفه همه ماست که از اساتید محترم کمومتریکس که همواره با تمام توان خود در خدمت مردم و ارتقاء علمي کشور مي باشند قدرداني نمائیم .اینجانب به نوبه خود از این عزیزان سپاسگزارم و براي همه آرزوي سلامتي و موفقیت هاي بیشتر را دارم .

با تقدیم احترام
تقي خیامیان
مهر 96

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Thursday

Time Schedule of 6th Iranian Biannual Chemometrics Seminar

First Session	
Time	Program
8:00-9:00	Registration and Reception
9:00-9:10	Reading the Qur'an and playing the anthem
9:10-9:20	Presentation of the seminar secretary's report and greetings
9:20-9:40	Speech by Dr. Shamsipour, head of the Chemical Society of Iran
9:45-10:00	Speech by Dr. Naseri, Chairman of the Chemometrics Committee
10:00-10:30	Coffee break

Seconde Session: Oral presentations		
Chairmen: Dr. Kompany Zareh and Dr. Ghasemi		
Time	Title	Presenter
10:30-11:00	A Generalized Constraint for Achieving the Unique Solution in Self Modeling Curve Resolution Methods based on Duality Principle	Dr. Abdollahi
11-11:30	Big (Bio)Chemical Data Mining Using Chemometric Methods: A Need for Chemists	Dr. Parastar
11:30-11:50	Quantitative Structure Sequence Modeling of Angiotensin-I-Converting Enzyme Peptide Originated from Milk Using Amino Acid Indices based on Quantum Topological Molecular Similarity	Maryam Bahadori
11:50-12:10	QSAR classification models for Bcl-2 and Bcl-xL inhibitors using Supervised Kohonen maps and Linear Discriminant Analysis methods	Marzieh Sadat Neiband
12:10-13:30	Pray and Lunch	

Thursday

	Third Session: Oral presentations		
	Chairmen: Dr. Naseri and Dr. Parastar		
Time	Title		Presenter
13:30-14:00	Chemometrics-Assisted Resolving of Net Faradaic Current Contribution from Total Current in Electroanalytical Methods		Dr. Hemmateenejad
14-14:30	Systems pharmacology		Dr. Gharaghani
14:30-14:50	Pushing back the limits in the analysis of mass spectrometry images of biological tissues by using parallel factor analysis		Mahsa Rezaiyan
14:50-15:10	Untargeted GC×GC-MS metabolic profiling of lettuce exposed to contaminants of emerging concern using wavelet transform-multivariate curve resolution followed by partialleast squares-discriminant analysis		Saeed Moayedpour
15:10-16	Coffee break and Poster presentation		

	Fourth Session: Oral presentations		
	Chairmen: Dr. Gharaghani and Dr. Abdollahi		
16:00-16:30	A reasonable compromise between the magnitude of L_1 and L_2 norms in multivariate curve resolution for deconvolution of GC-MS data		Dr.Mani
16:30-16:50	Joint approximate diagonalization of eigenmatrices (JADE) as new approach for analysis of hyphenated and comprehensive two-dimensional gas chromatographic data		Maryam Zarghani
16:50-17:10	Detection of gasoline adulteration using colorimetric sensor array based on Au\Ag bimetallic nanoparticles and pattern recognition methods		Mohammad Mahdi Bordbar
17:10-17:30	Study of monoprotic acid–base equilibria in methanol-water association using spectrophotometry and equilibrium modeling		Saheleh Sheikhizadeh

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Friday

Fifth Session: Oral presentations		
Chairmen: Dr. Hemmateenejad and Dr.Mani		
Time	Title	Presenter
8:30-9:00	Common Factor Analysis	Dr.Kompany Zareh
9:00-9:20	Particle swarm diagonalization of fourth order cumulants tensor for estimation of least dependent components	Saeed Bagheri
9:20-9:40	The role of chemometrics in metabolomics studies	Maryam Khoshkam
9:40-10:00	A generalized multivariate method for quantification in gray systems	Mahdiyeh Ghaffari
10:00-10:50	Coffee break and Poster presentation	
Sixth Session: Oral presentations		
Chairmen: Dr. Masoum and Dr. Niazi		
10:50-11:20	Optimization of preconcentration and extraction processes by single and multi-response experimental design	Dr.Naseri
11:20-11:40	Investigating error structure effect on possible solutions in the three-way models	Nematollah Omidikia
11:40-12:00	Model based design of experimental procedures for efficient investigation of some chemical equilibria	Reza Lotfi Khatoonabadi
12:00-12:20	Chemometrics description and systematic investigation of measurement error in smartphone based spectrometer	Fereshteh Matinrad
Pray and Lunch		

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Posters

A Generalized Constraint for Achieving the Unique Solution in Self Modeling Curve Resolution Methods based on Duality Principle

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There is a natural duality between the row and column vector spaces of the data matrix using minimal constraints. First time Henry [15] has introduced the duality principle in chemometrics and later Rajkó [16] showed that there is a natural duality between the row and column vector spaces of a bilinear data matrix using only the non-negativity property of data set. It is remarkable that this mathematical relation between row and column space provides an efficient tool to transfer the information of the considered space to the dual space. The duality concept is a general principle that can be formulated in an easy way.

Simply the duality principle states that each data point corresponds to one special directed hyper-plane in the dual space. This relation can be used for any point in the considered space. Thus, a unique solution as a point fixes a unique directed hyper-plane as its dual subspace. Hence the conditions for achieving the unique solution can be studied simply based on this general principle. Undoubtedly, the necessary condition to get a unique solution is the definition of the directed hyper-plane in the dual space. So according to this concept, there is a generalized constraint for achieving the unique solution.

We have shown that implying constraints like trilinearity, known values and local rank constraint can be interpreted based on the duality principle. Similarly, we have explored that other conditions which result in the unique solution such as extracting the net analyte signal and resolution theorem conditions just fulfill the duality principle.

References:

[1] R.C. Henry, Duality in multivariate receptor models, Chemometrics and intelligent laboratory systems, 77 (**2005**) 59-63.

[2] R. Rajkó, Natural duality in minimal constrained self modeling curve resolution, J. Chemom., 20 (**2006**) 164-169.

Big (Bio)Chemical Data Mining Using Chemometric Methods: A Need for Chemists

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ABSTRACT

Large and complex chemical data sets generated by modern analytical technologies have led to the so-called Big (Bio)Chemical Data (BBCD) era [1]. These data sets can be produced using modern analytical instruments such as multi-dimensional chromatography, high-resolution and multi-dimensional spectroscopy, hyperspectral imaging and DNA/RNA microarrays [2]. These huge data sets are difficult to manage and analyze using conventional statistical methodologies and software tools [3]. Chemometric methods have shown potential to analyze BBCD especially in omics sciences and chemical toxicology/drug discovery [4]. Therefore, this contribution aims to demonstrate abilities to analyze BBCD with multivariate chemometric methods and to show some of the more important challenges of modern analytical research. In this regard, the capabilities and versatility of chemometric methods will be discussed in light of the BBCD challenges that are being encountered in chromatographic, spectroscopic and hyperspectral imaging measurements, with an emphasis on their application to omics sciences. In addition, insights and perspectives on how to address the analysis of BBCD are provided along with a discussion of the procedures necessary to obtain more reliable qualitative and quantitative results. In this work, the importance of Big Data and of their relevance to (bio) chemistry is first discussed. Then, analytical tools which can produce BBCD are presented as well as some basics needed to understand prospects and limitations of chemometric techniques when they are applied to BBCD are given. Finally, the significance of the combination of chemometric approaches with BBCD analysis in different chemical disciplines is highlighted with some examples.
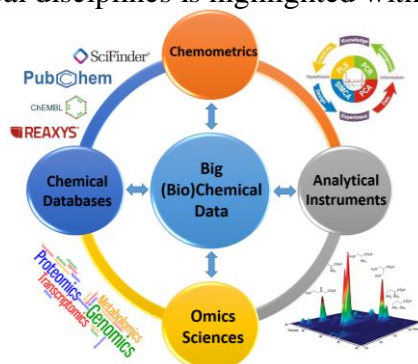
Keywords: Big Data; Chemometrics; Chromatography; Mass Spectrometry; Omics Science.

References:
[1] Gibb, C., *Nat. Chem.*, **2013**, 5, 248- 249.
[2] May, J.C., McLean, J.A., *Ann. Rev. Anal. Chem.*, **2016**, 9, 387-409.
[3] Tetko, I.V., Engkvist, O., Koch, U., Reymond, J.L., Chen, H., *Mol. Informatics,* **2016**, 35, 615-621.
[4] Martens, H., *J. Chemom.*, **2015**, 29, 563-581.

Quantitative Structure Sequence Modeling of Angiotensin-I-Converting Enzyme Peptide Originated from Milk Using Amino Acid Indices based on Quantum Topological Molecular Similarity.

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ABSTRACT

Numerous casein and whey protein-derived angiotensin-I-converting enzyme (ACE) inhibitory peptides/hydrolysates have been identified. Clinical trials in hypertensive animals and humans have shown that these peptides/hydrolysates can bring about a significant reduction in hypertension[1].

In this work, quantum topological molecular similarity (QTMS)amino acids indices [2,3] were utilized in QSAR/ QSAM studies to predict the activity of a set of milk-driven peptides with ACE property. To show the importance of the studied peptides it should be noted that Casokinins and lactokinins which are Casein and Whey Protein-derived ACE inhibitory peptides of milk respectively, have special importance in pharmaceutical industry as the pharmaceutical peptides. Besides they consist of numerous sequences of different lengths and with different IC_{50} values. In the current project, by combination of QTMS descriptors with Auto cross covariance (ACC) methodology[4] , the QSAM model was built and evaluated to predict the pIC_{50} value of ACE peptides derived from Bovine Casein and Whey with different number of residues. The model established an acceptable relationship between the selected variables and the pIC_{50} of the peptides for example for casein data set R^2_{train}, R^2_{CV} and R^2_{test} were obtained equal to 0 .85, 0.81 and 0.82 respectively.

For estimating performance of our proposed method and its regression models, different hypertension mammals' peptides sequences of casein and whey were obtained from human, goat, bovine and sheep. In this regard, each sequences were broken virtually by trypsin and chymotrypsin enzyme. After ACC preparation, pIC_{50} value of each peptide was estimated by using the suggested QSAM models to predict and synthesize new peptides to control hypertension disease as pharmaceutical targets.

Keywords: angiotensin-I-converting enzyme (ACE), quantum topological molecular similarity, Casokinins, lactokinins, Auto cross covariance, Amino acid

References:
[1]   L. Sciences, È. Milchforschung, È. Chemie, R.J. Fitzgerald, H. Meisel, Milk protein-derived peptide inhibitors of angiotensin-I-converting enzyme, (2000) 33–37.
[2]   S. Yousefinejad, B. Hemmateenejad, A.R. Mehdipour, New autocorrelation QTMS-based descriptors for use in QSAM of peptides, J. Iran. Chem. Soc. 9 (2012) 569–577. doi:10.1007/s13738-012-0070-y.
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QSAR classification models for Bcl-2 and Bcl-x$_L$ inhibitors using Supervised Kohonen maps and Linear Discriminant Analysis methods

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ABSTRACT

Bcl-2 and Bcl-X$_L$ are key apoptosis regulators whose their inhibition is a very attractive strategy for cancer therapy [1-3]. The aim of this study was to apply linear and nonlinear QSAR classification approaches to classify of Bcl-2 and Bcl-X$_L$ targets from Binding database. To this end, we created a large database of 1374 molecules which was divided into the active and inactive classes on the basis of their activity values. To classify the data set, molecules were categorized into four classes: Class 1: active selective inhibitors of Bcl-2; Class 2: active selective inhibitors of Bcl-x$_L$; Class 3: inactive compounds for Bcl-2, and Class 4: inactive compounds for Bcl-x$_L$. The classification models of Bcl-2 and Bcl-x$_L$ inhibitors were proposed in two different ways: 1) Development of an active-active classifier for separating active inhibitors of Bcl-2 from active inhibitors of Bcl-x$_L$. This model promoted the design of selective inhibitors and the extraction of important pharmacophores which induced selectivity for Bcl-2 or Bcl-x$_L$ targets. 2) Development of an active-inactive classifier, that identified the key structural for differentiating active inhibitors of Bcl-2 and Bcl-x$_L$ from inactive ones. The general aim of the classification models discovered a discriminatory hyperplane in the feature space to facilitate separation active from inactive inhibitors of Bcl-2 and Bcl-x$_L$ and helped to design selective and potent inhibitors. The genetic algorithm (GA) was used to select most efficient subsets of the molecular descriptors. The model containing eight descriptors based on the GA- supervised kohonen maps (SKM) showed a better predictive ability than GA- linear discriminant analysis (LDA). The prediction accuracy of the training set was 83.9%, 91.8%, 82.5% and 79.4% for SKM, and 82.4%, 80.7%, 80.3% and 69.9% for LDA, respectively. The comparison study show that GA-SKM method can be used as a powerful modeling tool For classification molecules according to their activity values and therapeutic targets.

Keywords: Bcl-2, Bcl-x$_L$, Supervised Kohonen maps, linear discriminant analysis

References:
[1] Adams J, Cory S. Oncogene 2007, 26, 1324–1337.
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Chemometrics-Assisted Resolving of Net Faradaic Current Contribution from Total Current in Electroanalytical Methods

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ABSTRACT

Total current in the electroanalytical data is assumed to be consisting of three main constituents: faradaic current, step charging current and induced charging current. Both charging currents can cause an interfering effect on precise determination of faradaic currents, and hence insert direct effects on sensitivity and detection limit of the electroanalytical techniques. Despite the widespread techniques introduced until now, the extraction of the net faradaic current from total current still remains a challenge. By using multivariate curve resolution-alternating least square (MCR-ALS) as a powerful curve resolution-based chemometrics method, a straightforward method has been introduced for resolving faradaic current from the two types of charging currents (step charging current and induced charging current) in single potential step and staircase cyclic voltammetric methods [1]. By simultaneous analyses of the current data matrices for different electrochemical systems, the three sources of current were successfully identified and their contributions in the total signal were easily calculated. We show that the suggested method can be used to estimate the cell-time constant. Also, by monitoring the changes in the net faradaic current as function of the concentration of analyte, one can derive calibration curve at early time of experiment with higher sensitivity comparing to conventional method [2]. Moreover, this method allowed us to investigate the effects of the type of electrode and the nature of supporting electrolyte on the contribution of charging current in total current [3].

Keywords: Electroanalytical, Chemometrics, Faradaic current, Charging current

References:
[1] Safavi, A., Hemmateenejad, B., Honarasa, F., Analytica Chimica Acta, **2013**, 766, 34-46.
[2] Hemmateenejad, B., Safavi, A., Honarasa, F., Journal of Electroanalytical Chemistry, **2015**, 755, 221-227.
[2] Tashkhourian, J., Hemmateenejad B., Ahmadpour, S, Talebanpour-Bayat, E., Journal of Electroanalytical Chemistry, **2017**, In press.

Systems Pharmacology

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ABSTRACT

The "one-target, one-drug, one-disease" model has long been the standard strategy for discovering new drugs in pharmaceutical research. In spite of the fact that this paradigm allowed discovering new drugs, a meaningful decrease in the rate of new drug candidates has been observed. In the last decade, many failures in drug development have occurred in the clinical trial stage, and the number of new drugs approved by the US Food and Drug Administration's (FDA) has decreased. The main reason for this is that, whereas the multiple activities of drugs against several targets might be beneficial, it can also lead to dramatic side effects and toxicity. Nowadays increasing evidence that several drugs exert their biological effects through interactions with multiple targets is boosting the development of new research such as systems polypharmacology and chemogenomics [1]. Therefore the purpose of drug discovery has changed from one-drug, one-target strategy to a multi-drug, multi-target approach by systems pharmacology [2]. Systems pharmacology is the application of network biology principles to the field of drug discovery. Systems pharmacology seeks to understand how drugs affect the human body as a complex biological system (on specific pathways, on different cell types and in different tissues/organs/diseases). The complex biological system may include drug-protein, protein-protein, genetic, signaling and physiological (at cellular, tissue, organ and whole body levels). It uses bioinformatics and statistical techniques to integrate and interpret these networks. In this lecture, I will describe the current state of multi-target drug discovery and the concepts of systems pharmacology, drug repurposing, polypharmacology, chemogenomics, and phenotypic screening.

Keywords: Systems pharmacology, polypharmacology, chemogenomics

References:
[1] Hopkins, A.L. Nat. Chem. Biol.,**2008**, 4, 682-690.
[2] Medina-Franco, José´ L., Giulianotti, Marc A., Welmaker, Gregory S., Houghten, Richard A., Drug Discovery Today, **2013**, 18, 495-501.

Pushing back the limits in the analysis of mass spectrometryimagesof biological tissues by using parallel factor analysis

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ABSTRACT

For much of the past decade, hyperspectralimaging (HSI) has been an area of active research and development which has been introduced in many applications in chemistry, medicine, agriculture, mineral exploration, and environmental monitoring.Mass spectrometry imaging (MSI)is one of the most powerful HSI techniques that extends the capability of traditional imaging techniques by obtaining spatial images of a sample at a series of (>100) continuousmass to charge ratios (m/z)[1].A MSIimage is a three-dimensional (3D) hyperspectralcube which is composed of vector pixels containing spectral information (of m/z values) as well as two-dimensional spatial information (of *x*rows and *y*columns).Due to the complexity of MS images, chemometric methods have shown potential forthe analysis of MSI data [2]. In the present contribution, a chemomtricstrategy based on binning approach for image compression and parallel factor analysis (PARAFAC) [3] for image resolution was developed for analysis of MS images obtained from different sections ofmouse lung.Due to the huge size of MS image of mouse lung sections(10 billion elements of 49×132 pixels and 500000 m/zvalues), images were compressed using binning approach in m/z direction (bin size=0.275) as the most common compression way. In this way, the number of elements was reduced from 10000 million elements to 1.2 million ones ($49 \times 132 \times 6000$)which is approximately 1% of the original size. Then, the number of components in the analyzed section was determined using core consistency diagnostics (CORCONDIA)which was 10 in this case. Then, the trilinear model assumption of the data was tested using singular value decomposition (SVD) of the row-and column-wise augmented data. The results confirmed the trilinearity of the image cubes. Therefore, PARAFAC was used for image resolution with GRAM/DTLD as initial estimates to start ALS optimization. Also,non-negativity constraintwas applied tothreedatamodes[3]. Using this method, both spatial distribution and spectral information of analyzed samples wereobtainedwith lack of fit (LOF) values below 10%.The 2D distribution maps for different components were then obtained using a post-processing step.

Evaluation of the results showedthree different lung regions based on differences in resolved mass spectra anddistribution maps.These three regions were related to external membrane of the lung, parenchyma region and blood vessels in the lung. Finally, the results of this study were compared with multivariate curve resolution-alternating least squares (MCR-ALS) which was the aim of previous studies [2]. Inspection of the results showed the equivalence of the results of both methods. It is concluded that combination ofMSIand advanced data analysis tools suchas PARAFAC has allowed the extraction of valuableinformation from a highly complex massive datasetlike mouse lung.

Keywords: Chemometrics,Hyperspectral imaging,Mass spectrometry imaging; Parallel factor analysis.

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Untargeted GC×GC-MS metabolic profiling of *lettuce* exposed to contaminants of emerging concern using wavelet transform-multivariate curve resolution followed by partial least squares-discriminant analysis

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ABSTRACT

Metabolomics is systematic study of metabolic profiles, their composition, and changes in metabolome caused by genetical, environmental, nutritional, or other factors. Thus, it has important role in detecting potential biomarkers in various samples. Contaminants of emerging concern (CECs), including pharmaceuticals and personal care products, are increasingly being detected at low levels in irrigation waters and cause significant reproductive effects. Presence of CECs in irrigation waters lead to changes in plant's metabolome in order to adapt to environmental stressors [1]. However, measurement of all metabolites is an analytical challenge due to the complexity of the sample matrices. In this regard, two-dimensional gas chromatography-mass spectrometry (GC×GC-MS) has emerged as a powerful separation technique to tackle the incomplete separation issue in complex samples matrices [2]. In the present contribution, an untargeted metabolomic study based on chemometrics was developed on control *lettuce* (*Lactuca sativa* L) samples and exposed samples to 11 CECs by irrigation. The aim of this study was identification of lettuce metabolites with significant profile alteration induced by CECs exposure. In this regard, raw GC×GC–TOFMS data from eight lettuce sample extracts (i.e., control and exposed samples) were column-wise augmented. However, due to the huge size of augmented matrix (~20 gigabytes (GB)) it was necessary to use a proper data compression approach to reduce data size without missing relevant information. For this purpose, wavelet decomposition and compression (level-2) was applied independently on every column (m/z) of the augmented matrix. Compressed augmented data matrix for eight samples was then analyzed by multivariate curve resolution-alternating least squares (MCR-ALS) using proper constraints [3]. The number of components in the data matrix was determined using singular value decomposition (SVD) which was 80 in this study. Also, orthogonal projection approach (OPA) was used to calculate initial spectral estimates to start ALS optimization. On this matter, fifty MCR-ALS components were unambiguously assigned to characteristic lettuce metabolites. Then, the peak areas of the MCR-ALS resolved elution profiles in every sample analyzed by GC×GC-TOFMS technique were arranged in a new data matrix that was then modeled by partial least squares-discriminant analysis (PLS-DA). The control and CECs exposed *lettuce* samples were discriminated by PLS-DA and the most relevant metabolites were estimated using Variable Importance in Projection (VIP) scores and Selectivity Ratio (SR) values. Finally, the metabolic pathways of the identified significant metabolites were found using Kyoto Encyclopedia of Genes and Genomes (KEGG) and they were interpreted from biochemistry point of view.

