

Danail SIMEONOV¹, Lyubomir SPASOV² and Pavlina SIMEONOVA^{3*}

STATISTICAL CALIBRATION OF MODEL SOLUTION OF ANALYTES

MODEL STATYSTYCZNEJ KALIBRACJI ROZTWORÓW ANALITÓW

Abstract: A new method based on spectrophotometric-partial least-squares procedure was proposed for simultaneously determination of thorium and zirconium using SPADNS (4,5-Dihydroxy-3-(p-sulfophenylazo)-2,7-naphthalene disulfonic acid, trisodium salt) as a color reagent. Absorbance measurements were made in the range of $\lambda = 541\div 620$ nm with 1.0 nm steps in buffered solutions at pH 3.5. The linear ranges were obtained for $0.5\div 11.5$ and $1.5\div 14.5$ $\mu\text{g cm}^{-3}$ for Th^{4+} and Zr^{4+} ions, respectively. The limits of detection were determined 0.4 and 1.2 $\mu\text{g cm}^{-3}$ for thorium and zirconium, respectively. The standard deviation ($n = 3$) and recovery percent of 10 samples in the prediction set were obtained in the amplitude $0.22\div 0.38$ $\mu\text{g cm}^{-3}$ and $91.3\div 109.2$, respectively. The proposed method was used for simultaneously determination of mentioned ions in spiked real water samples and wastewater. The results show that the method is applicable for the analysis of samples with similar matrix.

Keywords: spectrophotometry, partial least-squares method, SPADNS, thorium, zirconium

For a number of reasons, spectroscopy is one of the most powerful methods in quantitative analysis of chemical mixtures since it is relatively easy to generate a good data set in short time. However, getting useful results from a set of spectral data is not always straightforward. Determining the amounts of the components of a mixture can often be a problem without a prior separation steps because of the overlap of spectral response. For this reason, the analysts have increasingly turned to chemometrics in dealing with spectral data [1].

Quantitative spectrophotometry has been greatly improved by the use of variety of multivariate statistical methods such as *classical least square* (CLS), *inverse least squares* (ILS), *principal component regression* (PCR), and *partial least squares* (PLS). Multivariate

¹ Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences, 1113 Sofia, Acad. G. Bontchev Bl. 11, Bulgaria, email: alusil@abv.bg

² Institute of Catalysis, Bulgarian Academy of Sciences, 1113 Sofia, Acad. G. Bontchev Bl. 11, Bulgaria, email: lubomir@srv.igic.bas.bg

³ Laboratory of Environmental Physics, Georgi Nadjakov Institute of Solid State Physics, 1184 Sofia, Tzarigradsko Chaussee Blvd. 72, Bulgaria

* Corresponding author: poly-sim@issp.bas.bg

calibrations are effective in spectrophotometric analysis because the simultaneous inclusion of multiple spectral intensities can greatly improve the precision and applicability. The widespread use of these methods is due to the proliferation of commercial software for laboratory computers and detectors capable of recording full spectra very rapidly [2-4].

Partial least-squares modeling is a powerful multivariate analysis of spectroscopic data. The use of PLS method in chemical analysis was pioneered by Wold and coworkers [5]. Detailed studies of multivariate calibration by PLS were carried out for many spectrophotometric determinations of metals [6-9].

Heavy metal ions represent a major environmental problem and their detection and monitoring in wastewater outlets, rivers, reservoirs or sources of drinking water is necessary. Thorium is a naturally occurring element that has a number of industrial and medical applications. It is present in very small quantities in virtually all rock, soil, water, plants and animals. Where high concentrations occur in rock, thorium may be mined and refined, producing waste products such as mill tailings. If not properly controlled, wind and water can introduce the tailings into the environment [10]. Zirconium is used in a wide range of applications including nuclear caps, catalytic converters, surgical appliances, metallurgical furnaces, superconductors, ceramics, lamp filaments, anticorrosive alloys and photographic purposes. Hence nanogram level determinations of zirconium are critically important.

