1-1-2005

Extraction-Spectrophotometric Determination of Trace Amounts of Barium and Strontium by 18-Crown-6 and Rose Bengal Using Partial Least Squares

JAHAN B. GHASEMI

ALIREZA NIKRAHI

ALI NIAZI

Extraction-Spectrophotometric Determination of Trace Amounts of Barium and Strontium by 18-Crown-6 and Rose Bengal Using Partial Least Squares

Jahanbakhsh GHASEMI[1*]**, Alireza NIKRAHI**[1] **and Ali NIAZI**[2]

[1]*Department of Chemistry, Faculty of Sciences, Razi University, Kermanshah-IRAN*
e-mail: jahan.ghasemi@tataa.com
[2]*Department of Chemistry, Faculty of Sciences, Azad University of Arak, Arak-IRAN*
e-mail: ali.niazi@gmail.com

Partial least squares modeling is a powerful multivariate statistical tool applied to extraction-spectrophotometric simultaneous determination of mixtures of barium and strontium. The method is based on the formation of the ternary complexes of 18C6 and rose bengal (RB) with barium and strontium. The 18C6-Ba-RB and 18C6-Sr-RB ternary complexes are quantitatively extracted into dichloromethane and the resolution of the mixtures is accomplished by partial least squares (PLS). In this study, the calibration model is based on absorption spectra in the 500-600 nm range for 25 different mixtures of barium and strontium. Calibration matrice's ranges were 0.05-5.50 and 0.03-4.50 μg mL^{-1} and detection limits were 0.036 and 0.017 μg mL^{-1} for barium and strontium, respectively. A series of synthetic solutions containing different concentrations of barium and strontium was used to check the prediction ability of the PLS model. The RMSEP for barium and strontium was 0.1323 and 0.0327, respectively. The method was successfully applied to the analysis of spiked water (natural, tap and waste waters) samples.

Key Words: Partial least squares, Extraction-spectrophotometric determination, Barium, Strontium.

Introduction

Liquid-liquid extraction methods for the separation and determination of barium and strontium are limited. Macrocyclic crown ethers are well known as selective ligands for various ions[1]. Some such complexes can be extracted from aqueous solutions into an organic phase. Although the extraction properties of crown ether complexes have been widely studied[2−7], their applications for the determination of metal ions are still rather limited[8−10]. The application of highly molar absorbance anionic dyes or counter anions with large molar absorptivities could lead to a sensitive method for trace metal determinations.

---

[*]Corresponding author

Among the most widely used analytical methods are those based the ultraviolet (UV)/visible spectrophotometry techniques, due to the resulting experimental rapidity and simplicity and their wide application. However, the simultaneous determination of barium and strontium by traditional spectrophotometry techniques is difficult because, generally, the absorption spectra overlap in a bright region and the superimposed curves are not suitable for quantitative evaluation.

Under computer-controlled instrumentation, derivative techniques and multivariate calibration methods play a very important role in the multicomponent analysis of mixtures by ultraviolet (UV)/visible, molecular absorption spectrophotometry[11−13]. The application of quantitative chemometrics, particularly partial least squares (PLS), to multivariate chemical data is becoming more widespread owing to the availability of digitized spectroscopic data and commercial software for laboratory computers.

The theory and application of PLS in spectrometry have been discussed by several authors[14−20]. Several multicomponent determination of inorganic substances based on the application of these methods to spectrophotometric data has also been reported[21−29]. A particularly detailed study of multivariate calibration by PLS was carried out for the spectrophotometric determination of metals[30].

In the present work, the simultaneous extraction-spectrophotometric determination of barium and strontium is reported. The method is based on the formation of the ternary complexes of 18-crown-6 and rose bengal (RB) with barium and strontium. The 18C6-Ba-RB and 18C6-Sr-RB ternary complexes are quantitatively extracted into dichloromethane and the resolution of this mixture of these cations was accomplished by partial least squares. The optimum value of pH and the concentration of reagents were obtained. This study is a preliminary step for further applications for the routine determination of barium and strontium in water samples.