Keywords: Metabolomics, Multivariate curve resolution, Partial least squares, GC×GC-MS.

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A reasonable compromise between the magnitude of L_1 and L_2 norms in multivariate curve resolution for deconvolution of GC-MS data

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ABSTRACT

Sparse non-negative matrix factorization (SNMF) is a recently developed technique for finding parts-based linear representations of non-negative data. The present contribution is about the implementation of sparsity constraint in multivariate curve resolution-alternating least square (MCR-ALS) techniques for analysis of GC-MS/LC-MS data. The GC-MS and LC-MS data are sparse in mass dimension, and implementation of SNMF techniques would be useful for analyzing such two-way chromatographic data. In this work, the L_1-and L_2 regularization paradigms have been implemented in each iteration of the MCR-ALS algorithm in order to force the algorithm to return sparser spectral profiles. Multivariate Elastic net regression (ENR), least absolute shrinkage and selection operator (Lasso) and minimum absolute deviation regression (MADR) were used instead of the ordinary least square in MCR methods. A comprehensive comparison has been made between MCR-ALS, ENR-MCR-ALS, Lasso-MCR-ALS and MADR-MCR-ALS algorithms for deconvolution of the simulated two-component GC-MS data. The comparison has been made thorough the calculation of the values of sum of square errors (SSE) for 5000 times repetition of both algorithms using the random spectral/concentration profiles as initial estimates. The results revealed that regularization of L_1-norm of the spectral profiles is more effective than confining the values of L_2-norm. Implementation of L_1-constraint in spectral profiles prevents occurrence of overfitting in ALS algorithm and this increases the probability of finding "true solution" after the deconvolution procedure. Moreover, the effect of this "sparsity constraint" has been explored on the area of feasible solutions in MCR methods. The results in work revealed that implementation of L_1-constraint reduces the extent of rotational ambiguity. Finally, a graphical user interface (GUI) has been developed for easy implementation of this constraint on ALS algorithm. This GUI can be used for analysis of two component GC-MS/LC-MS data with high degrees of overlapping in mass/concentration profiles.

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Joint approximatediagonalization of eigenmatrices (JADE)as anew approachfor analysis of hyphenated and comprehensive two-dimensional gas chromatographic data

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ABSTRACT

Hyphenated techniques combine separation and spectroscopic detection technique to exploit the advantages of bothand theyhave attractedattention of chemists to analyze complex mixtures. However, inadequate separation challenges still exist especially in theanalysis ofcomplex samples[1]. Therefore,two-dimensional chromatographic systems such as comprehensive two-dimensional gas chromatography-mass spectrometry(GC×GC-MS) have been proposed for the analysis of complexsamples due totheirhigherresolution and higherpeak capacity.However, oneof the main challenges in GC×GCisrelated to the difficulty of the analysis and interpretation of thehugeamount of data. Additionally,complete separation of all detectable components still cannotbe achieved.Therefore, the objective of the present work was development of joint approximatediagonalization of eigenmatrices (JADE) as a member of ICA family[2], for the analysisofGC-MSandGC×GC-MSdata.In this regard,simulatedGC-MSand GC×GC-MS data sets with different number of components, different degree of overlapandnoise levels were evaluated.Also, column-wise augmentation was used for GC-MS and GC×GC-MS dataarrangement before JADE analysis.The performance of JADE was evaluated in terms of statistical parametersof lack of fit (LOF), mutual information (MI) and Amari index[3]as well asanalytical figures of merit (AFOMs)obtained from calibration curves. In addition,the area of feasible solutions (AFS) was calculatedby two different approachesofMCR-BANDs and polygon inflation algorithm (fackpack). Furthermore, JADE performance was compared with multivariate curve resolution-alternation least squares (MCR-ALS) and other ICA algorithms of mean-field ICA (MFICA) and mutual information least dependent component analysis (MILCA).In all cases, JADE could successfully resolve the elution and spectral profiles in GC-MS and GC×GC-MSdata with acceptable statistical and calibration parameters andtheir solutions were in the AFS. To check the applicabilityof JADE in real cases, JADE was used for resolution and quantification of phenanthrene and anthracene in heavy fuel oil (HFO) analyzed by GC×GC-MS. Surprisingly, pure elution and spectral profiles of target compounds were properly resolved in the presenceof baseline and interferences using JADE. Once more, the performance of JADE was compared with MCR-ALS. On this matter, the MI values were 1.01 and 1.13 for resolved profiles by JADE and MCR-ALS, respectively. In addition, LOD values (µg/mL) were respectively 1.36 and 1.24 for phenanthrene and 1.26 and 1.09 for anthracene using MCR-ALS and JADE which showed outperformance of JADE over MCR-ALS.

Keywords: Independent component analysis, Gas chromatography, JADE,GC×GC,MCR-ALS.

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Detection of gasoline adulteration using colorimetric sensor array based on Au\Ag bimetallic nanoparticles and pattern recognition methods.

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ABSTRACT

The quality control of gasoline is the serious and important economic and environmental in many manufacturing industries and other activities [1]. The negative effects of adulterated gasoline such as engine damage and air pollution and destructive effects in fuel oil industries because of using fraudulent mixing of low-priced reagents with higher-priced fuels are necessary reasons for investigating the quality of gasoline [2, 3]. So, the development of the high sensitive and safe portable sensor for on-site analysis of gasoline is a great goal in last decade. Herein, we present a novel colorimetric sensor array based on 30 types of Au\Ag bimetallic nanoparticles which preparation with green reducing agent including lemon juice, pomegranate juice, orange juice and chemical agent such as citric acid, gallic acid and ascorbic acid. This array was used to discriminate the petroleum-based products such as gasoline, diesel, thinner, ethanol, methanol, kerosene and detection the amount of these species in fake gasoline. Changing in color sensing elements is based on aggregation or destruction of nanoparticles which produce unique color change profiles for each specific analytes can be monitored with an ordinary flatbed scanner. The discriminatory ability of proposed sensor array was investigated by different chemometrics methods of classification such as principle component analysis (PCA), hierarchical cluster analysis (HCA) with 100 % classification accuracy.

Keywords: Adulteration, Bimetallic nanoparticle, Classification methods, Image analysis, Sensor array.

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Study of monoprotic acid–base equilibria in methanol-water association using spectrophotometry and equilibrium modeling

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ABSTRACT

Methanol–water mixtures are widely used as solvents in chemistry such as HPLC separations. Previous studies showed a methanol-water mixture cannot be considered as a simple binary system. So the system is assumed to contain clusters of methanol (M), water (W), and methanol–water (M-W), contains water and methanol in the molecular ratio of unity [1]. So the solute molecules in such mixture are known to be distributed between different solvent clusters. To clarify the issue, we considered acid - base equilibria of dye as indicator in methanol-water mixture. In this model, the protonated and deprotonated form of indicator can be distributed between M, W and M-W clusters, with different distribution constants. So, three components exist for each of the protonated and deprotonated forms. Also it should be noted that there is an acid-base equilibrium with a different protonation constant in each clusters (Schematic 1).

$$(A)_M \quad + \quad (H^+)_M \quad \xleftrightarrow{K'_p} \quad (AH^+)_M$$

$$k_1 \updownarrow \qquad\qquad k_3 \updownarrow \qquad\qquad k_5 \updownarrow$$

$$(A)_W \quad + \quad (H^+)_W \quad \xleftrightarrow{K_p} \quad (AH^+)_{MW}$$

$$k_2 \updownarrow \qquad\qquad k_4 \updownarrow \qquad\qquad k_6 \updownarrow$$

$$(A)_{MW} \quad + \quad (H^+)_{MW} \quad \xleftrightarrow{K''_p} \quad (AH^+)_{MW}$$
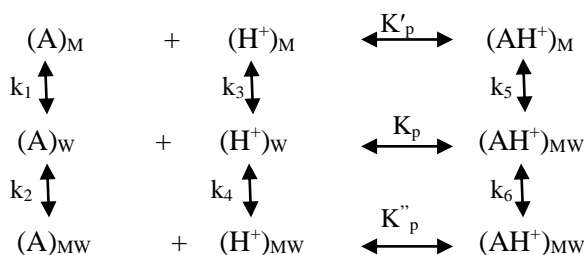
Schematic 1: A model for acid–base equilibrium of the indicator in methanol-water mixture.

where, $(A)_W$, $(A)_M$ and $(A)_{MW}$ are deprotonated indicator in water, methanol and methanol-water clusters with the protonation constants of K_p, K'_p and K''_p, respectively. The protonated indicator in water, methanol and methanol-water clusters are shown as $(AH^+)_W$, $(AH^+)_M$ and $(AH^+)_{MW}$, respectively. k_1, k_2, k_3, k_4, k_5 and k_6 were distribution constants of desired analytes between water, methanol and methanol-water clusters. At first, the solvation of protonated and deprotonated form of the indicator in different methanol/water compositions was studied spectrophotometrically to calculate of distribution coefficients of solute between clusters and association constant methanol-water cluster. Then, the spectrophotometric data obtained from acid-base titration of the indicator in methanol and water was used for calculating of protonation constant of dye in these solvents. Finally, global analysis of spectrophotometric data obtained from acid-base titration of the indicator in mixture of methanol/ water was used for calculating of protonation constant of dye in M-W cluster.

Keywords: Methanol/water association, Acid–base equilibria, Equilibrium modeling, Distribution coefficient, Spectrophotometry, Global analysis

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Common Factor Analysis

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ABSTRACT
Generally defined, factor analysis (FA) is any method that decomposes a data matrix (or, in a more general case, a data tensor) into a bilinear (or multilinear) model of lower dimensionality. Principal components analysis (PCA) is the most popular FA technique in chemistry [1]. Another popular FA technique is a maximum likelihood based common factor analysis (MLCFA or CFA) technique [2,3] which is available in the Statistical toolbox of Matlab, as *factoran.m*. Although both are ML based, MLCFA is different from MLPCA [4]. Principal axis factoring (PAF) is another common factor analysis technique [5,6] that is similar to CFA in that it decomposes data into specific factors in addition to common factors. This report is a comparison of CFA, PAF and PCA regarding their resulting profiles and subspaces.

Simulated data sets including multivariate normal and non-multivariate normal (chromatographic and spectral kinetic) data were considered, in addition to an experimental data set including fatty acids of different groups of fish samples. Different types of noise, including independent and identically distributed (*iid*), column heteroscedastic and general heteroscedastic were added to the simulated data, in different levels.

In presence of *iid* noise, results from CFA, PAF and PCA are almost the same and the angle between calculated and true profile subspaces are higher when using non-multivariate normal data. In the presence of heteroscedastic noise, the subspace of CFA and PAF profiles are closer to that of the true profiles compared to PCA. In the presence of heteroscedastic noise, CFA and PAF result in different profiles and reconstruct the covariance matrix of data better than PCA, which assumes *iid* errors. In the case of multivariate normal (MN) data, a likelihood and chi-squared based statistical test can be applied for determining the optimum number of applied factors in the model. A major advantage of using PAF over CFA is the possibility of using PAF for "fat" data in which the number of samples (rows) is lower than the number of variables (columns). MLPCA results in best reconstructions of data covariance and lowest angle between subspaces of estimated and real profiles; however it needs the noise structure to be completely known.

Keywords: Factor Analysis, Maximum Likelihood, Principal Axis Factoring, Noise, Heteroscedastic, Multivariate Normal.

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Particle swarm diagonalization of fourth order cumulants tensor for estimation of least dependent components

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ABSTRACT

Least dependent components estimation is the main goal in many independent component analysis (ICA) techniques, such as ICA-JADE [1] and MILCA [2]. Extraction of information theoretically independent source vectors from signal mixtures matrix is the target of these techniques. An important chemical application of such techniques is in unsupervised clustering.

In ICA-JADE, the applied criteria for showing independence of components are elements of fourth order cumulants tensor (FCT), which is a crucial subject in higher order statistics (HOC). Variance and covariance are the second order cumulants, and kurtosis is a sort of fourth order cumulant. Diagonalized FCT for a set of profiles shows their information based independence.

Particle swarm optimization (PSO) belongs to the strong family of global optimization techniques, inspired by the social behavior of animals [3]. In PSO a swarm of particles flow in parameters space through pathways which are driven by their own and neighbors' best performances.

The proposed method is based on orthogonal rotation of whitened data (orthonormal and uncorrelated) or non-whitened data into the least dependent profiles. The angles of rotations in all possible direction of space are optimized by PSO to obtain super-diagonalized FCT. The method was successfully applied for clustering of ink samples using NIR spectra. The main advantage of the proposed PSO technique is flexibility in using different objective functions in place or in addition to FCT.

Keywords: Unsupervised Clustering, Particle Swarm Optimization, Independent Components Analysis, Orthogonal Rotation, NIR Spectra.

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The role of chemometrics in metabolomics studies

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ABSTRACT

Metabolomics is a growing area in the field of systems biology [1]. In this study the role of chemometrics in metabolomics is considered. Chemometrics can be used throughout the steps involved in metabolomics including data acquisition, raw data pre-processing, pattern analyses and identification of important features. The real challenge is to identify the biomarkers of a particular disease from hundreds of metabolites identified by metabolomics [1-4]. Data acquisition in appropriate platform generates a data file commonly called as raw data. The process of obtaining meaningful information from raw data for further analysis is called data pre-processing [3].

Following pre-processing metadata or the data matrix has been obtained and further analysis for pattern analyses and identification of important feature are crucial steps. It involved multiple statistical steps to identify a robust biomarker of a set of biomarkers [1]. Depending on complexity of the data matrix and between or within group variations, both uni- and multivariate statistical methods can be used in order to identify biomarkers [4]. Some practical examples of metabolomics in presence of different pre-processing methods and their effect on metabolite identification has been considered.

Keywords: Metabolomics, pretreatment, pattern recognition, metabolite identification

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A Generalized Multivariate Method for Quantification in Gray Systems

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ABSTRACT

Analyte determination in the presence of unexpected sample constituents, i.e., those not taken into account in the calibration phase, is one of the important subjects in the field of chemometrics. Multivariate calibration methods are a group of techniques based on factor analysis with the goal to develop the mathematical models relating unselective multiple instrumental signals with analyte concentrations. The area of calibration can be divided in zero, first and second-order, etc. A given instrument may yield first-order (vector) data for a single sample, which, when several samples are combined into a matrix, produces a two-way array. Principal component regression (PCR) and Partial Least Square (PLS) are two well-established algorithms in first-order multivariate calibrations which allow the simultaneous determination of multiple analytes in the same sample. In first-order calibration methods, calibration samples must contain the same potential interferents as unknown samples [1]. Several modified first order calibration methods tried to quantify analytes in the presence of unexpected constituents (in gray samples). Unfortunately all of those methods can only give a possible solution because of lack of information needed for unique solution [2]. In this work the main aim is introduction of a general method to calculate all of the possible solution in a very simple way. In addition, all information that must be added to these systems to cause uniqueness has been discussed. Based on duality relation it is obvious that any information about the spectra of interferents could be useful in the accuracy of analyte quantification. Now the question is what is the least information that would be useful in accuracy of quantification?
In the last step, a graphical user-friendly interface (GUI) has been designed to make the program easier to use. Simulated data sets and real systems have been used to evaluate the performance of proposed method. In this work quercetin as an antioxidant has been determined in honey and onion as real samples.

Keywords:

Multivariate calibration methods, gray systems, first order data

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Ss

Optimization of preconcentration and extraction processes by single and multi-response experimental design

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Detection and determination of analytes in real samples at low level by simple analytical techniques are difficult. In such cases, preconcentration and extraction processes can be coupled with analytical techniques. Several sample preparation methods have been developed for the analysis of analytes, such as SPE, SPME, LLE, LPME, DLLME AALLME and AALLME-SFOD. In the AALLME-SFOD method, a low toxic and low density solvent with a melting point about room temperature is used as an extraction solvent.

Different factors affect the performance of extraction steps, so the optimizations of these parameters are more important. Response surface methodology (RSM) is frequently used for this optimization. Multi-response optimization (MRO) is a branch of response surface methodology that can be applied in modeling and optimization. The desirability function approach is one of the most extensively applied methods for optimizing multiple response processes. The goal in desirability function approach is the finding of conditions where the independent variables leading to optimal or nearly response variables optimal values. In this lecture, some of works were done in our research group are presented.

An air assisted liquid–liquid microextraction by applying the solidification of a floating organic droplet method coupled with a multivariate calibration method, namely partial least squares was introduced for the fast and easy determination of Atenolol, Propanolol and Carvedilol in biological samples via a spectrophotometric approach. Derringer and Suich multi-response optimization were utilized for simultaneous optimizing the parameters.

An air-assisted liquid–liquid microextraction method coupled with a multivariate calibration method, namely partial least squares (PLS), was developed for the extraction and simultaneous determination of benzoic acid (BA) and sorbic acid (SA) via a spectrophotometric approach. In this work, a two-step microextraction method was used. In the first step, analytes were extracted from acidic aqueous solution into octanol, as an organic solvent, and in the second step, the analytes were simultaneously back-extracted into an alkaline aqueous solution.

In another work, we synthesized polymeric nanoparticles and used it as sorbent in magnetic solid-phase extraction. In the first step of study, a novel super para magnetic nanosorbent was prepared using $Fe_3O_4@SiO_2$ nanoparticles as a core and Acrylic Acid and Acryl Amide as monomers. Central composite design was used to design experiments and optimize extraction conditions.

Also, a simple, rapid and efficient method has been developed for extraction, and preconcentration of copper and nickel ions in water samples by AALLME-SFOD coupled with graphite furnace atomic absorption spectrometry. Derringer and suich method was used to find the optimal conditions for simultaneous extraction of both analytes.

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Investigating error structure effect on possible solutions in the three-way models

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ABSTRACT

The main assumption behind most of chemometrics tool is identical independent distribution (i.i.d) for noises structure [1]. Alternating lest-squares and principal component analysis provides maximum likelihood (ML) estimation in the i.i.d condition [1]. Unfortunately this assumption will be violated in most of experimental cases. Hence, maximum likelihood paves the way to a modification on the basic chemometrics tools [2]. MLPCA and MLPARAFAC are state of art chemometrics tool for the analysis of fallible two-way and three-way data sets [3]. Error structures can be categorized in six different cases and these cases encompass all of the possible structures that will be dealt with. Error structure of a data set can be a combination of these cases [4]. Different MLPARAFAC algorithms were developed in order to a trilinear decomposition of three-way data sets [3].

The aim of this contribution is two-folded. 1) The effect of noise structure on the possible solution of multi-way models will be highlighted. In other words calculation of feasible regions will extended to the MLPARAFAC models. Data sets with different known error structure were simulated and feasible regions were calculated. It was shown that the error effect is non-uniform and complex on the possible solutions.

2) In the same analogy with MLPCA-MCR-ALS, MLPCA-MA-MCR-ALS will be used for handling error structure of three-way data sets. It should be highlighted that MLPCA-MCR-ALS provides reliable estimation of profiles such as MCR-WLAS in noisy measurements [4,5]. Finally, the results confirmed that the resolved profiles obtained by MLPCA-MA-MCR-ALS are practically identical to those obtained by ML-PARAFAC and that they can differ from those resolved by ordinary PARAFAC-ALS, especially in the case of high noise. In MLPCA-MA-MCR-ALS with trilinearity constraint, MLPCA is only used as a preliminary data pretreatment before MA-MCR analysis and this is the possible advantage over MLPARAFAC and it does not require changing the traditional PARAFAC algorithm.

Keywords: Maximum Likelihood Estimation, MLPARAFAC, Error structure, Feasible region, MLPCA-Matrix augmented MCR-ALS.

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Model based design of experimental procedures for efficient investigation of some chemical equilibria

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ABSTRACT

The chemical model which governing a chemical process can be the basis for selecting or designing an appropriate laboratory method. In an equilibrium system, the model defines a mathematical function which in expresses the relationship between equilibrium concentrations and thermodynamic parameters. The mass balance equations, which are the main basis for the expression of an equilibrium chemical model in a system, can be used for designing laboratory methods for the study of equilibrium processes [1].

A common method for studying equilibrium systems is to change the concentration of components through titrations. But some of the equilibrium systems which is studied by this way do not provide enough information about some species. Therefore, the data would not well-fitted to the model [2]. There may also be some linear dependency between some species in the system. Thus, the system will be faced rank deficiency problem [3]. In this case, although the parameters of the model could be achieved by data fitting, but the signals could not resolve properly. Augmentation of different data sets with various initial conditions is one of the offered solutions for these problems in the literature.

The goal of this research is to proper designing of the chemical equilibrium reactions based on the chemical models. So that, the gained information which collected by several data sets in a classic method could be achieved only by a data set.

For example, as the metal ion Ni^{+2} forms 1:1,1:2 and 1:3 complexes with tryptophan amino acid, the pH metric titration of 1:1 ratio of Ni^{+2} and tryptophan with NaOH lead to least information about 1:3 complex. Same results are achieved for 1:1 complex in titration of 1:3 ratio of metal-amino acid with NaOH. For achieving enough information about all complexes in one data set, it can be possible to start with 1:1 ratio and adding tryptophan as the second titrant during the procedure. The fitting results of formation constants of all complexes in this condition are comparable with augmented data sets of different conditions. Also for the case of rank deficiency system, acid-base titrations of a mixture of three nucleic bases (adenine, cytosine, and uracil), were investigated. The acidic and basic forms of nucleic bases are spectroscopically active. Due to the linear dependency between concentration profiles, the rank of mixed solution is 4 instead of 6. For this case, during the titration of this mixture with NaOH, a nucleic acid is added as the second titrant. So, the linear dependency is disappeared.

Keywords: Equilibrium reactions, Chemical models, Data fitting.

