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SHORT COMMUNICATION

QUANTITATIVE DETERMINATION OF FORMALDEHYDE BY SPECTROPHOTOMETRY UTILIZING MULTIVARIATE CURVE RESOLUTION ALTERNATING LEAST SQUARES

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ABSTRACT. Formaldehyde is a vastly used material in industry. Nowadays, it is proven that formaldehyde is toxic and carcinogenic. Thus providing a reliable method for its quantitative determination is very important. This study proposes a UV-Vis spectrophotometric based method for determination of formaldehyde. The method is based on reaction between the analyte and Fluoral P. Spectral changes during the time were mathematically analyzed using a chemometrics technique, called "multivariate curve resolution alternating least squares" (MCR-ALS). Data processing by this chemometrics technique enhanced the reliability of the UV-Vis spectrophotometry for quantitative analysis of formaldehyde in real samples.

KEY WORDS: Formaldehyde, Fluoral P, UV-Visible, Multivariate curve resolution alternating least squares; Quantitative analysis

INTRODUCTION

Formaldehyde is known as a very toxic, mutant and carcinogen causing chemical which affects human eyes, membranes, and respiration systems. Its irritant properties such as dermatitis, eye irritation, respiration, asthma and pulmonary edema have been reported previously [1]. Formaldehyde has been classified as one of the major pollutants due to its toxicity. It tends to form nitric acid and peroxide acetyl nitrate through a photochemical reaction [2, 3]. It is also known as a pollutant which has the potential to react with hydrochloric acid to form bis(chloromethyl)ether, a well known carcinogen. The high production and consumption rates of formaldehyde in various industries such as detergents, plastics, polymers, tires raise further concerns in view of its harmful effects both on human and the environment.

Determination of formaldehyde in different environments and samples is a very important task. Several analytical methods are available for determination of formaldehyde. Gas chromatography (GC), high performance liquid chromatography (HPLC), GC with electron-capture detector (ECD) or flame ionization detector (FID) are some of the confirmed methods. Combination of the HPLC and pre-concentration by solid-phase extraction (SPE) with C18 cartridges has been also reported as a sensitive technique. Solid phase spectrophotometric method in association with flow injection analysis is also used for determination formaldehyde with direct spectrophotometric measurement in C18 material [4]. Trace amount of formaldehyde in textiles was determined by discoloring kinetic spectrophotometry [5]; food samples are also analyzed by flow injection spectrophotometry using phloroglucinol as chromogenic agent to determine formaldehyde [6]. Utilizing spectrophotometry for determination of formaldehyde, several reagents such as 5,5-dimetil-1,3-sikloheksadione (Dimedone), 2,4-dinitrophenyl-hydrazine (DNPH) [7] have been applied. There is a selective reagent named Fluoral P for determination of formaldehyde. Reacting with formaldehyde, it forms a yellow complex,

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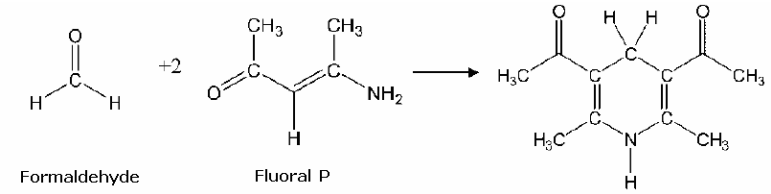
possible to be analyzed quantitatively by spectrophotmetry. The complex formation reaction is gradual, providing a series of spectrophotometric data to be processed, interpreted and manipulated. Nowadays, every analytical technique is coupled with a chemometrics technique for improving the capabilities, performing more reliable models and achieving more precise results. In the other words, chemometrics is the tool for data interpretation and manipulation. There are several chemometrics techniques which can provide more reliable results. Artificial neural networks (ANN) is an example in determination of formaldehyde [8].

