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Simplex design method in simultaneous spectrophotometric determination of silicate and phosphate in boiler water of power plant and sewage sample by partial least squares

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Abstract

Partial least squares modeling as a powerful multivariate statistical tool was applied to the simultaneous spectrophotometric determination of silicate and phosphate in aqueous solutions. The concentration range for silicate and phosphate were 0.02-0.6 and 0.4-3 μg ml^{-1}, respectively. The experimental calibration set was composed with 30 sample solutions using a mixture design for two component mixtures. The absorption spectra were recorded from 500 to 900 nm. The optimum conditions were obtained by simplex optimization method. The values of root mean square error of prediction (RMSEP) for silicate and phosphate using partial least squares (PLS) were 0.0017 and 0.02 μg ml^{-1}, respectively. The effects of various cations and anions on detection of silicate and phosphate were investigated. The method was successfully used for determination of silicate and phosphate in boiler water at power plant, well water and sewage samples.

Keywords: Phosphate; Silicate; PLS; Boiler water; Sewage; Simplex.

1. Introduction

Phosphate is added to boiler water of steam and combined cycle power plant under mixed water treatment (MWT) regime for two reasons. It prevents scale formation, by converting calcium ion in the boiler water to insoluble precipitate which is discharged with blow down water from the system. It also adjusts the pH of water, so that prevent scaling of magnesium ion and corrosion. However, the concentration of phosphate must be in an optimum range to keep the boiler feed water slightly alkaline (pH~9.0). In other word, if the amount of phosphate is too little, it can not lower the concentration of Ca^{2+} and Mg^{2+} sufficiently, so in the presence of silicate ion, $CaSiO_3$, $MgSiO_3$ and other type of scale is formed; and if too excess amount of phosphate is added, formation of $NaFePO_4$, Fe_3PO_4 and phosphate hide out phenomenon occur; which cause the swelling and eventually bursting of boiler water pipe [1].

The concentration of silicate ion in the steam is directly dependent on boiler pressure; and must be controlled and kept below the authorized level (0.02 mg L^{-1} as SiO_2). An excess amount

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of silicate ion in boiler water apt to lead to silicate carry over in the steam; which results in silicate deposition on the turbine blade and slowly ruined the turbine balance and shorten the effective lifetime of the blades [1].

Phosphate and silicate have also been considered as an environmental pollutant. Phosphate is introduced into lake from inadequately treated sewage. The excess amounts of phosphate in lake water cause the death of living organisms by stimulating the growth of alga. Silicate serves as micronutrient for diatomaceous alga which converts soluble silicate to solid silicate, and thus increases the insoluble material in water [2]. Thus, monitoring of the concentration of phosphate and silicate ions in boiler water and environmental water sample is essential.

The standard spectrophotometric method for determination of phosphate and silicate in water and waste water is based on reaction of both ions with molybdate in acidic medium [3]. However simultaneous determinations of both ions are not possible due to mutual interference between them, unless a proper masking agent is used. Furthermore, determination of silicate by this method required use of the hazardous solution of mixture of 1-amino-2-hydroxy-4-naphthalenesulfonic acid, sodium disulfite, and sodium sulfite (ANSA solution). The ANSA solution has unpleasant smell, and long term exposure to it may cause respiratory disease. Numerous studies have been done to improve the sensitivity [4-5] and selectivity [6-7] of the standard method for simultaneous determination of phosphate and silicate, including, control of pH [8], separation by ion-exclusion chromatography [9-10], first-derivative spectrophotometry [11-12], sequential injection analysis [13-14], stopped flow injection analysis [15] and flow injection spectropotometry [16-19]. However these methods have some limitations such as needs for careful control of experimental conditions, decrease in signal to noise ratio, or needs for complex equipment and so on.

