Bull. Chem. Soc. Ethiop. **2016**, 30(3), 325-332.
Printed in Ethiopia
DOI: http://dx.doi.org/10.4314/bcse.v30i3.1
ISSN 1011-3924

APPLICATION OF 4-(2-PYRIDYLAZO)RESORCINOL FOR FLOTATION-SPECTROPHOTOMETRIC DETERMINATION OF IRON

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(Received June 9, 2015; revised March 21, 2016)

ABSTRACT. Optimum conditions for flotation-spectrophotometric determination of iron with 4-(2-pyridylazo)resorcinol (PAR) based on a 1:2 Fe^{II}-PAR complex were found to be as follows: flotation solvent (chloroform), shaking time (2 min), pH (4.5±0.5), concentration of PAR (2.0×10^{-4} mol L^{-1}), reducing agent (hydroxylamine hydrochloride), solvent for the floated compound (dimethylsulphoxide, DMSO), wavelength for spectrophotometric measurements (718 nm), and volumes of the organic solvents (5 mL of chloroform and 3 mL of DMSO). Calibration graphs were compared for different volumes of the aqueous phase – 10 mL and 40 mL; the corresponding linear ranges were 0.30–1.3 μg mL^{-1} and 0.25–1.0 μg mL^{-1}. The iron content was successfully determined in soil samples, reference standard materials (PS-1, COOMET No. 0001-1999 BG, SOD No. 310a-98; PS-2, COOMET No. 0002-1999 BG, SOD No. 311a-98; and PS-3, COOMET No. 0003-1999 BG, SOD No. 312a-98) and zinc sulfide concentrates.

KEY WORDS: Iron(II), Fe-PAR complex, Flotation, Spectrophotometry, Soils, Zinc sulfide concentrates

INTRODUCTION

4-(2-Pyridylazo)resorcinol (PAR) is one of the most popular analytical reagents. It forms colored complexes with many metal ions and can be used for their spectrophotometric determination. A well-known disadvantage of this reagent is its insufficient selectivity [1]. Commonly used approaches for increasing the selectivity are masking, precise pH control, introduction of additional reagents for the formation of ternary/multicomponent complexes, derivative spectrophotometry, and application of separation/preconcentration steps, which often demand expensive equipment, high running costs, and well-trained personnel. Usually, a combination of these approaches is needed. As a result, the procedures are complex, time consuming, and expensive.

Complexes of Fe^{II} or Fe^{III} and PAR have been investigated and by many authors [2-11]. Sometimes, the authors' opinions on various issues concerning the composition, iron oxidation state, or solubility of the complexes in different solvents are contradictory. For example, Hoshino and Yotsuyanagi [3] claim that the neutral Fe^{II}-PAR chelate $[Fe(HPAR)_2]^0$ can be extracted in chloroform. Arya *et al.* [5], in their turn, present results showing that the absorbance of this complex in the chloroform phase is zero after the extraction process. Our preliminary investigations on water-chloroform extraction systems containing Fe^{II} and PAR were in accordance with Arya *et al.* [5]. They showed that only protonated PAR species (H_2PAR) [12] are extracted in this solvent. Actually, the reddish-purple Fe^{II}-PAR complex accumulates during shaking on the phase boundary (and on the wall of the separating funnel), thus providing an opportunity to separate Fe^{II} quantitatively.

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In this work we propose a simple, low-cost, and fast spectrophotometric procedure for determining iron based on dissolving the "floated" Fe^{II}-PAR complex in appropriate solvent (dimethylsulfoxide, DMSO) and measuring the absorbance at a wavelength (λ = 718 nm) where the spectral interferences are limited. To the best of our knowledge, PAR has never been applied for flotation-spectrophotometric determination of any element in real samples. Previous investigations of two of us [13] were the first attempt in this area.