Multivariate curve resolution alternating least square (MCR-ALS) [9-12] is a chemometrics approach, which has been applied in different analytical aspects, e.g. complex study of evolving processes [13], multiequilibria systems using spectroscopic titrations (fluorescence, UV-Vis absorption, etc.) [14], resolution of multiple co-eluted peaks in chromatography [15], resolution and quantification of mixtures in flow injection analysis [16], kinetic reactions [17], spectroscopic images, multidimensional spectroscopy, electrophoretic studies of amino acids, voltammetric studies of metal complexes [18] and conformational variations [19]. Recently, determination of formaldehyde in alcoholic beverages has been reported using purpald screening and chromotropic acid spectrophotometry with multivariate curve resolution [20]. In the present study, MCR-ALS was utilized for quantitative determination of formaldehyde using spectrophotometric data obtained from formaldehyde and Fluoral P mixture during the course of reaction.

Formaldehyde reacts with Fluoral P and produces 3,5-diacetyle-1,4-dihydrolutidine (Scheme 1). This reaction course is more than 2 hours at room temperature since the start and it could be called as an iterative gradual reaction which could be treated by MCR-ALS.



Scheme 1. Complex formation between formaldehyde and Fluoral-P.

It was aimed to utilize the sensitive reagent Fluoral P, proposing a sensitive and reliable approach for determination of formaldehyde by coupling the sensitive reagent with MCR-ALS. This could be an idea to cover the lack of a model by which the reaction trend is also possible to be monitored. On the other hand, MCR-ALS needs least number of samples for making a reliable calibration model, determining the analyte in unknown samples, rapidly by simultaneous recovery of spectral information.

EXPERIMENTAL

Formaldehyde (36% w/v) was purchased from Fluka (St. Louis, USA); analytical grade acetyl acetone, acetic acid and ammonium acetate all from Merck (Darmstadt, Germany). Double distilled and de-ionized water was used for preparation of solutions purchased from Baran Moghattar (Iran). Spectrophotometric measurements were performed by a Shimadzu UV-160 apparatus (Tokyo, Japan) using a quartz cell.

Preparation of reagent. Fluoral P was prepared first by mixing 0.2 mL of acetyl acetone, 0.3 mL of acetic acid and 15.4 g of ammonium acetate and then by diluting to 100 mL with deionized water.

Preparation of calibration sample. Calibration model samples were prepared from stock solution (1000 mg/L) which was originally from the Fluka standard solution (36% w/v).

Preparation of validation and real samples. Validation sample was a formaldehyde solution with known concentration; the concentration of which was determined by constructed calibration model. Real sample was wastewater of a tire manufacturing factory. The laboratory of the factory declared the concentration of the formaldehyde in wastewater equal to 1 mg/L.

Spectroscopic determination. Formaldehyde was added to the Fluoral P solution in a 1:1 volume ratio. The reaction between formaldehyde and Fluoral P was monitored by spectrophotometry for 140 min. Absorbance of solution sample was determined at 1, 20, 40, 60, 80, 100, 120 and 140 min after start of process. The obtained absorbance data for standard, validation and real sample was processed by multivariate curve resolution alternating least square (MCR-ALS).

Data processing. Using MATLAB ver. 7.0 implemented MCR-ALS software the useful chemical information was extracted from UV-Vis spectra during the time. One of the main advantages of MCR is that it does not rely on the initial proposal of a specific model but estimates directly the changes in data. The concentration profiles are used as initial values in a constrained ALS optimization procedure which consists of two parts:
(1) An estimation of the unknown species spectra is obtained by least squares:

$$S = C'D^*$$

where D^* is the reproduced data matrix and C' is the pseudo inverse of C. The matrix S gives the current least-squares estimation of the spectra. The UV-Vis absorptivities must be positive. This constraint is applied accordingly during the least-squares optimization.

(2) A new estimation of the concentration profiles is obtained by least-squares:

$$C = D^*S'$$

where now S' is the pseudo inverse of the S matrix. In this case, the concentration derived from the equation is constrained to be positive. These 2 steps were repeated until the data matrix D was well explained within experimental error.