Chemometrics methods are playing a very important role in the analysis of multicomponent mixture by spectrophotometry [20-21]. Recently Afkhami et al. [22] used artificial neural networks (ANNs) for the simultaneous determination of phosphate and silicate in a variety of samples. ANNs is a nonlinear, nonparametric method that is called black box method as the weight of input variables is changed in each run. So the importance of these variables is not obvious. A powerful multivariate statistical tool that has been applied to the quantitative analysis is partial least squares (PLS) [23-24]. This is a linear and simple method. The theory and application of PLS in spectroscopy have been discussed by several workers [25-31].

In this study a simple, sensitive and selective method for simultaneous spectrophotometric determination of phosphate and silicate is developed. The analysis is based on the application of partial least squares (PLS) method to resolve the mixture of phosphate and silicate with molybdenum blue in aqueous solution at very low concentration. In this method, the reactions are at equilibrium and so the signal to noise ratio is at maximum. There is also no need for either expensive equipment, heating, masking agent or hazardous solution of ANSA.

2. Experimental

2. 1. Equipment

All absorption measurements were carried out on a JENWAY 6505 UV-Vis spectrophotometer (slit width 0.2 nm scan rate 500 nm min^{-1}), using 5.00-cm quartz cells. Measurement of pH was made with a JENWAY 3510 digital pH-meter with a combined glass–calomel electrode.

2. 2. Reagents

All chemicals were of analytical-reagent grade. Ultra purified water was used for the preparation of solutions. All flasks and glassware were socked in 1% HNO_3 solution, and was rinsed with ultra pure water before use. All solutions were stored in polyethylene vials. Silica stock solution (100 mg L^{-1} as SiO_2) were prepared by dissolving 0.4737 g of $Na_2SiO_3{\cdot}9H_2O$ in water and diluting to 1000 mL in a volumetric flask. Phosphate stock solution (1000 mg L^{-1} PO_4^{3-}) was prepared by dissolving 1.4334g of anhydrous potassium dihydrogenphosphate (dried at 110 °C for 2 h) in water and diluting to exactly 1000 mL in a volumetric flask. Ammonium molbdate (VI) solution (3.75%w/v) was prepared by dissolving appropriate amount of ammonium heptamolbdate tetrahydrate ($(NH_4)_6Mo_7O_{24}.4H_2O$) in 0.5 mol L^{-1} H_2SO_4 solution and diluting to 1000 mL in a volumetric flask. Ascorbic acid solution (1% w/v), was prepared by dissolving 5.00 g of ascorbic acid in water and diluting to 500 mL. The ascorbic acid solution was transferred to a dark polyethylene container and stored in the refrigerator. This solution should be prepared weakly.

2. 3. Computer hardware and software

All absorbance spectra were digitalized and stored at wavelengths from 500 to 900 nm in steps of 1 nm and then transferred via Dataway software (version 1.1.2348.27274) in ASCII format to a Pentium 4 1.7 GHz computer for subsequent manipulation by PLS program. The data pretreatment was done with MATLAB for windows (Mathworks, Version 7). PLS program for calibration–prediction and experimental design was written in MATLAB according to the algorithm described by Martens and Naes [25] and PLS routine of PLS Toolbox (Eigenvector Company, Version 2.1). Multisimplex software (2.1 trial version) was used to find the optimum conditions.

2. 4. Procedure

Twenty five mL of standard or sample solution containing not more than 15 and 75 µg of silicate and phosphate, respectively was transferred into a polyethylene beaker. 1 mL of ammonium molbdate solution (3.75% w/v) in 0.5 mol L^{-1} sulfuric acid was added, and the solution was allowed to stand for 5 min to ensure the formation of complexes of phosphor and silico-molybdic acid is completed. Then 1 mL of ascorbic acid solution (1% w/v) was added, to reduce the Mo(VI) to Mo(III). After 5 min, the blue complexes of both species were completely formed. Finally the solution was transferred into 5-cm quartz cell and the spectrum was recorded in the wavelength range of 500-900 nm on spectrophotometer against the reagent blank. The model was constructed with calibration and prediction sets containing 30 and 10 samples with different analytes concentration, respectively, and was used for analyzing of samples.