However, there are few reports on the determination of zirconium and thorium simultaneously. Although strong claims are made for the specificity and sensitivity of NAA, ICP-AES and ICP-MS, some of the interferences cause problems [11]. Therefore, spectrophotometric methods for thorium and rare earths continue to be of interest [12-14].

UV-Vis spectrophotometric techniques, due to both the simplicity and rapidness of the method, are the most widely used analytical methods in multicomponent analysis [15, 16]. However; the simultaneous determination of thorium and zirconium ions by the use the traditional spectrophotometry technique is difficult because, the absorption region and the superimposed curves are not suitable for quantitative evaluation. In most cases of analysis of complex samples, physical separation and non-universal instrumentation are required. Spectrophotometric techniques as well as chemometrics methods have been recently used for to solve these problems [9, 10, 17-19].

The goal of this study is to propose a spectrophotometric method by using partial least-squares multivariate calibration for simultaneous determination of Th(IV) and Zr(IV) ions in synthetic and real samples. The method is based on the reaction between these ions with SPADNS (4,5-Dihydroxy-3-(*p*-sulphophenylazo)-2,7-naphthalene disulfonic acid trisodium salt) as chromogenic reagent at pH 3.5.

Experimental

Reagents

All chemicals used were of analytical reagent grade. Doubly distilled water was used throughout. Standard solutions of Th(IV) and Zr(IV) ($1000 \mu\text{g cm}^{-3}$) were made using $\text{Th}(\text{NO}_3)_4 \cdot 6\text{H}_2\text{O}$ and $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$, respectively (Merck Co.). A 1.5×10^{-3} M solution of SPADNS as sodium salt was prepared and used daily. Adjusting the pH values of the working solution was carried out using acetic acid and sodium acetate solutions. The foreign ions were prepared with use from their suitable salts as analytical grade.

Apparatus

A carry 100 UV-Vis scanning spectrophotometer was used to record the absorbance spectra of Th-SPADNS and Zr-SPADNS complexes with a 1.0-cm path length quartz cell. The cell temperature is controlled by circulated water around the cell by thermostat. The slit width was set at 2-nm and a fast scan speed at 600 nm/min was used. The spectra were recorded between 400 and 700 nm at 1-nm intervals. A Metrohm 691 pH meter using a combined glass electrode was used for measurement of the pH. The software used was STATISTICA 7.0.

In order to determine the calibration curve for each element as an analyte, 1.0-cm³ 1.5×10⁻³ M SPADNS as reagent, 2.0-cm³ buffer pH 3.5 and appropriate amounts of the metal ion solution were added to 10-cm³ volumetric flask and made up to the mark with double distilled water. The concentration of Th(IV) and Zr(IV) ions were 0.50÷11.50 and 1.50÷14.50 µg cm⁻³, respectively, that means the proposed method is a valuable method for simultaneous determination of Th⁴⁺ and Zr⁴⁺ in a sample. The absorbances were measured at λ = 580 nm, against a reagent blank for thorium and zirconium ions, respectively.

To a series of 10-cm³ volumetric flasks, 1.0-cm³ 1.5×10⁻³ M SPADNS as reagent and 2.0-cm³ buffer pH 3.5 were added. The appropriate amount of each metal ion containing 5.0÷115.0 µg of Th(IV) and 15.0÷145.0 µg of Zr(IV) were also added and the solutions were made up to the mark with distilled water. These solutions were used for preparation of data sets of calibration and prediction in PLS multivariate calibration method. Excess concentration of SPADNS has been applied to ensure quantitative formation of the complexes in the whole range of calibration. The absorbance of the solutions were measured in the range of 561÷640 nm with 1.0 nm steps and therefore 80 experimental points (λ) per spectrum were obtained.

Results and discussion

SPADNS can be used as an indicator for determination of zirconium and thorium. The complexes stoichiometry of Th(IV):SPADNS and Zr(IV)-SPADNS is 1:1 and 2:1, respectively. Both normal absorption spectra of Th-SPADNS and Zr-SPADNS complexes show maximum absorption (λ_{max}) value at λ = 580 nm; whereas free ligand has λ_{max} = 510 nm (Fig. 1). Therefore, a calibration curve was obtained with absorbance measurement of standard solutions of metal complex versus concentration of each metal ion. As seen from Figure 1, since overlapping of obtained spectrums in the range 560÷640 nm, the presence of each metal ion is interfere in measurement of the other ion. Thus, multivariate calibration such as partial-least squares method can be used to determination two analytes in a mixture sample.

