Simultaneous determination of phosphate and silicate in complex unknown mixtures by H-point curve isolation method and H-point standard addition method

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ABSTRACT

The present work examine the capability of standard addition method to correct the matrix effect and the advantages of the curve isolation of data using H-point standard addition method (HPSAM) and H-point curve isolation method (HPCIM) for determination in unknown mixtures. By a successive standard addition of the analyte was performed. The average of the created spectra was calculated. The subtraction of obtained averaged spectrum from the initial solution spectrum gives constant cumulative spectrum for interferents. The proposed procedure was based on the formation of phosphate- and silico-molybdenum blue complexes in the presence of ascorbic acid. Molybdenum blue is not relatively free from the interferences caused by the other ions, therefore several cations and anions (such as As^{5+}, V^{5+}, Sn^{2+}, Zn^{2+}, Fe^{3+}, S^{2-}, MnO_4^-, F^-, I^-) can react with this reagent. It is also not necessary to condition carefully the medium to remove interfering species. Hence due to the standard addition of analyte in sample solution more accurate results will be produced. This method was validated for the determination of phosphate and silicate in sea water, river water, mineral water, waste water, urine, detergent and soft drink samples.
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KEYWORDS

INTRODUCTION

Recent years witnessed an increase in the number of people using computational chemistry. This increase has been facilitated by the development of computer software. Chemometrics is involved in the process of producing data and in the extraction of the information from them. The key to chemometrics is involved in the process of producing data and in the extraction of the information from them. With a multivariate calibration model, usually, it is required that there is (are) no new constituent(s) in the samples being analyzed. In order to accurate determination of new constituent(s) a recalibration including this new constituent will be necessary. In the literature, for multiway data, there are a number reports to resolve the overlapping spectra. Among these methods, are partial least squares[1,2], rank annihilation method[3,4], Kalman filtering multivariate

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curve resolution-alternative least squares (MCR-ALS)[7,8], generalized rank annihilation method[3], PARAFAC[9], and more recently PARALIND[10], have made great efforts and improvements in multivariate calibration models. All these methods, except partial least square and Kalman filtering which were based on second-order advantage, require three-way data to resolve overlapping spectra.

Although, these techniques can give much information about interaction between examined parameters but several factors can be responsible for the breakdown the accuracy of this information. Strongly, matrix effect can alter the sample analytical signal relative to that of a standard of the same analyte concentration[11]. It means that in the presence of matrix effect, the applicability of these methods is hindered. In the other words, when the sensitivity of the response depends on the matrix composition, quantitative predictions based on pure standards may be affected by differences in the sensitivity of the response of the analyte in the presence and in the absence of chemical matrix of the sample. Hence, standard addition can be applied for most analytical techniques in order to solve the matrix effect problem e.g. compensate non-spectral interferences and certain types of spectral interferences (e.g. non-analyte absorption), which enhance or depress the analytical signal of the analyte concentration.

HPSAM is a modification of the standard addition method that transforms the incorrigible error resulting from the presence of a direct interference in the determination of analyte into a constant systematic error[12]. In 1988, HPSAM was presented based on the principle of dual-wavelength spectrophotometry and the standard addition method[13-15]. The greatest advantage of HPSAM is that it can remove the presence of an interference and reagent blank[16]. In order to apply HPSAM to resolve mixtures, the interferent(s) species should be known. Two methods namely generalized H-point standard addition method (GHPSAM)[17-19] and HPCIM[20] were proposed to solve this problem. Curve resolution procedure for isolating the spectra of unknown interferent(s) from the sample spectrum in order to determine analyte based on the HPSAM and *K*-ratio-HPSAM was proposed[21-23]. Safavi *et al*., developed combination of HPCIM and HPSAM for spectral deconvolution of

solute-miceller systems[24]. Also Abdollahi and Zeinali used HPCIM and HPSAM for spectrophotometric studies of complex formation equilibria[25].

In a previously reported work, we introduced a new strategy for solving the matrix effect and the determination of an analyte in the presence of unknown interferents using the combination of HPCIM and HPSAM. Compensation of matrix effect was performed using successive standard addition of the analyte to the sample solution. The spectrum of the analyte was calculated by averaging the resulting spectra obtained by subtraction of the solutions spectra after and before standard addition. The result at simulated and real data sets (pharmaceutical, biological and alloy samples) showed that proposed strategy for considering matrix effect was quite efficient[26].