3. Results and discussion

3. 1. Absorption spectra

The absorbance spectra of aqueous solution of complexes of silico-molybdate blue and phosphor-molybdate blue were recorded in the range of 500-900 nm, the results of this study is shown in Fig. 1 a and b, respectively. As it is demonstrates, the curves overlap significantly in all wavelength, so in a mixture of both species, spectrophotometric determination of individual complex is not possible unless a chemometrics method is used.

3. 2. Optimization of conditions

Optimization of condition was done with Multisimplex software (2.1 trial version). In Multisimplex program, modified simplex method was used as appropriate algorithm with coefficients of reflection(R)=1, contraction=0.5, contraction of R=0.5, and expansion of R=2. The factors that influence the formation of complex and absorbance signal ratio such as; amount of ammoniummolbdate, sulfuric acid, ascorbic acid and required time for complication of reaction were optimized. Table 1 represents simplex conditions for both silicate and phosphate optimization and also final optimum values. Since silicate concentration in boiler water is less than phosphate, optimization was done with respect to silicate determination. In the initial optimization experiment the solution of sulfuric acid (0.5 mol L^{-1}) and ammoniummolbdate were prepared separately, but once the optimum conditions was obtained, the two solutions were combined and was used for further study.

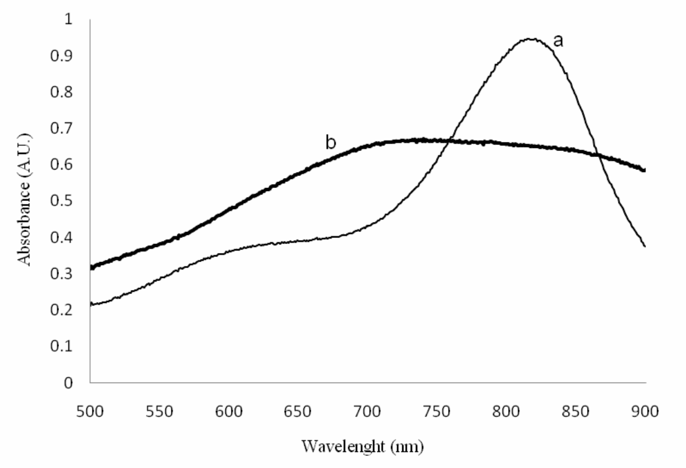

Fig. 1. Absorption spectra of 0.6 µg ml^{-1} of silicate (a) and 3 µg ml^{-1} of phosphate (b) at optimum conditions.

Table 1
Simplex condition for both silicate and phosphate optimization.

Variable	Ref. value	Step	Optimum value for Silicate	Optimum value for Phosphate	Optimum value for Both anions
Sulfuric acid (0.5 mol L^{-1}) volume (mL)	2	0.5	1.1	0.8	1
A^* (mL)	2	0.5	0.95	1.3	1
B^* (sec)	180	30	305	208	300
Ascorbic acid (1% w/v) volume (mL)	2	0.5	1	1.4	1
C^* (sec)	180	30	308	208	300

*A; ammoniummolbdate (3.75% w/v) solution volume, B; time duration after addition of acid and ammoniummolbdate solution, C; time duration after addition of ascorbic acid

3. 3. Calibration and prediction data sets

Multivariate calibration methods are suitable for the analysis of large number of samples containing few analytes. However, this method is not advisable for analysis of samples with large numbers of analytes due to complexity of the calibration matrix. Moreover, the preparation and analysis of the standards belong to the calibration set are the most time consuming step in the multivariate calibration procedure. Multivariate calibration methods such as PLS require a suitable design of the standards belonging to the calibration range. To obtain the linear dynamic range of each component the separate calibration curve was constructed at λ_{max} of each analytes. The linear range was found to be 0.02-0.6 and 0.4-3 µg ml^{-1} for silicate and phosphate, respectively. Next, a synthetic set of 30 solutions of mixtures of silicate and phosphate with respect to liner range of each component were prepared (Fig. 2) for calibration. Ten predicted solutions, was also prepared so that the concentration of each analytes was within the range of calibration set.