RESULTS AND DISCUSSION

The UV-Vis spectra of formaldehyde, Fluoral P and formaldehyde-Fluoral P complex between 300-1000 nm demonstrated that formaldehyde had no signal, a signal due to Fluoral P between 300-400 nm and due to formaldehyde-Fluoral P complex between 360-460 nm. It was observed that while there are no informative signals in the spectra of single component formaldehyde samples, the binary mixture showed an intensive band due to complex formation. The main informative spectral region for formaldehyde-Fluoral P complex was 360-460 nm, which was applied in further analysis and data processing. Formaldehyde contains C=O functional group which can have $\pi \rightarrow \pi^*$ transition but the related absorbance of this transition occurs at near-UV. Fluoral P contains C=O group conjugated with C=C. This shifts the absorbance related to $\pi \rightarrow \pi^*$ transition to higher wavelengths. Formaldehyde-Fluoral P complex has C=O, C=C and nitrogen with lone electron pair. These three groups are conjugated, causing the absorbance related to $\pi \rightarrow \pi^*$ transition to shift to higher wavelength than the absorbance of Fluoral P.

Multivariate curve resolution alternating least squares (MCR-ALS). MCR-ALS involves decomposing the experimental data into two matrices: a matrix of concentrations and a matrix of spectra. In the first step, the data matrix is built up. The different individual spectra obtained in different times would form the rows of this data matrix and the measured absorbance values at each spectral wavelength are in the columns.

Principal component analysis (PCA) is a widely accepted method that reduces complex spectral data into much fewer dimensions using principal components (eigenvectors) and scores. PCA is performed to estimate the possible number of components [21]. It is assumed that a bilinear relation exists between experimental data, concentrations and spectra of the components of analogues structure. This relation is supposed to be an example of the generalized of Lambert-Beer law. If this bilinear model is set in matrix form, it is expressed as:

$$\mathbf{D} = \mathbf{C}\mathbf{S}^{\mathbf{T}} + \mathbf{E}$$

where **D** is experimental data matrix, **C** is concentration profiles' matrix , $\mathbf{S}^{\mathbf{T}}$ is the spectra matrix and **E** is the experimental error matrix.

It is assumed that data matrix **D** is bilinear, i.e., the spectroscopic signal can be decomposed into the sum of individual contributions, each described by a concentration profile in matrix **C** and by a pure spectra in matrix $\mathbf{S}^{\mathbf{T}}$. The number of components or contributions, to be considered in the mathematical decomposition of mentioned equation can be initially estimated by singular value decomposition (SVD) analysis. The initial estimate of the concentration profiles can be obtained by evolving factor analysis (EFA) process. Given the measurements matrix **D**, MCR has to estimate the pure variables **C** and $\mathbf{S}^{\mathbf{T}}$ in terms of the bilinear model and using some generic knowledge about these variables. In other words, one seeks for the estimates of the pure variables that minimize the following error criterion:

$$\min_{\mathbf{C},\mathbf{S}^{\mathrm{T}}} ||\mathbf{E}||^2 = \min_{\mathbf{C},\mathbf{S}^{\mathrm{T}}} ||\mathbf{X} - \mathbf{C}\mathbf{S}^{\mathrm{T}}||^2$$

The least squares error criterion is the most commonly used error criteria, although there are some MCR techniques using weighted or normalized least squares errors. Both the resolved concentration profiles and spectra can be rotated without changing the residuals associated with the model (rotational ambiguity). Additionally, the intensity of the concentration profiles and the spectra is not unique either since the profiles can be multiplied by a non-zero number, what is compensated by dividing its associated spectrum by the same number (intensity ambiguity). Minimizing of the previous equation will therefore lead to multiple solutions of the pure variables. Using constraints one can force a certain spectral or temporal profile to fulfil a defined feature, reducing thus the ambiguity of the solution. A multivariate curve resolution-alternating least squares (MCR-ALS) algorithm, like the one used here, relies on an iterative ALS optimization of the matrixes **C** and $\mathbf{S}^{\mathbf{T}}$ under applying constraints:

$$\min_{\mathrm{C}} ||\mathbf{X} - \mathbf{C}\mathbf{S}^{\mathrm{T}}||^2 \text{ and } C \text{ fulfilling constraints}$$

$$\min_{\mathrm{S}^{\mathrm{T}}} ||\mathbf{X} - \mathbf{C}\mathbf{S}^{\mathrm{T}}||^2 \text{ and } S^T \text{ fulfilling constraints}$$