EXPERIMENTAL

Reagents and instruments

Stock solutions (1 mg mL^{-1}) of iron(II) and iron(III) were prepared by dissolving $(NH_4)_2SO_4 \cdot FeSO_4 \cdot 6H_2O$ and $(NH_4)_2SO_4 \cdot Fe_2(SO_4)_3 \cdot 12H_2O$ in distilled water containing H_2SO_4 [14, 15]. Working solutions with a concentration of 2.2×10^{-4} mol L^{-1} were obtained by a suitable dilution of the standardized stock solutions with distilled water. The PAR solution (2×10^{-3} mol L^{-1}) was prepared by dissolving an appropriate amount of PAR (96%, Sigma-Aldrich Chemie GMBH, Steinheim, Germany) in slightly alkalized distilled water. Freshly prepared aqueous solutions (50 mg mL^{-1}) of hydroxylamine hydrochloride or ascorbic acid were used for the reduction of Fe^{III} to Fe^{II} [10, 14, 15]. The organic solvents were chloroform (redistilled) and dimethylsulfoxide (DMSO; Sigma-Aldrich, ≥99.9%). The acidity of the aqueous medium was set by the addition of buffer solution, prepared by mixing 2.0 mol L^{-1} aqueous solutions of CH_3COOH and NH_4OH. The resulting pH was checked by a Hanna HI 83141 pH meter (Romania). A Camspec M508 spectrophotometer (United Kingdom), equipped with 10 mm path-length cells, was used for the absorbance measurements.

Procedure for establishing the optimum flotation-spectrophotometric conditions

Aliquots of iron solution, reducing agent solution, PAR solution, and buffer solution (3 mL; pH ranging from 3.5 to 7.5) were introduced into 125-mL separatory funnels. The resulting solutions were diluted with distilled water to a total volume not higher than 100 mL. Then 5 mL of a water-immiscible organic solvent (e.g. chloroform) were added and the funnels were shaken for a fixed time (5-180 s). After separation of the phases, they were both carefully removed, leaving the precipitate accumulated on the wall of the funnels. Fixed amounts (2-5 mL) of a polar organic solvent (e.g. DMSO) were added to dissolve the complex. Portions of the obtained colored solutions were transferred into cells and the absorbances were measured against blanks.

Analytical procedure

An aliquot of the analyzed sample solution was placed in a separatory funnel. A 1.0 mL aliquot of the hydroxylamine hydrochloride solution, 1.0 mL of the PAR solution, and 3.0 mL of the buffer solution (pH 4.5) were added. The resulting solution was diluted with distilled water to a total volume of 10 mL. A 5 mL volume of chloroform was added and the funnel was shaken for 2 min. After separation of the phases, they were both carefully removed, leaving the precipitate accumulated on the wall of the funnel. A 3 mL volume of DMSO was added to dissolve the complex. A portion of the obtained solution was transferred into a cell. The absorbance was measured at 718 nm against DMSO and the iron concentration was found from a calibration graph.

RESULTS AND DISCUSSION

It is known that a neutral chelate complex can be formed by mixing aqueous solutions of Fe^{II} and PAR [5, 8, 10]. Our optimization experiments for the flotation-spectrophotometric

determination of the total iron included the following steps: (i) choice of a flotation solvent and a solvent for dissolution of the floated compound; (ii) choice of wavelength for spectrophotometric measurement; (iii) choice of pH of the aqueous phase; (iv) choice of PAR concentration; (v) choice of shaking time; (vi) choice of a reducing reagent for Fe^{III}; (vii) choice of volume of the organic solvents; (viii) choice of volume of the aqueous phase; and (ix) finding a region where the calibration graph is linear. Step 6 was performed with Fe^{III} solutions and the results were compared with these for Fe^{II} solutions. Fe^{II} was used in all remaining steps.

Choice of solvents

Several water-immiscible solvents were tested for the flotation of the Fe^{II}-PAR complex: chloroform, 1,2-dichloroethane, dichloromethane, benzene, toluene, carbon tetrachloride, hexane and cyclohexane. Chloroform was the most suitable flotation solvent since it ensured efficient separation of the complex. This solvent was successfully used in our previous paper [13] and in the work of Shabazi *et al.* [16].