Assay conditions such as pH of the solutions were investigated for optimization. The effect of pH on the spectrum of each complex was studied separately in pH range of 2.0÷5.0. The absorbance of each complex solution at a constant concentration of metal ion was measured at λ_{max} of it and as a function of pH. In the case of both the formed complexes, the absorbance of solutions increased up to pH 3.5 then diminished in the pH above 3.5 for Th-SPADNS, whereas, the absorbance of Zr-SPADNS was decreased in the pH above 4.5. Therefore, the pH value of 3.5 of acetate buffer was selected as an optimum pH for simultaneous determination of Th⁴⁺ and Zr⁴⁺ ions. This pH was achieved via addition of 2.0-cm³ buffer solution (pH 3.5) per 10 cm³ final solution. Excess concentration of

SPADNS (1.5×10^{-4} M) has been applied to ensure quantitative formation of the complexes in the whole range of calibration.

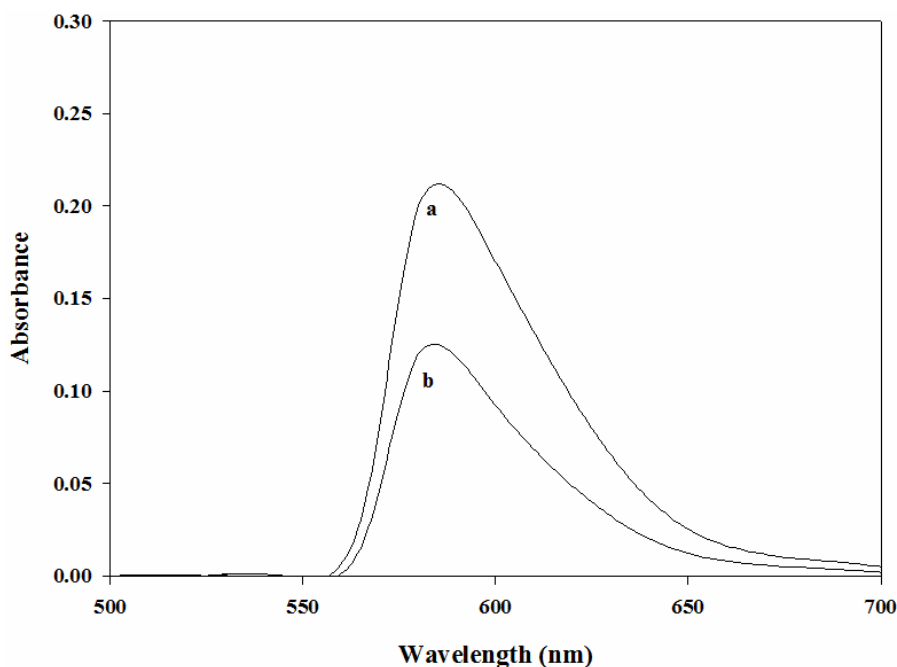


Fig. 1. Absorbance spectra of (a) Th-SPADNS and (b) Zr-SPADNS against reagent blank, conditions: $C_{\text{SPADNS}} = 1.5 \times 10^{-4}$ M, $C_M = 2 \mu\text{g cm}^{-3}$, pH = 3.5 and $t = 25^\circ\text{C}$

In order to find the linear range of concentration of each metal ion, one component calibration was performed for each analyte. In a 10-cm^3 volumetric flask, 1.0-cm^3 SPADNS 1.5×10^{-3} M, 2.0-cm^3 acetate buffer 3.5 and different volumes of $100 \mu\text{g cm}^{-3}$ solution of thorium(IV) ion were added and diluted to the mark with distilled water. The absorbance of the thorium(IV) ion standard solutions was read at λ_{max} of Th-SPADNS complex (580 nm). The same procedure was followed for zirconium and the absorbance of the solutions was read at 580 nm. The linear ranges were obtained in the amplitude of $0.50 \div 11.50$ and $1.50 \div 14.50 \mu\text{g cm}^{-3}$ for Th^{4+} and Zr^{4+} ions, respectively. The R^2 values for thorium and zirconium calibration curves were obtained 0.9987 and 0.9981, respectively. The limits of detection also were determined 0.4 and $1.2 \mu\text{g cm}^{-3}$ for thorium and zirconium, respectively.

