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Multivariate curve resolution-alternating least squares applied to kinetic spectrophotometric data for the determination of mixtures of aliphatic amines

Masoumeh Hasani[a,*], Tayebeh Sayarpour[a], Abbas Karami[a], Masoud Shariati-Rad[b]

[a]*Faculty of Chemistry, Bu-Ali Sina University, Hamedan 65174, Iran*

[b]*Department of Chemistry, Faculty of Science, Razi University, Kermanshah, Iran*

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Abstract

Kinetic spectrophotometric second order data based on the reaction of 1,2-naphthoquinone-4-sulphonate (NQS) coupled with multivariate curve resolution-alternating least squares (MCR-ALS) has been proposed for simultaneous determination of ethylamine, propylamine and butylamine. Using second-order advantage, MCR-ALS methodology can solve problems of quantitation of analyte in the presence of unknown and uncalibrated interferences. Ethylamine, propylamine and butylamine differentially react with NQS at pH 9.5. Therefore, determination of these amines has been carried out due to the difference between their reaction rates. Quantitative determination of each amine in the mixture has been performed using a synthetic standard solution containing only the amine of interest. The quantitative determination of these amines in different synthetic mixtures and some real samples such as river water, well water, tap water and soil has been performed and the results have been found to have good recoveries.

Keywords: MCR-ALS; aliphatic amines; kinetics; UV/Vis spectroscopy.

Introduction

Aliphatic amines are of industrial interest as important precursors in the synthesis of dyes, pharmaceuticals, stabilizers, emulsifiers and corrosion inhibitors [1]. Due to their commercial applications and widespread uses as intermediates in the chemical and pharmaceutical industries, they are widely distributed in the nature. In addition to their industrial application, aliphatic amines may occur as biodegradation products of proteins and amino acids, or other nitrogen-containing compounds. Most of alkylamines have toxic characteristics and are dangerous to health especially when react with nitrite, in order to form carcinogenic nitrosamines [2]. Therefore, there is a growing need in the determination of aliphatic amines in various types of samples.

High-performance liquid chromatography (HPLC) [3-6], and gas chromatography (GC) coupled with different detectors [2,7-9] have been recognized as the techniques most widely used for the determination of

*Corresponding author: Masoumeh Hasani
Tel: +98 (81) 38282807, Fax: +98 (81) 38380709
E-mail: E-mail: hasani@basu.ac.ir

aliphatic amines in environmental samples. But in these techniques it is crucial to convert amines to detectable derivatives. Derivatization requires efficient and effective reagents and mild conditions to obtain stable derivatives with minimum by-products. Moreover, chromatographic methods usually require expensive instrumentation. So, other simpler methods are of great interest.

Spectrophotometry is an easy and convenient analytical technique that can be used for the determination of a number of different compounds [10-13]. Therefore, spectrophotometric method can be considered as a good alternative to the separation techniques. However, the lack of selectivity of UV-Vis absorption measurements limits its application in complicated systems with overlapped absorption bands. So, multicomponent analysis with UV-Vis spectrophotometers continues to be a difficult problem where there is no spectral differences [11]. In such cases, using chemometric methods in resolving the overlapped spectra into their individual components will help.

Coupling the kinetics of a reaction with chemometric approaches provides the necessary data for analytical applications. Therefore, in the last decade simultaneous determination of compounds with similar structures/properties has been achieved using differential kinetic methods and chemometric treatments [12-14]. For quantitative and qualitative measurement purposes, methods with second order advantages can successfully resolve [15,16] the spectral profiles and the relative concentrations of each component in the system. A very appropriate analysis method is multivariate curve resolution based on alternating least squares (MCR-ALS) [17]. MCR-ALS, as a soft-modelling methodology, is able to extract the information of the evolving systems without using the underlying kinetic model. The time evolution of spectra for a reacting system constitutes second order instrumental data which can be subjected to MCR-ALS that permits analyte quantitation in samples containing unexpected components, i.e. components not included in the calibration set. There are some reports on using kinetic spectroscopic data to achieve the second order advantage for quantitative purposes [18-22].

The main limitation of all MCR methods is the rotational ambiguity which is undesirable. This can lead to finding no unique solution for the concentration and spectral profiles of the system under study. However, by applying different constraints such as nonnegativity of the concentration and absorption spectra, unimodality of concentration profiles and other constraints the unique solution may be achived. This subject has been studied by Abdollahi et.al in detail [23].