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Chemometrics description and systematic investigation of measurement error in smartphone based spectrometer

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ABSTRACT

Analytical chemistry is the science of chemical measurements, and inherent in any chemical measurement is the principle of measurement error [1,2]. Proper data analysis necessarily implies knowledge of the nature of error, with all the contributions that configure its correlated or uncorrelated nature. Once this is known, the whole error structure can be associated with physical factors and, eventually, be corrected or be taken into account in the data analysis through weighting schemes. In here we have investigated the underlying noise structures in a homemade smartphone spectrophotometer.

Smart mobile phones with the digital camera associated as an attractive consumer electronic product and a small piece of digital versatile disks (DVDs) are capable of being used as portable analytic optical devices [3,4]. The images of transmitted light through cuvette were captured by smartphone rear camera and then analyzed by a home-built MATLAB program. The miniature spectrometer was used to acquisition of sampling replicates of transmittance spectrum from Orange G and Indigo Carmine solutions. The error structures of the transmittance spectra were investigated through for assessing error covariance and correlation matrices. PCA, MCR-ALS and PARAFAC were used to extract possible sources of noise.

The effect of concentration change and cell positioning on error structure were investigated. To estimate the error covariance matrices, thirty five images were taken from each solution as replicates. These replicates were taken while the placed sample in the apparatus was not moved and replacing. These two conditions were done to check the effect of sample cell replacement on noise structures. In order to understand the error structure in absence of the signal of analyte, the same image acquisition procedure was done on the empty cell and the cell filled by deionized water (blank sample).

This study revealed four main sources of noise in recorded signals: a) constant offset noise, b) colors border noise, c) heteroscedastic noise (uncorrelated independent error) which is proportional to transmittance spectrum and it is specific for different dyes, d) peak broadening noise which is observed when there is a broadening in of each RGB colors. This study can be used to improve instrumental setup and finding error among with it. This leads to use of measurement error information to enhance data analysis that make more accurate and precise inexpensive spectroscopic assays.

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QSAR coupled to principal component analysis-adaptive neuro-fuzzy inference systems-Artificial Neural Network (PCA-ANFIS-ANN) and docking studies for the modeling of the flavonoid compounds

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ABSTRACT

Flavonoids are phenolic compounds, secondary metabolites of plants that cause several benefits to our health, including helping the treatment against HIV [1] Quantitative structure–activity relationship (QSAR) methods are used to predict the pharmaceutically relevant properties of drug candidates whenever it is applicable. The aim of this study was to use three different techniques, namely principal component analysis (PCA), adaptive neuro fuzzy inference system (ANFIS) and artificial neural networks (ANNs) in predicting the activity (i.e. pIC_{50}) of flavonoids compounds. Docking study was performed using HEX program on all the compounds. Using docking study, it has shown that all the studied DATAs derivatives bind to the Human immunodeficiency virus 1 receptor and have a common binding modes. These computational studies can offer useful references for understanding the action mechanism and molecular design or modification of this series of the anti-HIV agents [2].

Keywords: Flavonoids compounds - Principal component analysis (PCA) - QSAR - adaptive neuro-fuzzy inference systems (ANFIS)-Artificial Neural Network (ANN) -Molecular docking.

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Statistical optimization of the ultrasonic assisted removal of methylene blue by bituminous coal-based activated carbon nanosheets using experimental design

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ABSTRACT

Methylene blue (MB) as a thiazine cationic dye is the most commonly used dye for temporary hair colorants, wool, cotton, leather, silk and paper. Although MB not strongly hazardous, it can have numerous harmful effects. MB increases myocardial function in septic shock [1]. Bituminous coal as an inexpensive and abundant natural resource in Iran was used to produce nanoparticle and nanosheets of activated carbon (AC) for removal of methylene blue (as a cationic dye) from effluent. The structural features of these carbon nanoparticles and nanosheets were characterized by means of Fourier transform infrared (FTIR), Barret-Joyner-Halenda (BJH), X-ray diffraction (XRD), scanning electron microscopy (SEM) and transmission electron microscopy (TEM). In this work, rapid/assisted adsorption method followed by ultraviolet–visible spectroscopy (UV/Vis) detection has been used for efficient short time removal of MB. Combination of central composite design (CCD) and response surface methodology (RSM) has been applied to model and optimize the influencing variables on the MB adsorption by produced AC [2]. More specifically, the effects of influencing variables such as adsorbent mass, dye concentration, temperature and sonication time have been investigated. The best adsorption percentage, equal to 100%, was obtained under optimum conditions set as: 0.2008 g of adsorbent, MB concentration of 10.81 mg L^{-1}, temperature equal to 44.2 °C, and 7.3 min of sonication time. The results show that the Langmuir model and pseudo-second-order kinetic model fitted well to the adsorption experimental data [3, 4]. Proposed technique in comparison with the recently reported techniques for removal of cationic dye has several advantages such as low cost, abundance of raw materials, ease of production, fast adsorption kinetic and high adsorption capacity.

Keywords: Bituminous coal, Activated carbon, Methylene blue, Experimental design, Response surface methodology

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Experimental design approaches in the optimization of sorption potential of nano biomass derived from walnut shell for the removal of Malachite Green

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ABSTRACT

In the recent years, researchers have focused on the production of activated carbons from agricultural waste material as biomass because of their purity, stability of its resources and cheap prices for the removal of water pollutant. Dye waste water including malachite green (MG) is one of the significant pollutant source and is made by various industries including textile, pigment, leather, food, cosmetics manufacturing, rubber, paper printing and cotton [1]. MG is also used in aquaculture as an effective topical antiparasitic and antiprotozoan [2]. MG is a cationic triphenylmethane dye which is extremely toxic and harmful for human [3], hence scientists have worked on the MG properties and its influence on the human health and mammals [4]. Activated carbon based on walnut shell as a biomass material was synthesized and successfully applied for the removal of malachite green (MG) dye from aqueous solution. This biomass was characterized by several techniques such as Fourier transform infrared (FT-IR) spectroscopy, Transmission electron microscopy (TEM), Brunauer–Emmett–Teller (BET), Dynamic light scattering (DLS) and X-ray diffraction (XRD). Crucial operating parameters were screened and optimized by response surface methodology (RSM), in batch study considering removal efficiency as response. A five-level, three-factor central composite design (CCD) has been employed to determine the influence of operating parameters such as initial concentration of MG (16.5-33.5 mg L^{-1}), nano biomass dose (16.5- 33.4 mg) and contact time (13.0-47.0 min) on MG uptake from aqueous solution. Results showed that about 100% elimination was attained at initial MG concentration of 33.3 mg L^{-1}, nano biomass dose of 33.3 mg and contact time of 20.0 min. Four adsorption isotherms, including the Langmuir, Freundlich, Temkin and Dubinin–Kaganer–Radushkevich (DKR) isotherm models were used to analyze the experimental data and the results indicated the Langmuir isotherm was suitable to describe the adsorption behaviors. Finally the pseudo second order kinetic model described the MG sorption process with a well-fitting ($R^2 = 0.9897$).

Keywords: Walnut shell, Carbon nanoparticles, Nano biomass, Malachite Green, Response surface methodology

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Recognition of important chemicals in Engine oils affecting the value of oil viscosity indices using HS-SPME-GC-FID and PLS as a multivariate calibration technique

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ABSTRACT

Viscosity index is one of the important physicochemical properties of engine oils covered under the American Standards for Testing and Materials (ASTM) [1]. In this study, we focus on the combination of gas chromatography with Chemometric techniques to relate the viscosity index of engine oils to the important retention times of their chemical compositions. Extracting of compounds from engine oils was done using graphene/polyvinylchloride nanocomposite coated SPME fiber [2] under headspace mode. The effective parameters on HS-SPME extraction of chemical compounds were investigated by one-variable-at-a-time method with optimized circumstances (extraction temperature, $140\,^0C$; extraction time, 30 min; desorption temperature, $230\,^0C$; desorption time, 5 min; and stirring rate, 500rpm). Many preprocessing methods were done prior to partial least squares (PLS) technique, including asymmetric reweighted penalized least square (air-PLS), Savitzky-Golay filter and correlation optimized warping (COW). The results of the regression coefficient plot from PLS technique showed that the retention times of 12.78, 12.79, 12.97, 15.29, 15.65, 15.99, 16.91, 17.67 minutes have great positive effects on the value of viscosity indexes, and addition of such improver compounds in relation to these retention times can increase the value of viscosity index. Furthermore, the constructed model shows acceptable figure of merits (RMSEC= 2.35, R^2= 0.99, Q^2= 0.994 RMSECV= 1.95) which indicate the good performance and robustness of PLS model. The results in this work suggest that following the development of a robust model, it is possible to accurately determine which retention times are responsible for increasing the values of viscosity index of engine oils, using HS-SPME-GC-FID-PLS strategy. Moreover, the results demonstrated that the combination of HS-SPME-GC/FID with Chemometrics techniques is an appropriate and low-cost method for analysis of engine oils and evaluation of their viscosity index.

Keywords: Engine oils, viscosity index, Chemometrics, PLS, HS-SPME-GC-FID

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Chemometric analysis of highly overlapping voltammetric signals of chiral electrochemical sensor based on a nanocomposite of aspartame

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ABSTRACT

Chiral discrimination received attention not only as an interdisciplinary subject in science, but also as a safety issue in medical, pharmaceutical and food industries [1]. An electrochemical chiral sensor was designed based on graphene (GR) as a catalyst for signal enhancement. Aspartame (ASP), an artificial non-saccharide sweetener, has been immobilized as a chiral selector on GR to discriminate electrochemical signals of mandelic acid (MA) enantiomers. A two-step electrodeposition strategy was used to fabricate ASP-loaded overoxidized polypyrrole film (ASP-OPPy) on GR-modified glassy carbon electrode, which was successfully utilized as working electrode for electrochemical enantioselective recognition of MA enantiomers based on an inhibitory sensing mechanism. The modified surface properties and the recognition mechanism were investigated using electrochemical analysis and DFT calculations. Under optimal conditions, the chiral sensor exhibited a good linear relationship with MA enantiomers concentrations ranging from 1–25 mM with a detection limit of 0.25 mM. Due to the highly overlapping signals, partial least squares (PLS) regression was applied to distinguish the MA enantiomers in their mixtures. In addition, the genetic algorithm-based potential selection procedure used to optimize the number of PLS factors used in building the PLS calibration models and its predictive ability was also studied.

Keywords: Chiral discrimination, enantioselective electrochemical sensor, graphene nanocomposite, PLS-GA

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Gelatin Speciation Using Analysis of Mass Spectrometry-based-Proteomics Datasets

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ABSTRACT

Authentication of gelatin, an ingredient in food and drug products, is substantial with respect to some regulatory authorities and religion rules [1-3]. Muslim or Jewish people are concerned about gelatin derived from the porcine and fish without scales. The restrictions are released by regulatory authorities on the use of bovine gelatin in the case of the outbreak of Bovine Spongiform Encephalopathy (BSE) [4]. More specifically, the bovine skin-based gelatin is forbidden in Islam if the cattle are not slaughtered according to the religious rules.

Even though different studies have been done for characterizing animal source origin of gelatin in the literature [3], there is not a method for tissue specification. Thus, developing an accurate and precise method is of interest for differentiation of bovine, porcine and fish gelatin and besides bovine skin and bone gelatin in food and drug products. The gelatin samples were prepared in the proper concentration and processed with overnight trypsinization [5-7]. An appropriate volume of trypsinized sample was loaded on HPLC-ESI-QTRAP mass spectrometer and injected twice to the instrument. The generated High-Performance Liquid Chromatography-Mass Spectrometry (HPLC/MS) data sets involve MS spectrum of tryptic gelatin peptides of the gelatin extract samples. Pattern recognition methods, PLS/DA and PCA methods [8, 9] are used for mining HPLC/MS data set to define the pattern and also, peptide markers for discrimination the extracted gelatins. The detected peptides markers are applied for multiple reaction monitoring (MRM) mass spectrometry in routine works. The method was then tested on the extracts of gummy bears, marshmallow as well as pharmaceutical capsules used for drug delivery.

Results reveal that the proposed strategy is successful in the identifying of fish, bovine and porcine gelatin as well as bovine skin and bone gelatin in routine analysis of food and drug products.

To best of our knowledge, a method for specifying bovine skin and bone gelatin is introduced for firstly in this study.

Keywords: Gelatin, Mass spectrometry, Pattern recognition, Peptide markers, Origin

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Multivariate image – quantitative structure activity relationships of the antibacterial activity of pleuromutilin derivatives using different chemometrics methods

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ABSTRACT

Multivariate image analysis applied to quantitative structure-retention relationship (MIA-QSRR) has shown to be a useful tool to model the antibacterial activity of pleuromutilin derivatives. Antibacterial activity of 55 pleuromutilin derivatives used in this study was reported by Hirokawa et al. [1]. In MIA-QSPR [2], images are two-dimensional chemical structures, such as those drawn by using known programs like ChemDraw. These images (2D chemical structures) have shown excellent correlation with retention times and are supposed to codify chemical properties, like size of substituents, chains, branches and chiral centers.
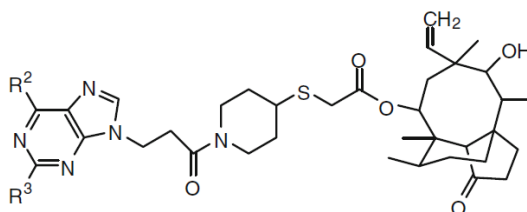
Chemical structure of pleuromutilin derivatives

In order to achieve this, different methods were employed in this study: partial least squares (PLS), genetic algorithm-PLS (GA-PLS), orthogonal signal correction-PLS (OSC-PLS) and PC-least squares-support vector analysis (PC-LSSVM) [3]. The results of all models are compared with statistical parameters such as RMSEP, RSEP, R^2 and Q^2. The resulted model showed high prediction ability with root mean square error of prediction of 0.0062 and 0.0024 for OSC-PLS and PC-LSSVM. Results have shown that the introduction of PC-LSSVM for pixel descriptors drastically enhances the ability of prediction in QSAR studies superior to other calibration algorithms.

Keywords: MIA-QSAR, Antibacterial activity, PLS, LSSVM, OSC, GA.

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DFT-Based QSAR Study of Toxicity of 2-(2,4-dichlorophenoxy)propanoic acid and 2-(3,4-dichlorophenoxy)propanoic acid Compounds

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ABSTRACT

In modern drug discovery process, ADME/Tox (absorption, distribution, metabolism, excretion, along with toxicity) properties should be determined as early as possible in the test cascade to allow a timely assessment of their property profiles [1]. Among ADME/Tox properties, drug metabolism is a key determinant of several important drug processes *in vivo*, such as metabolic stability, drug–drug interactions and drug toxicity [2]. Many physiological activities of molecules can be related to their composition and structures. Molecular descriptors, which are the numerical representation of the molecular structures, are used to perform Quantitative structure activity relationships (QSAR) analysis. Therefore, the DFT method is expected to lead to statistically more accurate QSAR model by comparing the semi-empirical methods. Aim of the present study is QSAR study to explore the correlations between activity and calculated molecular descriptors of 2-(2,4-dichlorophenoxy)propanoic acid and 2-(3,4-dichlorophenoxy)propanoic acid compounds. The ground state geometries of these compounds have been optimized by using density functional theory (DFT) at B3LYP/6-311G level of theory. We evaluated the overall predictive capacity of the models for the training set compounds and model derived predictions for the test set compounds. The computed properties of investigated compounds have been compared as well as available experimental data. The results also suggest that number and position of the substituents plays a dominant role in describing the toxicity. However, electronic factors are also important for the predictability of the models. The models built in the present study can be used for the prediction of toxicity of untested aldehydes against. The model based on factors scores of descriptors of different bonds was able to identify the important fragment responsible for the mediation of toxicity of 2-(2,4-dichlorophenoxy)propanoic acid and 2-(3,4-dichlorophenoxy)propanoic acid as corroborated by their established mechanism of toxicity.
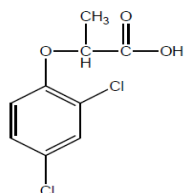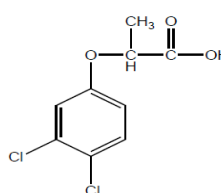
2-(2,4-dichlorophenoxy)propanoic acid   2-(3,4-dichlorophenoxy)propanoic acid
[Scheme]

Keywords: QSAR, DFT, 2-(2,4-dichlorophenoxy)propanoic acid, 2-(3,4-dichlorophenoxy)propanoic acid

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Approach to Accurate Models for Investigating the Chemical Processes in Non-Constant Ionic Strength

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Abstract

A proper chemical model should be close to the behavior of the system under study. In solutions which contains electronic charges for calculating the equilibrium parameters, using activities leads to somewhat better results that the use of concentration. So it seems necessary providing a more complete model to the apparent model. In this study, the effect of ionic strength of a solution on equilibrium systems has been studied. To investigate the effect of solution ionic strength, Titration of Bismuth($Bi+3$) with Chloride($Cl-$) was selected and spectrophotometric data is recorded [1]. Data is fitted two model (concentration and activity-base model). Calculated equilibrium constant of two model are different (due to the ionic strength of the solution). Also the effect of changing ionic strength of solutions on equilibrium perturbation, it could be a novel method to survey the equilibrium systems which are contains electrically charged species. For this purpose, we select Bromocresol green(BCG) dye and titred with electrolyte(NaCl) and spectrophotometric data is recorded. Data fitted to activity based model and thermodynamic equilibrium constant calculated ($pKa=4.79\pm0.005$). this result agree with that was reported in literature ($pKa=4.91\pm0.02$) [2]. Also in this research, we investigated resistance of electrolyte (which is used to stabilize ionic strength) against the change in ionic strength solution. So we indicated the required electrolyte concentration to fix ionic strength solution.

Keywords: Activity, Ionic Strength, Model fitting.

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QSAR Analysis of 6-chloro-N^2,N^4-diethyl-1,3,5-triazine-2,4-diamine Derivatives; a Theoretical Study

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ABSTRACT
The remarkable inhibitory effect is reinforced by the presence of heteroatoms such as sulfur (S), oxygen (O) and nitrogen (N) [1]. Density Functional theory (DFT) has been recently used [2], to describe the interaction between the activities and molecular structures. The molecular band gap was computed as the first vertical electronic excitation energy from the ground state using the time-dependent density functional theory (TD-DFT) approach as implemented in Gaussian 03. A quantitative structure–activity relationship (QSAR) study is performed on a set of 6-chloro-N^2,N^4-diethyl-1,3,5-triazine-2,4-diamine derivatives to reveal structural and quantum-chemical features influencing the toxic effect. All quantum-chemical calculations are carried out at DFT/B3LYP level of theory with 6-311++G** basis set Quantum-chemical calculations have been applied for electronic properties and wave function computations. Wave functions were further analyzed, and the properties derived from the analysis of electron density were applied to model the toxicity data. The results indicate that the charge on nitrogen atom plays an important role in the toxic behavior. Electron density, as well as kinetic energy densities influence the toxic effect of 6-chloro-N^2,N^4-diethyl-1,3,5-triazine-2,4-diamine compounds. Also, higher values of dipole moment indicate the higher toxicity in current compound series. Among the quantum topological descriptors electron density is believed to be the most influential. This study shows that the nature of substituents has very important determining role in toxicity of these compounds. Also, it was found that molecular charge distribution and strength of the bonds play vital role in stability of compound, which is directly related to its toxicity. Obtained QSAR models are beneficial for virtual screening of toxicity for new compounds of interest.
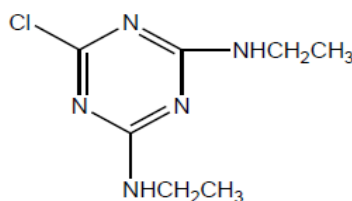
Scheme: 6-chloro-N^2,N^4-diethyl-1,3,5-triazine-2,4-diamine

Keywords: QSAR, DFT, 6-chloro-N^2,N^4-diethyl-1,3,5-triazine-2,4-diamine

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Molecular Docking Study of the Interaction of Ionic liquids with HSA as Potential Antimicrobial Agents

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ABSTRACT

The interaction between human serum albumin (HSA) and ionic liquids (ILs), as good potential microbial growth inhibitors, was investigated by molecular docking analysis [1]. All compounds were significant active against the tested bacterial and fungal strains [2]. The results of the molecular docking study showed that the studied ILs are able to firmly bind in the subdomain IIA of HSA. Molecular docking studies of one of ILs with the most antimicrobial activity shows the formation of a strong protein-ligand complex (Binding Energy = -6.49 kcal/mol). Two Hydrogen bonds were formed between protein and ligand. The first interaction (2.89 Å length) is formed between the Oxygen of the ligand and the NH-group of amino acid Arg218. The second interaction (2.80 Å length) is formed between NH-group of the ligand and the Oxygen of Asp451. The presence of two Hydrogen bonds in the protein-ligand system indicates the stability of this complex. Also, nine hydrophobic interactions were formed between hydrophobic substructures of the ligand and the protein. This study provides a better understanding of the binding of ILs to HSA and opens the way for their further biological and pharmaceutical investigations as candidates with antimicrobial properties.