Experimental

Instrumentation and software

A CECIL 9000 (slit width 0.2 nm and scan rate 500 nm/min) controlled by a computer and an equipment of a 1 cm pathlength quartz cell was used for UV-vis spectra acquisition. A Metrohm 692 pH-meter furnished with a combined glass-saturated calomel electrode was calibrated with at least 2 buffer solutions at pH 3.00 and 9.00.

The data were processed on an AMD 2000 XP (256 Mb RAM) microcomputer using MATLAB software, version 6.5 (The Mathworks). All absorption spectra were digitized and stored at wavelength range 500-600 nm with 1.5 nm steps and transferred in ASCII format for subsequent manipulation by PLS program. PLS calculus was carried out using 'PLS-Toolbox', version 2.0 (Eigenvectors Company).

Reagent and standard solutions

All the chemicals used were of analytical reagent grade. Sub-boiling, distilled water was used throughout the work. Stock solutions of barium and strontium (1000 μg mL^{-1}) were prepared from their commercial salts (nitrate or sulfate) and standardized titrimetrically. Standards of working solution were made by appropriate dilution daily as required. Stock solutions of RB (2.0×10^{-4} M) and 18C6 (4.0×10^{-3} M) were prepared by dissolving solid reagents. A universal buffer solution (pH 8.0) was prepared according to Lurie[31].

Procedure

After an aliquot of a sample containing barium and strontium was placed in a 10 mL volumetric flask, 4 mL of RB solution (2.0×10^{-4}M) and 4 mL of 18C6 (4.0×10^{-3} M) were added. Then the solution was diluted to the mark with distilled water. The solution was transferred into a 50 mL separatory funnel and 8 mL of dichloromethane was added. Then solution was shaken vigorously for 1 min. Then the phases were allowed to separate, the organic phase was separated, and its absorbance was measured at 500-600 nm.

Real sample

The real samples in this study were collected from surface waters of Tag-e-Bostan (spring water), and Gar-e-Soo (waste water). The impurities and solid particles in the collected water were firstly removed by filter paper. The concentrations of barium and strontium in calibration and prediction sets were 0.05-5.5 and 0.03-4.5 μg mL^{-1} for barium and strontium, respectively.

Results and Discussion
Selection of the optimum chemical conditions

Figure 1 shows the absorption spectra in dichloromethane solution of the individual metal ternary complexes and their mixture where the pH of the aqueous phase is 8.0. With the goal of determining barium and strontium in mixtures, the optimum working conditions are studied under the conditions previously established for each cation. The influence of pH values on the extraction of 18C6-Ba-RB and 18C6-Sr-RB complexes was studied over the pH range 2-12 at a constant concentration of each ion. The results are shown in Figure 2. As can be seen, the maximum extraction of the barium and strontium complexes occurred within the pH range 7-12. Thus pH 8 was chosen as the optimum value for the subsequent steps of the work.

