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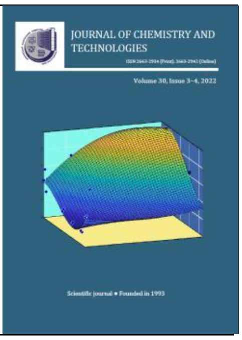

UDC 543.4

SPECTROPHOTOMETRIC STUDY OF ZIRCONIUM WITH DINITROBENZENE-AZOPYROCATECHOL AND MULTI-LIGAND COMPLEXES WITH OP-10

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Abstract

The proposed method was used to study the multi-ligand complex of zirconium with 1.2-dinitrobenzene-azopyrocatechol and OP-10 following spectrophotometric methods. The optimization procedure was confirmed by the Box Behnken design. Maximum extraction of zirconium complex occurred in the pH range of 1.0–3.8.

The effect of temperature, solvents and their volumes on the absorption was studied. Under optimal conditions: 500 μL of chloroform was selected as extraction solvent, 400 μL of acetone was used as a dispersive solvent,pH was 2.0, λmax = 560 nm. The linear range, limit of detection and lgβk were found to be 0.04–5.8 μg mL^{-1}, 0.08 μg mL^{-1} and 6.86, resp. Moreover, the effect of interference ions, which were present in water was investigated. The proposed method was applied for the determination of zirconium in various water samples.

Keywords: dinitrobenzene-azopyrocatechol; zirconium; Box-Behnken design; extraction.

СПЕКТРОФОТОМЕТРИЧНЕ ДОСЛІДЖЕННЯ ВЗАЄМОДІЇ ЦИРКОНІЮ З ДИНІТРОБЕНЗОЛ-АЗОПІРОКАТЕХОЛОМ ТА МУЛЬТИЛІГАНДНИМИ КОМПЛЕКСАМИ З ОП-10

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Анотація

Запропонована методика була використана для дослідження мультилігандного комплексу цирконію з 1.2–динітробензол-азопірокатехолом та ОП-10 за допомогою спектрофотометричних методів. Процедуру оптимізації підтверджено розрахунком за методом Бокса-Бенкена. Максимальне вилучення комплексу цирконію відбувалося в інтервалі pH 1.0–3.8.

Вивчено вплив температури, розчинників та їх об'ємів на поглинання. За оптимальних умов в якості екстракційного розчинника обрано 500 мкл хлороформу, в якості диспергуючого розчинника – 400 мкл ацетону, pH – 2.0, λmax = 560 нм. Встановлено, що лінійний діапазон, межа виявлення та lgβk складають 0.04–5.8 мкг/мл$^{-1}$, 0.08 мкг/мл$^{-1}$ та 6.86 відповідно. Крім того, досліджено вплив іонів-інтерферентів, які присутні у воді. Запропоновану методику застосовано для визначення цирконію в різних пробах води.

Ключові слова: динітробензол-азопірокатехол; цирконій; конструкція Бокса-Бенкена; екстракція.

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Introduction

Zirconium is widely used in industry. It increases the resistance of alloys to corrosion and their durability to mechanical impacts [1]. It is used in the nuclear industry [2], in the catalysis of organic reactions [3], in the pigment industry and in the production of ceramics [4; 5]. Therefore, the sensitive and selective analysis methods of zirconium are in high demand. The literature survey showed that different methods are used for analyzing zirconium, like spectrophotometric determination (SD) [6–8], flotation spectrophotometric determination (FSD) [9], molecular fluorescence spectrophotometry (MFS) [10], X-ray spectrophotometry [11], ultraviolet – visible spectrophotometry [12–15], simultaneous first order derivative spectrophotometric (SFODS) [16], sorption spectrophotometric determination – single sample on a two-layer support (SSD-SS TLS) [17] and others. However, the sensitivity and selectivity of these methods are too weak. As an extraction procedure, asolid phase extraction method with various adsorbents – C18 [18], glycerol – silica gel [19], chelating adsorbents [20], Amberlite XAD resin [21], Chromosorb resin [22], vinyl polymer resin [23], octadecyl silica-polyethylene [24], Amberlite XAD-2000 resin [14] and other sorbents [25–27] was applied.

Recently, a new liquid-liquid microextraction method namely, dispersive liquid-liquid microextraction (DLLME) was proposed [28]. It also enables the selective removal of components in a mixture. Liquid–liquid extraction is a separation method widely used in both laboratory scale and in industrial processes due to its simplicity, low cost, suitability for thermolabile and high-boiling compounds, and easy scalability. In some cases, the efficiency of a liquid-liquid extraction process can be strongly improved by modifying the distribution coefficient. This method has been applied for the determination of trace organic pollutants and metal ions in the environmental samples [29; 30].

In the presented work, the method of spectrophotometric analysis was combined with the method of liquid-liquid extraction for the analysis of zirconium. Liquid extraction method was used to concentrate the zirconium ions.