Every sub-step in the iterations is a least squares estimation of a part of the parameters temporarily fixing the remaining parameters. The MCR-ALS steps are briefly described as: constructing the initial estimates of the spectra ($\mathbf{S}^{\mathbf{T}}$), calculating least squares of **C** and then $\mathbf{S}^{\mathbf{T}}$ and finally, reproduction of **D**, using **C** and $\mathbf{S}^{\mathbf{T}}$. If the convergence criterion is fulfilled, the process is finished. If not, it is required to repeat from "least squares calculation" step. This procedure is valid when an initial estimate of $\mathbf{S}^{\mathbf{T}}$ is used. When using an initial estimate of **C**, the order of steps 2 and 3 should be reversed. We can also improve the resolution by applying

several constraints during optimization. These depend on the nature and structure of the data [22, 23]. Figure 1 shows a brief description of chemometrics procedure.

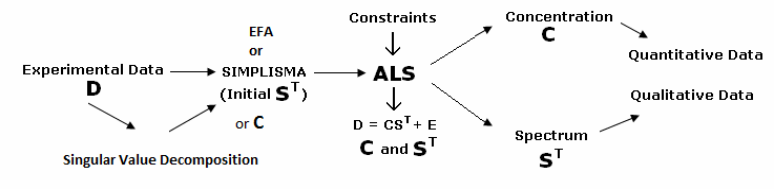


Figure 1. Schematic procedure of curve resolution.

The results obtained for determination of formaldehyde are shown in Table 1. Accuracy and precision of the results show this method can be a reliable approach compared to other methods reported in the literature [20]. Figure 2-A shows the spectrum of pure formaldehyde-Fluoral P complex and Figure 2-B shows resolved spectrum of the complex by MCR-ALS.

Table 1. Results obtained from determination of formaldehyde by UV-Vis spectrophotometry and MCR-ALS (concentrations in mg/L).

	Real	Determined	Relative error	n
Validation	0.50	0.49 (±0.11)*	2%	10
Real sample	1.00	1.04 (±0.24)	4%	10

*Standard deviation.

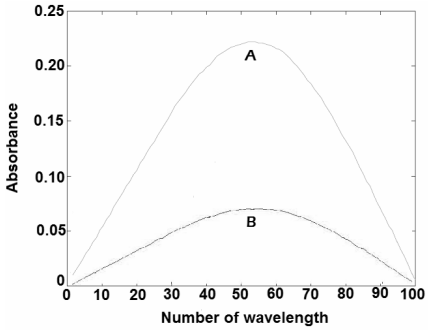


Figure 2. Spectrum of formaldehyde-Fluoral P complex (formaldehyde = 1 mg/L) 140 min after start of reaction (A) and pure spectrum of formaldehyde-Fluoral P resolved by MCR-ALS (B).

According to the MCR-ALS, it is possible to determine the amount (%w) of formed formaldehyde-Fluoral P complex (Table 2) during the time. It was assumed that the time for complete process is 140 min.

Table 2. Amount of produced complex (formaldehyde-Fluoral P) during time.

Time (min)	1	20	40	60	80	100	120	140
Complex (%w)	0.75	7.46	18.16	31.84	47.51	64.18	81.84	100

CONCLUSIONS

A new and easy method has been reported for determination of formaldehyde in industrial wastewater. In this method MCR-ALS chemometrics technique was used for processing the spectral data which were obtained by spectrophotometric measurement of reaction between formaldehyde and Fluoral P. This method needs least number of samples for making calibration model and is reliable. MCR-ALS is shown to be capable of determining formaldehyde using the new correlation constraint in unknown real samples. Although Fluoral P is a selective reagent for determination of formaldehyde, MCR-ALS was found to be a powerful method for determination of analyte in unknown mixture. The main advantage of using MCR-ALS relates to the simultaneous recovery of spectral information. The proposed method would be of great interest in environmental analysis.

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