Simultaneous spectrophotometric determination of phosphate and silicate by using partial least squares method

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Abstract

A very sensitive, simple and selective spectrophotometric method for simultaneous determination of phosphate and silicate based on formation of phospho- and silicomolybdenum blue complexes in the presence of ascorbic acid is described. Although the complexes of phosphate and silicate with reagent show a spectral overlap, they have been simultaneously determined by partial least squares (PLS). The linear range was 0.01-2.80 µg ml^{-1} for phosphate and 0.02-3.00 µg ml^{-1} for silicate. Interference effects of common anions and cations were studied and the proposed method was also applied satisfactorily to the determination of phosphate and silicate in synthetic detergents.

Key words: Phosphate; Silicate; Simultaneous determination; PLS; Ascorbic Acid; Synthetic detergents

1. Introduction

Phosphate and silicate have been involved in an environmental problem. The problem has serious consequence in view of the widespread utilization of phosphate and silicate in water softening, surfactants and many other applications. Synthetic detergents are one of the most famous and widely applied products that contain phosphate and silicate in a single formulation.

Among the most widely used analytical methods are those based on the UV-Visible spectrophotometric techniques due to the resulting experimental rapidly, simplicity and the wide application. Most spectrophotometric procedures [1,4] for the determination of phosphate and silicate are based on the formation of molybdoheteropoly acid and its reduction to molybdoheteropoly blue. However, the simultaneous determination of these ions by the use of the traditional spectrophotometry without the use of a masking agent [5] proper pH control [6] or preliminary separation [7] is difficult because generally, the absorption spectra overlap and superimposed curves are not suitable for quantitative evaluation. However, these methods are time consuming, require strict control of variables and involve tedious procedures. Dual wavelength [8] automated differential kinetic [9], flow injection [10] and derivatives spectrophotometry [11] procedures have been utilized for the simultaneous determination of phosphate and silicate. Quantitative spectrophotometry has been greatly improved by the use of multivariate statistical methods such as PLS method. Theory and application of PLS were discussed elsewhere [12,15]. There are actually two versions of the PLS algorithm: PLS1 and PLS2. We used PLS1 method. In PLS1, a separate set of scores and loading vectors is calculated for each constituent of interest.

The aim of this work was to develop a simple, sensitive, selective and inexpensive method for the simultaneous determination of phosphate and silicate in synthetic detergent. This method have the larger dynamic range and the lower detection limit rather than similar method with using derivative spectrophotometry [11] and also other methods that were previously reported such as refs. [8,10].

2. Experimental

2.1. Apparatus

UV-Visible absorbance digitized spectra were collected on a UV-VIS UVIKON 922 spectrophotometer, using a 1 cm quartz cell, at a scan rate of 3000 nm/min and slit width of 2 nm. The recorded spectra were digitized with an interval of 1 nm between consecutive points. Therefore 381 data point were used to represent a spectrum in the range of 500-880 nm. Measurements of pH were made with a PMT 1003 pH-meter using a combined glass electrode. The computations were made on a Pentium 133 MHz computer. All the programs were written in MATLAB (Mathworks, version 6) by the authors.

2.2. Reagents

All solutions were prepared with doubly distilled water. Chemicals used were of analytical grade and were purchased from E. Merck

Stock solutions of phosphate and silicate containing 1 mg ml^{-1} phosphorus and silicon were prepared by dissolving 1.0985 g and 1.0867 g of oven-dried potassium dihydrogenphosphate, KH_2PO_4, and sodium metasilicate, Na_2SiO_3, in 250 ml of water, respectively.

Solution of 0.02 M of Molybdenum (VI) was prepared by dissolving 6.1790 g of ammonium molybdate tetrahydrate, $(NH_4)_6Mo_7O_{24}.4H_2O$, in 250 ml of water

A solution of 1.25×10^{-1} M of ascorbic acid was prepared by dissolving 2.2 g of ascorbic acid in distilled water in a 100-ml volumetric flask.

Synthetic detergents of Tag, Shoma and Pak were prepared from Behdad, Tolypers and Pakvash co, respectively.