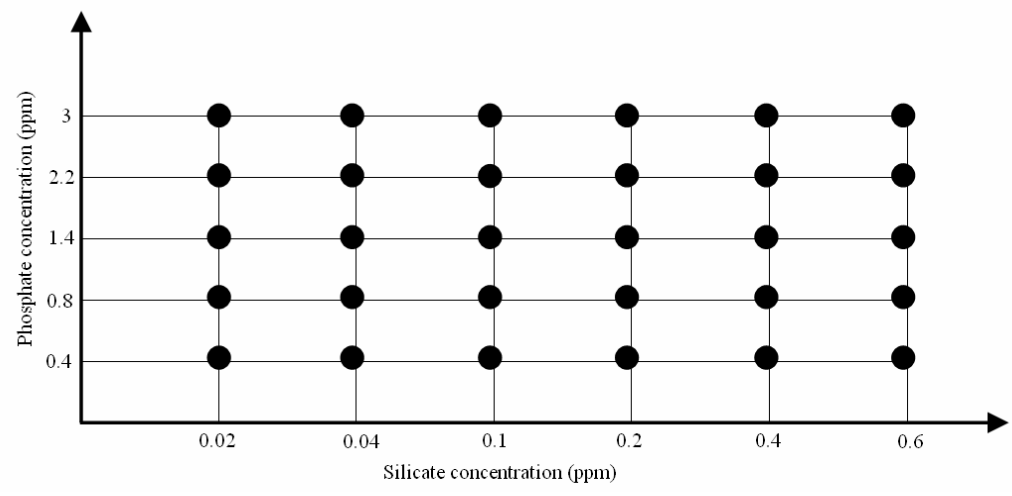

Fig. 2. Points of concentration data of different mixtures used in the calibration set for determination of silicate and phosphate. The concentrations levels of silicate and phosphate were 0.02, 0.04, 0.1, 0.2, 0.4, 0.6 and 0.4, 0.8, 1.4, 2.2, 3.0 µg mL^{-1}, respectively.

3. 4. Number of significant factors

To ascertain the number of significant factors (latent variables or pairs of score and loading vectors) in the PLS algorithm without over fitting, a cross-validation method leaving out one sample at a time was used. As the training set comprised 30 spectra of calibration set, the PLS calibration with first pair of score and loading vectors (i.e. the first significant factor), were performed on 29 of them and the concentration of the sample left out was predicted. The process was repeated 30 time (once for each sample), using this calibration datum. The concentration of all components in each sample was compared with the known concentration of the components in this reference sample and the prediction residual error sum of square (PRESS) was calculated. The PRESS was calculated in the same manner each time that a new factor was added to the PLS model.