The floated Fe^{II}-PAR complex can be dissolved in polar solvents such as DMSO, methanol, ethanol, n-butanol, and acetone. The most polar DMSO (dipole moment of 3.96 D) was used in our experiments. It is not volatile and the resultant intensive red-violet coloration remains stable for a long time (at least 2 days).

Absorption spectra

Spectra of the complex and blank in DMSO are shown in Figure 1. The complex has three maxima. The most important are these at 498 nm and 718 nm. As might be expected [2, 10], the first maximum is more intense. However, the second one is more promising from practical point of view since (i) the absorbance of the blank is practically zero (curve 2) and (ii) the selectivity towards some metal ions can be higher [10].

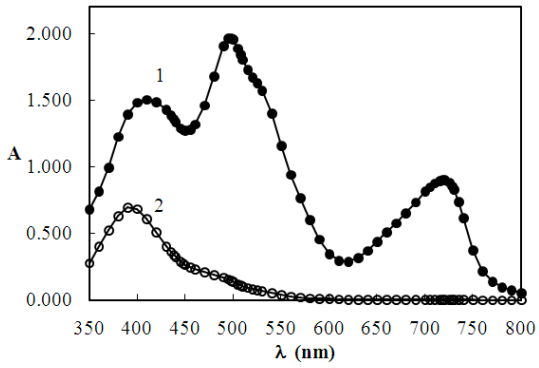

Figure 1. Absorption spectra of the Fe^{II}-PAR complex (curve 1) and the blank (curve 2) in DMSO. $C_{Fe} = 2.2\times10^{-5}$ mol L^{-1}, $C_{PAR} = 2.0\times10^{-4}$ mol L^{-1}, pH = 4.5 (ammonium-acetate buffer), $V_{aq.\ phase}$ =10 mL, V_{DMSO} = 3 mL.

Effect of pH

The effect of pH of the aqueous phase on the absorbance is illustrated in Figure 2. We used ammonium-acetate buffers to control pH. The decrease in absorbance at pH-values less than ca. 4.0 can be explained by the predominance of protonated PAR species in the solution. The decrease in absorbance at pH-values higher than ca. 5.5 can be attributed to hydrolysis.

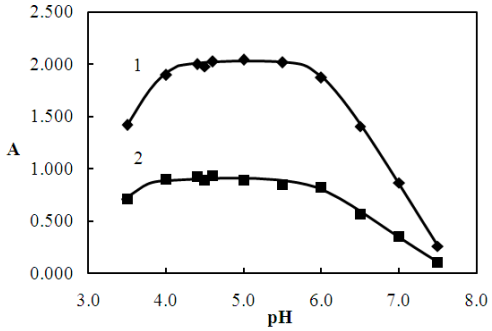

Figure 2. Effect of pH of the aqueous phase on the absorbance of the complex at 498 nm (curve 1) and 718 nm (curve 2). $C_{Fe} = 2.2\times10^{-5}$ mol L^{-1}, $C_{PAR} = 2.0\times10^{-4}$ mol L^{-1}, $V_{aq.\ phase}$ = 10 mL, V_{DMSO} = 3 mL.

Effect of PAR concentration

The effect of PAR concentration on the absorbance is shown in Figure 3. It can be seen that (i) the complex is stable (there is a sharp break in the saturation curve); (ii) the absorbance at 498 nm slightly decreases at PAR concentrations higher than 1.0×10^{-4} mol L^{-1}, while the absorbance at 718 nm is not affected by high PAR concentrations. We performed our further experiments with PAR concentration of 2.0×10^{-4} mol L^{-1}. This concentration provides sufficient PAR-to-Fe excess even when the solution contains foreign ions prone to form complexes with PAR. In addition, the maintenance of $C_{PAR} = 2.0\times10^{-4}$ mol L^{-1} allows performing reliable measurements at both wavelengths.