2.3. Procedure

Appropriate volumes of phosphate and silicate solutions (in their linear dynamic ranges), 1.5 ml of 0.5 M sulfuric acid and 2.0 ml of molybdate were added to 25-ml volumetric flask and was allowed to stand for 5.0 min, then was added 4.0 ml of 1.8 M sulfuric acid, 1 ml ascorbic acid and 10.0 ml of water. Then the solution was heated at 90 ^{o}C for 5 min, cooled and made up to the mark with water. For each measurement, about 2 ml of the above solution was transferred to a spectrophotometric cell and the spectrum was recorded 5.0 minute after preparation of a sample solution against of blank sample.

3. Results and discussion

Phosphate and silicate form colored complexes with molybdenum in the presence of ascorbic acid (Fig. 1). As shown in this figure, the absorption curves of these complexes have been overlapped with together. PLS method was used to determine two elements in presence of each other.

With the aim of investigating the possibility a simultaneous determination of phosphate and silicate in mixtures, the optimum working conditions were obtained as follow: 0.03

M sulfuric acid, 1.6×10^{-3} M molybdate and 5.0×10^{-3} M ascorbic acid. To prevent reduction of excess of molybdate by ascorbic acid, the phopho and silico molybdate complexes were reduced in highly acidic solution [11].

3.1. Univariate calibration

Under the optimum conditions the calibration graphs were obtained. The calibration graphs were constructed by plotting absorbance values as a function of analyte concentration. The linear regression equation for the calibration graph of phosphorus at λ= 827 nm for the concentration range of 0.01-3.00 µg ml^{-1} was $A = 0.0352 + 1.0814\ C$ ($r^2 = 0.9990$, n=12) and for silicate at λ=_810 nm on the concentration range of 0.01-5.00 µg ml^{-1} was $A = 0.0336 + 0.5617\ C$ ($r^2 = 0.9998$, n=15), where A is the absorbance and C is the analyte concentration in µg ml^{-1}.

3.2. Multivariate calibration

Multivariate calibration methods such as PLS require an experimental design of the standard belonging to the calibration set in order to provide good prediction. In this study, the random approach was used. This experimental design method involves randomly selecting samples throughout the calibration space. It is important that we use a method of random selection that does not create an underlying correlation among the concentrations of the components. The most common random design aims to assemble a calibration set that contains samples that are uniformly distributed throughout the concentration space. Two sets of standard solutions were prepared. The calibration set contains 27 standard solutions (Table 1). For prediction set, it was used of 16 test mixtures. Therefore data sets for calibration and prediction sets were 381×27 and 381×16, respectively. The concentration of each analyte solution was in linear dynamic range of the analyte for the prediction of each solution.

3.2.1. Selection of optimum number of factors

In PLS model, the method of cross-validation [16] (leave one out) was used to determine the number of principal components. In Fig. 2, PRESS obtained by optimizing the calibration matrix of the absorbance data with PLS is shown. One reasonable choice for the optimum number of factor would be that number which yielded the minimum PRESS. However, using the number of factors (h*) that yields a minimum press usually leads to some overfitting. A better criterion for selecting the optimum number of factors involves the comparison of PRESS from models with less than h* factors. The F-statistic was used to make the significance determination. Haaland and Thomas [17] empirically determined that an F-ratio probability of 0.75 is a good choice. We selected as the optimum number of factors for the PRESS value the F-ratio probability of which drops below 0.75. The numbers of factors selected as optimums by this procedure were 6 and 4 for phosphate and silicate, respectively.

The results obtained by applying PLS method to the 16 problem samples are listed in Table 2. This table also shows the absolute error for prediction of phosphate and silicate concentrations.

The plots of the predicted concentrations versus actual values are shown in Fig. 3 for phophate and silicate.