It has been reported that 1,2-naphthoquinone-4-sulphonate (NQS) reacts with amines and their derivatives due to the fact that lone pairs of electron on nitrogen of amines can attack the electron deficient center in NQS [24], namely the No. 4 carbon atom. NQS is a very well-known spectrophotometric reagent due to its capability in reaction with both primary and secondary amines [10,25-27].

The objective of this paper is to propose a method for the analysis of mixtures of aliphatic amines based on a two-dimensional kinetic spectrophotometric method coupled to chemometric decomposition method of MCR-ALS to take the advantage of second order data. This method is based on the difference of the chemical reaction rate of these amines with NQS

in basic medium. In this approach neither the extraction nor the separation of the analyte from the background are needed, because the quantitative determination of the analyte of interest is not affected by the presence of unknown interferences in the samples.

Multivariate curve resolution-alternating least squares (MCR-ALS) MCR-ALS is an iterative soft-modelling resolution method developed by Tauler and co-workers [17,28]. The aim of MCR-ALS is the optimal decomposition of a bilinear data matrix **D** with mixed information about a multicomponent system into the product of two small matrices, i.e. pure component spectra, $\mathbf{S}^T$, and the relative concentration profiles, ***C***. This decomposition is the result of the validity of Beer–Lambert's law for absorption measurements. Assuming the bilinearity of data matrix **D**, absorbance signal can be decomposed into the sum of individual contributions, each described by a concentration profile in the matrix **C** and by pure matrix spectra in matrix $\mathbf{S}^T$ [29].

$$\mathbf{D}_{(r\times c)}=\mathbf{C}_{(r\times n)}\mathbf{S}_{(n\times c)}^{T}+\mathbf{E}_{(r\times c)} \quad (1)$$

D is the original measurement and in kinetic processes contains as rows the r measured absorption spectra ordered as a function of the reaction time. The matrix **C** contains, as columns, the kinetic profiles of the n pure species involved in the process at r time points and $\mathbf{S}^T$ contains *n* rows with the related pure spectra. ***E*** is the error-related matrix that provides the data variation not explained by the proposed n contributions (components).

Decomposition of **D** is achieved by iterative least-squares minimization of ***E*** with the help of applying some constraints.

Iterative MCR-ALS method needs a preliminary estimation of $\mathbf{S}^T$ or **C** to start the ALS procedure. Different methods are used for this purpose like evolving factor analysis [30,31] or the determination of the purest variables [32,33]. These initial estimates are used to start the alternating least squares (ALS) constrained optimization through an iterative process. The algorithm proceeds in cycling steps in which **C** and $\boldsymbol{S}^T$ are iteratively updated by solving alternatively the two following least-squares matrix equations, (Eqs. (2) and (3)) to have a least square solution for Eq. (1) i.e.at each iterative cycle the **C** and $\boldsymbol{S}^T$ matrices that minimize the error in the description of the raw dataset is found

$$\mathbf{S}^T=(\mathbf{C})^{+}\mathbf{D} \quad (2)$$

$$\mathbf{C}=\mathbf{D}\,(\mathbf{S}^T)^{+} \quad (3)$$

Where $(\mathbf{S}^T)^+$ and $(\mathbf{C})^+$ are the pseudoinverses of the $\mathbf{S}^T$ and **C** matrices, respectively [34]. The resolution was improved by applying several constraints during optimization. A figure of merit of the optimization procedure is the percent of lack of fit (% LOF). LOF is defined as the difference between the input data **D** and the data reproduced by the $\mathbf{CS}^T$ product obtained by MCR-ALS. This value is calculated according to the expression (4).

$$\%LOF = 100\times \left(\sum(d_{ij}-d_{calij})^2/\sum d_{ij}^2\right)^{1/2} \quad (4)$$

Where d_{calij} and d_{ij} refer to the calculated and the real absorbance data objects, respectively.

Iteration continues until the relative difference in lack of fit between two consecutive iterations goes below a threshold value or when a preselected number of iteration is reached. The percentage of lack of fit (% LOF) is considered as a measure of the fit quality [35,36].

By comparing the area under the concentration profiles for the analyte in the standard and in the unknown sample, the quantification of analyte is possible (Equation 5).

$$C_{unk} = \frac{A_{unk}}{A_{std}} \times C_{std} \quad (5)$$

Here, C_{unk} and C_{std} are the concentrations of the analyte in the unknown and standard samples, respectively; A_{unk} and A_{std} are the areas below the concentration profiles in the unknown and in the standard samples, respectively.