The calibration set contains 30 standard solutions. The compositions of the calibration mixtures were selected, randomly, in the amplitude of calibration curve of each analyte. For preparation of each solution, different volumes of two analyte solutions ($25 \mu\text{g cm}^{-3}$) were added to 1.0-ml SPADNS 1.5×10^{-3} M and 2.0-cm^3 acetate buffer 3.5 in a 10-cm^3 volumetric flasks. The concentration of each cation was in the linear range of the cation in one component calibration. The calibration matrix used for the analysis is brought in Table 1. After 5 min, the absorption spectra of the prepared solutions were recorded.

Table 1

Concentration of the components [$\mu\text{g cm}^{-3}$] in calibration set

No.	Th(IV)	Zr(IV)	No.	Th(IV)	Zr(IV)	No.	Th(IV)	Zr(IV)
1	0.50	1.50	11	10.50	4.00	21	5.50	5.50
2	1.50	3.00	12	11.50	6.00	22	7.50	7.50
3	2.50	4.50	13	1.00	12.00	23	9.50	9.50
4	3.50	6.00	14	3.00	10.00	24	11.50	11.50
5	4.50	7.50	15	5.00	8.00	25	11.50	14.50
6	5.50	9.00	16	7.00	6.00	26	8.50	10.00
7	6.50	10.50	17	9.00	4.00	27	6.50	8.00
8	7.50	12.00	18	11.00	2.00	28	4.50	6.00
9	8.50	13.50	19	1.50	1.50	29	2.50	4.00
10	9.50	2.00	20	3.50	3.50	30	1.50	2.00

The selection of the number of the factors in the PLS algorithm is very important to achieve the best prediction. The number of factors was estimated in the PLS1 by cross-section validation method, leaving out one sample at a time and plotting the *prediction residual error sum of squares* (PRESS) versus the number of factors for each individual component [20, 21]. PRESS was computed using following equation:

$$\text{PRESS} = \sum (C_{\text{true},i} - C_{\text{pred},i})^2$$

where $C_{\text{true},i}$ is the known concentration for i -th sample and $C_{\text{pred},i}$ represents the concentration predicted by the model.

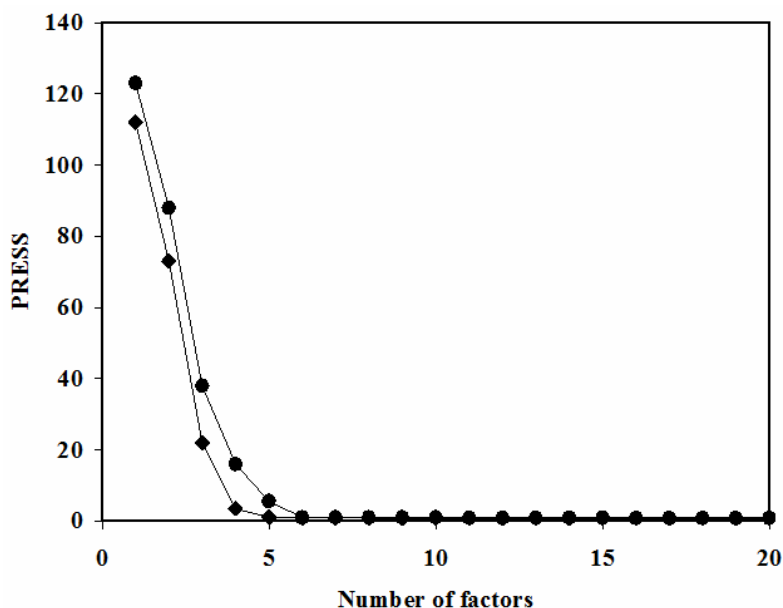


Fig. 2. Plot of PRESS vs number of factors: (♦) Th(IV) and (●) Zr(IV)