3.2.2. Statistical parameters

For the constructed model, three general statistical parameters were selected to evaluate the prediction ability of the model for simultaneous determination of phosphate and silicate. For this case, the predicted concentrations of each sample were compared with the actual concentrations. The first statistical parameter is the root mean square difference (RMSD). This parameter is an expression of the average error in the analysis for each component. RMSD was obtained by the following formula:

$$RMSD = \sqrt{\frac{1}{n}\sum_{i=1}^{n}(\hat{x}_i - x_i)^2}$$

The second statistical parameter was relative error of prediction (REP) that shows the predictive ability of each component, and is calculated as

$$REP(\%) = \frac{100}{\bar{x}}\sqrt{\frac{1}{n}\sum_{i=1}^{n}(\hat{x}_i - x_i)^2}$$

The square of the correlation coefficient (R^2), which is indicated the quality of fit of all the data to a straight line is calculated for the checking of each calibration.

$$R^2 = \frac{\sum_{i=1}^{n}\left(\hat{x}'_i - \bar{x}\right)^2}{\sum_{i=1}^{n}\left(\hat{x}_i - \bar{x}\right)^2}$$

Where x_i is the actual concentration of the analyte in the sample i, $\hat{x}_i$ the predicted concentration of the analyte by the PLS method in the sample i, $\hat{x}_i'$ the predicted concentration of the analyte by the linear equation between x_i and $\hat{x}_i$ in the sample i, $\bar{x}$ is the mean of true concentration in the prediction set and n is the total number of samples used in the prediction set.

The statistical results (RMSD, REP, R^2) are summarized in Table 3.

3.2.3. Interference Study

The interference study was performed by analyzing fixed concentrations of phosphorus (0.50 μg ml^{-1}) and silicon (0.30 μg ml^{-1}) and 300 μg ml^{-1} of each interfering ion. The results indicated that, many ions did not produce significant spectral interference. However, the tolerance limit (tolerance limit is defined as the foreign-ion concentration causing an error smaller than 3.0% for the determining 0.50 μg ml^{-1} of phosphorus and 0.30 μg ml^{-1} of silicon) was 300 fold (300 fold is the maximum tested concentration) for K^+, Na^+, Ca^{2+}, Al^{3+}, F^-, Cl^-, $SO_4^=$, NO_3^-, Cu^{2+}, Ba^{2+}, $Sn2^+$, Mg^{2+}, Mn^{2+}, Co^{2+}, Fe^{2+}; 100 fold for borate; 50 fold for Ag^+, Zn^{2+}, V^{5+}, Cd^{2+}, Li^+, Cr^{3+}, Hg_2^{2+} and 2 fold for AsO_4^{3-}. The results indicate that most of the cations and anions did not interfere.

3.3. Application

The proposed model was successfully applied to the simultaneous determination of phosphate and silicate in several synthetic detergent formulations. These samples were prepared according to ref. [11] and then 1.0 ml of this sample was subjected to the recommended procedure and the results were compared with those provided by reference methods [18], phosphate was determined by the vanadomolybdophosphoric acid and silicate was determined by the silicomolybdenum blue method with using oxalic acid as masking agent. The results were shown in Table 4. The good agreement between these results and reference method values indicates the successful applicability of the proposed model for simultaneous determination of phosphate and silicate in complex samples. The recoveries amounts after addition of different amounts of phosphate and silicate to these samples were also shown in Table 5.

4. Conclusion

Determination of phosphate and silicate based on formation of molybdoheteropoly blue with the PLS was established, with good prediction ability in the synthetic detergents. Results show that PLS is an excellent calibration method to determination of phosphate and silicate with higher sensitivity than previously reported methods. Analysis of the results for the two-component system revealed utility of this procedure for the simultaneous determination of phosphate and silicate in synthetic detergents.

Table 1

Concentration data for the different mixtures used in the calibration set for the determination of phosphate and silicate

(concentration in in µg ml^{-1})

Mixture no.	P	Si	Mixture no.	P	Si
1	0.03	0.02	15	0.16	0.40
2	0.07	0.02	16	0.80	0.40
3	0.01	0.03	17	0.12	0.56
4	0.10	0.03	18	0.80	0.56
5	0.04	0.04	19	0.28	0.80
6	0.08	0.04	20	0.68	0.80
7	0.04	0.06	21	0.12	1.20
8	0.10	0.06	22	0.20	1.00
9	0.04	0.08	23	0.16	1.40
10	0.04	0.10	24	1.20	0.24
11	0.12	0.02	25	1.04	0.48
12	0.03	0.05	26	1.20	1.20
13	0.40	0.12	27	2.80	2.00
14	0.36	0.28	28	0.80	3.00