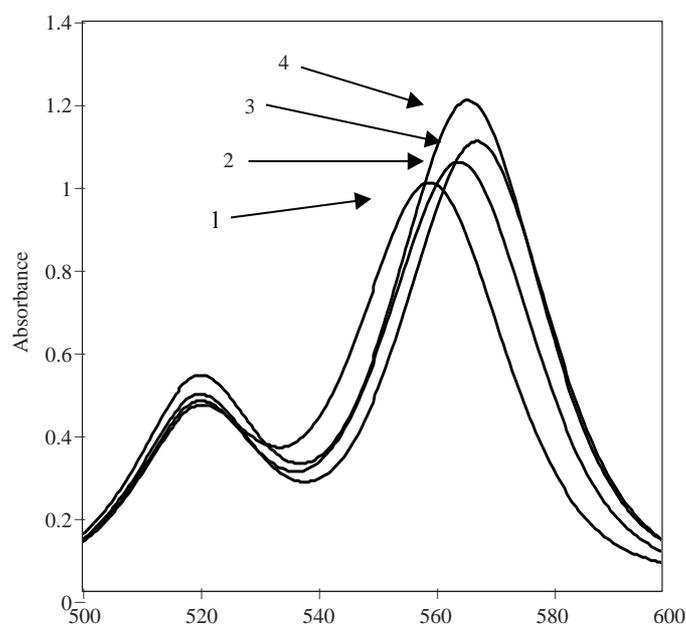**Figure 1.** Absorption spectra of barium and strontium ternary complexes and their mixture. (1) RB-18C6, (2) RB-Ba-18C6, Ba 5 μg mL^{-1}, (3) RB-Sr-18C6, Sr 4.5 μg mL^{-1} (4) mixture of Ba 4 μg mL^{-1} and Sr 3 μg mL^{-1}.
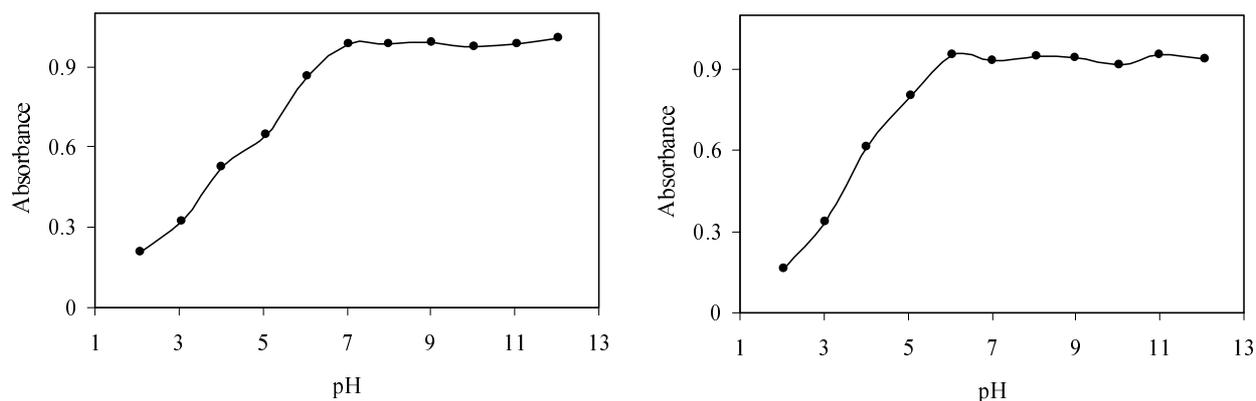
Figure 2. Effect of the pH of the aqueous phase on the extraction of barium and strontium into organic phase. Conditions: Ba^{2+} and Sr^{2+}, 4 μg mL^{-1}; 18C6, 1.6×10^{-3} M; RB, 1×10^{-5}M; dichloromethane, 8 mL; shaking time, 1 min.

The effect of the concentrations of RB and 18C6 on the extraction of the 18C6-Ba-RB and 18C6-Sr-RB complexes were also investigated. It is observed that the absorption of the organic phase increases with increases in both the RB and 18C6 concentrations in the aqueous phase. The maximum extraction of barium and strontium occurred when the reagent-to-metal ions mole ratio was about 40 and 130 for RB and 18C6, respectively. Excess amounts of 18C6 have no considerable effect on the measured absorbance, but increasing RB causes an increase in absorbance.

The extraction of the 18C6-Ba-RB and 18C6-Sr-RB ternary complexes under the conditions recommended in the procedure is rapid. A shaking time of 1 min was sufficient for complete extracting of the complexes. The extraction process was performed under optimal conditions with several organic solvents, such as 1,2-dichloromethane, chloroform, carbon tetrachloride, methyl isobutyl ketone and benzene. It was found that the ternary complexes is readily extractable in 1,2-dichloromethane. However, in the other solvents used, the colored complex could not be extracted into the organic phase as completely as occurred in 1,2-dichloromethane.