Experimental part

Reagents. A standard zirconium solution with a concentration of 135 μq mL^{-1} was prepared by dissolving "high purity" metallic zirconium in a mixture of HF+$HClO_4$. Then hydro fluoride acid is evaporated and separated and stirred with 4 M $HClO_4$ and 5 M H_2SO_4 [31]. 27 μg mL^{-1} of working solution of Zr (IV) was obtained by distilling primary solution with distilled water. 5×10^{-3} mol L^{-1} of dnBAP solution was prepared in 1,4-dioxane. Non-ionic surfactant (OP-10) solution (1 × 10^{-3} molL^{-1}) were prepared by distilled water. Doubly distilled water was used throughout. 0.5 molL^{-1} HNO_3 and NH_3 were used to regulate the pH. In addition, chloroform, tetrachloromethane, 1,2 dichloroethane, acetonitrile, acetone, ethanol were used in order to study the complexation conditions. All reagents used were of analytical grade.

The structure of 2,4-dinitrobenzene-azopyrocatechol is as follows (Fig. 1).

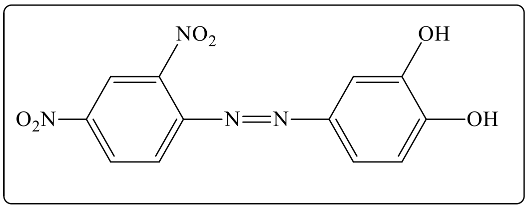

Fig. 1.The structure of 2,4 dinitrobenzene-azopyrocatechol

Apparatuses. Absorbtion of colored solutions was measured on UV-VIS Evolution 60S spectrophotometer and KFK-2 photoelectrocolorimeter, equipped with a 1.0 cm path length quartz cell. pH of all solutions was monitored using Cond./TDS/Temp universal pH-meter. All spectrophotometric measurements were performed at 25.0 ± 0.5 °C.

Extraction procedure. Sample, contained 15 μq·mL^{-1} of Zr (IV) was placed to the test tube. After, 250 μL from 5×10^{-3} mol·L^{-1} standard solution of 2,4 dinitrobenzene-azopyrocatechol (dNBAP), 250 μL from 1×10^{-3} mol·L^{-1} solution of OP-10 solution was added, and 400 μL of the dispersant was added. Then, 500 μL of extraction solution was added to the mixture and the pH 2.0 was set up using buffer solution. The total volume was made up to 10 mL with distilled water. Then, the solution was centrifuged at 3.500 rpm for 3 minutes. After, phase separation, the organic phase was collected from the bottom of the test tube with a pipette. The absorbance of the organic phase was measured at λ_{max}= 560 nm.

Absorption spectrum. The maximum absorbtion of the complex was measured in the wavelength range of 200–1100 nm (Fig. 2). The maximum absorbtion of the ligand was observed at 400 nm and the maximum absorbtion of the complex – at 560 nm. The molar absorbtion coefficient of the zirconium complex at 560 nm was 1.3×10^4 L mol^{-1} cm^{-1}.

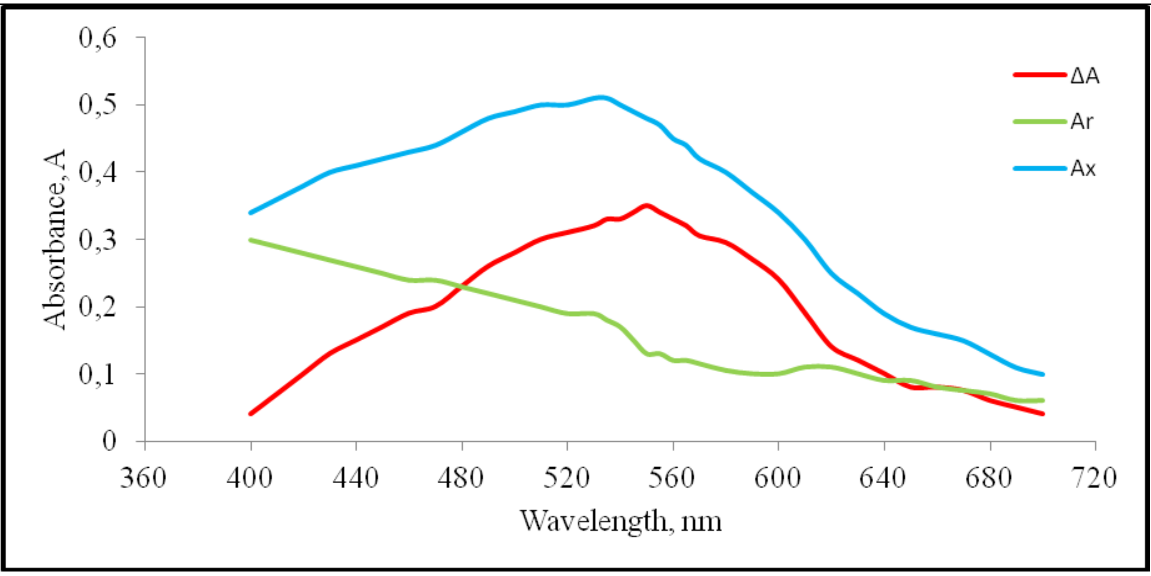

Fig. 2. Absorption spectrum of Zr-dnBAP-OP 10 complex: ($\Delta A = A_X - A_r$, A_r is the absorption spectrum of the ligand against a backdrop of distilled water, A_X is the absorption spectrum of Zr-dnBAP-OP 10 complex against a backdrop of ligand). Zr=0.4 µg mL^{-1}, C_{dnBAP} = 5×10^{-3} M, V_{dnBAP} = 4 mL.