Keywords: " Molecular docking , Ionic liquids , antimicrobial activity , human serum albumin (HSA) ,Inhibitors "

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High Diluted Homeopathic Dose Optimization using Central Composite Design (CCD) for *Oryza sativa* Seed Germination

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Abstract: Homeopathy is effective for human, animals and even plants and is the therapy based on the principle of "like-cures like." The finding that even plants respond to homeopathic remedies is fairly new and has become more widespread over the past few years. It is within the nature of homeopathy to determine the totality of symptoms and depending on that different remedies can choose. But plants cannot be consulted like human can. The only means to come to a remedy selection is possible by closely examining their symptoms and cause, and to interpret them as accurately as possible using the intuition. Some important remedy in agricultural homeopathy are Arsenicum album (Ars. alb.), Belladonna (Bell.), Natrum Sulphuricum (Nat. S.) and Sulphor (Sulp.) and has the properties including; seeds germination, reduces transplant shock, increases vigour and resistance of plants to pests, moulds, and mildew, aids water retention in plants growing on arid soils and stimulates flower growth, both in number and size. The aim of this study is to evaluate germination condition (irrigation (1 to 15 mL of water), temperature (4 to 40 °C), and light (with/without routine 24 day-night light)) with/without the presence of mentioned homeopathic remedies using central composite design (CCD). The *Oryza sativa* germination time, the amount of rooting and stemming and their length, total protein production was examined. The optimum concentration of homeopathic remedies under the evaluated factors are; Ars. alb.: C200, Bell.; C200, Nat.S.; C30 and Sulp; C200.

Keyword: Homeopathy, Central Composite Design, *Oryza sativa*, Seed Germination

Study the Metal (Ag) and Metal oxide (TiO$_2$ and ZnO) nanoparticles Interaction with Enzymatic detergents: Amylase, Cellulase and Lipase

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Abstract: Nanoparticles have special properties due to their size, as their size decreases their surface energy increases, which causes higher reactivity. Metal (Ag) and metal oxide (TiO$_2$ and ZnO) nanoparticles are applicable in different fields of industry; healthcare and agriculture caused by biochemical properties including antimicrobial or photo-degradation activity. One of the applications of mentioned nanoparticle is their deposition on clothes and textiles for their self-cleaning, shining and antibacterial activity. Moreover, different types of enzymes are important factors in the development of cleaning products, such as laundry detergents and dishwashing liquids. Utilizing enzyme detergents is more efficient, makes the washing environment milder and saves more energy. Modified textiles are being in contact with enzymes used in laundry detergents including amylase, cellulase and lipase while washing process, causing the loss of original properties of enzymes. The aim of this project is to investigate the interaction of metal (Ag) and metal oxide (TiO$_2$ and ZnO) nanoparticles and amylase, cellulase and lipase as detergent enzymes. In this case parameters influenced on their features including nanoparticle-enzyme ratio, time and temperature were monitored using central composite design (CCD). Finally the physiochemical and biochemical features and variations of enzymes as well as nanoparticles were investigated based on enzyme assay and model bacteria (model microorganisms including *Staphylococcus aureus* and *Escherichia coli*) survive. The activity of enzyme was studied using water contact angle and the nanoparticles physiochemical features variations were monitored using UV-Vis, CD and DLS.

Keywords: Enzymatic Detergent, Metal (Ag) and Metal oxide (TiO$_2$ and ZnO) Nanoparticle, Antibacterial, Cleaning Properties.

Application of TuckFMIN for Robust Estimating Tucker3 Solutions

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ABSTRACT
Despite MCR-FMIN [1] with trilinearity constraint which can be considered as a two-way analysis of three-way data sets, TuckFMIN is pave the way for the multi-way analysis of three-way data sets. TuckFMIN is an extended objective function minimization to preserve the Tucker3 features. Starting from higher-order singular value decomposition (HO-SVD)[2] loadings, TuckFMIN represents a new approach for obtaining three proper rotation matrices for transforming the HO-SVD loadings to physically and chemically meaningful solutions. In TuckFMIN, there are three rotation matrices S, T and U that are responsible for converting physically meaningless HO-SVD loadings (A, B, C) and non-sparse core of G to physically meaningful ones ($\tilde{A}, \tilde{B}$ and $\tilde{C}$) and sparse core ($\tilde{G}$). For each rotation matrix a special objective function ($f(S)$, $f(T)$ and $f(U)$) is regarded that is defined based on constraints non-fulfillment. FMIN is proposed for minimization of $f(total)$, where $f(total)=f(S)+f(T)+f(U)$. Every objective function is defined basis on suitable constraints such as normalization, non-negativity, trilinearity, sparsity, and etc [3]. For example $f(S)$ is defined as:

$f(S) = c_{norm}(S) + c_{non-neg}(S) + c_{tri}(S) + c_{spars}(S) + \cdots$. Trilinearity scalar function is defined because of the trilinear structure of $(\tilde{C} \otimes \tilde{B})'$. This trilinear scalar function can be efficient for obtaining robust convergence for full rank or rank-deficient data sets and decrease the risk of converging to the local minimum. TuckFMIN can sparse HO-SVD core by rotation of core elements using sparsity constraint. Simulated fluorescence data was exemplified to evaluate the feasibility of proposed method. For sake of comparison between different methods PARAFAC-ALS, HO-SVD and TuckFMIN are used. LOF (lack of fit) from TuckFMIN modeling is always as same as LOF of HO-SVD and less than LOF of the PARAFAC-ALS for noise free data sets. Despite the PARAFAC-ALS decomposition, TuckFMIN has the best fitting regardless to rank-deficiency or levels of noise . By means of simulation study, it is demonstrated that TuckFMIN with trilinearity and sparsity constraints can be helpful for faster convergence and obtaining the reproducible results.

Keywords: Non-linear constrained optimization, Rank-deficiency, Multi-way analysis, Trilinearity, Tucker3, Sparse core.

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Novel sorption-based on magnetic nanocomposite monolithic stir bar kit coupled to high performance liquid chromatography-ultraviolet detection for the determination of organophosphorus pesticides in environmental samples by optimizing the central composite design

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ABSTRACT

In this study, a novel stir bar sorptive kit based on magnetic nanocomposite monolithic material (MNM) was provided.The size and morphology of synthesized kits were characterized using field emission scanning electron microscopy (FESEM) equipped with energy dispersive X- Ray (EDX) spectroscopy system. The extraction and desorption analytical parameters, were optimized using a five-level three factor central composite design (CCD) and systematically, respectively. The prepared MNMSB kit was characterized and good preparation reproducibility was obtained with the relative standard deviations (RSDs) ranging from 3.73% to 7.97% (n = 3) in one batch, and from 5.39% to 10.84% (n = 3) among different batches. At optimum conditions method has linear response over 0.1–30 µg/mL for Ethion and 0.01–12 µg/mL for Phosalone, 0.1–25µg/mL for Diazinon, 0.06–7 µg/mL for Hexythiazox, 0.1–15 µg/mL for Chlorpyrifos and 0.1–10 µg/mL for total of OPPs, respectively. The limits of detection (LODs, S/N = 3) were found to be in the range of 9.60×10^{-6} µg/mL to 2.97×10^{-3} µg/mL. The RSDs of the method were in the range of 2.73–6.40% (n = 3, c = 1 µg/mL all of OPPs and 0.1µg/mL Phosalone) and the enrichment factors were from 2.23 to 14.52-fold.The results showed that MNMSBS kit could enrich the above-mentioned OPPs effectively. The MNMSBSE–LD/HPLC–UV methodology applied for the determination of OPPs real water samples.

Keywords: "Stir bar sorptive extraction, Magnetic nanocomposite monolithic material, High performance liquid chromatography-liquid desorption, Organophosphorus pesticides, Environmental samples, Centeral composite design"

Pesticides are widely used for agricultural activities due to their relatively low price and high effective ability to control pests, weeds, and diseases [1]. The increasing production of pesticides for agricultural and non-agricultural purposes has caused the pollution of air, soil, ground, and surface water which involves a serious risk to the environment and as well as human health due to either direct exposure or through residues in food and drinking water [2].

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Visualization of local rank information using microscopic structure of bilinear chemical data

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ABSTRACT

Multivariate Curve Resolution (MCR) is a methodology for analyzing chemical data used in many different application fields. However, MCR results are often complicated by the well-known rotational ambiguity problem. The reliability of the MCR results is highly dependent to the constraints that are used to apply the prior knowledge from the system under study. Local rank is one of the most powerful and widely used constraints in chemometrics [1]. Different methods in chemometrics rely on this constraint for building initial estimates [2], finding selective and/or zero concentration regions [3], and resolving concentration profile or spectra of analyte [4,5]. Furthermore, the prominent resolution theorems that define the uniqueness conditions in MCR are based on local rank information [6]. However, it has been shown very recently that local rank information may lead to incorrect solutions due to *local rank deficiency* problem [7]. More theoretical descriptions and generalizations are reported in this work to clarify the problem. Also, it is shown that the information related to the local rank can be extracted from the structure of data set by means of computational and geometry tools in addition to rank exploratory methods. Lawton-Sylvestre approach [8] in the case of two-componet and Borgen plot [9] in the case of three-component systems were used for this purpose.

Keywords: Multivariate curve resolution, Local rank constraint, local rank deficiency

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On the least size of first-order calibration model using multivariate curve resolution methods

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ABSTRACT

Several analytical applications of multivariate calibration methods require decision about the number of samples used for building the regression model. Calibration set should ideally be large enough and representative to produce reliable prediction [1]. In practice, however, the large number of calibration samples is costly in terms of time and effort. Some studies have been done to develop advanced regression techniques that are able to provide robust models from a limited number of calibration samples. In this work, a general rule for finding the minimum number of samples that must be acquired in a calibration problem is presented. The theoretical proofs, demonstrated both algebraically and geometrically, are based on the required number of known values for calculating the concentration profile of an analyte in a multicomponent system. The Partial least squares (PLS) [2], that often is referred to as a standard first order calibration, and also the correlation constraint multivariate curve resolution (CCMCR) [3] were used to assess the presented rules in several case studies.

Keywords: First-order calibration, Partial Least Squares, MCR-ALS, Correlation constraint

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Soft Trilinearity Constraints in Second Order Calibration

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ABSTRACT

Multivariate Curve Resolution (MCR) methods work by determining the pure component response profiles and their estimated concentrations when no prior information is available about the composition of the mixture. Experimental measurements generated by analytical instruments are so called second-order data when there is one matrix per sample and one measurement mode modulates the other, for example as in HPLC-DAD. If the second-order data follows a trilinear mathematical model this information can be applied as a constraint in MCR. Second-order data are obtained when measurements in a third-mode modulate the response matrices for each sample.

In practice, data analysis of trilinear data may be complicated by the fact that there are shifts in retention times of specific analytes from sample to sample. In such cases, a trilinear model is not valid and every analyte may not have the same elution profile in every sample, a strict requirement for trilinear behavior. Moreover, the sensitivity of the spectral response can change in the presence of different chemical matrix effects from sample to sample. In such cases the unique profiles normally obtained by strictly enforced "hard" trilinearity constraints may not necessarily represent the true profiles because the data set as a whole does not follow trilinear behavior. "Soft" constraints allow small deviations from constrained values and were first introduced by Gemperline [1]. He introduced a new algorithm using least squares penalty functions to implement constraints during alternating least squares steps. Later, Rahimdoust et.al visualized the effect of "soft" constraints on the accuracy of self-modeling curve resolution methods [2].

In this study, the use of soft trilinearity constraints rather than hard trilinearty constraints is investigated. For example, in the analysis of HPLC-DAD data, soft trilinearity constraints allow small deviations in HPLC peak shape or retention time. Simulated chromatography data sets are presented to evaluate the performance of the new algorithm, and a real case of an HPLC-DAD chromatogram of a three-compound system with two identified pesticides (azinphos-ethyl and fenitrothion) and one unknown interferent is analyzed. The results show that by imposing soft trilinearity constraints, a range of possible solutions is calculated that follow the trilinearity criteria, whereas by imposing hard trilinearity constraints, the unique solution that is calculated is not a correct solution and the result suffers from the presences of active constraints.

Keywords : "Multivariate Curve Resolution (MCR)" "Second-Order Data" "Soft Constraint" "Trilinearity" "Area of Feasible Solution (AFS)".

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Correlation constrained multivariate curve resolution for determination of polycyclic aromatic hydrocarbons in oil contaminated sea waters extracted by dispersive liquid-liquid micro-extraction and analyzed by gas chromatography

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ABSTRACT

Polycyclic Aromatic Hydrocarbons (PAHs) which are coming from incomplete combustion processes are very toxic organic pollutants and they can cause serious effects on the human health [1]. Due to the complexity of sample matrices including PAHs (e.g., oil contaminated waters), development of sensitive and selective analytical methods including a sample preparation technique followed by a separation technique (e.g., gas chromatography (GC)) is required for determination of PAHs. In this study, ultrasonic assisted extraction-dispersive liquid-liquid micro-extraction (UAE-DLLME) followed by gas chromatography-flame ionization detector (GC-FID) was proposed for simultaneous determination of thirteen polycyclic aromatic hydrocarbons (PAHs) in sea waters exposed to oil spills. The optimum extraction conditions obtained by response surface methodology (RSM) were 10 min sonication time, 14μL of tetrachloroethylene as extraction solvent and 1.2% (w/v) salt concentration. In order to have a comprehensive analysis, correlation constrained multivariate curve resolution-alternating least squares (CC-MCR-ALS) as a first-order calibration algorithm was used for resolution and quantification of the 13 target PAHs in the presence of uncalibrated interferences [2]. In this way, orthogonal projection approach (OPA) was used for estimation of the initial spectral values to start ALS optimization.

In this regard, calibration set for external calibration was randomly designed in concentration range 0.1-100 ngmL^{-1}. Then, multivariate analytical figures of merit (AFOM) including sensitivity (SEN), selectivity (SEL) and limit of detection (LOD) were calculated [3]. In all cases, the AFOMs were in acceptable ranges which confirm the validity of the proposed method. Finally, the proposed chemometrics-based strategy was successfully applied for determination of 13 PAHs in oil contaminated sea water after removal of oil spill using standard addition calibration. On this matter, all 13 PAHs were found in sea water in concentration range 8.0-300.0 ngmL^{-1} with relative standard deviation (RSD) below 5.6 %.

It is concluded that combination of multivariate calibration methods with DLLME-GC-FID can be a straightforward and rapid technique to improve the identification and quantification ability of these methods for the simultaneous determination of target compounds in different sample matrices.

Keywords: Chemometrics, Multivariate curve resolution, Gas Chromatography, Liquid-liquid micro-extraction, Polycyclic aromatic hydrocarbons.

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Investigating the Deep Eutectic-Water Binary Solvents Association by Vibrational Spectroscopy and Chemometrics methods

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ABSTRACT

Solvent–solvent interactions are important for probing chemical, industrial, environmental and biological processes in the liquid phase [1]. Therefore, investigating the behaviour of newly introduced solvents in the presence of other solvents such as water is essential. Deep eutectic solvents (DESs), introduced as novel green solvents by Abbott at 2003, are defined as eutectic mixtures of two or three non-toxic natural components that are able to generate intermolecular hydrogen bonds [2]. Choline chloride-glycerol deep eutectic solvent (GDES) was selected as a common DESs to study its behaviour in the presence of water. Combinations of vibrational spectroscopy (Raman and FTIR) and MCR-ALS were used to explore the association of solvents in the binary mixture of GDES and water. Preservation of intermolecular hydrogen binding between constituents of GDES during solvation with water was another aim of this study. Therefore, the behaviour of DESs and its components was compared. The binary mixture of glycerol (Gly), one of the liquid constituents of GDES, and water has been explored under the same conditions.

This work utilizes the power of multi-technique (Raman and FTIR) and multi-experiment (GDES and Gly) data analysis for the proper description of complex processes of water and GDES interaction. Two binary solvent systems of GDES-water and Gly-water were studied. For each solvent system, a total of 20 binary solvent mixtures with different mole fractions of co-solvent varied from 0% to 100% (in 5% intervals) were prepared by mixing the proper weights of the pure solvents. The ATR-FTIR and Raman spectra of each prepared binary mixtures were recorded and the digitized spectra of each solvent system were collected in different data matrices. For each solvent system, two data matrices were provided; a data matrix of Raman intensities and a data matrix of IR absorbancies. MCR-ALS was utilized to analyze the obtained IR and Raman data matrices. As a result, five species were obtained for GDES-water interaction. Pure water, GDES, GDES-water association, Gly and Gly-water association were components that were achieved from MCR-ALS analysis of the GDES-water binary mixture. The stoichiometry of GDES-water association was 0.1 of mole fraction of GDES. It exhibits the considerable role of GDES even in very low mole fractions in the presence of water. In addition, concerning both GDES and Gly interaction in the presence of water by multi-technique and multi-experimental technique, identified GDES as a distinct solvent from its constituent (Gly).

Keywords: Deep eutectic solvents; Deep eutectic-water binary solvents; MCR-ALS; Solvent–solvent interactions; Vibrational spectroscopy.

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Evaluation of saffron adulteration by means of thin layer chromatography-image analysis and chemometrics methods

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ABSTRACT

Saffron, the dried stigmas of Crocus *sativus* L., is one of the most precious spices in the world, due to its delicate aroma and special color. Because of its limited production owing to the laborious process required, saffron become an expensive spice and therefore is considered as one of the major candidates for economically motivated fraud [1-2]. In the present work, thin layer chromatography-image analysis (TLC-IA) combined with chemometrics has been employed for detection of saffron adulteration and identification of the adulterant. Seven saffron natural and artificial adulteration including sumac, turmeric, safflower, common madder, quinoline yellow, sunset yellow and tartrazine were used to simulate artificial counterfeit mixtures of saffron. Overall, 6 mixtures containing saffron and 5-30% (w/w) of plant adulterants were prepared and analyzed for each adulterant and thus eight classes, including the authentic saffron samples, were defined. The saffron metabolites were extracted with a mixture of ethanol/water and analyzed by TLC. The images of the TLC plates were recorded under visible light and subsequently imported into the MATLAB software. The images were compressed, inverted, baseline corrected using asymmetric least squares (AsLS), aligned by correlation optimization warping (COW) and finally converted to RGB chromatograms. To eliminate the artificial sources of variations, the chromatograms were normalized toward total peak area. The data were mean centered and Pareto-scaled prior to data analysis [3]. Eventually, the preprocessed data were randomly divided into training and test sets for further classification analysis. Different pattern recognition techniques including principal component analysis (PCA) and K-means were used to explore the general structure of the obtained data. Moreover, supervised pattern recognition was carried out through partial least squares discriminant analysis (PLS-DA). The model parameters for fitting, cross-validation and external validation including sensitivity, specificity and accuracy for all the groups were equal to 1.00. In order to obtain a better understanding of the model, two different variable selection methods including variable importance projection (VIP) and PLS loading weights were used. The results indicated that even after reducing a large number of the variables, the model performance was acceptable. Finally, the model was successfully utilized to predict the potential adulterants in real samples.

Keywords: "Adulteration"; "Chemometrics"; "Image analysis"; "Saffron"; "Thin layer chromatography"

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Receptor guided QSAR studies of S-trityl-L-Cysteine analogues as potent Eg5 inhibitors.

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ABSTRACT

kinesin Eg5, a member of the kinesin-5 superfamily, is responsible for the formation and maintenance of bipolar spindle in the early prometaphase stage of mitosis. Since Eg5 plays a crucial role in cell division, inhibition of this protein causes mitotic arrest, which can lead to cell death. In the past few years, a large number of chemicals were synthesized and evaluated as Eg5 inhibitors [1, 2]. Kosielski and coworkers introduced S-trityl-L-cysteine (STLC) as a potent Eg5 inhibitor.

In the recent years computational drug design methods have gained significant contribution to the development and optimization of drugs, which may shorten the cycle of the drug development [3]. Among the theoretical methods, quantitative structure–activity relationship (QSAR) is a well-established technique to quantitative correlate the physicochemical properties of molecules to their biological properties.

In the present report, we performed a hybrid docking-QSAR approach to obtain a statistical QSAR model to the study of the structural features of STLC analogues synthesized by Wang et al. that influenced in Eg5 inhibitory activity [4]. In the first step, in order to consider the conformational change of STLC analogues in Eg5 binding site the favorable conformation of STLC analogues in the binding site of Eg5 was obtained from the docking methods. Then the structural molecular descriptors of these optimized conformers were computed to developed statistical QSAR models. Multiple linear regression was applied to choose the best subset of descriptors. The selected descriptors explain that the gravitation index [all pairs], and H attached to C_1 (sp^3)/C_0 (sp^2) play important roles in Eg5 inhibition. Multiple linear regression (MLR), square support vector machine (SVM), and artificial neural network (ANN) were used as QSAR models, respectively. The results of this model reveals the superiority of SVM models over two others models. The squared correlation coefficient (R^2), root mean square error (RMSE) and standard error (SE) for SVM are: R^2=0.964, RMSE=0.16 and SE=0.150 for the training set, and R^2=0.920, RMSE=0.287 and SE=0.25 for the test set. Leave one out cross validation test was used for assessment of the predictive power and validity of models which led to cross-validation correlation coefficient (Q^2) of 0.941 and standardized predicted relative error sum of squares (SPRESS) of 0.225 for SVM model.