Phosphorus can be found in the environment most commonly as phosphates. Phosphates are important substances in the human body, because they are a part of DNA materials and they take part in energy distribution. Phosphates can also be found commonly in plants[27]. Phosphates have many effects upon organisms. The effects are mainly consequences of emissions of large quantities of phosphate into the environment due to mining and cultivating. During water purification phosphates are often not removed properly, so that they can spread over large distances when found in surface waters. The increasing phosphor concentrations in surface waters raise the growth of phosphate-dependent organisms, such as algae and duckweed. These organisms use great amounts of oxygen and prevent sunlight from entering the water[28].

The enrichment of silicate can promote the growth of diatoms and the other algal species and change the dominance of few Cyanobacteria and Chlorophyte species. Therefore, it can elevate the algal biodiversity of an aquatic ecosystem and weaken the cyanobacterial blooms to a certain degree[29].

The molybdenum blue reduction has been known since the 1930s. A conventional spectrophotometry as the molybdenum blue is not so sensitive or selective. This is because of its relating high interference from coexisting ions. Selectivity or sensitivity towards each ion is achieved by careful conditioning of sample solution to remove interferences.

El-Sayed applied first-derivative spectrophotom-

etry for simultaneous determination of phosphate and silicate[30]. The derivative methods do not have good sensitivity. An unwanted effect of the derivative methods is the decrease in *S/N*. This decrease follows from the fact that noise always contains the sharpest features in the spectrum. So the more sensitive methods for simultaneous determination of them were interested.

Recently, we used artificial neural networks (ANNs) assisted by principal components analysis for simultaneous determination of phosphate and silicate[31]. In general, using ANNs techniques is time suming and difficult to be carried out with the data of entire spectral overlapping for simultaneous multicomponent determination. Also at ANNs as similar as multiplicative calibration methods, all of components should be considered in calibration step. It means that in presence of new interferences (unknown interferences) recalibration will be necessary. So applicability of ANNs in the presence of matrix effect or unknown interferences is hindered.

The proposed method based on combination of HPCIM and HPSAM allows the quantitative analysis of phosphate and silicate in the presence of several unknown interfering components without any separation steps. The quality of the results obtained is not a function of overlapped unknown spectra. It is very interesting with respect to improve the sensitivity and selectivity for phosphate and silicate determination that experiments can be performed in a solution without removing interfering ions or compensation of their effect by selection of proper blank. The results from experimental data set relating to the spectrophptometric determination of phosphate and silicate in synthetic mixtures were presented. The method was successfully applied to the determination of phosphate and silicate in sea water, river water, waste water, mineral water, and urine and detergents powder.

HPCIM for extraction the spectra of interferents in unknown mixture

The HPCIM can be used for obtaining the pure spectrum, which is sum of interferents spectra. We will use the term interferent, instead of sum of interferents for simplicity. Consider the total absorbance of solution defines by following equation:

$$S_i = A_i + I_i \tag{1}$$

where i is i*th* wavelength and S, A and I are sample absorbance, analyte absorbance and interferent absorbance, respectively. By standard addition of known amounts of analyte on sample solution, the new values will be obtained as follows:

$$S_{i,k} = A_i + I_i + A_{i,k} \tag{2}$$
$$S_{i,n} = A_i + I_i + A_{i,n}$$

where, because of standard addition of analyte on sample solution, $A_{i,k}$ and $A_{i,n}$ are added values to previous absorbance value. If Eq. (2) subtracted from Equation (1), new values, containing the matrix effect presented in solution, will be created, too. The average of these values can be use as analyte spectrum, as follows:

$$A_{A,i} = \frac{\sum_{k}^{n}(S_{i,k} - S_i)}{n} \tag{3}$$

The reference wavelength selected from the created spectrum by Eq. (3). Then the K_i is defined as:

$$K_{i,ref} = \frac{A_{A,ref}}{A_{A,i}} \tag{4}$$

$A_{A,ref}$ is the absorbance of analyte at reference wavelength. If we use the analyte spectrum and select reference wavelength from this spectrum, the analyte contribution to the signal, can be canceled by subtraction S_{ref} - $K_{i,ref}S_i$, where S_{ref} is the absorbance of solution at the reference wavelength. Rearrangement gives:

$$S_{ref} - K_{i,ref}S_i = I_{ref} - K_{i,ref}I_i \tag{5}$$

The equation shows that the result is related only to interferent. The later equation can be written in the following way

$$I_i = \frac{(S_{ref} - K_{i,ref}S_i) - I_{ref}}{-K_{i,ref}} = S_i - \frac{S_{ref} - I_{ref}}{K_{i,ref}} \tag{6}$$