It should be mentioned that, the quantitative extraction of ternary complexes of the barium and strontium was completed by single-stage extraction using 8 mL of organic phase under optimal experimental conditions. Individual calibration curves were constructed with several points as absorbance vs. metal ion concentration in the range 0.05-5.50 and 0.03-4.50 μg mL^{-1} and 565.0 and 567.5 nm for barium and strontium, respectively (Figure 3). The detection limits were 0.036 and 0.017 μg mL^{-1} for barium and strontium, respectively. Linear regression results, line equations and R^2 shown in Figure 3.

Calibration and prediction data sets

Multivariate calibration methods are suitable for the analysis of large numbers of samples. However, they are not recommended for the determination of large numbers of analytes because the complexity of the calibration matrix. Moreover, the preparation and analysis of the standards belong to the calibration set are the most expensive step in the multivariate calibration procedure. Multivariate calibration methods such as PLS require a suitable experimental design of the standards belonging to the calibration set in order to provide good predictions.
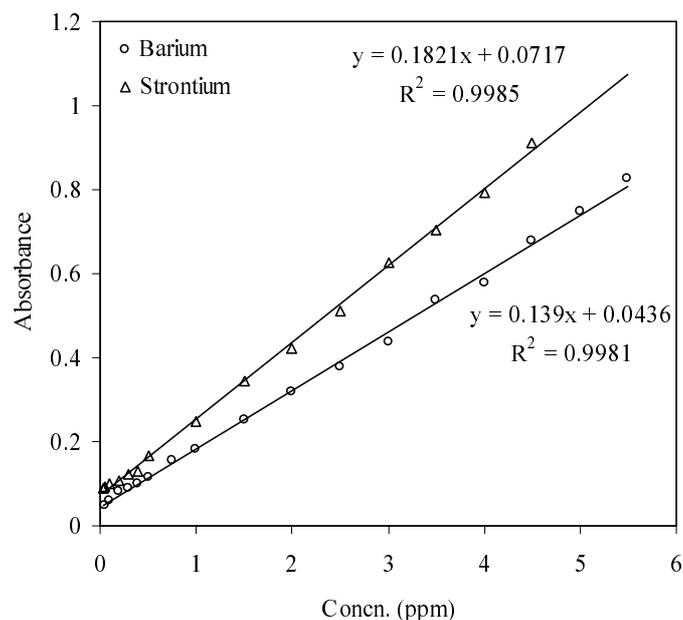
Figure 3. Analytical curve for univariate determination of barium and strontium complexes.

The calibration matrix was designed over the concentration ranges 0.05-5.50 and 0.03-4.50 μg mL^{-1} for barium and strontium, respectively. According to the following basic rules, first, the calibration standards should be mixtures of components in order to compensate for effects on absorbance from interactions between the components. Second, the peak absorbance of each standard should be less 2.5 in the analytical wavelength range. Finally, the concentration of all of the components must be independently varied within the set of standards.

A synthetic set of 34 solution mixtures of barium and strontium were prepared. Twenty-five of the solutions were chosen for the calibration set (Table 1) and the other 9 were used as the prediction set (Table 2). The spectral region is between 500 and 600 nm and each spectrum is digitized with 1.5 nm steps, and 67 experimental points (λ) per spectrum is obtained.

Table 1. Calibration set data for the different mixtures of barium and strontium (μg mL^{-1}).