Keywords: QSAR, kinesin Eg5, S-trityl-L-cysteine (STLC), Molecular descriptor, SVM

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The application of multivariate curve resolution-correlation optimized warping method for simultaneous solving coelution and time shift-related artifacts in complex GC-MS signals; toward obtaining the through comparative study of chemical variability of citrus aurantium L. peel samples

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ABSTRACT

Multivariate curve resolution of the coeluted multicomponent signals based correlation optimized warping (MCR-COW) was proposed as an efficient alignment method in correcting the undesirable elution time shifts where coeluting and shift occurred at the same time and the use of COW algorithm on the raw data often fails [1]. For this purpose, the primarily implementation of extended multivariate curve resolution-alternating least square in a multiset analysis of three samples helped to reduce the underlying complexity of GC-MS data representing the pure elution and spectral signatures. Afterward, the resolved elution profiles aligned component by component using COW algorithm. Reconstituting of the corrected multiset data was conducted by multiplying of aligned augmented elution profiles with their spectral profiles to reanalysis by MCR-ALS under triliearity constraint [2]. The results obtained from the proposed strategy (MCR-COW-MCR) compared to two common methods MCR-ALS and COW-MCR under application of the same constraints in statistical terms such as lack of fit (LOF), percent of variance explained by model (R^2) and spectral correlation coefficient (R). Inspection of the results shows that by avoiding of aligning the non-corresponding elution information and improving the initial application of COW algorithm in MCR-COW-MCR method, the quality of the chemical variability of the chromatographic profiles related to the constituents of three varieties of citrus aurantium L. peel extracts were correctly assessed by PCA modeling. Hereby, the presented strategy by improving the accuracy of quantitative and qualitative results provided an opportunity to reach a comprehensive comparative study from the composition and content of volatile constituent's points of view in the studied samples. According to the obtained results, it can be concluded that relevant similarities among volatile constituents of desired varieties related to the predominant presence of monoterpene and sesquiterpene hydrocarbons. In addition, the oxygenated compounds derived from these hydrocarbons in relatively low content were considered as an indicator of high quality of peel samples [3]. On account the highest content of oxygenated compounds in variegated sour orange in comparison to other verities, it can be concluded that the variety can affect the amount of oxygenated compounds and as a result on the sample quality. Furthermore, each variety contains the constituents in minor quantities that differ between them and can be used in identifying and authenticity the various extracts because of they are responsible for the specific flavor and odor of citrus fruits.

Keywords: "Correlation optimized warping", "Multivariate curve resolution", "Gas chromatography-mass spectrometry", "Citrus aurantium L.", "Variety".

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Simultaneous UV-Vis spectrophotometric quantification of Auramine O and Acridine orange dyes by partial least squares

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ABSTRACT

One of the main difficulties in quantification of dyes in industrial wastewaters is the fact that dyes are usually in complex mixtures rather than being pure. Auramine O (AU) and Acridine orange (AO) in aqueous solutions were selected as two model dyes whose UV-Vis absorption spectra highly overlap each other. The spectral overlap between AU and AO dyes is extreme and this will retard their direct quantification by simple spectrophotometry without separation. Therefore, univaraite calibration is not applicable for the current sorption system and an analysis must be performed by chromatographic procedures or multivariate calibration methods in order to overcome such degree of overlapping [1,2]. Partial least squares (PLS-1) is factor-based chemometric method which can analyze highly collinear noisy data [3]. We developed one rapid and powerful method for spectral resolution of a highly overlapping binary dye system in the presence of interferences. The calibration samples were built by random number generation method with dye concentrations ranging from 3–32 mg/L. Once the calibration/training has been done, the final PLS-1 model may be further used to predict the concentrations of new samples. The spectra of an independent test dataset consisting of 10 samples were applied to the PLS-1 model. High accuracies in prediction of AU and AO dyes were obtained and all predicted values being close to the reference ones. A number of important statistical parameters such as correlation coefficient (R^2_{pred}), root mean square error of prediction (RMSEP) and relative error of prediction (REP) were calculated. In the case of a river water sample, taking into account the complexity of the matrices available in natural waters, the prediction power of PLS-1 model for these dyes can be considered acceptable with recoveries between 92-98%.

Keywords: Acridine Orange, Auramine O, Partial least squares

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application of response surface methodology for the obtaining optimization removal of crystal violet from aqua sulotion

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ABSTRACT

before discharging wastewaters to aquatic ecosystems, it is necessary to reduce dye concentration in the wastewater. Ultraviolet-Visible (UV-Vis) spectrophotometric techniques have received increasing attention in the area of simultaneous determination of dyes, especially during the last decade [1]. Silicate was prepared by extraction from straw. Also, synthesis of SBA-15 mesoporous silica nanoparticles was performed and characterized by means of X-ray diffraction, Fourier transform infrared spectroscopy, scanning electron microscopy, and N2 adsorption–desorption [2]. The BET surface area and average pore diameter of synthesized SBA-15 were obtained to be 602 $m^2 g^{-1}$ and 4.5 nm, respectively. SBA-15 mesoporous silica nanoparticles used as adsorbent for the removal of crystal violet (CV) cationic dye from aqueous solution. Four factors including the pH, adsorbent dosage, initial dye concentration and ageing time have been optimized by response surface modeling (RSM) using design expert software (version 8.0.7.1) for removal of crystal violet by SBA-15 nanoparticles. Results indicated that longer contact times (14 min), higher initial concentrations (28 mg L^{-1}), lower adsorbent dosages (0.1 g L^{-1}) and basic pH (9) results in the best adsorption capacity of SBA-15 with response surface methodology. The combined effect of factors on the adsorption uptake of SBA-15 nanoparticles is shown as contour plot and response surface plots. Finally, the maximum adsorption capacities of 166 mg g^{-1} at optimum experimental conditions was obtained for crystal violet. The SBA-15 nanoparticles have the potential to be applied in real industrial wastewaters for the removal of cationic dyes such as crystal violet.

Keywords: crystal violet, SBA-15, response surface modeling

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Binning approach combined with multivariate curve resolution-alternating least squares for quantitative mass spectrometry imaging

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ABSTRACT

Large and complex data sets generated by modern instruments during the last decade have led to the so-called Big Data era. High resolution mass spectrometry imaging (HRMSI) instrument is one of the most powerful instruments which generates such Big Data and it has a central role in modern analytical chemistry. On this matter, MSI data are difficult to analyze using conventional tools. Chemometric methods have shown potential to fill the gap in the analysis of MSI data especially for quantitative MSI [1]. The aim of this work was quantification of chlordecone as a carcinogenic organochlorinated pesticide ($C_{10}Cl_{10}O$) in mouse liver using matrix-assisted laser desorption ionization MSI (MALDI-MSI) method [2]. The MSI data sets were corresponded to 1, 5 and 10 days of mouse exposure to the standard of chlordecone in quantity range of 0 to 450 μg/g. The raw data size was 70 gigabytes (GB) for one sample. Therefore, binning approach in m/z direction was necessary to group high resolution m/z values and to reduce the data size. To consider the effect of bin size on the quality of the obtained results, three different bin sizes of 0.25, 0.5 and 1.0 were chosen. In this regard, the number of m/z values was reduced from 101205 to 2400, 1200 and 600, respectively. Afterwards, the three-way MSI data arrays (two spatial dimensions and one m/z dimension) for seven standard samples (calibration set) and four unknown samples (test set) were column-wise augmented with m/z values as common mode. Then, these data sets were analyzed using multivariate curve resolution-alternating least squares (MCR-ALS) using proper constraints [3]. Singular value decomposition (SVD) and orthogonal projection approach (OPA) were used to determine the number of components and initial estimates of spectral profiles, respectively. The resolved mass spectrum was used for identification of chlordecone in the presence of complex background and interferences. Additionally, augmented spatial profiles were post-processed to obtain 2D images for each component in different samples. Then, these images were used to set the calibration curve and to obtain analytical figures of merit (AFOM). Finally, the obtained results by MALDI-MSI-MCR (bin size 0.25 as optimum size) were compared with previous results using gas chromatography-mass spectrometry (GC-MS) and MALDI-MSI using msiQuant software. The obtained results using MALDI-MSI-MCR method were higher than MALDI-MSI and lower than GC-MS which confirms the performance improvement of MALDI-MSI using chemometric method. As an instance, the chlordecone quantity for data set II (five days of exposure) was 141.9 μg/g by GC-MS, 77.7 μg/g by MALDI-MSI-MCR, and 15.0 μg/g by MALDI-MSI. All of these results confirmed the potential of chemometrics as an alternative way for quantitative MSI.

Keywords: Mass spectrometry imaging, Big data, Multivariate curve resolution, Binning approach

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Prediction of surface tension of alcohol + water solutions using Feed-Forward neural networks and thermodynamic model at various temperatures

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ABSTRACT

Feed-Forward Neural Networks(FFNNs) are among the most important neural networks that can be applied to wide range of forecasting problems with a high degree of accuracy[1-2]. The aim of this study, was predicting surface tension of aqueous solution of methanol, ethanol, 1-propanol and 2-propanol in range temperatures of 293.15-323.15K using with two entrance variables, mole fraction and temperature, one hidden layer(with 1-10 neuron) and one output neuron. In this work, a set of experimental data of alcohol/water mixtures at various temperatures have been collected from the literature [3].The optimal FFNN structure model was determined based on the maximum value of R^2 and the minimum value of the APD of the testing set for each system. The obtained results for R^2 and APD values, showed that the best FFNN architectures for binary mixtures of water/methanol, ethanol, 1-propanol and 2-propanol are (2:4:1), (2:5:1), (2:3:1) and (2:6:1), respectively. As it is obvious from Fig. 1, the calculated values of training, validation and testing sets are located around the bisection, and this indicates the accuracy of the results and the ability of the used FFNN model for predicting the desired property (water/methanol systems). In Fig. 2, the differences between the experimental and calculated values for water/ 1-propanol system are potted versus the experimental data. This figure shows that the range of error for surface tension is (-0.38 to 0.33), other systems had a same pattern. The obtained results confirm that the FFNN is a powerful method for predicting the surface tension of high-polar binary mixtures of water/alcohols. Finally, to check the performance of the FFNN model, its estimations are compared with thermodynamic model base on chemical equilibrium and discussed from a theoretical point of view [4].
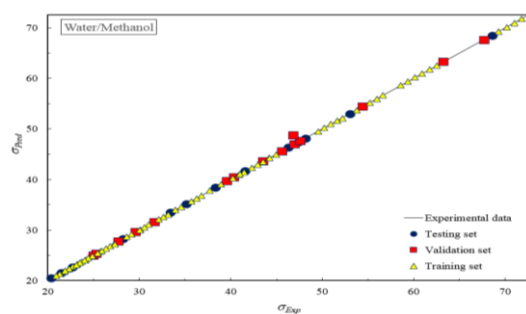
Fig. 1. Calculated results of surface tension with FFNN technique versus reported experimental for water/methanol systems.
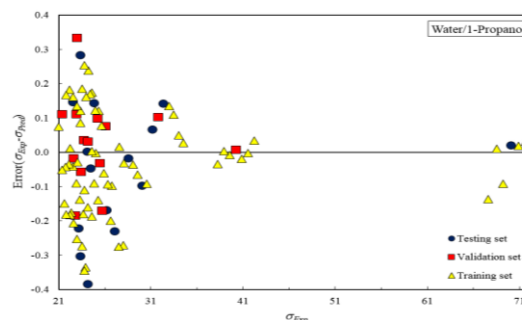
Fig. 2. Williams plot describing applicability of surface tension for water/1-propanol systems by the FFNN method.

Keywords:
Prediction, Surface tension, Feed-Forward Neural Network, Neuron number.

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Simultaneous spectrophotometric determination of nitroaniline isomers after dispersive liquid-liquid microextraction by

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ABSTRACT

A new method for simultaneous spectrophotometric determination of nitroaniline isomers is developed by dispersive liquid-liquid microextraction (DLLME) preconcentration[1]and chemometrics methods[2]. In the proposed method, dicholoromethaneand asetonitrileare selected as extraction and dispersive solvent. The optimization strategy is carried out by using two level full factorial designs. Results of the two level full factorial design (24) based on an analysis of variance demonstrated that the pH, ionic strength, amount of dispersive and extraction solvents are statistically significant. Optimal condition for three variables: pH, ionic strength, amount of dispersive and extraction solvents are obtained by using Box-Behnken design. Under the optimum conditions, the calibration graphs are linear in the range of 0.05-15.0, 0.03-14.0 and 0.04-15.0$\square$g mL-1with detection limit of 0.016, 0.011 and 0.15$\square$g mL-1($3\square$B/slope) and the enrichment factor of this method for uranium reached at 150. The method is successfully applied to the determination of trace amount of nitroaniline isomers in different water samples. DLLME [3] coupled with orthogonal signal correction-partial least squares (OSC-PLS) algorithm for data processing for determination of uranium in synthesis and real samples. DLLME-OSC-PLS method was presented for the first time in this study. The root mean squares error of prediction for nitroaniline isomersdetermination using PLS and OSC-PLS models were 0.651, 0.542, 0.712and 0.103, 0.098, 0.127, respectively. This procedure allows the determination of nitroaniline isomerssynthesis and real samples such as waste water with good reliability of the determination.

Keywords: Nitroaniline isomers, Determination, DLLME, Box-Behnken design, PLS, OSC-PLS.

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QSAR study for inhibitory activities of Phosphodiesterase

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ABSTRACT
A quantitative structure-activity relationship (QSAR) study has been done on the inhibitory activity of some phosphodiesterase. QSAR models were based on multiple linear regression (MLR), genetic algorithm (GA) and successive projection algorithm (SPA). First, stepwise MLR was used as a linear descriptor selection procedure and then SPA and GA was employed as a non-linear descriptor selection method. Finally, selected descriptors were employed for constructing model by supported vector regression (SVR) and MLR techniques. Comparison of the statistical results after cross validation was indicated the priority of nonlinear methods to MLR models.

Keywords: Quantitative structure–activity relationship (QSAR); Inhibitory activity; Phosphodiesterase, IC50

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Calculation and Simulation of Thermal Degradation Kinetics by Artificial Neural Network

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ABSTRACT

The thermal degradation of materials such as plastics, cartons, municipal wastes, etc. has received renewed attention due to the possibility of converting these wastes into useful energetic products or into valuable chemicals. The thermogravimetric analysis (TGA) is one of the most commonly used techniques to study the reactions of thermal decomposition of solids [1-2].

On the other hand, it has been proved in many cases that the appropriated kinetic model can explain a set of TG dynamic data with a single set of kinetic parameters regardless of the heating rate [3].

In this paper, we introduces a new approach based on artificial neural network (ANN) to study the kinetics of thermal decomposition reactions of polymeric material, using dynamic thermogravimetry analysis (TGA) at several heating rates. A multilayer neural network model was trained and tested using experimental data, allowing the proposed model a very good correlation of the weight-loss data. As an example, the same kinetic model has been applied to simultaneously fit runs performed at different heating rates.

Keywords: ANN, TGA, Polymer, Kinetic, Degradation.

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Model Free and Hybrid Genetic Algorithm Coupled Direct Search Methods for Pyrolysis Kinetics: Thermal Decomposition of Waste PET

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ABSTRACT

Model-free approach that are implemented till date for evaluating the optimum overall pyrolysis kinetics parameters usually used traditional gradient base optimization techniques. Since polymer decomposition is a complicated process, serious uncertainties arise about an accurate description of decomposition kinetics by using simplified equations expressing a rate of the process only via mass loss [1-5].

To overcome such drawbacks and uncertainties, we have, used the modern evolutionary optimization method (i.e. hybrid genetic algorithms (HGA) technique). The experimental thermogravimetric analysis (TGA) data was used in this technique to attain the globally optimum kinetics parameters. Also, we compare the experimental and simulated data to obtain the possible mechanism to take place during pyrolysis. As case study, we used thermal decomposition of polyethylene terephthalate (PET). The suitability of the models is also tested using the AICc score. Also, the nth order model demonstrations good AICc score and well predicted the experimental TGA data.

Keywords: Genetic Algorithm, TGA, Polymer, Kinetic, Degradation**.**

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Quantitative structure–activity relationship analysis of a series of 2,3-diaryl imidazole as selective cyclooxygenase-2 inhibitors

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ABSTRACT

COX-2 is an oxido-reductase having a role in prostaglandin biosynthesis, inflammatory responses and in cardiovascular events. Cyclooxygenase 2 (COX-2) inhibitors are common non-steroidal anti-inflammatory drugs that could be useful in the therapy of inflammatory and painful conditions including rheumatoid arthritis, soft tissue lesions, fever and respiratory tract. The imidazole's are a group of COX-2 inhibitors [1-3]. In this work, 2D-QSAR analysis has been carried out on eighty-five 1,2-diaryl imidazole. The genetic algorithm (GA), stepwise and GFA algorithm used as variable selection method. Correlations between inhibitory activities and calculated predictor variables were established through multiple linear regression (MLR) and partial least-squares regression (PLS) method. The results were compared and the best model was selected. This model was further used to predict the COX-2 inhibitory activity of 25 test set of compounds and good results were obtained.

Keywords: QSAR, COX-2, GA, MLR, PLS.

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A QSAR study of 5α –reductase inhibitors using multivariate image analysis

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ABSTRACT

Testosterone and its more potent metabolite, DHT, are essential hormones for male phenotype sexual differentiation and maturation through their actions at the androgen receptor. This hormone convert to dihydrotestosterone (DHT) by the enzyme 5α -reductase (5AR) that this conversion is related to the development of many endocrine diseases such as prostatic cancer. Also 5AR play an important role in other physiological processes. 5α -Reductase is a system of two isozymes: 5α reductase Type 1 and 5α -reductase Type 2 [1-3]. In this study, we applied quantitative structure-activity relationship (QSAR) analysis to a series of 38 compounds of 4-X-17-Y-4-Azaandrost-3-ones as 5α -Reductase Type 2 inhibitors. we investigate the effect of pixel selection by application of genetic algorithms (GA) and orthogonal signal correction (OSC). In order to find correlations between inhibitory activities and calculated predictor variables, partial least-squares regression (PLS) model were developed and the resulted model showed high prediction ability.

Keywords: QSAR, 5α -reductase, GA, OSC, PLS.

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Structure-retention time modeling of some anthraquinone-based dyes by considering chain lengths of organic modifiers in the eluent of micellar HPLC

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ABSTRACT

Micellar liquid chromatography (MLC) is a green liquid chromatographic technique which is dramatically growing in last decade [1]. In this technique, an aqueous solution of a surfactant along with an alcoholic modifier is usually employed as mobile phase composition. Quantitative predictive/descriptive models are usually useful tools to predict and elucidate chromatographic behavior in MLC systems. In this work, a quantitative structure–activity relationship (QSPR) model was proposed for retention time of anthraquinones in reverse phase MLC system. Retention time of 96 chromatographic samples (16 antraquinones evaluated by using 6 different organic modifiers) were experimentally determined and used as the independent variables of the QSPR model. Five small-chain alcohols (methanol, ethanol, propanol, butanol and pentanol) as well as acetonitrile were used as the eluent modifiers. The matrix of the dependent variables of the model was build using structural descriptors of antraquinones and empirical parameters of organic modifiers in the applied MLC [2]. It should be noted that not-retained chromatographic mixtures were excluded from QSPR modeling. After deleting the not-retained samples (t_R < 2.5 min), the matrix containing both the structural properties of antraquinones and the empirical scales of the modifies were entered to the variable selection and multiple linear regression model construction steps. A five-parameter model was proposed for the logarithm of the retention time values which covered about 96% and 95% variance of data in training and cross validation, respectively. The correlation coefficient of the external test set was 0.97 which showed the prediction ability of the proposed model as well as its good applicability domain that was checked using standardized residual-leverage plot. The stability and significance of the proposed model were tested by applying model on different random-selected training and test sets. It was concluded that both structural properties of analytes (antraquinones) and properties of organic modifiers are contributed in the proposed quantitative structure-retention time relationship.

Keywords: Antraquinones, Descriptive models, Micellar liquid chromatography, Multiple linear regression, Quantitative structure–activity relationship

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Gas Chromatographic Fingerprint Analysis of Secondary Metabolites of *Salvia* using Pattern Recognition Techniques for Source Identification and Quality Control

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ABSTRACT

Chromatographic fingerprinting is a common method for classification, authentication and quality control of natural complex samples such as plant extracts [1]. In this regard, gas chromatography (GC) is the best option for fingerprinting and identification of chemical composition of such samples, as GC can provide reliable qualitative and quantitative information about the sample [2]. On the other hand, due to the complexity of natural sample matrices and lack of selectivity in analytical instruments, multivariate chemometric methods have been largely used to extract maximum useful information from chromatographic fingerprints [1,3]. In the present contribution, a chemometrics-based strategy is proposed for GC fingerprints analysis of *Salvia* for source identification and quality control. On this matter, ultrasonic-assisted extraction-dispersive liquid-liquid microextraction (UAE-DLLME) was used for extraction of chemical components of twenty-eight *Salvia* samples from eight populations. The optimum extraction conditions were obtained using factorial based response surface methodology (RSM). The optimum parameters were 60 mg of powdered aerial parts of dried *Salvia* sample, 2.5 mL of methanol as first extraction solvent, 45 min first sonication time, 40°C extraction temperature, 30 μL of tetrachloroethylene as preconcentration solvent, 2 min second sonication time and NaCl 7% (w/v). The GC profiles were arranged in a data matrix and this data matrix was autoscaled before cluster analysis. The data was then analyzed using principal component analysis (PCA), hierarchical cluster analysis (HCA) and *k*-nearest neighbors (*k*NN) clustering methods to explore similarities and dissimilarities among different *Salvia* samples according to their secondary metabolites. As an instance, PCA with three PCs could explain 85.8 % variance of data. In general, three clear-cut clusters were determined using PCA score plot and HCA and kNN dendrograms. In addition, according to the PCA loading plot and kNN dendrogram of selected variables by different variable selection methods, the chemical markers (chemotypes) responsible to this differentiation were characterized. Finally, a reference chromatographic fingerprint was developed for each cluster which can be used for quality control. It is concluded that the proposed strategy in this work can be successfully applied for comprehensive analysis of chromatographic fingerprints of complex natural samples.

Keywords: Chromatographic fingerprinting, Salvia, Multivariate classification, k-nearest neighbors.