Experimental

Apparatus and software

UV-visible absorbance digitized spectra were collected on an Analytic Yena Specord 210 spectrophotometer, using a 1 cm quartz cell within the wavelength range 280-600 nm. The pH of the solutions was measured with a Metrohm 827 pH meter using a combined glass electrode. All calculations related to multivariate resolution with alternative least squares were performed using MATLAB 7.11 environment utilizing a personal computer with windows 7 operating system. MCR-ALS software, freely available in the literature has been used [37].

Solution and reagents

All chemicals were of analytical reagent grade and used without further purification. All aqueous solutions were prepared with distilled water. Stock solutions of ethylamine, propylamine (4.99×10^{-2} M, Merck) and of buthylamine (1.49×10^{-2} M, Merck) were prepared by dissolving the appropriate amount of each compound in water. A 3.69×10^{-3} M stock solution of 1,2-naphtoquinone-4-sulphonate (NQS) was prepared by dissolving 4.8 mg of sodium salt (Merck) in water in a 5 mL volumetric flask. This solution was prepared fresh for each experiment and was stored in the dark at room temperature. Working standard solutions were prepared by suitable dilution of the stock solutions as required. Solutions with different pH have been prepared by mixing amines and NQS in the corresponding buffer solutions (i.e. acetate buffer for pH=5, phosphate buffer for pH=6-8, and carbonate buffer for pH=9-11). In each case the concentration of buffer was 0.2 M.

Preparation of soil and water sample

The analyzed samples were water samples collected from tap water, well water and river water of Hamedan as well as an agricultural soil sample. The water samples were filtered through a filter paper for removal of possible particulate contaminants before use. A 2.0 g of soil sample were stirred in 10 mL distilled water for 30 min at room temperature to extract soluble constituents. The resulting solution was centrifuged at 4000 rpm for 10 min, and filtered through a filter paper. Then, 1.0 mL of this solution was added to a 5 mL volumetric flask and diluted to the mark with distilled water.

Procedure

Here, 1.0 mL of stock NQS solution and 2.0 mL of the carbonate buffer solution (pH 9.5, 0.2 M) were transferred into a 5 mL volumetric flask. This solution was diluted to volume with water and mixed well. After mixing, 2.5 mL of the above solution was transferred to a spectrophotometric cell. The absorbance spectrum was recorded at 280-600 nm with respect to the distilled water blank. Then 50 µl of ethylamine, propylamine, buthylamine or mixtures

of them in certain concentration was injected to the spectrophotometric cell and mixed well. Then immediately the spectrophotometer started to record the UV-Vis spectra every 30 s for 30 min, over the wavelength range of 280-600 nm. For each sample, 60 spectra were sequentially recorded. The recorded spectra were digitized every 1 nm. Therefore, the absorbance-time data matrix was 60×321. Quantitative experiments were carried out using the synthetic mixtures given in Table 1.

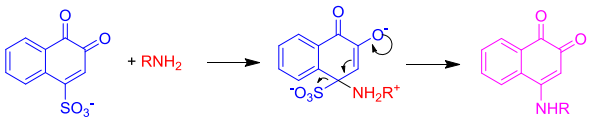
Table 1. Composition of the three standard solutions ([E],[P],[B]) and four analyzed mixtures

	Concentration (M)		
	Ethylamine (E)	**Propylamine (P)**	**Butylamine (B)**
[E]	7.35×10^{-5}		
[P]		7.35×10^{-5}	
[B]			7.35×10^{-5}
[EP]	3.92×10^{-5}	3.43×10^{-5}	
[EB]	2.45×10^{-5}		4.90×10^{-5}
[PB]		2.94×10^{-5}	4.41×10^{-5}
[EPB]	3.92×10^{-5}	1.96×10^{-5}	1.47×10^{-5}

Results and discussion

Spectral features

NQS is able to react in basic medium with both primary and secondary amino group to produce spectrophotometrically detectable derivatives [24]. According to the literature [27,38,39], the reaction equation is as Scheme 1.



Scheme 1.