Optimization procedure. The effects of pH, extractant volume (EV), dispersive solvent volume (DSV), ligand volume (LV) and effect of the temperature (T) on the extraction process were studied. Calculations were performed using the Box-Behnken design to characterize the optimal values of these independent parameters in the extraction process (Table 1).

Table 1

Values of statistically independent variables with the Box-Behnken design program

Independent variables	Symbol	The lowest value	The highest value
pH	pH	1.0	3.8
Centrifugation time, minute	CT	2	10
Volume of ligand, (µL)	VL	50	400
Volume of extraction solvnt, (µL)	VES	300	700
Volume of dispersive solvent, (µL)	VDS	200	600
Temperature, ºC	T	10	40

The effect of pH. The formation and extraction of the Zr (IV) complex was significantly dependent on pH. The effect of pH, was studied in the range 0.5–8. The pH was adjusted using HNO_3 and NH_3 (0.5 mol·L^{-1}). It was found that the absorbance of the complex was highest in the range of 1.0–3.8 (Fig. 3). Subsequent experiments were performed at pH = 2.0.

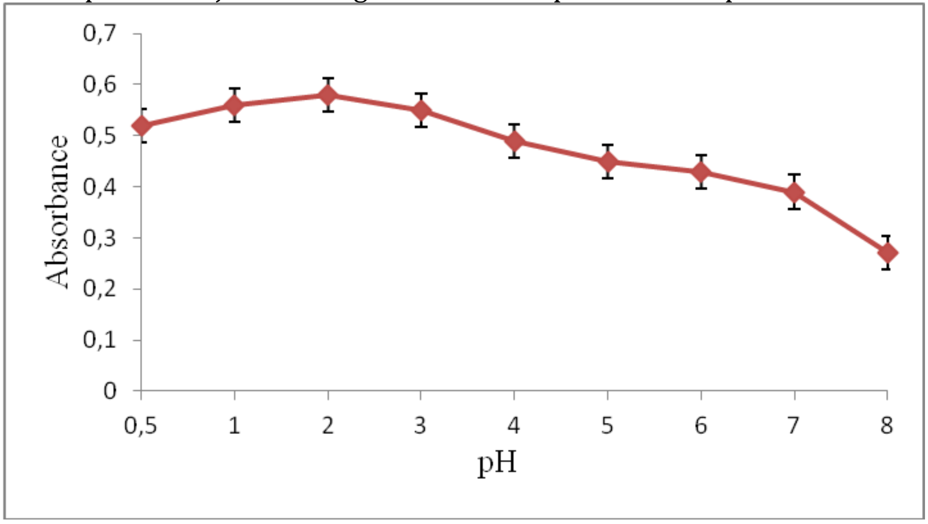

Fig. 3. Effect of pH on adsorption of Zr (IV) complex

Selection of extractant and dispersant and their volume. For this purpose, 3 types of solvents were selected: tetrachloromethane (TCM), 1,2-dichloroethane (DCE), chloroform (CF), (Figure 3). According to the results, the best solvent for the extraction of Zr (IV) complex was selected chloroform (recovery 99 %). Absorption of chloroform at 500 µL was maximal. The effect of the dispersant solution on the extraction, which facilitates the distribution of the Zr (IV) complex between the two phases, was studied. Acetonitrile, acetone and ethanol were used as dispersive solutions. These solvents are well soluble in both extraction solutions and in the aqueous phase. As a result, acetone was selected as the dispersant solution with maximum absorption of the complex, and the optimal volume of acetone was 400 µL (Fig. 6).