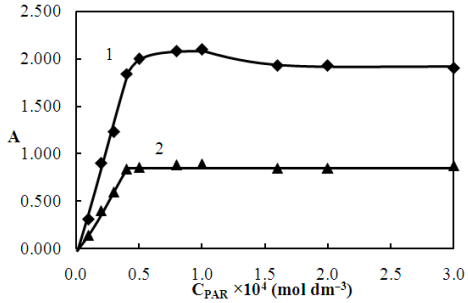

Figure 3. Effect of the PAR concentration of the absorbance in DMSO at 498 nm (curve 1) and 718 nm (curve 2). $C_{Fe} = 2.2\times10^{-5}$ mol L^{-1}, pH = 4.5, $V_{aq.\ phase}$ = 10 mL, V_{DMSO} = 3 mL.

Effect of shaking time

Experiments with different shaking times were performed (Figure 4). The results show that 1.0-1.5 min are sufficient for the quantitative formation and flotation of the complex. For safety reasons the shaking period in our further experiments was 2 min.

Choice of reducing agent

Both Fe^{II} and Fe^{III} form complexes with PAR at slightly acidic conditions. The Fe^{II}-PAR complex described by Arya *et al.* [5] is neutral, well-extractable in polar organic solvents (n-butanol) and has an analytical application for the spectrophotometric determination of ascorbic

acid–a reducing agent for Fe^{III}. Since only Fe^{II} form a complex with PAR that quantitatively can be isolated by flotation, it is important to add appropriate reducing agent before determining the total iron content. The literature [5, 14, 15] describes details on the Fe^{III} reduction with hydroxylamine hydrochloride and ascorbic acid. That is why we checked the applicability of these reagents at our optimum conditions. The results obtained with 1 mL portions of freshly prepared 50 mg mL^{-1} solutions showed that they both can be used successfully. Further, we used hydroxylamine hydrochloride because of its lower price and considerations described by Ferreira and Nano [15] (greater stability of its solutions).

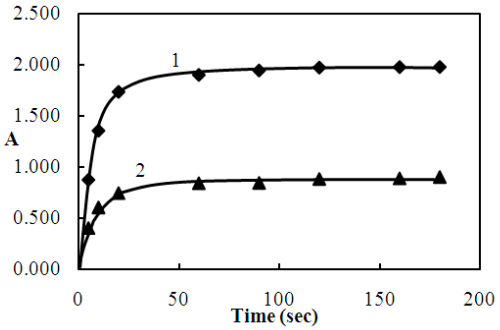

Figure 4. Effect of shaking time on the absorbance of the complex at 498 nm (curve 1) and 718 nm (curve 2). $C_{Fe(II)} = 2.2\times10^{-5}$ mol L^{-1}, $C_{PAR} = 2.0\times10^{-4}$ mol L^{-1}, pH = 4.5, $V_{aq.\ phase}$= 10 mL, V_{DMSO} = 3 mL.

Volumes of the solvents

The selected volume of the added flotation solvent (chloroform) was 5 mL, as in the work of Shabazi *et al.* [16]. We experimented with different volumes of the aqueous phase. The course of the obtained experimental curves (Figure 5) suggested that the increase in the volume over 40 mL is pointless.

The optimum DMSO volume was 3 mL. Smaller volumes resulted in insufficient repeatability of the results.

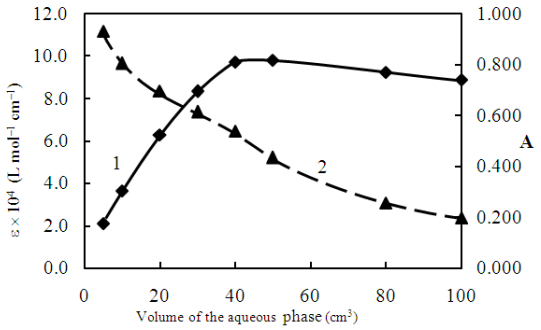

Figure 5. Effect of the volume of the aqueous phase on the conditional molar absorptivity ε (curve 1, left ordinate) and the absorbance of the complex at 718 nm (curve 2, right ordinate). $C_{Fe} = 2.2\times10^{-5}$ mol L^{-1}, $C_{PAR} = 2.0\times10^{-4}$ mol L^{-1}, pH = 4.5, V_{DMSO} = 3 mL.