Sample absorption spectra related to the mixture of NQS (7.5×10^{-4} M) and propylamine (7.5×10^{-3} M) as a function of time at room temperature are shown in Figure 1. Ethylamine, propylamine and butylamine have no absorption in the range of 280-600 nm. NQS has an absorbance maximum at 480 nm. But adding aliphatic amines to NQS gives rise to changes absorption in the visible range during a 30 min waiting period. The spectral shapes resulting from the individual reactions of these amines are very similar and the resulting derivatives show spectra with considerable overlapping which complicates the analysis of the spectral data set without a multivariate approach. Figure 2 shows this similarity. As seen from Figure 1, the spectra of propylamine and also two other amines (not shown) in reaction with NQS are time dependent. Amino group of these amines gives a substitution reaction with sulphonate group of NQS (Scheme 1) and yielded

new compounds that their absorption increase with elapse of time. The formation of these products was utilized in the development of a kinetic spectrophotometric method for the simultaneous determination of ethylamine, propylamine and butylamine. Preliminary investigations showed that the reaction rates for these three amines with NQS are different and the absorbance in the wavelength range studied changes differently with elapse of time for each analyte. Figure 3 shows the variation of the absorbance versus time at 480 nm for ethyl-, propyl- and butylamine in the reaction with NQS under the conditions used in this work.

Therefore, simultaneous determination of these analytes on the basis of their kinetic properties with NQS was carried out because of the difference between their reaction rates. MCR-ALS seems to be the appropriate method for this goal.

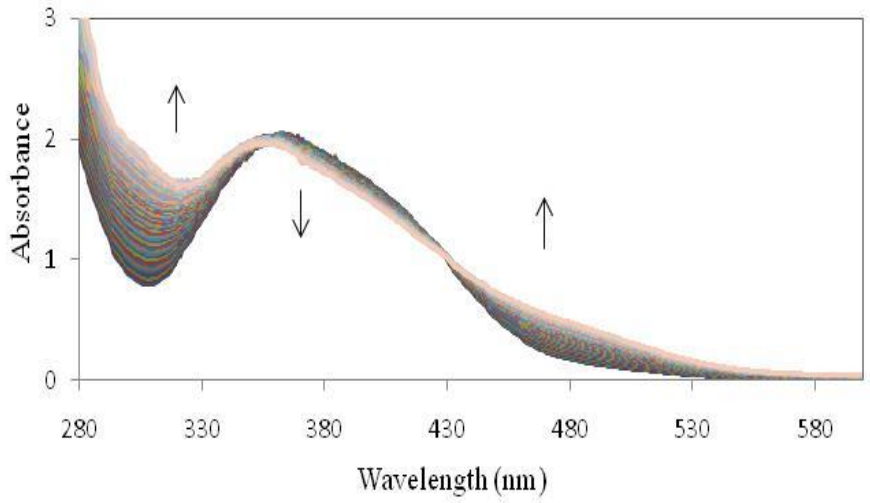


Figure 1. The spectra of propylamine (7.35×10^{-5} M) in presence of NQS (7.5×10^{-4} M), at pH=9.5 during a 30-min time period

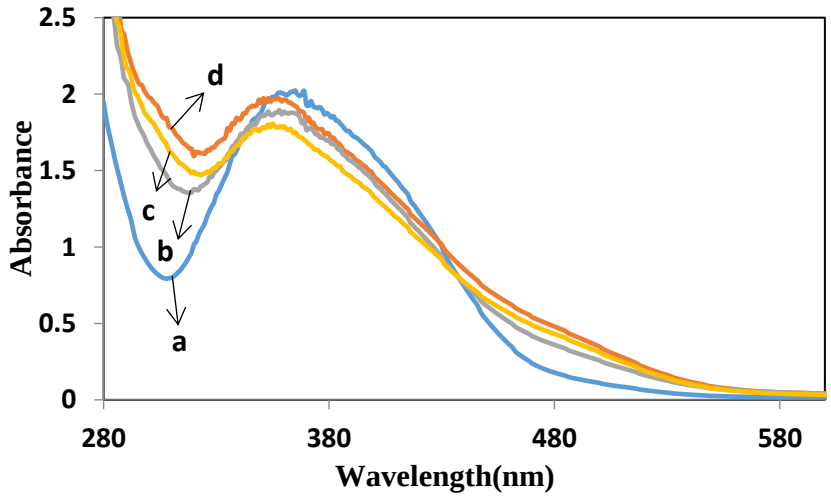


Figure 2. The spectra of a) NQS alone ($7.\ 5\times10^{-4}$M) b) ethylamine c) propylamine d) butylamine (all 7.35×10^{-5} M) in the presence of $7.\ 5\times10^{-4}$ M NQS at pH= 9 after 30 min.