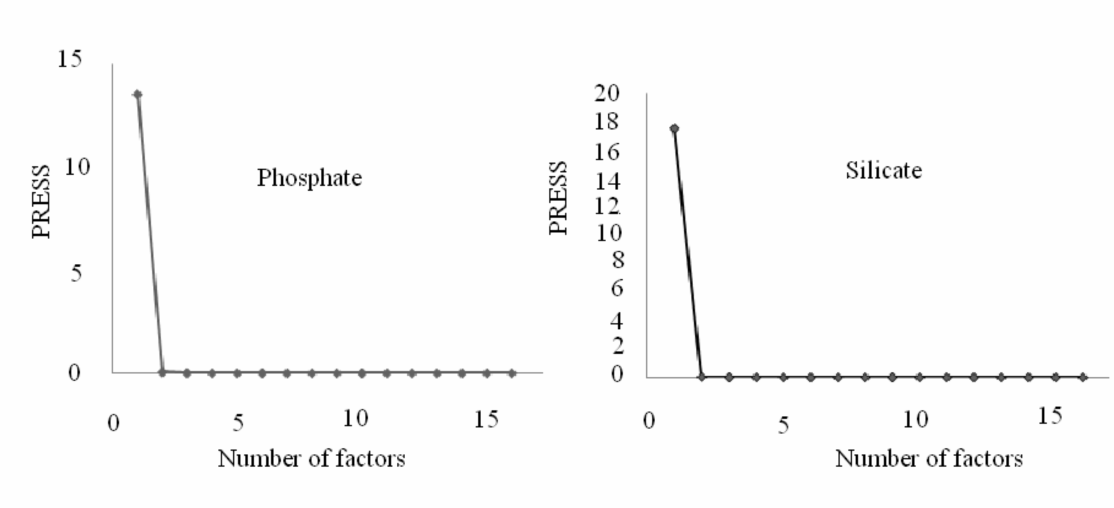

Fig. 3. PRESS values as a function of number of factors.

One reasonable choice for the optimum number of factors is a number that yields the minimum PRESS. However, using the number of factors (h^*) that yields the minimum PRESS, usually lead to some over fitting. A better criterion for selecting the optimum number of factors, involves the comparison of PRESS from model which is not significantly greater than PRESS from the model with h^* factors. The maximum number of factors used to calculate the optimum PRESS was selected as 16 (half of the number of standard plus one). The PRESS values are minimum, when the number of Latent variables is 2 for silicate and phosphate. The PRESS obtained by optimizing the calibration matrix of the absorbance data with PLS method is shown in Fig. 3. The results obtained by applying optimized PLS calibration model to prediction samples are given in Table 2.

Table 2
Analysis of prediction set.

Solution	Added (μg mL^{-1})		Found [a] (μg mL^{-1})		Recovery%	
Number	Silicate	Phosphate	Silicate	Phosphate	Silicate	Phosphate
1	0.250	0.50	0.249±0.003	0.49±0.04	100	98
2	0.080	2.40	0.083±0.003	2.40±0.02	104	100
3	0.450	1.80	0.448±0.004	1.79±0.02	100	99
4	0.030	0.90	0.030±0.003	0.90±0.01	100	100
5	0.550	2.20	0.550±0.002	2.23±0.02	100	101
6	0.150	0.60	0.152±0.001	0.59±0.04	101	98
7	0.300	2.90	0.300±0.003	2.93±0.03	100	101
8	0.050	1.30	0.049±0.002	1.33±0.03	98	102
9	0.160	2.50	0.163±0.001	2.53±0.03	102	101
10	0.060	0.70	0.059±0.003	0.71±0.04	98	101

[a] The numbers are average and standard deviation of five independent analyses

3. 5. Figures of merit

For the constructed model, four parameters, root mean square error of prediction (RMSEP), the square of the correlation coefficient (R^2), the relative error of prediction (REP), and the prediction residual error sum of square (PRESS) were selected to test the prediction ability of the model for simultaneous determination of silicate and phosphate. The result of this investigation is summarized in Table 3.

Table 3
Statistical parameter of the optimization matrix using the PLS model.

Anion	Number of factors	PRESS	RMSEP	REP (%)	R^2
Silicate	2	29 (μg $L^{-1})^2$	1.703 μg L^{-1}	0.819	0.99
Phosphate	2	0.004 (μg $mL^{-1})^2$	0.02 μg mL^{-1}	1.27	1.03

3. 6. Effect of foreign ions

In order to evaluate the selectivity of the method, the effects of foreign species on the simultaneous determination of phosphate and silicate were investigated by analyzing the samples containing 0.2 mg L^{-1} of silicate, 1.4 mg L^{-1} of phosphate and various amounts of other species. The tolerated limit was taken as the concentrations of interference causing an error of less than ±5%. The amount of foreign ions was chosen at 800 μg ml^{-1}, but once interference was observed its concentration was lowered until the error was less than ±5%. The results of this investigation are shown in Table 4 and as it demonstrates most of the common co-existing species have no significant effect on the determinations of both analytes.