This equation also shows that spectrum of interferent can be calculated by entering an appropriate value of I_{ref}, because every parameter in this equation is known except I_{ref}. So the next step is to estimate the I_{ref} value. The maximum absorbance at the reference wavelength should not be higher than the absorption of the solution which analyzed at this wavelength. Also the minimum value is the smallest absorbance value that provided non-negative absorbance value for the products at some wavelengths calculated by Eq. (6).

It is possible to plot the several spectral from Eq.

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(6) by considering the range between maximum and minimum absorbance values for interferent.

The real interferent spectrum will be one of all calculated spectra. To calculate the absorbance of the interferent at this reference wavelength, it is necessary to find of wavelength with the same absorbance values, although different in magnitude, from one spectrum to another. In order to find wavelengths, it is sufficient to find them on the maximum and the minimum spectra, since they are most different. Having set of λ_m and λ_n with $I_m = I_n$, there are following three following equations and three unknowns

$$S_{ref} - K_{m,ref}S_m = I_{ref} - K_{m,ref}I_m$$
$$S_{ref} - K_{n,ref}S_n = I_{ref} - K_{n,ref}I_n$$
$$I_m = I_n$$

So the real value of I_{ref} can be calculated from:

$$I_{ref} = s_{ref} - k_{m,ref}s_m + \frac{k_{m,ref}[(s_{ref} - k_{m,ref}s_m) - (s_{ref} - k_{n,ref}s_n)]}{k_{n,ref} - k_{m,ref}} \quad (7)$$

Since this equation is only dependent on known quantities, it is possible to estimate the interfernts spectra by that.

At this point, this spectrum belongs to the sum of interferents. By applying HPSAM, analyte concentration in each sample can be calculated. The concentration of each component is then calculated from intersection point of calibration curves by standard addition of analyte on selected wavelength pairs.

EXPERIMENTAL

Reagents

All chemicals were of analytical reagent grade and doubly distilled water was used throughout the experiments. A stock solution of phosphate (100 mg L^{-1}) was prepared by dissolving oven dried potassium dihydrogen phosphate (Merck) in water. A stock solution of silicate was prepared by appropriate dilution of a sodium silicate solution (Merck) with water. A sodium molybdate solution (0.02 mol L^{-1}) was prepared by dissolving an appropriate amount of $(NH_4)_6Mo_7O_{24}.2H_2O$ in 0.2 mol L^{-1} nitric acid. Ascorbic acid, 3×10^{-2} mol L^{-1}, was prepared by dissolving appropriate amounts of ascorbic acid (Merck) in 100.0 mL of distilled water. The detergent and mineral water were brought from local markets.

Apparatus

A detection system consisting of analytic Jena SPECORD 250-222P169 UV/VIS double beam spectrophotometer with 1 cm path length quartz cell was used. The slit length was 1 nm and scan speed of 100 nm s^{-1} was selected. The spectra recorded at 1 nm intervals. Simple programs was written for performing selection of wavelength pairs performing the selection of the wavelength pairs in MATLAB 7.1.

Individual calibration graphs

A set of sample solutions with different ions concentrations was prepared and measurements were carried out according to the experimental procedure. The calibration curves of analyte measured at different ranges were linear in the ranges 0.025- 4.50 mg L^{-1} and 0.020 - 6.00 mg L^{-1} for phosphate and silicate, respectively. Typical equation of the calibration curves were as follows: A= 8.81×10^{-2} + 1.2×10^{-3}, r^2 = 0.9997 and A=6.91 $\times$ 10^{-2} + 1.5×10^{-3}, r^2 = 0.9995 for phosphate and silicate, respectively. Limits of detection (LODs) were determined as 0.012 mg L^{-1} and 0.0023 mg L^{-1}, for phosphate and silicate, respectively. Also limit of quantitation (LOQs) were determined as 0.0332 mg L^{-1} and 0.0750 mg L^{-1}, for phosphate and silicate, respectively.