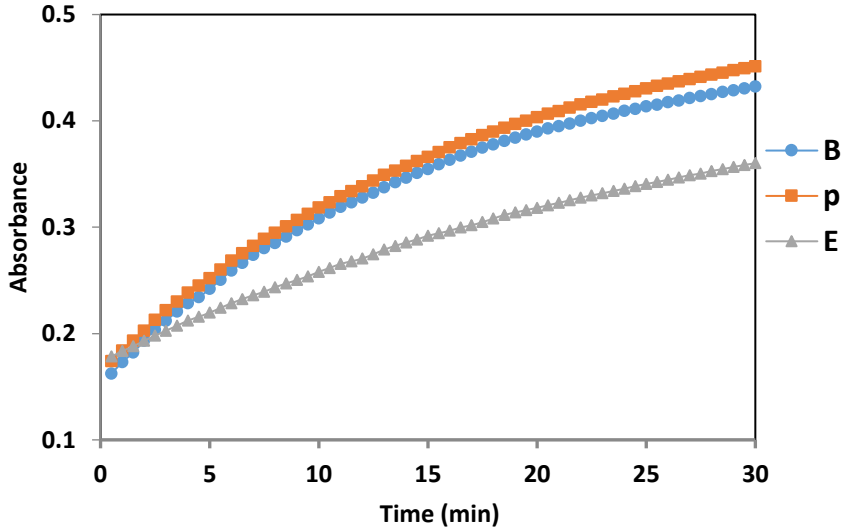


Figure 3. Absorbance-time plots for ethylamine (E), propylamine (P), and butylamine (B) (all 7.35×10^{-5} M) in the presence of NQS (7.5×10^{-4} M), pH=9.5 at λ=480nm

Optimization of experimental conditions

The optimum conditions for the development of the method were established by varying the parameters one at a time while keeping the others fixed and observing the effect produced on the absorbance of the colored product. These studies were to establish the experimental condition resulting in the greatest possible discrimination between the kinetic behavior of these amines and greatest value of signal. So, the effect of various parameters such as pH and concentration of NQS were studied at 480 nm.

Influence of pH

The effect of pH on the absorbance of the reaction between NQS and ethylamine, propylamine and butylamine was separately studied in the pH range of 5 to 10. For this purpose, changes in absorbance at different pHs at 480 nm over 30 min following the initiation of the reaction were monitored and ΔA (ΔA_{total}-ΔA_{blank}) signal is plotted against pH (Figure 4). The signal ΔA(ΔA_{total}-ΔA_{blank}) between 0.5 and 30 min was considered as analytical signal. At pH 5-7, ΔA of the product is close to 0, indicating that under medium acidity, ethylamine, propylamine and butylamine have difficulty reacting with 1,2-naphtoquinone-4-solphonate. The possible reason may be that the amino group ($-NH_2$) of these amines is protonized and turn into protonated amine salts ($-NH_3^+$). So it loses nucleophilic capability for 4-sodium sulphonate of NQS and the nucleophilic substitution reaction cannot take place easily. At pH greater than 7, the absorbance of the solution increases with growth of pH. It may be that protonated amino groups ($-NH_3^+$) turned into $-NH_2$ and nucleophilic substitution reaction happens more easily. At pH 9.5 the ΔA reaches its maximum probably due to higher degree of nucleophilic substitution. But because of good nucleophilic ability of hydroxide ion the reaction may be hindered at higher pH. In order to keep the high sensibility for determination of ethyl-, propyl- and butylamine, pH 9.5 (carbonate buffer) was selected for the optimal experimental conditions.

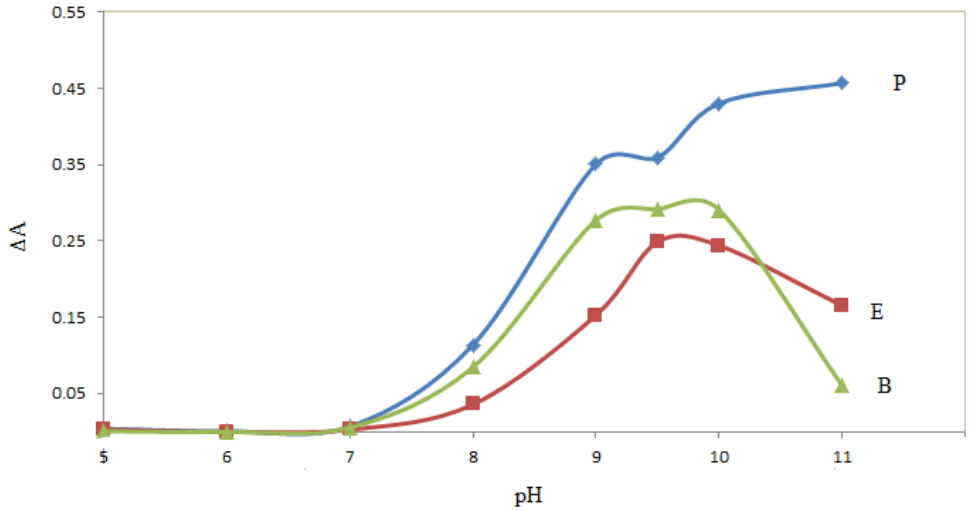


Figure 4. The effect of pH on the ΔA signals of ethylamine (E), propylamine (P), butylamine (B), (2.0×10^{-4} M) in the presence of NQS (7.5×10^{-4} M), pH=9.5