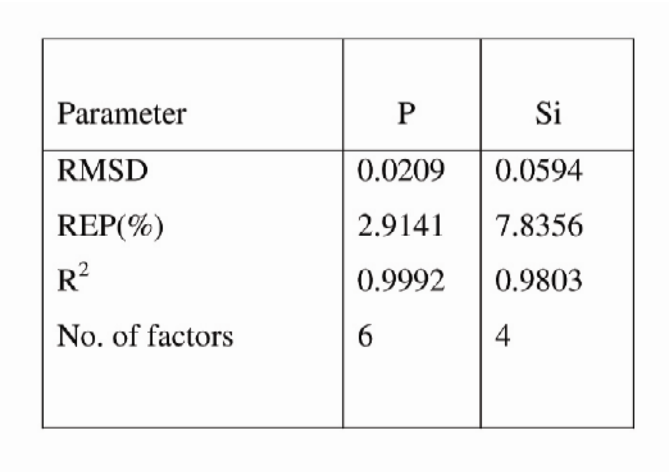
Table 2

Simultaneous determination of phosphate and silicate in prediction set (concentration in µg ml^{-1})

Added		Found		Error	
P	Si	P	Si	P	Si
0.07	0.03	0.07	0.04	0.00	0.01
0.06	0.06	0.07	0.06	0.01	0.00
0.03	0.12	0.04	0.10	0.01	-0.02
0.08	0.12	0.08	0.11	0.00	-0.01
0.08	0.07	0.08	0.08	0.00	0.01
0.40	0.40	0.40	0.42	0.00	0.02
0.36	0.56	0.36	0.56	0.00	0.00
1.20	0.56	1.17	0.46	-0.03	-0.10
1.12	0.80	1.12	0.63	0.00	-0.17
0.48	1.20	0.48	1.13	0.00	-0.07
0.72	1.00	0.74	0.93	0.02	-0.07
0.52	0.68	0.54	0.66	0.02	-0.02
0.16	0.80	0.18	0.82	0.02	0.02
0.32	0.48	0.34	0.52	0.02	0.04
0.20	1.12	0.19	1.14	-0.01	0.02
2.40	1.20	2.46	1.27	0.06	0.07

Table 3

Statistical parameters obtained by applying the PLS method to the prediction



Parameter	P	Si
RMSD	0.0209	0.0594
REP(%)	2.9141	7.8356
R^2	0.9992	0.9803
No. of factors	6	4

Table 4

Determination of phosphate and silicate in synthetic detergent samples (Concentration in μg ml^{-1}, n=3 for both methods)

Sample	This Method		Reference Method	
	Phosphorus	Silicon	Phosphorus	Silicon
Tag Powder	8.0 ± 0.3	19.5 ± 0.7	7.60 ± 0.02	18.80 ± 0.06
Pak Powder	7.3 ± 0.2	10.0 ± 0.2	7.40 ± 0.02	10.03 ± 0.03
Shoma Powder	10.3 ± 0.4	11.4 ± 0.3	10.60 ± 0.03	11.43 ± 0.04

Table 5

Recovery percent of phosphate and silicate in synthetic detergent samples (concentration in μg ml^{-1})

Sample	Phosphorus			Silicon		
	Added	Found	Recovery %	Added	Found	Recovery %
Tag Powder	0.0	8.0	-	0.0	19.5	-
	3.0	10.5	95.4	1.0	22.5	109.8
	2.0	10.0	100.0	3.0	23.2	103.1
	1.0	10.0	111.1	2.0	21.0	97.7
Pak Powder	0.0	7.3	-	0.0	10.0	-
	40.0	57.5	121.6	10.0	18.2	91.0
	3.0	11.8	104.4	2.0	12.5	104.2
	2.0	8.8	94.6	1.5	12.0	104.3
Shoma Powder	0.0	10.3	-	0.0	11.4	-
	5.0	16.8	109.8	5.0	15.0	91.5
	10.0	23.0	113.3	10.0	18.5	86.4
	25.0	32.0	90.6	15.0	27.2	103.0