Mixture	Barium	Strontium	Mixture	Barium	Strontium	Mixture	Barium	Strontium
1	0.05	0.03	10	1.40	4.50	19	4.10	3.10
2	0.05	1.10	11	2.70	0.03	20	4.10	4.50
3	0.05	2.20	12	2.70	1.10	21	5.50	0.03
4	0.05	3.10	13	2.70	2.20	22	5.50	1.10
5	0.05	4.50	14	2.70	3.10	23	5.50	2.20
6	1.40	0.03	15	2.70	4.50	24	5.50	3.10
7	1.40	1.10	16	4.10	0.03	25	5.50	4.50
8	1.40	2.20	17	4.10	1.10			
9	1.40	3.10	18	4.10	2.20			

Selection of the optimum number of factors

In order to determine the optimum number of factors (latent variables) for the PLS calibration model, the cross validation procedure was applied. There are several cross validation routines and "leave one sample

out" was used in our experiments. As the calibration set was constructed of 25 spectra, the calibration was performed on 24 of them. The process was repeated 25 times and the predicted concentrations were compared with known concentrations. The predictive residual error sum of squares (PRESS) was computed, which is defined as follows:

$$PRESS = \sum (y_i - \hat{y}_i)^2$$

where y_i is the known concentration for the ith sample and $\hat{y}_i$ represents the concentration estimated or predicted by the model. The Haaland and Thomas criterion[32] was applied to determine the optimum number of factors. The optimum number was determined rather than the selection of the model, which yields a minimum in prediction error variance or PRESS; the model selected is the one with the fewest number of factors such that the PRESS for that model is not significantly greater than the minimum PRESS. In our case, 13 factors (half the standards + 1) were used as the maximum number of initial factors. A plot of the PRESS against the number of factors for each individual component indicates a minimum value for the optimal number of factors. For finding the fewest number of factors the F-statistics were used to determine the significance[32]. The optimum number of factors obtained by the application of the PLS model is summarized in Table 3. In all cases, the number of factors for the first PRESS values whose F-ratio probability drops below 0.75 was selected as the optimum number. As shown in Table 3, the PRESS values are abnormally high, reflecting the high overlapping of the spectral traces. On the other hand, some nonlinearity or rank deficiency in spectral direction may be responsible for the observed high values of the number of significant factors in the final model.

Table 2. Prediction set results of the synthetic mixtures of barium and strontium by PLS.

Mixture	Added (μg mL^{-1})		Found (μg mL^{-1})		Recovery (%)	
	Barium	Strontium	Barium	Strontium	Barium	Strontium
1	0.20	2.00	0.20	1.95	100.0	97.5
2	1.10	3.80	1.06	3.78	96.4	99.5
3	5.50	1.40	5.71	1.40	103.8	100.0
4	1.40	0.10	1.43	0.08	102.1	80.0
5	3.00	1.30	3.00	1.29	100.0	99.2
6	3.10	2.20	3.09	2.26	99.4	102.7
7	2.30	5.00	2.28	4.96	99.1	99.2
8	4.80	0.25	4.47	0.26	93.1	104.0
9	4.30	4.70	4.26	4.67	99.1	99.4

Table 3. Statistical parameters of the optimized matrix using PLS.

Cation	NPC*	PRESS	RMSEP	RSEP (%)
Barium	11	0.1637	0.1323	3.9921
Strontium	11	0.1392	0.0327	1.1383

*Number of components

Determination of barium and strontium in synthetic mixtures

The predictive ability of the method was determined using 10 two-component mixtures of metal ions (their compositions are given in Table 2). Nine different solutions, which their concentrations were in the linear