RESULT AND DISCUSSION

Preliminary study of the system

In the acidic media and in the presence of an appropriate catalyst and reducing agent the reaction of orthophosphate and silicate with molybdate produces the colored product of phosphor-molybdenum blue and silico -molybdenum blue. For simultaneous determination of phosphate and silicate by molybdenum blue, the optimum working conditions were used as follows: 0.05 mol L^{-1} nitric acid (1.5 mL), molybdate 0.02 mol L^{-1} (1 mL) and 3×10^{-2} mol L^{-1} (1 mL) ascorbic acid.

The molybdenum blue method, for determination of phosphate and silicate, is not relatively free from the interferences caused by other ions. The most serious interfering ions are arsenate, vanadate, iron (III), nicke(II) and copper(II). Hence in order to evaluate applicability of the method for resolving real mixtures, simultaneous determination of phosphate and silicate

using molybdenum blue method in presence of different ions was investigated. For applying the curve isolation method, three different sample sets containing phosphate and silicate were prepared. First set contains phosphate, silicate and different cations (see Figure 1). Second and third sets contain anions (Figure 2) and both of cations and anions interferents, respectively (see TABLE 1 for more details).
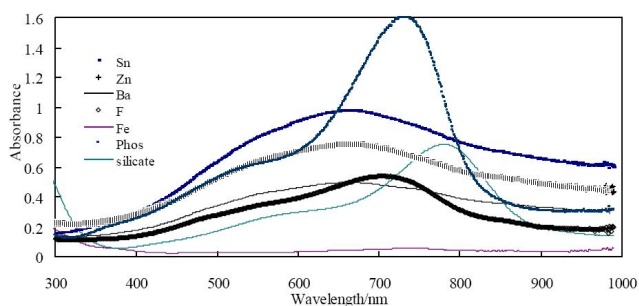

Figure 1 : Spectral features of the components for data set 1 (see text for more details).

TABLE 1 : Composition of three data sets assayed.

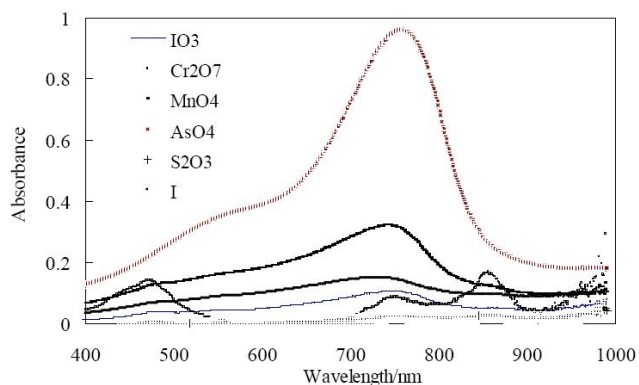| Sample set	Interferents	Sample composition
1	Cation	P(0.2 mg L^{-1}), Si(0.4 mg L^{-1}), Zn^{2+}(3.0 mg L^{-1}), Sn^{2+}(2.0 mg L^{-1}), Ba^{2+}(2.0 mg L^{-1})
2	Anions	P(0.2 mg L^{-1}), Si (0.4 mg L^{-1}) I^{-} (0.2 mg L^{-1}), SCN^{-}(0.4 mg L^{-1}), IO3^{-}(1.0 mg L^{-1}), AsO$_4$$^{-}$(2.0 mg L^{-1}), Cr$_2O_7$$^{2-}$(0.2 mg L^{-1})
3	Both	P(0.2mg L^{-1}), Si(0.4 mg L^{-1}), Zn^{2+}(3 mg L^{-1}), Sn^{2+}(2 mg L^{-1}), Ba^{2+}(mg L^{-1}) F^{-} (0.2 mg L^{-1}), SCN^{-}(0.4 mg L^{-1}),IO$_3$$^{-}$(1.0 mg L^{-1}), AsO$_4$$^{-}$(2.0 mg L^{-1}), Cr$_2O_7$$^{2-}$(0.2mg L^{-1})

Figure 2 : Spectral features of the components for data set 2 (see text for more details).