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Preconcentration and simultaneous multicomponent spectrophotometric determination of lead and cadmium using modified maghemite nanoparticles by WOSC-PLS and OSC-PLS

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ABSTRACT

A novel and fast solid phase extraction method for simultaneous preconcentration and determination of lead and cadmium ions in real samples was developed by using sodium dodecyle sulphate-coated maghemite nanoparticles (SDS-coated γ-Fe_2O_3 NPs) as a new extractor. The chemical co-precipitation method was used in the preparation of the γ-Fe_2O_3 NPs. The maghemite nanoparticles were synthesized according to a method proposed elsewhere [1]. The coating of nanoparticles by SDS was performed according to the method proposed elsewhere [2]. After preconcentration, the absorbance of the extracted ions was measured using tiazolylazo-Resorsinol (TAR) as a complexation reagent in the wavelength range of 300–700 nm. The influence of effective parameters on the separation and preconcentration of the analytes, such as amount of adsorbent, pH, amount of SDS, contact time, volume and concentration of eluent and extraction volume were investigated. PLS modeling is a powerful multivariate statistical tool and can be performed with easily accessible statically software. The basic concept of PLS was originally described by Wold et al. and consequently different application for PLS modeling were reported [3]. The wavelet orthogonal signal correction with the partial least squares (WOSC-PLS) method was then applied for simultaneous determination of adsorbed metal ions. Under optimized conditions, the calibration curves were linear in the range of 0.2 - 4.7 and 0.04 -3.02 μg L^{-1} for Pb (II) and Cd (II), respectively. Limits of detection and enrichment factors for lead and cadmium were 0.039-0.019 μgL^{-1} and 240-250, respectively. The proposed method was successfully applied for the simultaneous determination of lead and cadmium in drink samples.

Keywords: nanoparticles, wavelet, orthogonal signal correction, partial least squares, Chemometrics

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Chemometrics assisted liquid chromatography–mass spectrometry in full scan mode for quantification of two immunosuppressant drugs in whole blood samples

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Immunosuppressant drugs are used increasingly to prevent allograft rejection in organ transplant patients. Cyclosporine A and the structurally related macrolides tacrolimus, sirolimus and everolimus are increasingly used for maintenance of immunosuppression in combination with a steroid and mycophenolic acid. All of these agents have narrow therapeutic indices and, as a result of highly variable inter-subject pharmacokinetics, require therapeutic drug monitoring to individualize dosage based on target concentration ranges [1]. In the present study, a strategy that combines three-way liquid chromatography–mass spectrometry (LC–MS) data with second-order calibration methods based on multivariate curve resolution-alternating least squares (MCR-ALS) algorithm and alternating trilinear decomposition(ATLD) algorithm were developed for simultaneous determination of two immunosuppressant drugs in human blood samples. Acceptable resolution and quantification results in the presence of matrix interferences were achieved and the second-order advantage was fully exploited. The average recoveries were between 90% and 110% with average relative standard deviation of less than 10% in both methods.Indicating that the strategy could provide satisfactory prediction results for multi-drug assay in human blood samples only using liquid chromatography -mass spectrometer in full scan mode[2]. Considering the advantages of fast, low-cost, high sensitivity, and no need of complicated chromatographic and tandem mass spectrometric conditions optimization, the proposed strategy is expected to be extended as an attractive alternative method with respect to LC-MS/MS, to quantify analyte(s) of interest in complex systems such as cells, biological fluids, food, environment, pharmaceuticals and other complex samples[3].

Keywords: Cyclosporine A, Tacrolimus, Liquid chromatography–mass spectrometry (LC–MS), Multivariate curve resolution-alternating least squares (MCR-ALS) algorithm, Alternating trilinear decomposition (ATLD) algorithm.

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Application of genetic algorithms for pixel selection in MIA-QSAR study of CK-1δ inhibitors as neuroprotective agents

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ABSTRACT

Amyotrophic Lateral Sclerosis (ALS) is a progressive neurodegenerative disease which results in paralysis, muscle wasting and death. Death of the motor neurons of the cortex, spinal cord and brain stem is a characteristic of this disease which eventually leads to death of the patient usually resulting from respiratory failure, mostly within 3-5 years from the appearance of symptoms. Among the reported isoforms and splice variants of CK-1 protein superfamily, CK-1δ is known to phosphorylate different serine and threonine sites on TDP-43 protein in vitro and the thus qualifies as potential target for ALS treatment. Quantitative structure-activity relationships (QSAR) model [2] has been developed for the CK-1δ inhibitors of 37 various N-Benzothiazolyl-2-Phenyl Acetamide derivatives [1].
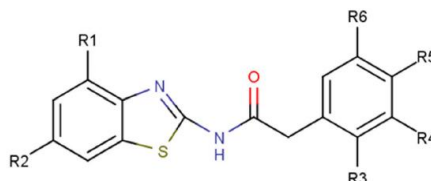
Bidimensional images were used to calculate some pixels [2]. Multivariate image analysis [3, 4] was applied to QSAR modeling of the CK-1δ inhibitors of these compounds by means of multivariate calibration such as principal component regression (PCR) and partial least squares (PLS). In this study we investigate the effect of pixel selection by application of genetic algorithms (GAs) for PLS model. GAs is very useful in the variable selection in modeling and calibration because of the strong effect of the relationship between presence/absence of variables in a calibration model and the prediction ability of the model itself. The subset of pixels, which resulted in the low prediction error, was selected by genetic algorithm. The resulted model showed high prediction ability with RMSEP of 0.0985, 0.0763 and 0.0103 for PCR, PLS and GA-PLS models, respectively. Furthermore, the proposed QSAR model with GA-PLS was used for modification of structure and their activity predicted.

Keywords: QSAR, CK-1δ inhibitors, PCR, PLS, GA-PLS.

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Quantitative Structure Activity Relationship (QSAR) modeling of opioid activities for some morphine derivatives by linear & non-linear procedures

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ABSTRACT

QSAR studies have been performed on forty-four molecules of morphine derivatives. With studies on opioid activities for some morphine derivatives [1] and determining the amount of agonist potency relative to morphine [2], tow techniques: multiple linear regression (MLR) and support vector machine (SVM) were used to design the relationship between molecular descriptor and agonist potency morphine derivatives (14-Acylaminomorphinones and 14-alkylaminomorphinones). Semi- empirical quantum chemical calculation (AM1 method) was used to fine the optimum 3D geometry of the studied molecules. Among these 44 molecules, 35 (79%) were selected as the training set molecules based on structural diversity and the remaining 9 (21%) molecules were used as test set. The modeling was estimated by Stepwise selection method using different descriptors obtained from Dragon software. Four hundred thirty-six descriptors were calculated. The coefficient of determination (R-square) of 0.9 was observed between experimental and predicted activity value of training set and R-square of 0.821 was observed for test set by MLR. The coefficient of determination of 0.939 was observed for training set and R-square of 0.863 was observed for test set by SVM. The standard error was calculated 0.344 for training set and 0.364 for test set by MLR and it was calculated 0.077 for training set and 0.218 for test set by SVM. High correlation between experimental and predicted activity values was observed, indicating the validation and the good quality of the derived QSAR models.

Keywords: Quantitative structure – activity relationship, Opioid activities, MLR procedure, SVM procedure, Morphine derivatives.

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QSPR Study of Chemicals Adsorption on the MWCNT using Bee Algorithm as Descriptor Selection Method

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ABSTRACT

Adsorption of chemicals on nanomaterials is an effective and important issue in nanotechnology. It can be studied as the main subject for complicated interactions between nanoparticles (NPs) with target molecules when they are used as drug delivery [1] diagnostic tools or environmental adsorbents. In this study, a new quantitative structure–property relationship (QSPR) methodology was used to model and predict the adsorption coefficients of some small organic compounds on multiwall carbon nanotube (MWCNT) based on bee algorithm (BA) method. The 3-D structures of these compounds were optimized using Hyper Chem software (version 7.0) with semi empirical AM1 optimization method. After optimization a total of 3224 0-, 1-, 2-, and 3-D descriptors were generated using Dragon software (version 3.0). A major problem of modeling is the high dimensionality of the descriptor space; therefore, descriptor selection is one of the most important steps. For descriptor selection in the first step, the bee algorithm program was written in Matlab (Ver. 7.0.4). In this paper, bee algorithm (BA) was used to select the best descriptors. Bee algorithm is a new population-based optimization algorithm, which is derived from the observation of real bees and proposed to feature selection [2]. Four descriptors were selected and used to model building by multiple linear regression (MLR) method. Root mean square error (RMSE) and determination coefficient (R^2) were obtained as 0.157 and 0.9642, respectively. Then the data set was divided to training and test sets and the RMSE and R^2 were obtained for two sets using four selected descriptors by BA. The RMSE and R^2 were obtained as 0.148 and 0.9545 for the training set and 0.2630 and 0.9366 for the test set.

Keywords: QSPR, Descriptor selection, Bee algorithm, Adsorption, MWCNT

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Identification and quantification of ciprofloxacin, enrofloxacineanddifloxacin in milk through excitation emission fluorescence and chemometricsmethods

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ABSTRACT

Though there are many analytical methods available to determine antibiotic residues in milk, most of them are rather complicated[1].In this workamethod for simultaneous determination of ciprofloxacin, enrofloxacine and difloxacin in milk was proposed by fluorescence spectroscopy combined with chemometrics.

Antibiotics are becoming available for use in animal husbandry. This, along with the possibility of the development of antibiotic resistant human pathogens, make it an important class of drug for which methodology is required for the monitoring of residues in food[2].Rank annihilation factor analysis (RAFA) is employed to analyze matrices of spectrofluorimetric data in two and three component mixture. Annihilation of the contribution of one chemical component from the original data matrix is basis of RAFA. In order to apply RAFA for the determination of an analyte in an unknown sample, a standard second order data of the analyte with rank one should generally be available[3].The determinations were performed in methanol/water medium (60/40% v/v) at pH 9.1, provided by adding a tris buffer solution in the difference concentration of antibiotic samples. Using RAFA for excitation–emission matrix fluorescence successfully achieved quantitative analysis of the three residues antibiotics simultaneously. This algorithm achieves the second-order advantage, and is in principle able to overcome the problem of the presence of unexpected interferences [4].

Keywords: second order advantage, Rank annihilation factor analysis, spectrofluorimetry, ciprofloxacin, enrofloxacine, difloxacin

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Using chemical hard modeling for designing optimum pH sensor arrays

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ABSTRACT

pH measurement is widely demanded in biomedical, environmental, and industrial fields [1]. pH is an important physiological signal that plays a critical role in maintaining cellular and tissue homeostasis. Sensing and monitoring minor pH changes, especially at pHs of 5.4–7.4, are thus of great importance. Optical sensors have attracted the attention of many researchers with respect to cost, freedom from electrical interference, safety and the possibility of remote sensing [2]. Optical pH sensors based on the use of pH indicators have two major limitations, i.e. narrow dynamic range and non-linear response for pH measurement. A linear response is desirable because it leads to a simple calibration of the pH sensors, and more importantly, a constant sensitivity and precision in pH measurement over the entire linear range [3]. The useful pH sensing range is centered on the dye's dissociation constant [4]. Thus, there is a need to fine-tune the probe pK_a in a predictable way [5]. There is a body of literature showing how micelle composition can be used to control dye pK_a, and chemical model of distribution of solutes between aqueous phase and micellar pseudo-phase in aqueous micellar solutions had been studied [6]. In this study, we have used chemical hard modeling to predict indicator pK_a shift, in different micellar pseudo-phase or in different concentration of a micelle. Hard modeling as a systematic approach has been used to design optimum pH sensor array, which has linear response over a broad pH range. To ensure the largest sensing dynamic range, it is helpful to fine-tune the sensor pK_a to match the pH of the sample under analysis. In order to increase sensitivity in this pH range, we have designed a sensor array, include 10 sensor which difference indicator pK_a in each sensor was 0.2 unit. Using sensor array instead of individual sensor increases sensitivity and linear pH range. Two pH indicators, Alizarin yellow and cresol red in micellar solution of CTAB (Cetyltrimethylammonium bromide), allow the determination of pHs in the range 1 to 12.

Keywords: Hard-modeling, optical pH sensor array, pH indicator, Micelle, Spectrophotometry

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Modeling of reversed-phase direct immersion microextraction of acrylamide by feed forward neural network

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ABSTRACT

Acrylamide even in trace amounts is a potential cause of cancer in humans and can be created in many foodstuff that are cooked at high temperatures [1], therefore it is of importance to detect and quantify it in brown bread and potato chips and crisps. In this work, a novel reversed-phase direct immersion single drop microextraction was developed, optimized and used for the determination of acrylamide at low levels in potato crisps samples [2]. Then, a computational modeling method based on a feed-forward neural network was established to construct a predicting model for the determination of acrylamide using the results obtained empirically. The inputs of feed-forward neural network model were pH, extraction time, extraction temperature, stirring rate, drop volume, and sample volume; and the output was peak areas of acrylamide in the chromatograms. The BFGS Quasi-Newton algorithm was used to train feed forward neural network by the patterns gathered through experiments. The patterns used for modeling were divided in three subsets: 70% for training data set, 15% for validation data set, and 15% for testing data set. As an activation function, hidden neurons use hyperbolic tangent sigmoid function $tansig(s) = 2/\left(1 + e^{-2s}\right) - 1$, where $-1 \leq tansig(s) \leq 1$ and output neuron uses a linear transfer function $purelin(s) = s$ where $-\infty \leq purelin(s) \leq +\infty$. A neural network with 4 hidden neurons was considered for modeling purpose. In order to assess the efficiency of model for the prediction of acrylamide, root mean square error (RMSE) and determination coefficient (R^2) were used. The RMSE of obtained predictor model in training data was 32.0, in validation data set was 34.15, and in testing (unseen) data set was 36.35. A regression plot is created for each of three mentioned data sets to verify the relationship between forecasted outputs by model and actual outputs of patterns. The resulted R^2 value was 0.92, 0.90, and 0.90 for training, validation and unseen data sets, correspondingly that means there is a linear relation between the outputs of network and experimental outputs.

Key words: Feedforward neural network, Microextraction, Acrylamide

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Classification of different kinds of rice in the north of iran using IR spectroscopy combined with multivariate analysis

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ABSTRACT

Rice agriculture plays an important role in the country's economy. Rice is the main foodstuff for about half of the world's population. For the last decades, rice consumption has been expanding beyond the traditional rice-grown areas particularly in Asia and Europe [1]. Many of the traditional methods of analysis for determining the physical, chemical and mechanical properties to ensure the quality of rice are time consuming, destructive, require expensive harmful reagents [2]. The desire is to replace the traditional methods to find its quality with rapid, non-destructive, noninvasive methods. for this purpose, four kinds of rice were selected from the agricultural lands in the tonekabon in the north of Iran. Ten samples from each kind of rice were prepared. The objective of this study is to classify rice samples based on the fingerprints of the IR region by using the Infrared Spectroscopy (IRs). Therefore, thirty spectra were recorded such as ten samples with three replicates. IR spectra were taken on every four kinds of rice in the range of 400 to 4000 cm^{-1}. All the spectral data were processed statistically and resulting, the rice samples were classified using Principle Component Analysis (PCA). Application of principal component analysis (PCA) to our experimental data resulted in satisfactory classifications for all kinds of rice. Rice samples were effectively distinguished in four discrete groups.

Keywords: "classification" "multivariate classification" "principal component analysis" "PCA" "IR spectroscopy"

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Three-Dimensional Quantitative Structure- Activity Relationship (3D-QSAR) Model for Predicting Toxicity of Ionic Liquids Towards Leukemia rat cell line IPC-81

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ABSTRACT

Ionic liquids (ILs) are generally known as designer solvents due to their unique physicochemical properties by various combination of organic and inorganic cations and anions which caused that they have been applied in multifarious fields such as analytical chemistry [1], chromatography [2], electrochemistry [3], separation and extraction techniques [4], drug design [5] etc. But it is essential to note to their potential to produce toxic effects on living ecosystems like other chemicals. Therefore, it is required to understand ILs' toxicological consequence to design ILs which are structurally safe for environment. In this study, multivariate linear and nonlinear analysis such as partial least squares (PLS) and support vector machines (SVMs) were applied for constructing 3D-QSAR model using extracted alignment independent descriptors derived from GRID molecular interaction fields (MIFs) [6] in order to relate the structure of ILs to their cytotoxicity towards Leukemia rat cell line IPC-81. Genetic Algorithm as a powerful tool was used in order to select the best and interpretative subset of variables for building predictive models. These QSAR models provided acceptable predictions in both internal and external validation sets and made it possible to develop the predictive model for a large set of 269 ILs containing 9 cationic core and 44 types of anions. The effect of nature of the cation, anion and substituents on the subsequent toxicity were evaluated and discussed.

Keywords: Ionic liquids, Cytotoxicity, Alignment independent 3D-QSAR, PLS, SVM

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Synthesis of magnetic core-shell Fe$_3$O$_4$@MCM-41-NH$_2$ and its application for the removal of Alizarin Red S from wastewater samples and optimization by Response Surface Methodology (RSM)

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Abstract

A core-shell Fe$_3$O$_4$@MCM-41-NH$_2$ was synthesized by hydrothermal method and it modified by 3-aminopropyltriothoxysilane (APTES) as amine function on surface nanocomposite as a magnetic mesoporous nanocomposite to be used as an adsorbent for the effective and rapid removal of anionic dye, Congo Red. The Fe$_3$O$_4$@MCM-41-NH$_2$ nanocomposite were characterized by FT-IR, SEM, TEM and XRD. The 26 experiments were designed by response surface methodology. The selected removal conditions, obtained with a Central Composite Design (CCD) under Response Surface Methodology (RSM). Quadratic model was used to predict the variables .Analysis of variance was used for investigation of variables and interaction between them. High F-value (54.38), very low P-value (<0.00001), non-significant lack of fit, the determination coefficient (R^2 = 0.9899) demonstrate good correlation between experimental and predicted values of the response. The optimum parameters are achieved: pH 3.68, mass of adsorbent 0.012gr, stirring time 4 min and dye concentration 9 mg/l. At these conditions maximum dye removal efficiency was obtained 98.53 %. The maximum sorption capacity was obtained for ARS, 192.27 mg g^{-1}. The adsorption isotherms at different temperatures were fitted well with Langmuir model. Various kinetics models were examined and the results showed that pseudo-second-order could be best model to the adsorption

Multi-Criteria Decision Making in High-Submicellar Liquid Chromatographic Separation of Reducing Sugars by using UV-Detection

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ABSTRACT

Di- and mono-saccharides are compounds with similar property and high hydrophilicity. Therefore, the analysis of saccharides is challenging. The colorimetric methods can provide the total amount of carbohydrates but it is nonspecific. Because of the lack of effective chromophores or fluorophores in the structure of monosaccharides, the application of high performance liquid chromatography (HPLC) method is greatly limited. Specialized carbohydrate columns in combination with refractive index detector (RID) was often used in direct HPLC analysis of monosaccharides. However, the RID was not as common as ultraviolet (UV) or fluorescence (FL) detector for most of the researchers and the sensitivity was usually not satisfying [1]. Besides, since monosaccharides are non-volatile, direct gas chromategraphy (GC) method is also not applicable [2]. In this study, a simple and sensitive pre-column derivatization method for analysing reducing sugars is developed with labelling reagents of the containing chromophore moieties. The reagent 1-phenyl-3-methyl-5-pyrazolone (PMP) with strong UV absorbance at 245 nm is used as one of the popular labels that can react with reducing carbohydrates under mild conditions, requiring no acids catalyst and causing no desialylation and isomerisation. PMP derivatization increased the hydrophobicity of carbohydrates; therefore HPLC is quite suitable for analyzing PMP derivatives. Therefore the labelled di- and monosaccharides were separated by high-submicellar chromatographic (HSC) technique and detected by UV detector. In this technique, the surfactant monomers exist in the mobile phase, which are dissolved in the hydro-organic medium. The mobile phases were prepared with acetonitrile and an aqueous solution of sodium dodecyl sulphate (SDS) according to a face-centred cube central composite design. The considered factors in modelling were SDS concentration, mobile phase pH and volume percentage of acetonitrile. Multiple linear regression method was used for the construction of the best model based on experimental retention times. Pareto-optimal method was used to find suitable compatibility between separation quality and analysis time of sugar derivatives (manose, glucose, galactose, xylose and maltose) based on the prediction of the retention behaviour through empirical retention models. The optimum mobile phase composition for separation and determination of the saccharide analytes were [SDS]=0.03 molL^{-1}, 30% v/v acetonitrile and mobile phase pH 5.

Keywords: Derivatization, Reducing sugars, High-submicellar liquid chromatography, 1-phenyl-3-methyl-5-pyrazolone (PMP).

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Application of random forest regression in the modelling of a newly synthesized compound as potent HIV-1 reverse transcriptase inhibitors

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ABSTRACT

AIDS that is caused by HIV-1, threatens human life and spreads rapidly worldwide because of no effective vaccine. HIV-1 non-nucleoside reverse transcriptase inhibitors (NNRTIs), as an ingredient of highly active antiretroviral therapy (HAART), have played an important role in drug therapy [1, 2]. In this study, random forest (RF) model was developed for modeling and accurate prediction of anti HIV-1 inhibitory activities of azabenzene (pyrimidine, pyridine, pyridazine and triazine) derivatives as potent NNRTIs [3-7]. The chemical structure of each compound was converted to 29 molecular properties descriptors by Dragon software and 12 newly docking derived descriptors. Among total 41 descriptors, only 25 descriptors were selected after removing descriptors with pairwise correlation above 0.9 and used as significant descriptors, which relate the activity data to the molecular structures. The optimized RF model was developed and its prediction ability was evaluated by prediction of some compounds in the external (test) data set (n=10). The mean square error (MSE), mean absolute error (MAE) and correlation coefficient (R^2) for test set were 0.0618, 0.2067 and 0.9546, respectively. The results obtained showed the superior prediction ability of the proposed model in the prediction of anti HIV-1 inhibitory activities.