range of the system, were prepared in the optimum conditions. The spectra of these solutions were recorded at 500-600 nm and the data were digitized. The results obtained by applying the PLS model to 9 synthetic samples are listed in Table 2. Table 2 also shows the recovery for prediction series of barium and strontium mixtures. The plots of the predicted concentration versus actual values are shown in Figure 4 for barium and strontium (line equations and R^2 values are also shown).
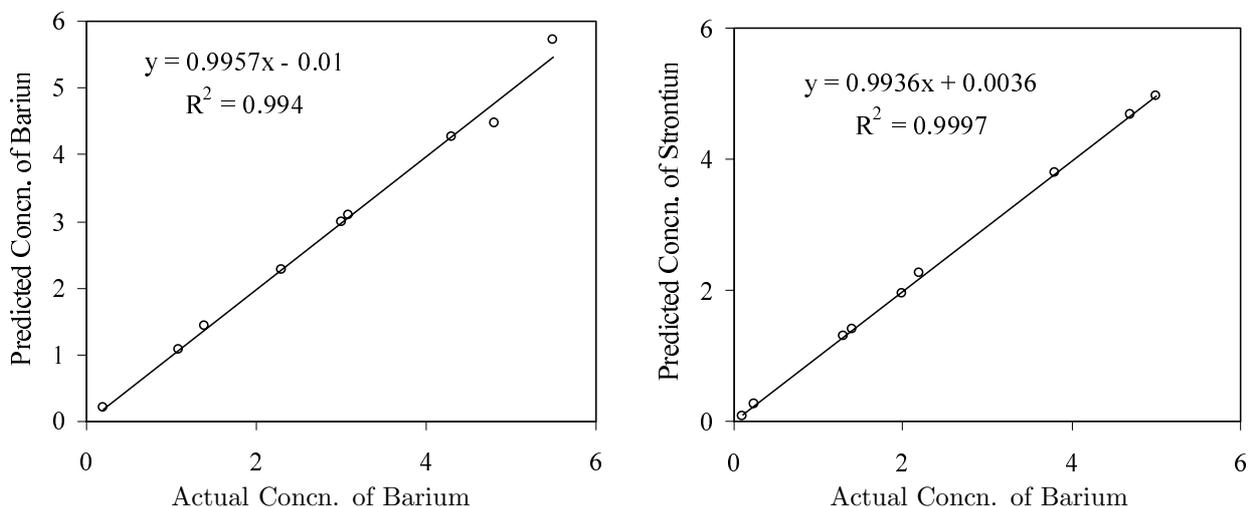

Figure 4. Plots of predicted concentration versus actual concentration for barium and strontium by PLS method (μg mL^{-1}).

A good agreement between the obtained results (using PLS) and the known values is an indication of the successful applicability of the proposed method for extraction-spectrophotometric simultaneous determination of barium and strontium in complex samples. Good results were achieved in the PLS model, with recovery ranges from 93.1 to 103.8 and 80.0 to 104.0% for barium and strontium, respectively.

Statistical parameters

For the evaluation of the predictive ability of a multivariate calibration model, the root mean square error of prediction (RMSEP) and relative standard error of prediction (RSEP) can be used[28,33]:

$$RMSEP = \sqrt{\frac{\sum_{i=1}^{n} (y_{pred} - y_{obs})^2}{n}}$$

$$RSEP(\%) = 100 \times \sqrt{\frac{\sum_{i=1}^{n} (y_{pred} - y_{obs})^2}{\sum (y_{obs})^2}}$$

where y_{pred} is the predicted concentration in the sample, y_{obs} is the observed value of the concentration in the sample and n is the number of samples in the validation set. The value of RMSEP and RSEP(%) for barium and strontium summarized in Table 3.

Determination of barium and strontium in real samples

In order to test the applicability of the proposed method in the analysis of real samples, the analysis of different real spiked samples was carried out. The real sample matrix based of barium and strontium liquid

alloys is prepared according to Naber et al.[34]. These metals are the main gradient of the liquid alloy from the corresponding pure metals. The formed liquid alloy must be analyzed for the 2 cited metal contents on very small samples. Table 4 shows the results obtained for real and spiked matrix samples. The precision of the method was investigated by the analysis of 3 identical specimens for each sample. The results showed that the relative standard deviation (R.S.D.) obtained was acceptable (Table 4). Therefore, the PLS model is able to predict the concentrations of barium and strontium ions in the real matrix samples.

Table 4. PLS results applied on the real matrix and spiked samples.