We suppose phosphate to be an analyte, so standard addition of phosphate to the sample solution was

performed (see Figure 3). The spectra after and before standard additions was recorded. These spectra were subtracted by initial sample solution to obtain spectra of phosphate by considering matrix effect. Average of obtained spectra was calculated and used at HPCIM procedure as phosphate spectrum. Phosphate obtained spectra was used to isolate cumulative interferents spectra. For beginning of HPCIM the wavelength 700 nm was selected as reference wavelength. Interferents cumulative spectrum can be calculated according Eq. 6. For this purpose, the minimum and maximum possible values of I$_{700}$ were determined. The maximum selected absorbance for I$_{700}$ was absorbance of solution at wavelength 700 nm (0.574 AU). Also, the minimum value was 0.005 absorbance unit. It is worth considering that feeling absorbance values less than the minimum value (0.005) in the present wavelength (700 nm), generates negative absorbance values at some wavelengths. Figure 4 shows created absorption spectra of hypothetical interferents spectra at the range 0.005-0.574 AU. This means that real interfernts spectrum will be one of these created spectra. In order to obtain the absorbance value of interferets, it is necessary to find wavelength pairs with nearly the same absorbance values in spectral range. Several wavelength pairs (wavelength meeting the requirement of not more than 2 % difference in their absorbance value) were selected.
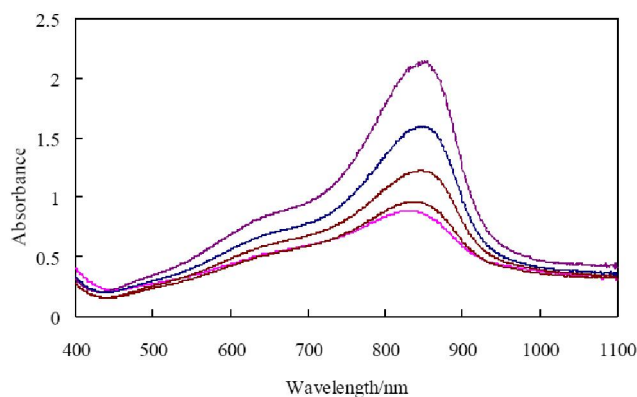

Figure 3 : Obtained spectra after standard addition of phosphate on the sample solution of set 1.

According to Eq. (6), new values for I$_{700}$ were calculated and with these new values, new spectra can be obtained for interferents (see Figure 4). As Figure 5 shows the maximum and the minimum values of upper and lower spectra was changed (after three cycle HPCIM). Calculation was repeated until the absorbance

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interval became an acceptable small value. At this point, the average value of I_{700} was calculated and substituted in Eq. (6) to obtain data for final cumulative spectrum of inteferents (see Figure 6).
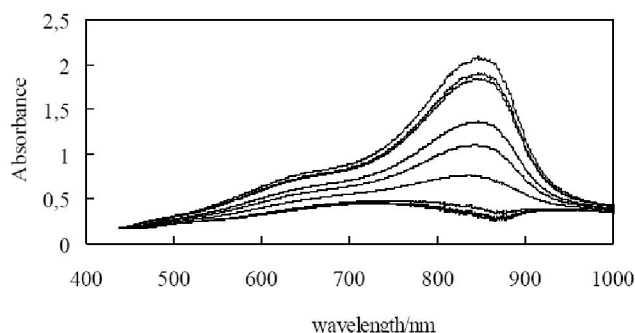
Figure 4 : Various spectra obtained for cumulative spectra of interferents between maximum and minimum predicted values using HPCIM min order to remove phosphate contribution from sample spectrum
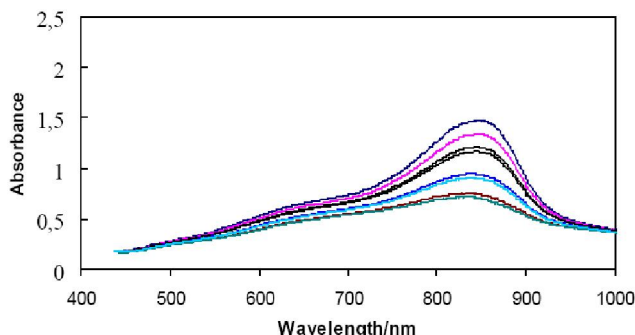
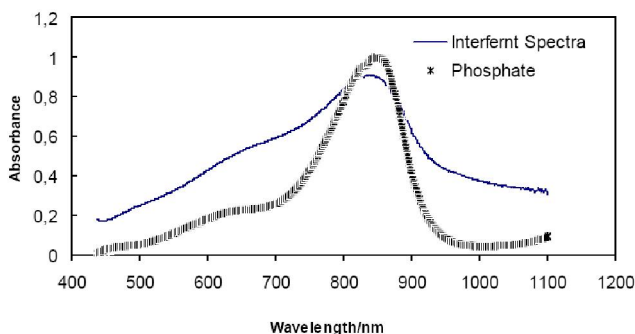**Figure 5 : The spectra obtained after three times applying HPCIM**

Figure 6 : The predicted cumulative spectrum for interferents in solution (-) and phosphate spectrum(*).