The PLS calibrations were performed on the 29 spectra from set of 30 calibration spectra. The components in the sample left out during calibration were predicted with using this calibration. This process was repeated 30 times and in each step of calibration, one sample left out. The prediction residual sum of squares was calculated by comparing the predicted concentration of components in each sample with known concentration of components in standard solutions. To optimize the number of factors, the F-statistic with F-ratio probability of 0.75 was used. The optimum the number of factors was selected for the first PRESS values the F-ratio probability, which drops below 0.75. The Figure 2 shows, the PRESS obtained by optimizing the calibration matrix of the absorbance data with PLS. The optimal number of factors for thorium and zirconium was obtained 5 and 6, respectively.

To evaluate prediction ability of a multivariate calibration model, the *root mean square error of prediction* (RMSEP), the square of the correlation coefficient (R^2) and *relative standard error of prediction* (RSEP) can be used:

$$\text{RMSEP} = \sqrt{\sum_{i=1}^n (C_{\text{pred}} - C_{\text{true}})^2 / n}$$

$$R^2 = \frac{\sum_{i=1}^n (C_{\text{pred}} - \bar{C}_{\text{true}})^2}{\sum_{i=1}^n (C_{\text{true}} - \bar{C}_{\text{true}})^2}$$

$$\text{RSEP}(\%) = 100 \times \sqrt{\sum_{i=1}^n (C_{\text{pred}} - C_{\text{true}})^2 / \sum_{i=1}^n (C_{\text{true}})^2}$$

where: C_{pred} is the predicted concentration in the sample, C_{true} is the true value of the concentration in the sample, $\bar{C}_{\text{true}}$ is the mane of true value of the concentration in the sample and n is the number of samples in the prediction test.

Table 2
Concentration of the components [$\mu\text{g cm}^{-3}$] in prediction set, predicted values and recovery percent

No.	True value		^a Predicted value		Recovery [%]	
	Th(IV)	Zr(IV)	Th(IV)	Zr(IV)	Th(IV)	Zr(IV)
1	0.50	1.50	0.52±0.25	1.37±0.25	104.0	91.3
2	1.50	3.00	1.53±0.27	2.96±0.24	102.0	98.7
3	1.50	10.00	1.60±0.22	10.92±0.28	107.0	109.2
4	4.00	3.00	3.86±0.28	3.06±0.31	96.5	102.0
5	4.00	12.00	4.16±0.25	11.96±0.25	104.0	99.7
6	10.00	2.50	10.28±0.38	2.33±0.27	102.8	93.2
7	10.00	10.00	9.78±0.25	10.10±0.25	97.8	101.0
8	5.00	1.50	5.36±0.26	1.60±0.30	107.2	106.7
9	5.00	8.00	5.42±0.33	7.77±0.28	108.4	97.1
10	11.50	14.50	11.28±0.25	14.24±0.35	98.00	98.2

^a Mean±S.D. (n = 3)

Simultaneously determination of thorium and zirconium was made on the 10 synthetic test samples by the proposed method. Figures 3 and 4 show plots of predicted concentrations versus true concentrations using the optimized model. Predicted results and

their recovery percent are given in Table 2. The standard deviation and recovery percent of 10 samples in the prediction set were obtained in the amplitude $0.22 \div 0.38 \mu\text{g cm}^{-3}$ and $91.3 \div 109.2$, respectively. Also, the values of RMSEP, R^2 , RSEP [%] and number of factors according the obtained results for prediction test are summarized in Table 2.