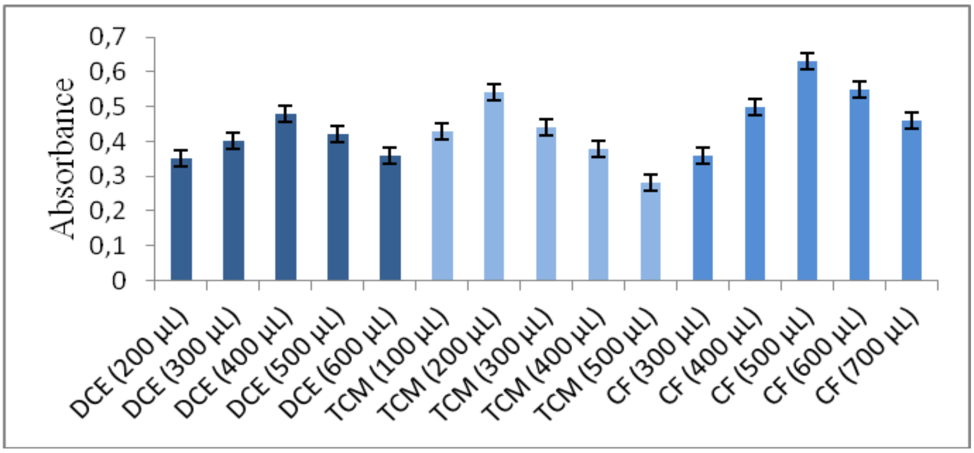

Fig. 4. Effect of extraction solvents and their different volumes on absorption

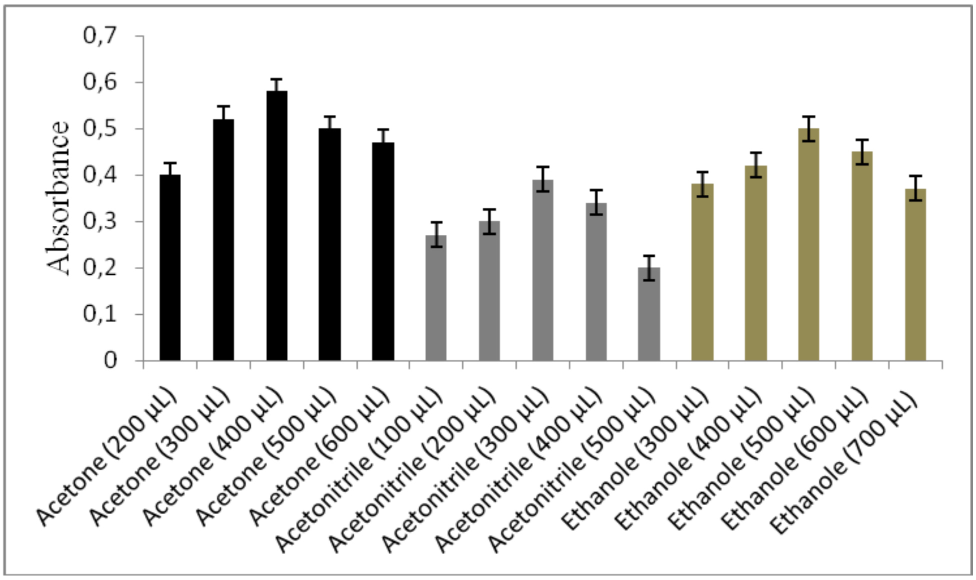

Fig. 5. Effect of dispersive solvents and their volumes on absorption

Effect of ligand volume. The absorbtion of the complex was measured after the addition dinitrobenzene in the range of 50–400 µL to 10 mL of samplecontaining 15 µq Zr (IV) at optimal acidity (pH = 2.0) (Fig. 6). According to the results was obtained, the adsorption of the complex solution was maximal when the volume of the ligand was 250 µL. Therefore, the optimal volume of the ligand, 250 µL was selected for subsequent experiments.

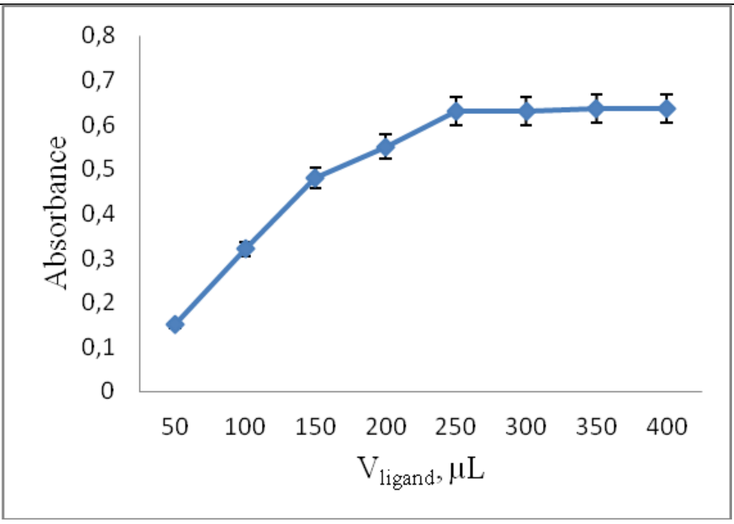

Fig. 6. Effect of ligand volume on absorption.

Effect of volume of surfactant. In order to study the effect of the volume of the nonionic surfactant on the extraction of the Zr (IV) complex, an experiment was conducted in the volume range of 50–350 μL of surfactant (Fig. 7). According to the results obtained, maximum absorption was observed at 250 μL surfactant.