Phosphate concentration in sample can be calculated based on HPSAM equation. Regarding cumulative predicted spectrum, it is possible to select several pairs of wavelength where they present the same absorbance for interferents. After this the selected wavelength pairs were sorted following the criteria to give the higher value in the difference of slopes of cali-

brations lines for standard solutions of phosphate. Figure 7 shows the HPSAM lines obtained at selected wavelengths.
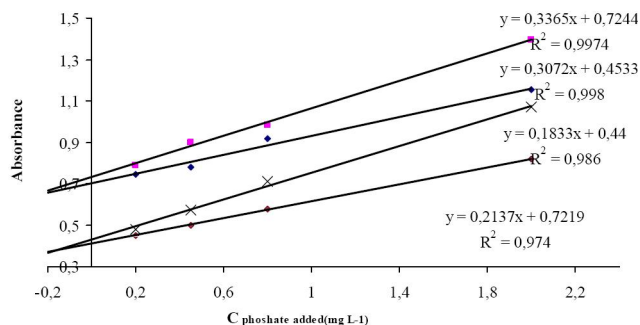
Figure 7 : Plot of HPSAM for determination of phosphate in the solution at selected wavelength pairs.

TABLE 2 : Selected wavelength, calculated concentration and recovery data for synthetic mixtures given in TABLE 1 using HPCIM and HPSAM for samples

Set	Analyte	Wavelength	Calculated concentration	% Recovery
1	P	637-908	0.192±0.03	96
	S	652-770	0.420±0.02	105
2	P	655-797	0.208±0.03	104
	S	579-812	0.421±0.02	105
3	P	741-889	0.211±0.03	105.5
	S	566-819	0.418±0.02	104.5

TABLE 3 : Effect of foreign ions on the simultaneous determination of phosphate and silicate (0.8 mg L^{-1} each of phosphate and silicate)

Foreign ion	Tolerance limit/mg L^{-1}	
	Phosphate	Silicate
Zn^{2+}	10	10
Sn^{2+}	8	10
$Cr_2O_7^{2-}$	15	10
SO_4^{2-}	700	1000
IO_3^-	50	50
SCN^-	600	>600
$S_2O_3^{2-}$	>1000	>1000
VO_4^{2-}	5	5

Same procedure for determination of silicate in mixtures was applied. Standard addition of silicate was performed and after subtraction of spectra after and before standard additions, the cumulative spectrum of interferents, using HPCIM procedure was extracted. HPSAM was applied to estimate silicate concentration. The results and selected wavelength pairs are given in TABLE 2.

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In same way, for quantitative determination of phosphate and silicate in second and third sets standard addition of phosphate and silicate was performed and the cumulative spectra of interferents were resolved. Concentration of silicate and phosphate was determined. The results and selected wavelength pairs are given in TABLE 2. As the results shows, proposed procedure is suitable for determination of phosphate and silicate in various media. The results show that the predictive applicability of method not only is independent on the type or the number of interferents but also it is independent on the amount of analytical signal overlapping of the components.

Study of diverse ions

In our previous work[31], the effects of foreign species on the simultaneous determination of phosphate and silicate were investigated by measuring the absorbance of solution containing 0.80 mg L^{-1} of phosphate and silicate in the presence of various amounts of the other ions. In this study the interference effect of the other ions was investigated. The results are shown in TABLE 3. The interfering effect of ions was not removed. Because the proposed method can extract cumulative spectrum of unknown interferents, it is possible to select the wavelength pairs on this spectrum which interferents absorbance is the same as other wavelength.