Effect of concentration of NQS

In order to find the optimal concentration of NQS, the effect of its concentration on the reaction of each amines was studied by carrying out the reaction at pH 9.5 and varying concentration of NQS in the range of 1.87×10^{-4} to 1.13×10^{-3} M (four concentration level). At concentration lower than 3.75×10^{-4} M, the reaction rate is quite slow and at concentration higher than 1.13×10^{-3} M the absorbance at wavelengths below 380 nm was too high to allow a precise measurements (A>2). Therefore concentration of 7.5×10^{-4} M was selected as a suitable concentration value.

Data analysis

The experimental data in this work consist of a series of kinetic runs monitored for different amine standards and mixtures. The recorded experimental data has been ordered in a data matrix D (r×c). In the rows of this data matrix are the spectra measured at different times and in the columns the absorbance measured values at different wavelengths. In our datasets, r is 60 and c is 321 in all cases. The total number spectra were 60 per run. Before starting the resolution process, an estimation of the possible number of contributions to the experimental response D must be obtained using singular value decomposition [34]. It is assumed that the singular values associated to the chemical components are much larger than singular values associated with other possible sources of variation such as experimental errors.

Rank analysis of the data sets

The singular values were calculated for all individual data sets. When the spectral data matrices of standards were analyzed by SVD, two factors were found to be significant in all cases. Considering the reported reaction between NQS and amines in the literature,[25,36,37] it is acceptable that the number of components present in the standard solutions are two, consisting of NQS and NQS-amine final adduct (Scheme 1). In fact the standard data are not rank deficient. In the case of binary and ternary mixtures the expected number of species was 3 and 4, respectively i.e. NQS and each amine-NQS final products. As seen from Table 2 the number of significant components estimated by SVD is the

same as the expected ones for binary mixtures. For ternary mixture the right number of significant components has been obtained after augmentation of the matrix of NQS with that of the ternary mixture. Table 2 shows the 9 first singular values obtained by SVD in 9 different situations. In each case, the estimation of the singular values associated with noise is achieved using the second SVD of pure NQS at pH=9.5. This value is reported in Table 2 and can be chosen as a threshold to estimate the rank i.e., the contributions with singular values higher than the threshold are considered significant.

Table 2. The results of singular values decomposition of the individual and augmented data sets

Factor	NQS	P	E	B	PE	PB	BE	BEP	[NQS;BEP]
1	**26.69**	**164.19**	**153.99**	**152.73**	**152.81**	**162.27**	**153.83**	**145.49**	**147.91**
2	0.50	**14.10**	**10.66**	**13.58**	**13.19**	**14.01**	**11.66**	**11.84**	**11.85**
3	0.05	0.49	0.45	0.51	**0.57**	**0.92**	**0.57**	**0.59**	**1.24**
4	0.01	0.33	0.27	0.40	0.45	0.49	0.35	0.27	**0.59**
5	0.009	0.29	0.24	0.25	0.36	0.39	0.29	0.24	0.28
6	0.008	0.26	0.22	0.22	0.26	0.32	0.21	0.17	0.19
7	0.008	0.21	0.19	0.19	0.20	0.25	0.20	0.14	0.17
8	0.008	0.20	0.15	0.15	0.18	0.23	0.16	0.13	0.14
9	0.007	0.19	0.14	0.13	0.16	0.19	0.15	0.12	0.13
Limit[a]	0.50								
Rank[b]	1	2	2	2	3	3	3	3	4

[a] Second singular value from the pure NQS data set
[b] Estimated rank of the data matrix