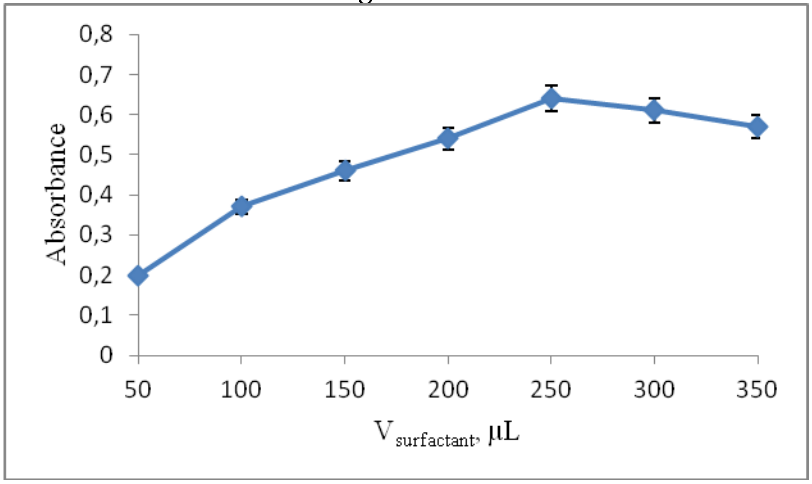

Fig. 7. Effect of surfactant volume on absorption.

Effect of other experimental conditions on extraction efficiency. To study the effect of temperature on the extraction process, experiments were performed in the temperature range of 15–40 °C. Absorption was found to be higher when the temperature was 25 °C. At low temperatures, a decrease of absorption was observed due to the poor complex formation. Also, when the temperature increased, the absorption value decreased due to the changes in the stoichiometric composition of the complex.

The effect of extraction time was studied at 1, 3, 5 minutes, and it was found that extraction time did not affect absorption. It was observed that the organic phase was better separated when the centrifuge speed was 3500 rpm. The results of the experiments conducted in the interval of 2–10 minutes were also compared, and the best results were obtained at 3 minutes of the centrifugation.

*Optimization of analytical results***.** Box Behnken statistical analysis method was used to optimize the extraction process of zirconium (IV) complex (Minitab 19). For this purpose, value ranges of independent variables were defined. Fifteen experiments with different values of 3 parameters compiled by the Box Behnken program were conducted and statistical analysis was performed based on the results of the experiments. An equation was obtained expressing the relationship between dependent and independent variables.

The relationship between the parameters by means of statistical analysis was expressed by 3D graphs. Figure 8 shows the effect of pH, VL, and VDS-independent variables on the absorption for the extraction process. Looking at the effect of VL and pH on absorption, keeping the mean value of VDS constant at 400 μL, it is clear that VL has a greater effect, especially when VL = 250 μL, the absorption is greater than 0.50 (Figure 8a). When the pH = 2.5 is constant, the absorption is still high at VL = 250 µL. The pH value does not appear to be as effective as VL (Fig. 8b). Examination of both graphs reveals that the VL-independent variable has a greater effect on absorption during the extraction process. As a result, comparing the effects of 3 independent variables, it is clear that VL has a greater effect on the extraction process. According to the results of statistical analysis, the optimal values of independent variables are pH = 2, VL = 250µL and VDS = 400 µL to achieve the highest absorption.

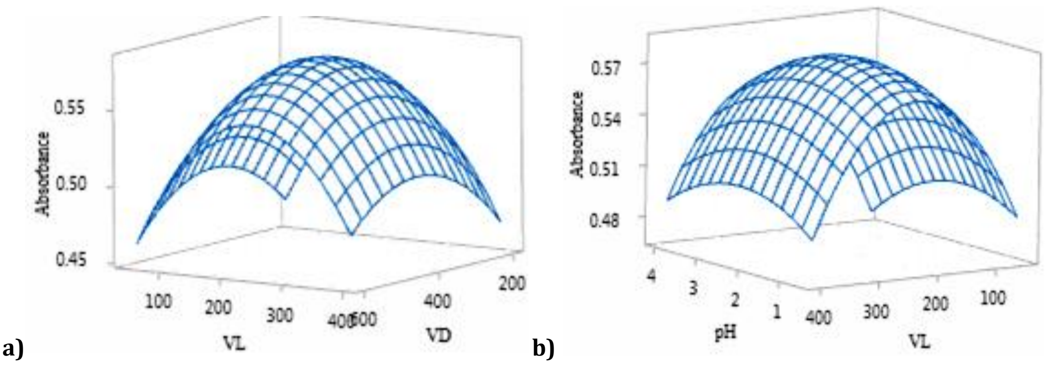

Fig. 8. The effect of pH and ligand volume and volume of dispersant solution on absorption during extraction.

Analytical performance. Samples of zirconium of known concentration were added to 1000 mL of water and analyzed by the proposed method. The limit of detection (LOD) and limit of quantitation (LOQ) of zirconium, as well as the absorption recovery were determined in each water sample. The best analytical results were obtained in an experiment with tap water. The coefficient of determination and sensitivity were studied by adding different amounts of zirconium samples to distilled water. Sensitivity was studied by inter-day and intra-day experiments. The results are shown in Table 2.