Type of water	Added (μg mL^{-1})		Found (μg mL^{-1})		Recovery (%)	
	Barium	Strontium	Barium	Strontium	Barium	Strontium
Waste water	4.00	1.20	4.43(2.10)*	1.53(1.46)	110.8	127.5
River water	5.00	0.40	5.10(1.88)	0.41(2.31)	102.0	102.5
Tap water	1.70	3.80	1.65(2.06)	3.83(1.86)	97.1	100.8
Cooling water of Bistun Power Plant	5.0	3.0	4.95(1.40)	3.03(1.2)	99.0	101.0
Milk Factory of Bistun (waste)	4.0	2.0	4.02(2.2)	1.98(2.0)	101.5	99.0
Gamasiab River	- - -	3.0	0.30 (3.0)	3.03(2.3)	- - -	101.0
Ba-Sr Liquid Alloy (5 ppm of each)[a]	- - -	- - -	4.90(2.1)[b]	4.92(2.4)[b]	98.0	98.4
			4.89(1.3)[c]	4.90(1.4)[c]	97.8	98.0

*Relative standard deviation for n = 3, [a]Ref. 34. [b]This method, [c]Atomic absorption method.

Effect of diverse ions

The extent of interference by diverse ions was investigated by measuring the absorbance of the mixture solutions of 1 μg mL^{-1} of barium and strontium and various amounts of diverse ions. The criterion for an interference was an absorbance value varying by more than $\pm 5\%$ from the expected value of the solution mixture of barium and strontium. The results presented in Table 5 shows that a large excess of different cations and anions, which are usually associated in the determination of barium and strontium, do not interfere in the analysis. It should be noted that, with regard to the different interference effect of K$^+$ and Ca^{2+}, the greater the interference effect of the K$^+$ with respect to the Ca^{2+} the greater is the coincidence of the ionic radius of K$^+$ to the cavity size of the 18C6 than the Ca^{2+}. In the other words, the crown cavity has size recognition to accept an ionic sphere in its cavity.

Table 5. The maximum tolerance values of various cations and anions on the measurement of mixture barium and strontium containing 1 and 1 μg mL^{-1}, respectively.

Ions	Tolerance Limit (μg mL^{-1})
Cu^{2+}, Cd^{2+}, Zn^{2+}, Ni^{2+}, Co^{2+}, Ce^{4+}, Bi^{3+}, Li^+, Rb^+, Tl^+, As^{3+}, Cl^-, NO_3^-, F^-, I^-, Br^-, CH_3COO^-, CN^-, ClO_4^-, SCN^- N_3^-, SO_3^{2-}, $S_2O_3^{2-}$, IO_4^-, IO_3^-, BrO_3^-, WO_4^{2-}	500
Cs^+, Zr^{4+}, Ga^{2+}	400
In^{3+}	300
Sn^{2+}, Pd^{2+}, La^{3+}, Ca^{2+}, Mn^{2+}, NH_4^+	200
PO_4^{3-}, $C_2O_4^{2-}$, CO_3^{2-}	50
Al^{3+}, Mg^{2+}, Fe^{2+}, Fe^{3+}	10
SO_4^{2-}	5
K^+	3
Hg^{2+}, Pb^{2+}	1

Conclusion

In this paper, we have described a single and sensitive extraction-spectrophotometric method for the simultaneous determination of barium and strontium. The method is based on the formation of the ternary complexes with 18C6 and RB with barium and strontium. The 18C6-Ba-RB and 18C6-Sr-RB ternary complexes were quantitatively extracted into dichloromethane and the resolution of this mixture of these cations was accomplished by PLS. The barium-strontium mixture is an extremely complex system due to high spectral overlapping of the absorption spectra for the components. For overcoming the drawback of spectral interferences PLS multivariate calibration approaches were applied. The results showed the ability of the PLS model in the deconvolution of mixture spectra. The points of merit, limit of detection and good R.S.D. values, indicate the potential and versatility of the method in the simultaneous determination of barium and strontium spectrophotometrically in various water samples.