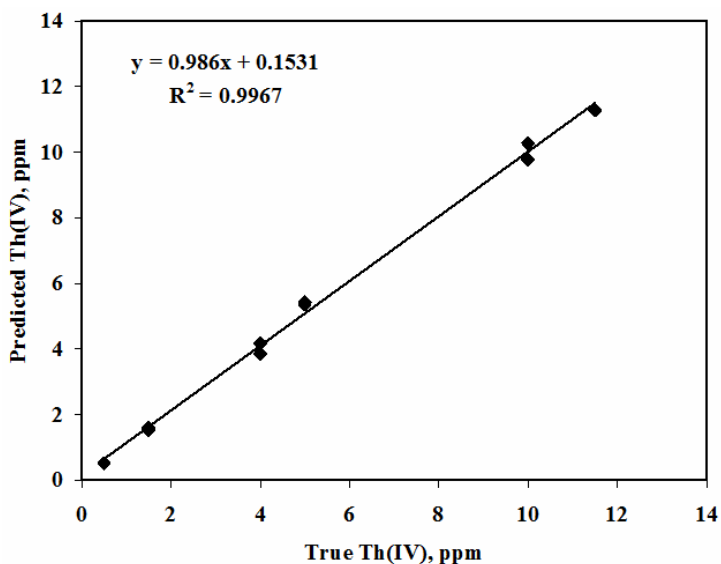


Fig. 3. Plots of predicted concentration vs true concentration for Th(IV) ion in the prediction set

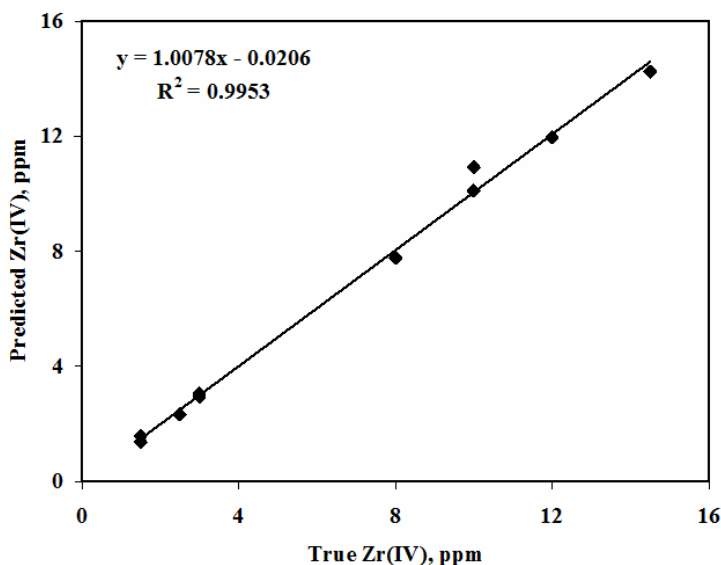


Fig. 4. Plots of predicted concentration vs true concentration for Zr(IV) ion in the prediction set

Table 3

Statistical parameters of the test matrix

Analyte	No. of factors	RMSEP	R ²	RSEP [%]
Th(IV)	5	0.0448	0.9967	2.18
Zr(IV)	6	0.0535	0.9953	1.18

The interference due to several cations and anions on the determination of two components ($5 \mu\text{g cm}^{-3}$) has been investigated by multivariate calibration method. The tolerance limit for each foreign ion is obtained when its presence at tested weight ratio produced a variation in concentration of analytes lower than 5%. The results (Table 4) indicate that the most of the cations and anions did not show any significant spectral interference at weight ratio greater than 1000.

Table 4

Tolerance limits for the divers ions in the determination of Th(IV) and Zr(IV) ions

Interfere ion	Tolerance limit ($w_{\text{Ion}}/w_{\text{M}}$)
Li^+ , Ag^+ , K^+ , NH_4^+ , Mg^{2+} , Sr^{2+} , Ba^{2+} , Ca^{2+} , HCO_3^- , I^- , Br^- , Cl^- , F^- , NO_3^- , NO_2^- , $\text{S}_2\text{O}_8^{2-}$, SO_4^{2-} , SCN^- , $\text{S}_2\text{O}_3^{2-}$, IO_3^- , ClO_3^-	1000
Hg^{2+} , Ti(IV) , Mo(VI) , Cr(VI) , Mn(VII)	500
Cr^{3+} , Sn^{4+} , Sn^{2+} , Ti(III) , V(IV) , V(V)	100
Mn^{2+} , Co^{2+} , Ni^{2+} , Zn^{2+} , Cu^{2+} , Cd^{2+} , Pb^{2+} , Bi^{3+} , HPO_4^{2-} , H_2PO_4^-	50
Fe^{2+} , PO_4^{3-}	10
F^- , Fe^{3+} , Al^{3+}	1