Table 2

Analytical features of the proposed method

Zirconium (ng L^{-1})	Coefficient of determination (R^2)	Precision (%)			
		Inter-day		Intra-day	
		Concentration, (ng L^{-1})	Error, %	Concentration, (ng L^{-1})	Error, %
4	0.9954	4.02	0.40	4.02	0.60
20	0.9936	20.28	1.40	20.24	1.20
40	0.9986	40.44	1.10	40.64	1.60
60	0.9925	60.24	0.40	60.12	0.20
80	0.9940	80.05	0.06	80.07	0.09
100	0.9913	101.11	1.11	100.08	0.08

Influence of foreign ions. The concentration limit of foreign ions that could interfere with the determination of zirconium was studied (Table 3). For this purpose, a mixed solution was prepared by adding 1µg mL^{-1} of foreign ions and zirconium to natural water. Results showed no more than ≤ 5 % error. Due to the strong acidic environment of the reaction medium, foreign ions could not form complexes with dnBAP, which lead to a high tolerance limit.

Table 3

The effect of foreign ions on the determination of 1µg mL^{-1} concentrated zirconium.

Interfering ion	Tolerance limit mass ratio
Na^+, K^+, Ca^{2+}, Mn^{2+}, NO^-, $C_2O_4^{2-}$	1:2000
Mg^{2+}, PO_4^{3+}, IO_3^-, Co^{2+}	1:1200
Tl^+, Th^{4+}, Ba^{2+}, Pb^{2+}, Cr^{3+}	1:800
Si^{4+}, Ti^{4+}, Al^{3+}	1:650
Zn^{2+}, Cu^{2+}, Sr^{2+}	1:430
Sm^{3+}, Fe^{2+}, Cs^+, Y^{3+}	1:200
Mo^{6+}, Be^{2+}, Hg^{2+}, V^{4+}	1:140

Compared to different methods of analysis of zirconium (according to the Beer-Lambert law and limit of detection values), this method can be considered to be a sensitive and selective

(Table 4). The simplicity of the method allows to perform analysis in the laboratory with less time and simple devices.

Table 4

Comparison of analytical results of the method with other methods

Reagent	Method	Analized obyect	Linear range	λ$_{max}$, nm	Molar absorptivity, L mol^{-1} cm^{-1}	Limit of detection	Reference
Xipamide.	SD	Water, soil	0.2–3.6 μg L^{-1}	333	5.60×10^4	0.0451 μg L^{-1}	6
Arsenoza lll	SPE	Water and soil samples	5–300 ng mL^{-1}	534		1.3 ng mL^{-1}	27
Xylenol orange	FSD	Water	7–120 ng mL^{-1}	429	6.9×10^5	5.8 ng mL^{-1}	9
2-(2-benzothiazolylazo) -3-hydroxyphenol	SPS	Water	0.25–3.7 μg mL^{-1}	569	1.97×10^7	0.08 μg L^{-1}	1
Diacetylmonoxime salicyloylhydrazone	SFODS	Oil	0.30–3.20 μg mL^{-1}	405	1.82×10^4		16
dnBAP	SD	Tap water	0.04–5.8 μg mL^{-1}	560	1.3×10^4	0.08 μg mL^{-1}	This work

Conclusions

In this study, DLLME was developed and used for preconcentration of the zirconium complex. According to experimental and statistical studies, the pH, the volume of the ligand and the volume of the dispersant solution have a greater impact on the absorption value. These values indicate that the experimental results can be expressed as statistical results. It was found that the adsorption of the complex was higher when 500 μL of chloroform, 400 μL acetone as a dispersant solution were used for the extraction of zirconium complex in the range of pH = 1.0–3.8. The estimated stoichiometric composition of the complex Zr : dnBAP : OP-10 was found to be 1 : 2 : 2. As well, The 15-step experiment optimization procedure was conducted. The influence of foreign ions was studied. The amount of zirconium was determined in various water samples to show the applicability of the developed method.

References

[1] Amin, A. S. (2015). Novel approach for the determination of zirconium by solid-phasespectrophotometry, *Journal of Taibah University for Science*, *9*(2), 227–236. https://doi.org/10.1016/j.jtusci.2014.11.003

[2] Hedrick, J. B. (2007). Rare Earths (Advanced Release), Minerals Yearbook; U.S. Geological Survey: Reston, VA, USA, 2009. http://www.usmagneticmaterials.com/documents/USGS-RE-MineralsYearbook.pdf

[3] Ghasemi, J. B., Zolfonoun, E. (2010). Simultaneous spectrophotometric determination of trace amounts of uranium, thorium, and zirconium using the partial least squares method after their preconcentration by alpha-benzoin oxime modified Amberlite XAD-2000 resin. *Talanta*, *80*(3), 1191–1197. doi.org/10.1016/j.talanta.2009.09.007

[4] Abbaspour, A., Baramakeh, L. (2002). Simultaneous determination of zirconium and molybdenum by first-derivative spectrophotometry. *Anal. Sci.*, *18*(10), 1127–1130. doi.org/10.2116/analsci.18.1127

[5] Lide, D. R. (2007). CRC Handbook of Chemistry and Physics. *J. Am. Chem. Soc.*, *129*(3), 724. https://doi.org/10.1021/ja069813z.