Keywords: Azabenzene derivatives, Docking descriptors, Molecular properties descriptors, Random forest (RF)

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Combined molecular docking and molecular dynamicssimulationto investigation of aflatoxin B1interaction with human serum albumin

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ABSTRACT

Aflatoxin, a group of toxic fungal metabolites, is called Mycotoxin and is produced by a mildew called Asparicillus, which grows on some foods and can cause Aflatoxicosis in humananddomestic animals. aflatoxins are species B1, B2, G1, G2, M1 and M2. B1 is more abundant than others and its toxicity is higher than other types. These compounds are more important than other fungal toxins due to the effects ofcancer and acute poisoning [1]. These compounds, after entering the human body, can be linked to proteins in the bloodstream and distributed throughout the body. One of the most important of these proteins is human serum albumin (HSA).HSA is the major soluble protein constituents of the circulatory system and has many physiological functions.Its principal function is that it involves the binding, transport, and delivery of numerous drugs to their target organs. One of the most important factors affectingthe distribution and the free, active concentration of many drugs is binding affinity for HSA [2].One way of investigation these interactions is to use computational techniques such as molecular dynamics simulation and molecular docking. The combination of the two techniques in a protocol where docking is used for the fast screening of large libraries and MD simulations are then applied to explore conformations of the protein receptor, optimize the structures of the final complexes, and calculate accurateenergies, is a logical approach to improving the drug-design process and investigate these types of interactions[3]. In this study, AutoDock 4.2were used to determine the binding site and free energyof bindingof aflatoxinto human serum albumin. Then the conformation with the lowest binding energy was chosen from the mostpopulated cluster and the corresponding ligand-protein complex was used for further MD studies. The MD simulations were performed with GROMACS 5.4.1 software package, employing the CHARMM27 force field.The results showed that the free energy of binding of the high affinity site on HSA for Aflatoxin B1 was -8.58 kcal/mol and binding site was determined in domin I (in subdomain IB).The final structure of the complex was obtained and the RMSD value between it and the initialstructure of complex wasdetermined 0.33 Angstrom.The use combined Docking and MD Simulation can provide appropriate results for investigating the interactions of the ligand-protein.

Keywords: Molecular docking, Molecular dynamics simulation, Aflatoxin B1, Human serum albumin

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Application of orthogonal pixel correction for MIA-QSAR study of anilinquinolines

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ABSTRACT

The aim of this study was to investigate, for the first time, the possibility of using orthogonal signal (pixel) correction (OPC) and multivariate calibration methods for QSAR study of anilinquinolines [1] by image analysis. The results obtained, with and without using OPC algorithm as a preprocessing treatment of original data, were compared. The aim of this work is to propose OPC and PLS (OPC-PLS) method to modeling in QSAR study. To our knowledge this is the first report on the QSAR study. In the MIA-QSAR [2, 3] method, the descriptors are the pixels of images that can be two or three dimensional.
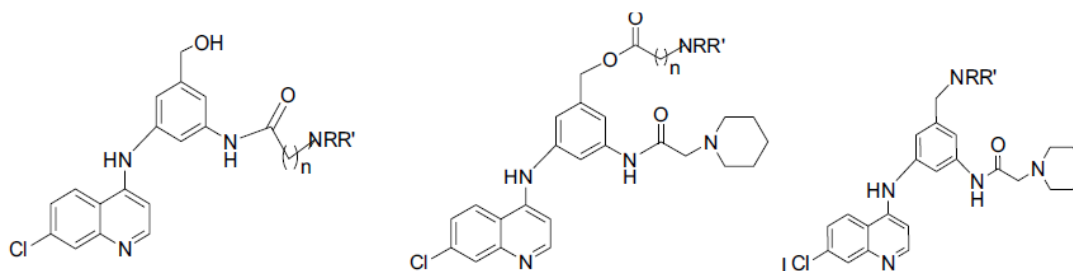
These pixels are correlated with dependent variables for making QSAR models [4]. Each image of dimension 120×150 pixels was unfolded to a 1×18000 row and then the 62 images were grouped to form a 62×18000 matrix. Columns with zero variance were removed to minimize memory, reducing the size of matrix to 62×1405. The resulted model showed high prediction ability with RMSEP of 0.0106 for OSC-PLS.

Keywords: QSAR, Anilinquinolines, Image analysis, PLS, OSC-PLS.

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Determination of the binding constant of some synthetic food dyes to human serum albumin using biopartitioning micellar chromatography and molecular docking

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ABSTRACT

Due to the high amount of artificial food colorants present in diets, their adverse effects have been of major concern among the literature. Artificial food colorants have been suggested to affect children's behavior, being hyperactivity the most common disorder[1]. Human serum albumin (HSA) is the most important artificial food colorants carrier in humans. Consequently, the study of the interaction of artificial food colorants with HSA is important[2]. Biopartitioning micellar chromatography (BMC) is a mode of micellar liquid chromatography that uses micellar mobile phases of Brij35 under adequate experimental conditions(the column temperature was kept at stable 36.5∘C to approach normal human body temperature, The pH of the micellar eluent was adjusted to 7.4 with 0.05 M phosphate buffer, prepared with disodium hydrogenphosphate and sodium dihydrogenphosphate, To reproduce the osmotic pressure of biological fluids, NaCl (9.2 g L−1) was added to the micellar mobile phase.). However, Mobile phases were prepared by aqueous solutions of 0.01 and 0.007 M Brij35. In this paper, relationships between the BMC retention data of artificial food colorants and binding constant of them are studied and the predictive ability of models is evaluated. Another method is the study of the interaction of the HAS-ligand by molecular docking. Molecular docking is one of the most widely used computing tools. Docking calculations simulate the interaction of an active compound and the active site of a protein. Hence, the results of this study are in good agreement with the results obtained from biochemical studies[3].

Keywords: Synthetic food dyes, Biopartitioning micellar chromatography, Human serum albumin, Chemometrics, Molecular docking

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Handling of highly coeluted chromatographic peaks by multivariate curve resolution for a complex bioanalytical problem: Quantitation of prednisolone, methylprednisolone and mycophenolic acid in human plasma

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Corticosteroids are prescribed as a critical medication in immunosuppressive regimens after solid organ transplantation. Due to numerous adverse effects and long term complications of corticosteroids, different multi-drug regimes have been advised by physicians to limit exposure[1]. One of the critical co-medications in this field is mycophenolic acid (MPA) which is the primary biologically active form of mycophenolate mofetil. In multi-drug protocols, therapeutic drug monitoring (TDM) plays an important role in the optimal use of immunosuppressants in patients carrying an organ transplant. So, developing a fast, easy and reliable analytical methodology for simultaneous quantitation of medications is highly valuable[2].

In the present study, prednisolone (Predl), methylprednisolone (Mpredl) and MPA are quantified in plasma samples by a fast high performance liquid chromatography with a diode array detector (HPLC-DAD) followed by multivariate curve resolution-alternating least square (MCR/ALS) modeling. The LC method optimized at isocratic reverse phase over a symmetric C18 column using an acetonitrile–phosphate buffer mobile phase (pH=3.5). The most challenges in the present study were: the highly coelution of analytes of interest with the matrix interferences and highly spectral similarity of selected corticosteroids and thus causing rank deficiency. To circumvent these drawbacks, the whole chromatographic run was divided into two sections. Then, the row-wise and column-wise augmentation strategies were implemented for the first and second regions, respectively. Highly acceptable resolution and quantification results were obtained. The calibration concentration ranged from 19 ng/mL to 1.6 µg/mL for Predl, 25 ng/mL to 2.4 µg/mL for Mpredl and 5 µg/mL to 14 µg /mL for MPA. The average recoveries for all components were acquired between 90 to 110 percent. Accurate and precise results, elimination of expensive and time consuming sample pretreatment steps and a very short chromatographic runtime, are among the advantages of the presented method.

Keywords: Corticosteroids, Mycophenolic acid, HPLC-DAD, MCR-ALS, Plasma.

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Discrimination of almonds (amygdalus) with respect to their genotype by using Fourier Transform Infrared Spectroscopy and chemometrics

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ABSTRACT

Fourier Transform Infrared Spectroscopy (FT-IR) is a well-established analytical tool in the chemical industry and analytical laboratory. Its utility arises from the generally well-resolved absorption bands found in FT-IR spectra and the consequent relative ease of chemical identification and quantitation. However, the application of this technique to food samples has only been seriously addressed recently due to developments in instrument design [1]. Spectroscopic techniques as generally applied to authenticity issues are non-selective, i.e. they do not detect the presence or absence of a single marker compound. Rather spectra contain information about the complete chemical composition and physical state of the material under analysis [2]. In this study, Fourier Transform Infrared spectroscopy (FT-IR) coupled to chemometrics is used to develop a fast and simple method for discriminating sweet, peanut, Prunus, Pistacia atlantica and bitter almonds (amygdalus). Spectra were recorded in the range of 400–3500 cm-1, and taking 15 scans per sample. The absorbance was computed against a background spectrum of Spectralon. The reflection window plate was carefully cleaned with a soft tissue to eliminate the presence of residues between measurements. FT-IR spectroscopy and an unsupervised pattern-recognition method, Principal component analysis (PCA), Linear discriminant analysis (LDA) based on the PCA and supervised counter propagation artificial neural network (CP-ANN) groupings, models were built to discriminate each types of almonds, show excellent discrimination between the almond groups and obtaining high levels of sensitivity and specificity for each classes, with more than 97% of the samples correctly classified and discriminated.

Keywords: almonds, Classification, PCA, LDA, FT-IR, CP-ANN

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Quantitative structure activity relationship study of quinazoline derivatives as tyrosine kinase (EGFR) inhibitors using scaled conjugate gradient artificial neural network

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ABSTRACT

Tyrosine kinases are important mediators of signal transduction process, leading to programmed cell death. Epidermal growth factor receptor (EGFR) which plays a vital role as a regulator of cell growth is one of the intensely studied tyrosine kinase targets of inhibitors. EGFR is overexpressed in many human cancers including non-small cell lung cancer, bladder cancer, and breast cancer. Since the hyper-activation of EGFR has been associated with these diseases, inhibitor of EGFR has potential therapeutic value and it has been extensively studied in the pharmaceutical industry [1, 2].

A nonlinear quantitative structure activity relationship study was presented for modeling and predicting epidermal growth factor receptor (EGFR) inhibitor data. Scaled conjugate gradient artificial neural network (SCG-ANN) was used to link molecular structures and inhibitory data. A data set consisting of 43 derivatives of analogues of quinazoline was used in this study [3]. Among a large number of calculated molecular descriptors by Dragon software, only six significant molecular descriptors were obtained by stepwise regression. The selected descriptors were combined with two (E_2 and $logK_i$) as newly docking derived descriptors and then they were used as inputs for neural network. The neural network architecture and its parameters were optimized. The prediction ability of the model was evaluated using the test set. The mean square errors and mean absolute errors for the test set data were 0.6934 and 0.6591, respectively. The results obtained showed the excellent prediction ability and stability of the proposed model in the prediction of inhibitory activity data of the corresponding analogues.

Keywords: Quantitative structure activity relationship (QSAR), Quinazoline derivatives, Epidermal growth factor receptor (EGFR), Docking, Artificial neural network (ANN)

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Docking Descriptor-Based QSAR Model for Prediction of Pyrimidine Series

Activities as Novel Phosphodiesterase10A Inhibitors

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ABSTRACT

Schizophrenia is a mental disorder that represents a vital unmet medical need [1]. Recently inhibition of phosphodiesterase (PDE10A) enzyme as an alternative approach is shown to have potential in treatment of schizophrenia [2, 3]. Objective of this study is investigating inhibition activity of 87 structurally diverse pyrimidine-based derivatives as a novel therapeutic drug candidate for PDE10A inhibition. A combination of docking and quantitative structure-activity relationship (QSAR) approaches were performed to characterize the relation between the structural features and the PDE10A inhibition activity. Molecular docking computation was performed by AutoDock 4.2 using the Lamarckian genetic algorithm. Conformations of pyrimidine inhibitors originating from docking with the lowest binding free energy were used to calculate molecular descriptors in a structure-based QSAR model. Molecular structural descriptors were calculated by BINding ANAlyzer (BINANA) Dragon, CODESSA and Accelrys Materials Studio software from docked conformers. The data set was divided into 69 training and 18 test sets based on hierarchical clustering method. The stepwise multiple linear regression as a variable selection method was carried out on the training set for selecting the most relevant descriptors. Among selected descriptors the most important ones, encoded topological features of molecules (e.g. the more branches, the more complex molecule) which can affect on steric interactions of ligand and the protein. Then support vector machine (SVM) was used to derive model based on obtained descriptors. The statistical parameters of R^2 and standard error for training set of SVM model were; 0.95 and 0.14, respectively, and were 0.93 and 0.18 for the test set. Leave one out cross validation test was used for assessment of the predictive power and validity of models which led to cross-validation correlation coefficient (Q_{Loo}^2) of 0.82.

Keyword: Molecular docking, QSAR, Molecular descriptor, Support vector machine

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Application of artificial neural network for prediction of dyes photo-degradation efficiency in UV/TiO2 condition based on structural information

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ABSTRACT

Wastewaters contaminated with dyes remained from the textile, paper, and other industries are source of environmental problems, especially in the third world countries. Synthetic dyes with wide variety of chemical structures and compositions of inorganic and organic compounds are one of the main groups of pollutants in wastewater [1, 2].

In this study, QSPR model based on Bayesian Regularized artificial neural network (BR-ANN) was developed for the modelling and accurate prediction of dyes degradation efficiency based on their chemical structures [3-5]. For this purpose, the photo-catalytic degradation of various dyes (31 dyes) have been investigated in TiO2/UV suspensions. Under constant condition of including amount of photo-catalyst (0.0100g), sample volume (50 ml) and pH of 7 the degradation efficiency of each dye was measured 15 minute under UV irradiation. Dyes structures were converted to the molecular descriptors using Dragon software and the most significant descriptors were selected and used as inputs in ANN modelling. After obtaining the best BR-ANN model, the prediction ability of the proposed model was evaluated by prediction of degradation efficiency of test set. The regression coefficient (R^2) for the test set was 0.85. The results obtained, showed the superior prediction ability of the proposed model in the prediction of degradation efficiency.

Keywords: "Artificial Neural Network", "Degradation", "Photocatalyst", "TiO2/UV", "Degradation efficiency"

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3D-QSAR analysis of Tacrine−4-Oxo-4H-chromene Hybrids as Multifunctional Agents for the Treatment of Alzheimer's disease by CoMFA and CoMSIA

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ABSTRACT

3D QSAR is a powerful tool for explaining the relationships between chemical structure and experimental observations [1]. 3D-QSAR studies have been carried out on a series of (29 compounds) of tacrine− 4-oxo-4H-chromene hybrids. Tacrine – 4 – oxo - 4H - chromene hybrids inhibit human acetyl- and butyrylcholinesterase (h-AChE and h-BuChE), being more potent than the parent inhibitor, tacrine [2]. They are also potent inhibitors of human BACE-1, better than the parent flavonoid, apigenin. To have a more reliable and flexible model before any data calibration the molecules were spliited to train and test sets.

An alignment rule for the compounds was defined using Distill option in SYBYL 1.3. It accomplished by selection of maximum common substructure by using the most active compound. Then according to database methodology will align all molecular stuctures on it. Models were validated using a data set obtained by dividing the data set into a training set and test set using hierarchical clustering, based on the CoMFA fields and biological activities (pIC50). QSAR model had good statistical parameters and yielded q2 = 0.568; r^2=0.853. The quality of CoMSIA was lower than that of CoMFA region focusing in terms of q^2 and r^2 values. The statistical parameters from the models indicate that the data are Well fitted and have high predictive ability.

Keywords: CoMFA, CoMSIA, tacrine−4-oxo-4H-chromene hybrids, acetylcholinesterase, inhibitor

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Simultaneous kinetic-spectrophotometric determination of mycophenolate mofetil and mycophenolic acid based on complexation with Fe(III) using MCR-ALS

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ABSTRACT

Determination of pharmaceutical analytes has been subjected to many investigations especially in transplantations in which accurate and precise detection of drugs is of importance. Mycophenolate mofetil (MPM) is a pro-drug that undergoes ester hydrolysis in liver and is converted to its active metabolite Mycophenolic acid (MPA) which inhibits purine biosynthesis and is responsible for pharmaceutical effects. Using this drug instead of MPA is because of higher safety and efficacy and lower costs of treatment. It has been shown that the lower concentrations of MPA in plasma correlate significantly with the risk of rejection while its high values increase the risk of toxicity in consumer patients so development of a simple and reliable method for fast and precise determination of MPM and MPA in pharmaceutical samples is of importance and a wide variety of analytical methodologies have been used for their determination [1- 4]. In this study, a simple and fast complexation reaction has been employed for simultaneous kinetic-spectrophotometric determination of these two immunosuppressant drugs which is based on the reaction between drugs and Fe(III) ions in the presence of sodium dodecyl sulfate as anionic surfactant by standard addition method. The effect of influential parameters including type of surfactant, concentration of Fe(III) ions and pH of the solution on complexation reaction have been studied and SDS was chosen as suitable surfactant while reaction proceeds with 0.1M Fe(III) at pH=4. Multivariate curve resolution-alternating least squares (MCR-ALS) has been employed for analyzing the multiset data obtained from augmentation of resulting standard addition matrices. Values for limit of detection (LOD) of method have been calculated as 2.1 µg. mL^{-1} and 5.8 µg. mL^{-1} for mycophenolic acid and mycophenolate mofetil respectively and Beer's law is obeyed over the concentration ranges 10-250 µg. mL^{-1} for both analytes. The proposed method was successfully applied for determination of drugs in plasma serum samples and the accuracy and reliability of the method was further ascertained by recovery experiments via standard addition procedure.

Keywords: MCR-ALS, Kinetic-Spectrophotometric, MPM, MPA, Complexation

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Optimization and simultaneous spectrophotometric determination of Thiosulfate and Sulfite in water samples based on insitu formation of AuNPs using PLSR

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ABSTRACT

Sulfite and thiosulfate are two reducing agents which have been extensively used in many industries for different purposes and as any other chemical pollutant in environment, intake of excess amounts of them can cause severe health problems. So various analytical methodologies have been employed for their determination in environmental samples [1, 2]. AuNPs present interesting optical properties due to their strong SPR absorptions in visible region of spectrum and their stability and ease of preparation. An interesting application in this field is the employment of reducing nature of analytes for insitu reduction of gold ions in solution and formation of AuNPs which can be used as colorimetric sensors for analyte determination [3- 5]. On the other hand, development of accurate and precise analytical methodologies for optimization and simultaneous multicomponent determination in analyzed samples has an undeniable importance which can be fulfilled by chemometrics especially in the case of spectroscopic data which usually have a well-defined bilinear behavior. In the present study, Partial Least Squares Regression has been used for simultaneous determination of thiosulfate and sulfite in water samples based on the redox reaction of analytes with Au(III) ions in the presence of SDS as surfactant and formation of AuNPs in solution which exhibit SPR absorptions proportional to the analyte concentration. The effects of various parameters on the formation of AuNPs including pH, time and concentrations of Au(III) and SDS have been studied and optimized using a four factor Central Composite Design. The spectra of samples were taken in ranges 400-800 nm with 1 nm intervals. Analytical figures of merit have been investigated and Beer's law obeyed over the concentration range $4*10^{-5}–1.6*10^{-4}$ mol. L^{-1}. The accuracy of method has been confirmed by recovery experiments.

Keywords: Sulfite, Thiosulfate, Experimental Design, AuNPs, PLSR

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Comparison of projection pursuit to independent component analysis

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ABSTRACT

Projection pursuit (PP) and independent component analysis (ICA) are two approaches to the blind source separation problem. In principle, ICA looks for maximum independence of resolved source vectors, while PP optimizes measures of non-Gaussianity. Similarities and differences between ICA and PP are considered in many sources, but the comparisons are largely vague. A number of reports state that PP is a sequential extraction technique, while ICA employs a simultaneous method [1]; however multivariate PP is simultaneous [2] and FastICA [3] is a sequential approach. One practical difference between ICA and PP is that the non-Gaussianity measure is enforced on the scores for PP and on the loadings for ICA. On the other hand, uncorrelated and non-Gaussian behavior are the basis criteria for resolved profiles from many PP and ICA algorithms. Thus, it is not hard to see why some believe PP and ICA are the same. In case of truly independent signals, such as those from acoustic sources, PP can separate real source vectors comparable to ICA. However, utilizing simulated and experimental data, it was observed that neither of the two methods could resolve spectrochemical data into the real source vectors. ICA [4], like PP [2] could be applied for clustering of the NIR spectra from ink samples and unsupervised classification of archeological data. Preprocessing is very effective on results from PP and ICA. Applying the same criterion as an objective function in PP and ICA, they can be regarded as essentially equivalent. When the real source vectors have maximum possible leptokurtic solutions with maximum kurtosis values (the solution that is most separated from Gaussianity) both PP and ICA can successfully be applied for the resolution of actual source vectors. It is not usually the case for spectrochemical data in which the real source vectors are not the most independent and non-Gaussian among the possible solutions. Although using different criteria, the results from PP and ICA are similar in their estimation of actual source vectors from some types of mixture signals but not from spectrochemical signals. The clustering ability of PP and ICA are comparable.

Keywords: Projection Pursuit, Independent Component Analysis, Ink Spectra, Gaussianity, Unsupervised Classification.