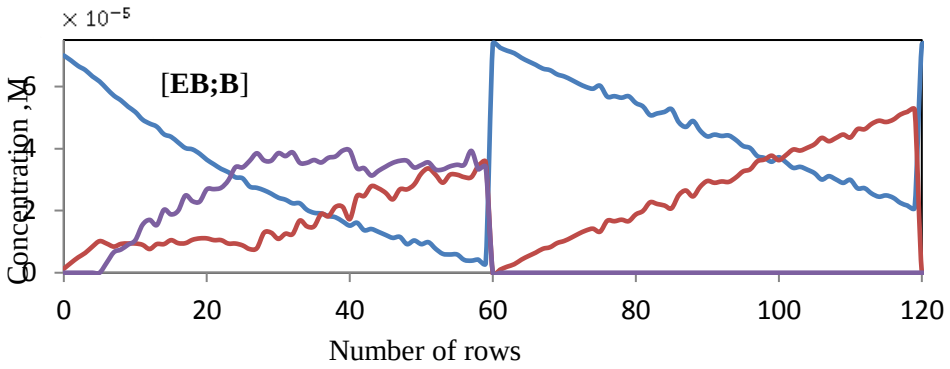
Quantification of binary and tertiary amine mixtures

The MCR-ALS procedure as described above has been applied firstly to synthetic binary and ternary mixtures of amines for the resolution and quantification of the analyte of interest. Quantitative experiments were carried out using the synthetic mixtures given in Table 1. In the analysis of all the mixtures, one of the compounds is considered as analyte to be quantified while the others are considered as unknown interferences. For example in the mixture of ethylamine and propylamine, firstly ethylamine was the compound to be determined and propylamine was the unknown interferent. These matrices are arranged in a column-wise fashion. The data matrix of the unknown mixture was augmented with a data matrix of pure ethylamine of known concentration.

Analysis was initiated with an initial estimate of the spectral profiles. The orthogonal projection approach (OPA) is an iterative procedure to find the pure or purest spectra (row) in a data matrix. A basic assumption of OPA is that the purest spectra are mutually more dissimilar than the corresponding mixture spectra. Therefore OPA uses a dissimilarity criterion to find the number of components and the corresponding purest spectra. These initial spectral estimates are used to start the alternating least squares (ALS)

constrained optimization through an iterative process. During this study, the non-negativity constraint in both concentration profiles and UV-Vis absorbances, unimodality constraint in concentration profiles and correspondence among the species [39] have been applied. Correspondence information is coded in the isp matrix that indicates with 1 and 0 the present and absent species, respectively. This matrix has a number of rows equal to the number of concentration submatrices (samples) in the analysis and a number of columns equal to the total number of components present in the system. This information is only available for the standards because the samples is supposed, to have an unknown composition [40]. Iterations continue until an optimal solution that fulfils the constraints postulated and the established convergence criteria.

Sample spectral and concentration profiles obtained from running MCR-ALS on the augmented matrices are shown in Figure 5. The quantity of each amine in the original mixture sample, was performed by comparing the areas below the concentration profiles for the analyte in the standard and in the unknown sample. These values were compared with the true values and percentage errors (%PE) are obtained. The obtained values of %PE are satisfactory showing that the predictive capability of this method is good. It is also remarkable that the reconstruction of the original data set is also good, with low lack of fit values. The results obtained from the analysis of mixture of ethyl-, propyl-, and butylamine are given in Table 3. The errors of prediction are not the same for different mixtures and are influenced by the composition. The LOF is poorer for ternary mixtures and for binary mixtures of butyl and propylamines with more similarly kinetic behavior. But generally good quantification is achieved for all the amines in the mixture.



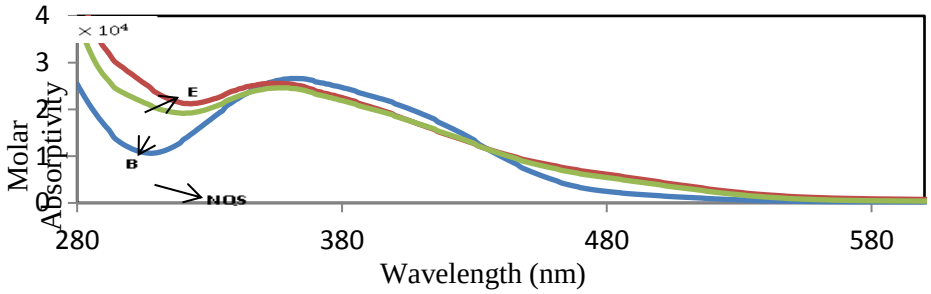


Figure 5. MCR-ALS resolved concentration (up) and spectral (down) profiles from the analysis of the augmented matrix [EB;E]

Table 3. The results obtained by MCR-ALS on the binary and ternary mixtures of ethylamine (**E**), propylamine (**P**) and butylamine (**B**)