[6] Al-Kady, A. S. (2012). Selective and sensitive spectrophotometric method for the determination of trace amounts of zirconium in environmental and biological samples using 4-chloro-N-(2,6-dimethylphenyl)-2-hydroxy-5-sulfamoylbenzamide. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, 97, 284–289. https://doi.org/10.1016/j.saa.2012.06.019

[7] Jain, A., Prakash, O., Kakkar, L. R. (2010). Spectrophotometric Determination of Zirconium with 5,7-Dibromo-8-hydroxyquinoline in presence of Thiocyanate. *Journal of Analytical Chemistry*, *65*(8), 820–824. https://doi.org/10.1134/s1061934810080101

[8] Lasheen, T. A., Hussein, G. M., Khawassek, Y. M., Cheira, M. F. (2013). Spectrophotometric determination of zirconium (IV) and hafnium (IV) with pyrazolo (1, 5-a) quinazolin-6-one derivative reagent. *Analytical chemistry an Indian Journal*, *12*(10), 368–376. https://www.tsijournals.com/articles/spectrophotometric-determination-of-zirconium-iv-and-hafnium-iv-with-pyrazolo-1-5a-quinazolin6one-derivative-reagent.pdf

[9] Pourreza, N., Parham, H., Shiri, S., (2010). Determination of Trace Amounts of Zirconium by Flotation – Spectrophotometric Method, *Journal of the Korean Chemical Society*, *54*(3), 283–286. DOI:10.5012/jkcs.2010.54.3.283

[10] Wang, Z.P., Qian, Y.H., Chen, G.S., Cheng, K.L. (1998). Studies on simultaneous fluorescence-spectrophotometric determination ofultratrace niobium(V), tantalum(V), and zirconium(IV) using partial least-squares algorithm, *Microchemical Journal*, *60*(3), 271–281. https://doi.org/10.1006/mchj.1998.1661

[11] Afzal, M., Hanif, J., Hanif, I., Qadeer, R., Saleem, M., (1990). Determination of zirconium and hafnium in solution by X-ray fluorescence spectrometry, *Journal of*

Radioanalytical and Nuclear Chemistry, *139*(2), 203–214. https://doi.org/10.1007/bf02061804

[12] Purohit, R., Devi, S. (1997). Determination of nanogram levels of zirco-nium by chelating ion exchange and on-line preconcentration inflow injection UV–visible spectrophotometry, *Talanta*, *44*(3), 319–326. doi: 10.1016/s0039-9140(96)02032-2

[13] Abbaspour, A., Baramakeh, L. (2002). Dual-wavelength-correction spectrophotometry for selective determination of Zr, *Talanta*, *57*(4), 807–812. doi: 10.1016/s0039-9140(02)00067-x

[14] Peralta-Zamora, P., Jose Martins, W. (1999). Anomalies in the spectrophotometric and extractive behaviour of zirconium and hafnium: Evidence of a synergistic effect, *Talanta*, *49*(4), 937–941. doi: 10.1016/s0039-9140(99)00090-9

[15] Uysal, U.D., Huseyinli, A.A., Guray, T. (2011). Rapid direct spec-trophotometric determination of zirconium (IV) in alloys with 2,2/3,4-tetrahydroxy-3/-sulpho-5-carboxyazobenzene reagent, *Journal of scientific and industrial research*, 70, 45–50.

[16] Varghese, A., George, L. (2012). Simultaneous first order derivative spectrophotometric determination of vanadium and zirconium in alloy steels and minerals, Spectrochimica Acta Part A Molecular and Biomolecular *Spectroscopy*, 95, 46–52. doi:10.1016/j.saa.2012.04.092

[17] Dedkova, V. P., Shvoeva, O. P., Savvin, S. B., (2013). Sorption–Spectrophotometric Determination of Zirconium and Chromium(VI) from a Single Sample on a Two-Layer Support Using Arsenazo III and 1,5-Diphenylcarbazide, *Journal of Analytical Chemistry*, *68*(2), 117–122. doi:10.1134/S1061934813020068

[18] Karve, M., Rajgor, R. V. (2007). Solid phase extraction of lead on octadecyl bonded silica membrane disk modified with Cyanex302 and determination by flame atomic absorption spectrometry, *Journal of Hazardous Materials*, *141*(3), 607–613. doi: 10.1016/j.jhazmat.2006.07.013

[19] Safavi, A., Iranpoor, N., Saghir, N., Momeni, S. (2006). Glycerol–silica gel: A new solid sorbent for preconcentration and determination of traces of cobalt(II) ion, *Analytica Chimica Acta*, *569*(1), 139–144. doi:10.1016/j.aca.2006.03.079