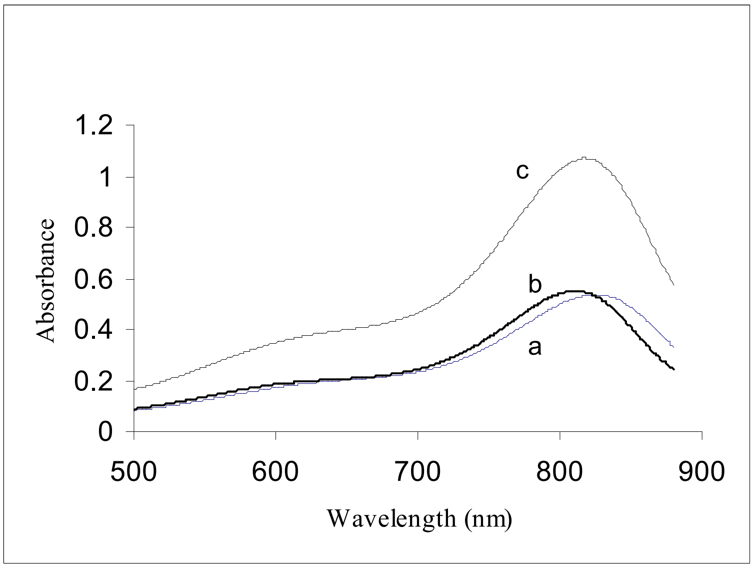


Fig. 1. Spectra of phosphomolybdenum blue complex (curve a) and silicomolybdenum blue complex (curve b) and a mixture of both complexes (curve c) at optimum condition. [P]=0.60 µg ml^{-1}, [Si]=0.80 µg ml^{-1}.

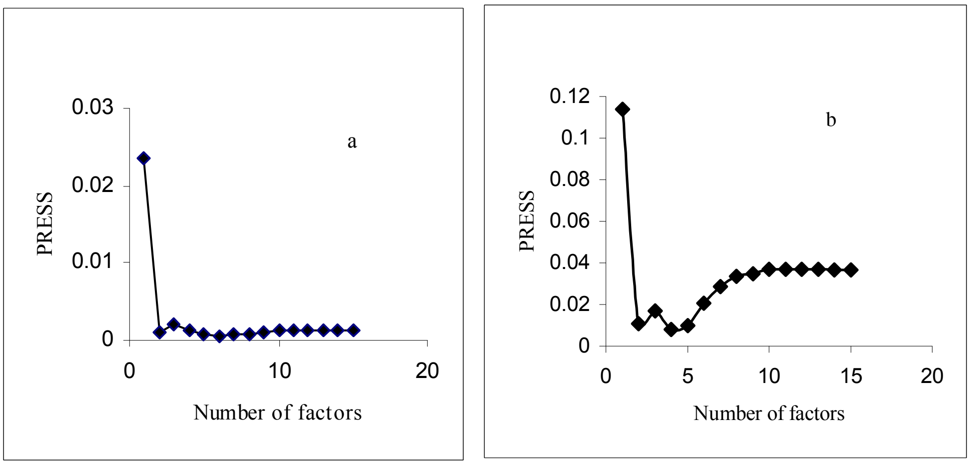


Fig. 2. Plot of PRESS vs. number of factors (a) Phosphorus (b) Silicon

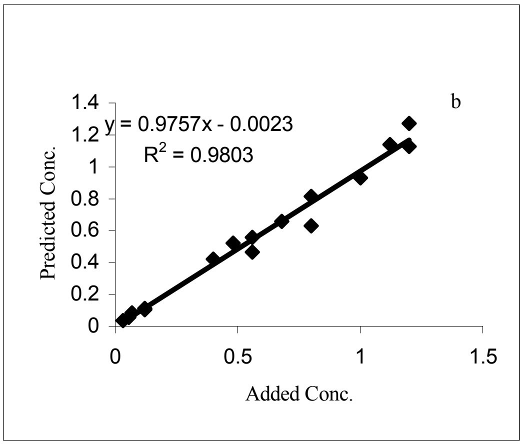


Fig. 3. Plots of predicted concentration vs. added concentration for (a): Phosphorus and (b): Silicon.

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