	Amines	Real conc. M	Found conc. M	%LOF	R^2	%PE	%Recovery
Sample 1	**E**	3.92×10^{-5}	3.90×10^{-5}	1.77	99.96	-0.51	99.48
	P	3.43×10^{-5}	3.43×10^{-5}	2.21	99.95	0	100
Sample 2	**B**	4.902×10^{-5}	4.90×10^{-5}	2.41	99.94	-0.04	99.95
	E	2.451×10^{-5}	2.32×10^{-5}	2.15	99.96	-5.34	94.65
Sample 3	**P**	2.94×10^{-5}	2.92×10^{-5}	2.11	99.96	-0.40	99.31
	B	4.41×10^{-5}	4.47×10^{-5}	3.87	99.94	1.36	101.36
Sample 4	**E**	3.92×10^{-5}	3.67×10^{-5}	18.7	99.89	-6.37	93.62
	P	1.96×10^{-5}	2.01×10^{-5}	20.2	99.81	2.25	102.55
	B	1.47×10-5	1.39×10^{-5}	18.5	99.87	-5.44	94.55

$$\%PE = 100(c_i^* - c_i)/c_i$$

$$\%Recovery = 100\times\sum\frac{c_i^*}{c_i}$$

Application

To investigate the possibility of the presence of these aliphatic amines in some environmental samples and subsequent determination of them, samples were prepared and treated following the procedure described in the experimental section. Three water samples from different sources in Hamedan, Iran, (i.e. tap water, river water and well water), and an agricultural soil sample collected from Azandarian village in Hamedan, Iran, were used for analysis. The analysis was performed exactly as for the synthetic mixtures. The collected data were analyzed using ALS optimization of an augmented matrix obtained by joining the kinetic data matrices of samples with matrices of standards for ethyl-, propyl- and butylamine in order to determine these amines respectively. Based on the results of MCR-ALS, these aliphatic amines were not

detected in the real samples except for ethylamine in agricultural soil. Therefore, the real samples were spiked by different mixtures of amines. These new samples were reacted with NQS under optimal experimental conditions and the collected spectral data matrices were again augmented with matrices of standards of interested analytes. Application of the MCR-ALS method on the resulted matrices showed satisfactory results that have been collected in Table 4.

Table 4. The results obtained by MCR-ALS on the spiked water and soil samples by ethyl-, propyl-, and buthylamine

	Spiked conc. M			Found conc. M			Recovery%		
Sample	**E**	**P**	**B**	**E**	**P**	**B**	**E**	**P**	**B**
Tap Water	3.92×10^{-5}	3.43×10^{-5}	0	3.96×10^{-5}	3.51×10^{-5}	0	98.98	102.33	0
	3.92×10^{-5}	0	1.47×10^{-5}	4.02×10^{-5}	0	1.35×10^{-5}	102.55	0	91.83
	0	7.35×10^{-5}	0	0	7.19×10^{-5}	0	0	97.82	0
Well Water	0	1.96×10^{-5}	1.47×10^{-5}	0	2.00×10^{-5}	1.36×10^{-5}	0	102.04	92.51
	3.92×10^{-5}	3.43×10^{-5}	0	4.11×10^{-5}	3.54×10^{-5}	0	104.84	103.20	0
River Water	3.92×10^{-5}	3.43×10^{-5}	0	3.61×10^{-5}	3.32×10^{-5}	0	92.09	96.79	0
	3.92×10^{-5}	0	1.47×10^{-5}	3.77×10^{-5}	0	1.23×10^{-5}	96.17	0	83.67
soil	3.92×10^{-5}	3.43×10^{-5}	0	3.05×10^{-5}	0	0	93.12	88.92	0
	3.92×10^{-5}	1.96×10^{-5}	0	1.78×10^{-5}	0	0	88.41	90.82	0

Conclusion

The application of MCR-ALS has been proven to be a useful method for quantitative analysis of aliphatic amines in multicomponent mixture samples. As a method for quantitative analysis, the experimental approach is simple and fast and there is no sample pre-treatment needed to suppress interferences. Advantages over separation techniques are that no clean-up and removal of interferences are needed for the analysis. Compared with multivariate calibration methodologies, the number of standards required is much smaller (one or two standard samples are sufficient) and there is no need to incorporate the information on the matrix interferences (neither the identity nor the concentration range) in the standard solutions. Rank deficiency has proved to be of minor importance for quantitative purposes using the second-order multivariate curve resolution method.

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