Table 4
Influence of foreign ions on the simultaneous determination of silicate and phosphate at 0.2 and 1.4 µg mL^{-1} level, respectively.

Species	Tolerance limit (µg mL^{-1})
K^+, Na^+, Pb^{2+}, NO_3^-, Al^{3+}	800[a]
SO_4^{2-}, Mg^{2+}, Ag^+, CO_3^{2-}, F^-	700
SCN^-	600
Zn^{2+}, Hg^{2+}	500
Fe^{3+}	400
Hydrazine, Fe^{2+}	5

[a] Maximum concentration studied

3. 7. Application

In order to test the applicability of the proposed method, the developed method was used for determination of silicate and phosphate in treated sewage and boiler water samples of Yazd combined cycle power plant. The sewage sample was diluted 100 fold before analysis. The accuracy of the method was determined by comparing the results with data obtained by standard methods [3]. The results are shown in Table 5.

Table 5
Determination of phosphate and silicate in sewage and boiler water samples of Yazd combined cycle power plant.

Sample	New method [a] (µg mL^{-1})		Standard method [a] (µg mL^{-1})	
	Phosphate	Silicate	Phosphate	Silicate
High pressure boiler drum 1	4.81±0.03	0.260±0.005	4.82±0.02	0.265±0.004
High pressure boiler drum 2	5.32±0.03	0.450±0.007	5.23±0.02	0.460±0.007
Low pressure boiler drum 1	2.62±0.01	0.105±0.002	2.63±0.01	0.106±0.002
Low pressure boiler drum 2	2.92±0.01	0.081±0.002	3.02±0.01	0.081±0.002
Treated sewage[b]	0.41±0.04	0.281±0.008	0.38±0.04	0.267±0.005

[a] The numbers are average and standard deviation of five independent analyses
[b] After 100 times dilution

As it is shown at 95% confidence interval there is no significant difference between the results of these two methods. The accuracy of the method was further determined by recovery experiments from samples spiked with different level of silicate and phosphate. The results of this investigation are summarized in Table 6 and as it is demonstrated the recoveries are satisfactory. Thus the method can be used for analysis of boiler water samples and samples with complex matrixes such as treated sewage.

Table 6
Recovery of phosphate and silicate for boiler water and treated sewage samples at power plant.

Sample	Phosphate (μg mL^{-1})			Silicate (μg mL^{-1})		
	Added	Found	Recovery %	Added	Found	Recovery %
High pressure boiler drum 1	0	4.81		0	0.26	
	1.4	6.11	93	0.1	0.358	98
	0.8	5.62	101	0.3	0.573	104
High pressure boiler drum 2	0	5.32		0	0.45	
	1	6.23	91	0.2	0.652	101
	0.8	6.15	104	0.4	0.831	95
Low pressure boiler drum 1	0	2.62		0	0.105	
	0.8	3.41	99	0.5	0.61	101
	0.2	2.83	105	0.15	0.252	98
Low pressure boiler drum 2	0	2.92		0	0.081	
	0.2	3.12	100	0.4	0.485	101
	0.6	3.52	100	0.25	0.325	98
Treated sewage[a]	0	0.41		0	0.281	
	3	3.26	95	0.1	0.383	102
	2	2.45	102	0.2	0.488	104
	1	1.36	95	0.3	0.59	103

[a] After 100 times dilution

4. Conclusion

In this paper a rapid and simple method for simultaneous determination of silicate and phosphate based on PLS modeling was developed. It has been demonstrated that the overlapped spectrum of phosphor and silico-molybdenum blue complexes can be resolved by PLS method. The reagents are safe, no heat is required and the total time of sample preparation and analysis is short.

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