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Spectroelectrochemical determination of Levodopa in the presence of interferents on gold nanoparticle-modified FTO electrodes using PARAFAC

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ABSTRACT

Levodopa is the precursor of dopamine neurotransmitter and the principal drug used in the treatment of parkinson's disease. Different side effects associated with the increase of systemic dopamine due to the enzymatic metabolization of levodopa in peripheral system, necessitates controlling the levels of dopamine and in fact levodopa in patients and therefore a wide variety of methods have been employed for its determination [1, 2]. Spectroelectrochemistry is a new field in analytical chemistry which not only can get the information about the electrochemical behavior of analyte, but its spectroscopic characteristics on the modified or even unmodified transparent working electrodes including mesh electrodes or semiconductor oxides like ITO or FTO [3]. The role of chemometrics in the analysis of spectroelectrochemical data will be cleared by considering the huge amounts of data obtained by spectroelectrochemistry from system under study and that it is an intrinsically trilinear technique [4, 5]. In this study UV-Vis spectroscopy was used in combination with electrochemical techniques like cyclic voltammetry and differential pulse voltammetry for determination of levodopa in the presence of some interfering compounds usually found in pharmaceutical formulations or biological medium during analysis like carbidopa or uric acid. Fluorine-doped tin oxide electrodes modified with electrodeposited gold nanoparticles were used as working electrodes and all experiments were done in a conventional 1-cm quartz cuvette with a homemade Ag/AgCl mini reference electrode and a Pt wire as counter electrode. PARAFAC was used for chemometrics analysis of obtained second order three-way data from standard addition procedure. Analytical figures of merit for determination of levodopa was evaluated and accuracy of method was further ascertained by recovery experiments. The proposed method was successfully applied for determination of levodopa in pharmaceutical samples.

Keywords: Spectroelectrochemistry, FTO, Levodopa, PARAFAC

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Three-dimensional quantitative structure activity relationship modeling of the rate of penetration of diverse compounds through the human skin by using GRIND descriptors

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ABSTRACT

The control of permeation is vital for the topical application of lotions, creams, and ointments, and for the toxicological and danger assessment of materials from environmental and occupational hazards. The skin permeability of industrial and household chemicals plays an important role in various fields including toxicology and risk assessment of hazardous materials, transdermal delivery of drugs and the plan of cosmetic products [1]. In this work, a three-dimensional quantitative structure–activity relationship (3DQSAR) model [2] has been developed to predict skin permeation of a variety of 210 compounds through human skin. Molecular descriptors were computed using GRid Independent Descriptors (GRIND) approach [3]. After variable selection via genetic algorithm method, 100 selected descriptors were correlated with skin permeability constants by various methods, such as PLS regression, support vector machine (SVM), and so on. Therefore, compounds are separated in two classification: 150 molecules as set of training and other compounds as set of test. The best results were obtained by PLS regression with the correlation coefficient of $R^2 = 0.61$ for calibration set. This strategy led to a final QSAR model that presented $Q^2 = 0.59$ and $R^2_{pred} = 0.64$. As a result, the hydrogen bonding donor and hydrogen bonding acceptor of investigated compounds greatly influences their ability to penetrate through human skin. Furthermore, it has been observed that permeability was enhanced by increasing hydrophobicity and decreasing molecular weight.

Keywords: skin permeability, 3D-QSAR, GRIND, molecular weight, *logkp*,

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Discrimination and Identification of Catecholamines Using Unmodified Gold Nanoparticles-Based Sensor Array

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ABSTRACT

Catecholamines (CAs) play various pivotal roles in the mammalian central and peripheral nervous systems both as neurotransmitters and hormones [1]. Therefore, detection of their abnormalities in the biological fluid, in terms of their concentrations and by products, is of quite importance.

Inspired by the superb performance of biological olfactory systems, "chemical nose" strategies have been developed for detection and differentiation of diverse families of analytes [2]. Unlike the traditional "lock-and-key" design, this alternative sensor architecture involves utilizing non-selective sensing elements to generate a fingerprint response pattern which is unique for each analyte [3].

Herein, a colorimetric sensor array based on unmodified gold nanoparticles was developed to sensitively detect and identify multiple structurally similar CAs including dopamine, epinephrine, norepinephrine, and L-dopa in aqueous media. Size dependency of assembly process encouraged us to employ AuNPs with four distinct particle sizes as sensing elements and visual differentiation tools to construct a colorimetric nanoarray. The target CAs seem to act as "molecular bridges", shortening the interparticle distance and inducing the aggregation of AuNPs. This aggregation produces changes in both the color and UV-vis spectra of AuNPs generating a visual molecular fingerprint of each analyte. The cumulative array responses were differentiated by principal component analysis (PCA) and hierarchical cluster analysis (HCA) with 100% classification accuracy demonstrating the versatility of this simple nanoarray platform. Furthermore, color difference maps were created to provide a visual tool for classifications and semi-quantitative analysis without exploiting any statistical techniques. The obtained results suggest that the proposed colorimetric nanoarray has promising perspective in clinical diagnostics.

Keywords: Colorimetric nanoarray, Catecholamines, Gold nanoparticles, Aggregation, Pattern recognition algorithms

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Hard-Soft PARAFAC to Study Catalytic Reduction of mixture of Nitrophenols

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ABSTRACT

PARAFAC is one of several decomposition methods for multi-way data. The popularity of this model in chemistry is due to its uniqueness properties [1]. The uniqueness of PARAFAC does not hold in cases with rank overlap, rank overlap can be simply found where components have similar spectral profiles or analytes appearing in identical proportions throughout an experiment. Although constraints such as non-negativity, unimodality and, hard modeling can still make PARAFAC model useful in this regard. The hard constraint forces some or all of the concentration profiles to fulfill an equilibrium model that is refined at each iteration cycle of PARAFAC optimization process. PARAFAC with hard constraint is called Hard-Soft PARAFAC [2].

Nitrophenol-type compounds are widely applied in industries such as chemistry, petrochemical, and pharmacy and are one of the most important raw materials for synthetic medicine, dye, herbicides, insecticides, resins, and explosives. Because nitrophenol-type compounds are cancer causing and highly poisonous, it is very important to test and analyze these compounds to avoid the harm and danger they may cause to humans. Simultaneous determination of nitrophenol-type compounds is very difficult because the similarity in their structures produces overlapping signals. In recent years, the reduction of 4-nitrophenol (Nip) to 4-aminophenol (Amp) by borohydride (BH4 $^-$) in aqueous solution has become such a model reaction that meets all criteria of a model reaction. It can be monitored easily with high precision by UV−vis spectroscopy. This is due to the fact that Nip has a strong absorption at 400 nm and the decay of this peak can be measured precisely as the function of time. Moreover, the reaction rate is small enough so that the conversion can be conveniently monitored over several minutes [3,4].

In this study, kinetic reaction of mixture of ortho, meta, and para-nitrophenol in the presence of excess BH_4^- has been investigated. The Uv-vis spectra were collected during the kinetic process in 15 samples. There are three first order reactions and PARAFAC does not have unique solution because of rank deficiency in concentration profiles. Use of HSPARAFAC leads to unique solution, therefore rate constants and concentration profiles can be calculated simultaneously. In our case, computed rate constants for meta, ortho and para-nitrophenol reaction are 0.0102, 0.0100, and 0.3830, respectively.

Keywords: PARAFAC, uniqueness, rank overlap, hard modeling constrain

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Computational modeling of liquid phase microextraction of malondialdehyde from human blood plasma by multi-layer perceptron

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ABSTRACT

Lipid peroxidation is the oxidative degradation of lipids. It is the process in which free radicals attack the lipids in cell membranes, resulting in cell damage. Malondialdehyde (MDA) is a compound which is released in human plasma during this process and can be used as an indicator of the level of lipid peroxidation. Therefore, determination of MDA is of high importance [1]. In this study, first MDA extraction from blood plasma was performed by the salt saturated single drop microextraction (SS-SDME) and its concentration was quantitatively determined by gas chromatography. All parameters of SS-SDME were optimized [2]. The data obtained here, were used to construct a predictive model based on multi-layer perceptron (MLP) for the determination of MDA in blood plasma. The inputs of MLP were stirring rate, pH, micro-drop volume, the volume of sample solution, extraction time, and temperature; and the output was relative peak area of MDA in chromatogram. The set of patterns used for modeling were 33 experiments and were divided in three subsets: 70% as training, 15% as validation, and 15% as testing sets. Given the training set, the scaled conjugate gradient method was used to train the MLP. The training epochs continue until the root mean square error (RMSE) between outputs of MLP and targets did not decrease during 6 continues epochs for patterns in validation set. As an activation function, hidden neurons use the hyperbolic tangent sigmoid function $tansig(s) = 2/\left(1 + e^{-2s}\right) - 1$, where $-1 \le tansig(s) \le 1$ and output neuron uses a linear transfer function $purelin(s) = s$ where $-\infty \le purelin(s) \le +\infty$. By performing some experiments, the number of 5 hidden neurons was considered for the MLP. The obtained RMSE for training, validation, and testing sets were 8.652259, 21.432824, and 16.158811, correspondingly. Regression diagrams were plotted for the three mentioned sets to investigate the relationship between predicted outputs of MLP and targets. The values of determination coefficients were 0.976524, 0.905604 and 0.905604 for training, validation and unseen data sets that states a good linear relation between outputs and targets. The linear range of the calibration curve was between 10-1000 µg.L^{-1}, with a detection limit of 0.76 µg.L^{-1}. At optimized conditions, a relative standard deviation of 8.66% was calculated for 5 successive analysis. The resulted predictive MLP model showed that it can save time, energy, and laboratory costs for optimization of the SS-SDME extraction of MDA from human blood plasma.

Keywords: Malondialdehyde, Multi-layer perceptron, Microextraction, Gas chromatography

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Study of fabrication of Fe3O4 nanoparticles polyether sulfone membrane (PES\Fe3O4 NPs) for the removal of methylene blue dye from aqueous solutions: Optimization through response surface methodology (RSM)

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ABSTRACT

A three factor, three-level Box–Behnken experimental design combining with response surface modeling (RSM) and quadratic programming (QP) by Design Expert Version 7.0.0 was employed for maximizing methylene blue removal from aqueous solution by Fe_3O_4 nanoparticles polyether sulfone membrane (PES\Fe$_3$O$_4$ NPs) based on 17 different experimental data obtained in a lab-scale batch study. Three independent variables (initial pH of solution (pH_0) ranging from 5 to 9, initial concentration of methylene blue (C_i) ranging from 5 to 15 ppm, and weight percent of modifier (M_p) ranging from 3 to 7 percent) were consecutively coded as x1, x2 and x3 at three levels (−1, 0 and 1), and a second-order polynomial regression equation was then derived to predict responses. The significance of independent variables and their interactions were tested by means of the analysis of variance (ANOVA) with 95% confidence limits ($\alpha = 0.05$). The optimum values of the selected variables were obtained by solving the quadratic regression model, as well as by analyzing the response surface contour plots. The experimental conditions were determined to be $pH_0 = 7.54$, $C_i = 11.16$ ppm, and $M_p = 4.20$, and the methylene blue removal efficiency was found to be about 91.58 %. Therefore, it is apparent that the response surface methodology not only gives valuable information on interactions between the factors but also leads to identification of feasible optimum values of the studied factors.

Keywords: Methylene Blue, Membrane, Response surface methodology (RSM), Poly ether sulfone, Iron Oxide Nanoparticles

Combination of Dispersive Liquid-Liquid Micro-Extraction by HPLC-UV and Response Surface Methodology to Optimize Determination of Ciprofloxacin in Infant Formula

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Abstract

A rapid, efficient, and environmentally friendly extraction method, namely dispersive liquid-liquid micro-extraction (DLLME) coupled with high performance liquid chromatography (HPLC), was applied for extraction of ciprofloxacin from infant formula. In this method, chloroform and acetone were used as the extracting and dispersing solvents, followed by HPLC analytical method. Using DLLME, ciprofloxacin contained in infant formula, was extracted and concentrated into the organic phase. Hence several parameters, such as type and volume of extraction and dispersive solvents, pH, salt addition, and extraction time, affect the DLLME extraction procedure efficiency, an optimization approach was used to attain the best extraction conditions [1]. Accordingly, initial screenings were first investigated by one factor at the time approach. Further optimization with Box-Behnken and response surface methodology showed that, pH, and volumes of extraction and dispersive solvents were effective variables, respectively [2, 3]. By fitting a second-order polynomial model to the experimental data, the optimum conditions for pH, volumes of extraction and dispersive solvents were found to be 4.25, 550µL and 760µL, respectively. The perfect agreement between the observed values and values predicted by the model were obtained in the light of Design of Experiment (DoE). Therefore, under optimized experimental status of DLLME-HPLC-UV method, a good linearity in the range of 50 – 1000 µg L^{-1}, detection limits of (10 µg L^{-1}), and recovery of 87% were obtained. In addition, considering the obtained figures of merit, the method proved to be reliable, precise and accurate. In fact, the method was successfully applied to determine ciprofloxacin in infant formula.

Keywords: DLLME, Box-Behnken Design, HPLC, infant formula, ciprofloxacin

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QSAR study of Quinazoline derivatives as tyrosine kinase inhibitors using multivariate image analysis and partial least squares

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ABSTRACT

A quantitative structure0activity relationship (QSAR) modeling was carried out for the prediction of inhibitory activity of Quinazoline derivatives as tyrosine kinase inhibitors [1]. QSAR is mathematical model of activity in terms of structural descriptors. The QSAR model is useful for understanding the factors controlling activity, prediction of activity and for designing new potent compounds. The main aim of QSAR studies is to establish an empirical rule or function relating the descriptors of compounds under investigation to activities or properties. This rule of function is then utilized to predict the same activities/properties of the compounds not involved in the training set from their descriptors [2-4].
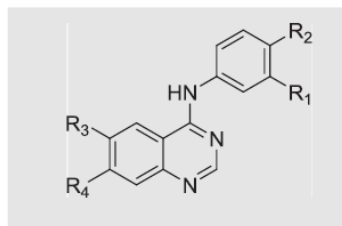
Partial least squares (PLS) algorithm was used for prediction of inhibitory activity as a function of the Bidimensional images. In the present study, it is investigated that the effect of pixel processing by application of orthogonal signal correction (OSC) for PLS model, because of the OSC is very useful in the preprocessing in modeling [5]. The results of all models are compared with statistical parameters such as RMSEP, RSEP, R^2 and Q^2. The resulted model showed high prediction ability with root mean square error of prediction of 0.0359 and 0.0107 for PLS and OSC-PLS. Results have shown that the introduction of OSC-PLS for pixel descriptors drastically enhances the ability of prediction in QSAR studies superior to other calibration algorithms.

Keywords: QSAR, Multivariate image analysis, Inhibitory activity, PLS, OSC-PLS.

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Multivariate curve resolution of organic pollution patterns in mangrove forests Sediment from Qeshm Island and Khamir Port—Persian Gulf, Iran

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ABSTRACT

Straight chain alkanes (n-alkanes) have been proposed as biomarkers to assess petroleum pollution sources in marine environments. In this work, three sampling sites were selected along Iranian protected mangrove forests in the Persian Gulf. Sample sites were chosen to represent different compositions and sources of n-alkanes in surface sediments (0-5 cm) from different locations in the Khamir port, in the Gulf middle part and in the Qeshm island. Samples were analyzed by gas chromatography-mass spectrometry (GC–MS), and the obtained n-alkanes were analyzed by Principal Component Analysis (PCA) and Multivariate Curve Resolution Alternating Least Squares (MCR-ALS) to deduce their possible sources and distribution patterns. Results revealed that n-alkanes have a dominant biogenic source in marginal Qeshm Island stations, which changed from biogenic to petrogenic sources in Khamir Port areas. Sediment samples from Khamir Port showed the significant presence of oil pollution due to transportation. These samples are being exposed to basic Persian Gulf currents entering from Hormoz Strait causing oil pollution spread over the entire Gulf area. Sediment samples of Middle part stations located between two other sites show a combined condition of the two previous sections, with petrogenic and biogenic contributions. The present study demonstrates that Hara Protected Area was already contaminated by background oil pollution as a result of continuous oil spills and war conflicts in the Persian Gulf.

Additionally, the MCR-ALS method is shown to be a powerful chemometrics tool for the investigation, resolution, identification, and description of pollution patterns distributed over a particular geographical area and environmental compartment. They can be used as well as parameters like unresolved to resolved ratio (U/R), pristane to phytane (Pr/Ph), n-C$_{17}$/Pr, n-C$_{18}$/Ph and unresolved complex mixture (UCM) to assess petroleum pollution sources in sediments.

Correlation of NDVI calculated with GreenSeeker and VNIR spectroscopy

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ABSTRACT

Optical sensors are recognized as non-destructive and cost effective methods to estimate different vegetation Indices. The objective of this study was to evaluate the reliability of normalized difference vegetative index (NDVI) values calculated by the GreenSeeker (GS) hand held sensor (Trimble, USA) as an indirect indicator of tomato and cucumber Nitrogen (N) status, and compare to the Visible-NIR (VNIR) spectra. NDVI index is commonly used to differentiate plant properties such as chlorophyll, biomass, and plant nutrition [1]. A reflectance VNIR system operating in the range 300-1100 nm was applied to evaluate performance of GS. The experiment was conducted in spring 2017 on tomato and cucumber planted in greenhouse which supplemented with five treatments of 46% Urea controlled release fertilizer (CRF). NDVI readings were recorded every weeks during the growth seasons and spectra of leaves earned in two stages (After the first and last repeated fertilization) like [2]. Sensors values were compared to actual leaf N concentration with Kjeldahl measurement. Results obtained by VNIR spectroscopy combined with chemometric analysis for the determination of N content. Spectra were analyzed by The Unscrambler software (version 10X, Camo, Norway) in order to build Partial least square (PLS) regression models able to estimate NDVI parameter of tomato and cucumber. Spectral data were normalized by Standard Normal Variate (SNV) and pretreated using a derivative transform calculation (Savitzky–Golaymethod) by 1st derivative [3]. Spectral data were elaborated by leave one-out cross validation (LOOCV) of PLS regression technique. High correlation models between spectral data and NDVI of GS and also Kjeldahl method were obtained for the N concentration ($0.75 < R^2 < 0.89$ and $0.81 < R^2 < 0.90$ for spectra-GS and spectra- Kjeldahl respectively). The GS readings of tomato's leaves were less correlated with leaf N concentration at early stages of establishment due to plants small size and background noise compared to wide leaves of cucumber.

Keywords: GreenSeeker, VNIR Spectroscopy, NDVI.

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Probing the chemical space regulated by DHFR homologs and pyrimidine-based inhibitors

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ABSTRACT

Ubiquitous Dihydrofolate reductase (DHFR) with an indispensable role in folate metabolism has been a major target for antineoplastic, antimicrobial and antiinflammatory drugs [1]. Despite the clinical effectiveness of current treatments, there is an urgent need for design and development of new drugs due to the resistance which is developing through mutations. One of crucial factors for the design of novel selective inhibitors against pathogen DHFRs, with the least side effect, is to understand factors influencing the ligand binding selectivity profiles among DHFRs. The hybrid scaffold containing pyrimidine ring is well-established as an effective scaffold for DHFR inhibition [2]. Hence, we applied proteochemometrics (PCM) approach to evaluate new pyrimidine-based derivatives as potent inhibitors for DHFR homologs [3]. Z-scales and GRID INdependent Descriptors (GRINDs) in addition to their cross-terms, have been correlated to biological activities through conducting partial least squares (PLS) regression. The final model was validated by several internal/external approaches. All calculated parameters have been in good accordance with acceptance criteria.

Keywords: Dihydrofolate reductase; Pyrimidine-based inhibitors; Structure-based descriptors; Sequence-based descriptors; Partial least squares regression method

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Analysis of Heavy elements, Cr, As, Hg, Cd, Pb in soil sample by ICP-MS and ICP-OES   and study of the distribution by Geochemometrics

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ABSTRACT

In this study distribution and effect of heavy elements, Pb, Cd, Hg, As, Cr on soil samples of Saduq in Yazd province was investigated. 335 soil samples were taken in Saduq, SS for Saduq, No for Nodushan and KH for Khezrabad was taken according to standard sampling methods. Sample digestion was done according to ASTM D4698 by 4-acid and fusion methods [1]. Analysis was done by ICP-MS, ICP-OES and AF and resulted data were processed by Geochemometrics methods. The concept of Geochemoemtrics contain Geo means the Earth and Chemometric which is a new method for receiving the most profitable data from a huge mass of complicated data [2]. PCA is the most useful mathematical method in chemometrics. The most important results of PCA algorithm are Score and Loading Plots and Biplot diagram which all help to have a better interpretation from gathered data. KNN method is used for classification and determination of the coherence between data [3].

The analysis of principle components was done according to heavy metals and three main components are PC1=22.94%, PC2=19.42% and PC3=16.91% which contain more that 59% of the change. Distribution of samples was studied according to the Score plots of the first and second principle components and SS158, SS156, SS154 in Saduq, NO-L29 and NO-S-10 in Nodushan and KH-S-23 in Khezrabad has got a significant variance. The effect of elements on samples was investigated by Biplot diagram and results show that AS and Cd has got an effect on distribution of NO-S-10, NO-L-29 and KH-S-23 respectively.

According to the studies about T^2-Hotelling the significant difference in KH-S-23, NO-L-29, NO-S-10, SS154, SS141 was obvious. KNN was used to study the correlation and clustering of elements and results show that Cd and Pb have got relative correlation in this region. In this plot B and Cr were placed in a different classification in compare with other elements also Hg and Cd are in this classification and have got closer correlation with As and Pb in comparison with Cr and B.

Results show that ICP-MS and ICP-OES analyses have got good accuracy and precision and the method is applicable in determination of trace elements in Geology. The method was presented to the Geology reference laboratory.

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