[20] Suvardhan, K., Kumar, K. S., Rekha, D., Jayaraj, B., Naidu, G. K., Chiranjeevi, P. (2006). Erratum to “Preconcentration and solid-phase extraction of beryllium, lead, nickel, and bismuth from various water samples using 2-propylpiperidine-1-carbodithioate with flame atomic absorption spectrometry (FAAS) *Talanta*, *68*(3), 735–740. https://doi.org/10.1016/j.talanta.2005.05.020

[21] Bulut, V. N., Gundogdu, A., Duran, C., Senturk, H. B., Soylak, M., Elci, L., Tufekci, M. (2007). A multi-element solid-phase extraction method for trace metals determination in environmental samples on Amberlite XAD-2000. *Journal of Hazardous Materials*, *146*(1), 155–163. https://doi.org/10.1016/j.jhazmat.2006.12.013

[22] Tuzen, M., Suylak, M., Elci, L. (2005). Multi-element pre-concentration of heavy metal ions by solid phase extraction on Chromosorb 108. *Analtica Chimica Acta*, *548*(1), 101–108. https://doi.org/10.1016/j.aca.2005.06.005

[23] Firdaus, M.L., Norisuye, K., Sato T., Urushihara, S., Nakagawa, Y., Umetani, S., Sohrin, Y. (2007). Preconcentration of Zr, Hf,Nb, Ta and W in seawater using solid-phase extraction onTSK-8-hydroxyquinoline resin and determination by inductivelycoupled plasma-mass spectrometry, *Analytica Chimica Acta, 583*(2), 296–302. https://doi.org/10.1016/j.aca.2006.10.033

[24] Faghihian, H., Tadi, M. K. (2010). A novel solid-phase extraction method for separation and preconcentration of zirconium, *Microchimica Acta*, *168*(1), 147–152. https://doi.org/10.1007/s00604-009-0273-9.

[25] Baytak, S., Turker, A. R. (2006). Application of ram horn powder (RHP) for the preconcentration and determination of copper in various samples by flame atomic absorption spectrometry. *Journal of Analytical Chemistry*, *61*(5), 483–489. https://doi.org/10.1134/S1061934806050091.

[26] Gode, F., Pehlivan, E. (2007). Sorption of Cr(III) onto chelating b-DAEG-sporopollenin and CEP-sporopollenin resins, *Bioresource Technology*, *98*(4), 904–911. doi:10.1016/j.biortech.2006.02.043.

[27] Pourreza N., Mouradzadegun, A., Mohammadi, S. (2011). Solid phase extraction of zirconium as arsenazo(III) complex on agar and spectrophotometric determination, *Journal of the Iranian Chemical Society*, *8*(4), 951–957. https://doi.org/10.1007/BF03246550

[28] Rezaee, M., Assadi, Y., Millani Hosseini, M. R., Aghaee, E., Ahmadi, F., Berijani, S. (2006). Determination of organic compounds in water using dispersive liquid–liquid microextraction, *Journal of Chromatography A., 1116*(1), 1–9. https://doi.org/10.1016/j.chroma.2006.03.007.

[29] Fatahi, N., Samadi, S., Assadi, Y., Milani Hosseini, M. R. (2007). Solid-phase extraction combined with dispersive liquid–liquid microextraction-ultra preconcentration of chlorophenols in aqueous samples, *Journal of Chromatography A., 1169*(1), 63–69. https://doi.org/10.1016/j.chroma.2007.09.002.

[30] Mohammadi, S. Z., Afzali, D., Taher, M. A., Baghelani, Y. M. (2009). Ligandless dispersive liquid–liquid microextraction for the separation of trace amounts of silver ions in water samples and flame atomic absorption spectrometry determination *Talanta*, *80*(2), 875–879. https://doi.org/10.1016/j.talanta.2009.08.009.

[31] Korestelev, P. P. (1964). [*Preparation of solutions for chemical and analytical works*]. M.: Nauka. (In Russian)/

[32] Bishgin, A. T., (2019). Surfactant-Assisted Emulsification ond Surfactant-Based Dispersive Liquid-Liquid Microextraction Method for Determination of Cu(II) in Food and Water Samples by Flame Atomic Absorbtion Spectrometry, *Journal of AOAC İnternational*, *102*(5), 1516–1522. https://doi.org/10.1093/jaoac/102.5.1516.

[33] Agarwal, K., Patel, K. S., Shrivas, K. (2009). Development of surfactant assisted spectrophotometric method for determination of selenium in waster water samples, *Journal of Hazardous Materials*, *161*(2-3), 1245–1249. https://doi.org/10.1016/j.jhazmat.2008.04.082.

[34] Shrivas, K., Dewangan, K. Ahmed, A. (2016). Surfactant-based dispersive liquid-liquid microextraction for the determination of zink in environmental water samples using flame atomic absorbtion spectrometry. *Analytical Methods*, *8*(27), 5519–5525. https://doi.org/10.1039/C6AY01277A.