Determination of Phosphate and silicate in surrounding waters

Results for the analysis of synthetic mixtures by the proposed methods (TABLE 2) showed satisfactory results for the simultaneous determination of phosphate and silicate. To demonstrate the applicability of the optimized method to real samples, the proposed procedure was applied to the simultaneous determination of phosphate and silicate in different water samples such as sea water, river water, waste water, mineral water and tap water. TABLE 4 shows the results and standard deviation of the results obtained for three replicates of each sample. The concentration of phosphate in natural waters seems to be relatively low, because phosphate precipitates as poorly soluble salts or assimilated by algae or bacteria unless there is any artificial pollution. Since the concentration of silicate in natural alters is relatively high, the results indicate the proposed method is helpful for the determination of phosphate and silicate in water samples. Concentration of phosphate and silicate in the samples were also determined by standard methods[32]. The amounts of ions obtained by the proposed method were in good agreement with those obtained by standard methods.

TABLE 4 : Amounts of silicate and phosphate found in real waters

Sample water	Phosphate (mg L^{-1})	Silicate (mg L^{-1})	Standard method	
			Phosphate (mg L^{-1})	Silicate (mg L^{-1})
Sea water (Persian Gulf, Bushehr, Iran)[a]	0.03±0.01	0.38±0.06	0.05 ± 0.01	0.40±0.02
Tap water (Bushehr, Iran)[b]	0.02 ±0.001	10.1 ± 2.0	0.03 ± 0.001	10.5 ± 1.0
River water (Hamedan) [b]	0.22 ±0.01	22.0 ± 2.0	0.25 ±0.030	22.5 ± 1.2
Mineral water (Damavand)[c]	0.50 ±0.04	1. 4 ± 0.03	0.52 ±0.05	1.5 ±0.03
Waste water[c]	0.34 ± 0.14	4.5± 2.0	0.35 ±0.05	5.0 ±0.03

[a]Determined without dilution; [b]Determined with 5-times dilution; [c]Determined with 10-times dilution

TABLE 5 : Amounts of silicate and phosphate found in spiked samples comparing with satandard methods

Sample	Phosphate		Recovery (%)	Standard method	Silicate		Recovery (%)	Standard method
	Added (mg L^{-1})	Found (mg L^{-1})			Added (mg L^{-1})	Found (mg L^{-1})		
Detergent Powder	0.0	2.5	-	2.3	0.0	6.25	-	6.20
	2.5	5.10	104.0		2.5	8.84	103.6	
Urine	0.0	3.10	-	3.12	0.0	0.0	-	ND[b]
	2.5	5.5	96.2		2.5	2.60	-	104
Coca cola[a]	0.0	0.090	-	0.085	0.0	0.0	-	ND
	2.5	2.70	104.4		2.5	2.60	104.5	

[a]Determined with 5-times dilution; [b]Not detected

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Recovery of spikes from real samples

Reliability of proposed procedure was also checked by spiking experiments. The results are presented in TABLE 5. The recoveries of the ions from a detergent, urine and soft drink samples were calculated. The recoveries of the ions were in the order of 96 – 104%. The recovery of spiked samples is satisfactorily reasonable and indicates the capability of the method in the determination of phosphate and silicate in the real samples.

CONCLUSION

The simultaneous determination of phosphate and silicate in materials samples utilizing a simple, rapid, low cost spectrophotometric procedure, selective and very sensitive method is introduced. Conventional spectrophotometry relating high interference effect from coexisting ions for the simultaneous determination of phosphate and silicate as the molybdenum blue is not so sensitive or selective. HPCIM presents advantages, it dose not require the total separation of data arrays to calculate the spectrum of interferents and also standard addition compensates matrix effect. So, precision and accuracy of the method are comparable with the existing methods, it has several advantages over them. The results of experiments in the presence of different ions improved, it dose not require knowing the interfernts species and the accuracy of method is not dependent on the number of interferents species, concentration of the overlapping species and the amount of overlapping analytical signals. A comparison of the proposed method with our previously reported work (see[31], shows a great advantage of the proposed method with respect to ANNs. For example, AsO_4^{3-} was tolerated in the determination of phosphate and silicate which the interferent effect of AsO_4^{3-} was removed by adding thiosulfate. This method cancels the process of the investigation of diverse ions influences. On the aspects of chemistry, it will rest the time of analysis. Another advantage of the proposed method is lower errors of the determinations whereas the matrices were more complex than previous study. Notice that ANNs for multi-component determination is not applicable when the matrix effect is presented. The effectiveness of the present method for the simultaneous determination of phosphate and silicate ions was demonstrated in practical application to the water quality monitoring, detergent and soft drink samples.

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