References

1. R.M. Lzatt, L. Pawlak, J.S. Bradshaw and R.L. Bruening, **Chem. Rev.** 91, 1721 (1991).

2. A. Ohki, P.J. Lu and R.A. Barstch, **Anal. Chem.** 63, 2282 (1994).

3. K. Suzuki, K. Watanabe, Y. Matsumoto, M. Kobayashi, S. Sato, D. Siswanta and H. Hisamoto, **Anal. Chem.** 64, 324 (1995).

4. Y. Takada, **Bull. Chem. Soc. Jpn.** 52, 2501 (1979).

5. L.M. Tsay, J.S. Shih and S.C. Wu, **Analyst** 108, 1108 (1983).

6. H. Koshima and H. Onishi, **Analyst** 111, 1261 (1986).

7. H. Parham and A.G. Fazeli, **Anal. Sci.** 16, 575 (2000).

8. K. Nakagawa, S. Okada, Y. Inoue and A. Tai, **Anal. Chem.** 60, 2527 (1988).

9. K. Chayama and E. Sekido, **Anal. Chim. Acta** 248, 511 (1991).

10. R. Escobar, C. Lamoneda, F. Depablos and A. Guiraum, **Analyst** 114, 533 (1989).

11. T.C. O'Haver and G.L. Green, **Anal. Chem.** 48, 312 (1976).

12. T.C. O'Haver, **Anal. Chem.** 51, 91A (1979).

13. P. Geladi and B.R. Kowalski, **Anal. Chim. Acta** 185, 1 (1986).

14. H. Martens and T. Naes, "**Multivariate Calibration**", John Wiley, New York, 1991.

15. A. Lorber, L.E. Wangen and B.R. Kowalski, **J. Chemometrics** 1, 19 (1987).

16. R. Marbach and H. M. Heise, **Chemometrics Intell. Lab. Syst.** 9, 45 (1990).

17. J.H. Kalivas, **J. Chemometrics** 13, 111 (1999).

18. J.H. Kalivas, **Chemometrics Intell. Lab. Syst.** 45, 215 (1999).

19. A. Hoskuldsson, **J. Chemometrics** 2, 211 (1988).

20. J.H. Kalivas, **Anal. Chim. Acta** 428, 31 (2001).

21. J. Ghasemi and A. Niazi, **Microchemical J.** 68, 1 (2001).

22. J. Ghasemi, A. Niazi and A. Safavi, **Anal. Lett.** 34, 1389 (2001).

23. J. Ghasemi, R. Amini and A. Niazi, **Anal. Lett.** 35, 533 (2002).

24. J. Ghasemi and D.E. Mohammadi, **Microchemical J.** 71, 1 (2002).

25. J. Ghasemi, A. Niazi and R. Leardi, **Talanta** 59, 311 (2003).

26. J. Ghasemi, N. Shahabadi and H.R. Seraji, **Anal. Chim. Acta** 510, 121 (2004).

27. J. Ghasemi, S. Saaidpour and A.A. Ensafi, **Anal. Chim. Acta** 508, 119 (2004).

28. J. Ghasemi and A. Niazi, **Talanta** 65, 1168 (2005).

29. J. Ghasemi and A. Niazi, **Anal. Chim. Acta** 533, 169 (2005).

30. M. Otto and W. Wegscheider, **Anal. Chem.** 61, 1847 (1989).

31. J. Lurie, "**Handbook of Analytical Chemistry**", Mir Publishers, Moscow, 1978.

32. D.M. Haaland and E.V. Thomas, **Anal. Chem.** 60, 1193 (1988).

33. K. Wiberg, A. Sterner-Molin and S.P. Jacobsson, **Talanta** 62, 567 (2004).

34. P. Naber, H. Elzinga, J. Huffman and J.B. van Zytveld, **J. Phys. F:, Met Phys.** 12, 981 (1982).