The proposed method was successfully applied for determination of thorium and zirconium in several real water spiked samples and wastewater after dilution (Table 5). Thorium and zirconium were not detected prior to spiking samples using AAS (*atomic absorption spectroscopy*) method. As seen from Table 5, good recovery and low standard deviation was obtained by the PLS method using absorbance data. Therefore, this proposed method can be used for the analysis of samples of similar matrix, effectively.

Table 5

Analysis of real samples

Sample	^a Spiked [$\mu\text{g/cm}^3$]		^b Found [$\mu\text{g/cm}^3$]		Recovery [%]	
	Th(IV)	Zr(IV)	Th(IV)	Zr(IV)	Th(IV)	Zr(IV)
Tap water	5.0	5.0	5.2 ± 0.2 ^c (5.1 ± 0.2)	4.8 ± 0.3 (4.7 ± 0.1)	104.0	96.0
River water	5.0	5.0	4.9 ± 0.3 (4.9 ± 0.2)	5.3 ± 0.1 (4.9 ± 0.3)	98.0	106.0
Spring water	5.0	5.0	4.8 ± 0.3 (4.9 ± 0.2)	4.6 ± 0.2 (4.7 ± 0.3)	96.0	92.0
^d Wastewater of AENTC			240 ± 6 (245 ± 5)	195 ± 4 (198 ± 4)		

^a Thorium and zirconium were not detected prior to spiking samples using AAS method, ^b Proposed method and mean $\pm$ S.D. (n = 3), ^c AAS, ^d The actual amounts of Th and Zr are 250 and 200 $\mu\text{g/cm}^3$, respectively.

Conclusions

Thorium(IV) and zirconium(IV) have chemical properties which can interfere with each other in their determination. For example, in spectrophotometric methods using color reagents for complex formation with these elements, the high spectral overlapping can be observed between the absorption spectra for these components. Thus, there are reliable methods for simultaneously determination these elements in the real samples. However, the partial least-squares (PLS) method shows two advantages in this work: (i) it is applicable for analysis of two analyte in a sample; (ii) there is not need to pretreatment in complex samples.

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MODEL STATYSTYCZNEJ KALIBRACJI ROZTWORÓW ANALITÓW

Abstrakt: Nowa metoda opiera się na procedurze spektrofotometrycznej - najmniejszych kwadratów, która została zaproponowana do równoczesnego oznaczania toru i cyrkonu z wykorzystaniem SPADNS (kwas 4,5-Dihydroksy-3-(*p*-sulfofenylazo)-2,7-naftaleno disulfonowy, sól trisodowa) jako odczynnika koloru. Pomiarów absorbancji dokonano w zakresie $\lambda = 541\div 620$ nm co 1,0 nm w roztworach buforowych o pH 3,5. Liniowy zakres uzyskano przy stężeniach jonów Th^{4+} i Zr^{4+} odpowiednio $0,5\div 11,5$ i $1,5\div 14,5$ $\mu\text{g cm}^{-3}$. Granice wykrywalności dla toru i cyrkonu wynosiły odpowiednio 0,4 i 1,2 $\mu\text{g cm}^{-3}$. Wyznaczono odchylenie standardowe ($n = 3$) i procent odzysku w serii 10 próbek odpowiednio w zakresie $0,22\div 0,38$ i $91,3\div 109,2$ $\mu\text{g cm}^{-3}$. Proponowana metoda została zastosowana do równoczesnego oznaczania wymienionych jonów w wzbogaconych próbkach rzeczywistych wody i ścieków. Wyniki pokazują, że ta metoda może być wykorzystywana do analizy próbek o podobnej matrycy.

Słowa kluczowe: spektrofotometria, metoda najmniejszych kwadratów, SPADNS, tor, cyrkon