Effect of foreign ions

Various ions which are often found together with iron in natural and industrial samples were used to test the selectivity of the proposed procedure. Their effect at λ = 718 nm is presented in

Table 1. Parallel measurement of the absorbance at 498 nm (against blank) showed that the selectivity at this wavelength is lower for the following ions: Al^{III}, Ba^{II}, Cd^{II}, Ce^{III}, Cr^{III}, Cu^{II}, In^{III}, Mn^{II}, Ni^{II}, Zn^{II}, and Zr^{IV}.

Table 1. Tolerance limits* of foreign ions in determination of 12 µg of Fe^{II} by the developed procedure.

Foreign ion, FI	FI to Fe^{II} ratio tolerance limit
NH_4^+, K^+, Na^+, Ca^{2+}, Ce^{III}, Cd^{II}, Cr^{III}, Mg^{II}, Zn^{II}, SO_4^{2-}, Br^-, HPO_4^-, HCO_3^-, Cl^-, NO_3^-, PO_4^{3-}, $H_2PO_4^-$	1000**
Al^{III}, Sr^{II}	500
Pb^{II}	250
Re^{VII}, Mn^{II}, Sn^{II}, Tl^{I}, CO_3^{2-}	100
Ba^{II}, Mo^{VI}, U^{VI}, W^{VI}, In^{III}	50
Ag^{I}, V^{IV}	10
Cu^{II}, Zr^{IV}	3
Nb^{V}, Ni^{II}	1

Conditions: $C_{PAR} = 2.0\times10^{-4}$ mol L^{-1}, pH = 4.5, λ = 718 nm, $V_{chloroform}$ = 5 mL, $V_{aq.\ phase}$ = 10 mL, V_{DMSO} = 3 mL. *Defined as the mass ratio of FI and Fe^{II} that cause a relative error less than ±3%. **Above which was not considered.

Calibration graph parameters and precision and accuracy

Calibration graphs were constructed at the optimal conditions (Figure 6) for different volumes of the aqueous phase: 10 mL and 40 mL. The results suggests that (i) the volume of the aqueous phase has a little effect on the lower limit of the linear range; (ii) the intercepts in both cases are statistically different form zero (Table 2).

Table 2. Statistical analysis of the calibration graphs

Parameters	Volume of the aqueous phase	
	10 mL	40 mL
Linear range (µg mL^{-1})	0.30–1.3	0.25–1.0
Slope ± standard deviation (A μg^{-1} mL)	0.778±0.012	3.012±0.055
Intercept ± standard deviation (A)	-0.143±0.009	-0.47±0.04
Correlation coefficient*	0.9994	0.9992

Conditions: $C_{PAR} = 2.0\times10^{-4}$ mol L^{-1}, pH = 4.5, λ = 718 nm, $V_{chloroform}$ = 5 mL, V_{DMSO} = 3 mL. *based on 7 calibration samples.

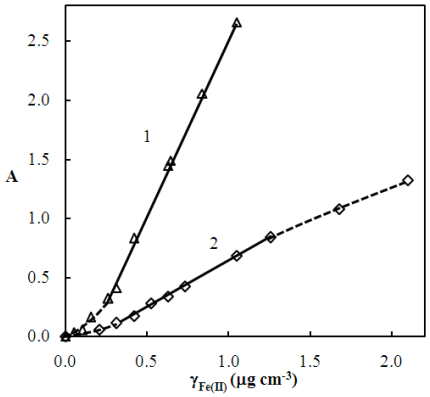

Figure 6. Calibration graphs for different volumes of the aqueous phase: 40 mL (1) and 10 mL (2). $C_{PAR} = 2.0\times10^{-4}$ mol L^{-1}, pH = 4.5, λ = 718 nm, $V_{chloroform}$ = 5 mL, V_{DMSO} = 3 mL.

The accuracy and precision of the proposed procedure were evaluated by the determination of iron in three standard soil samples. The following samples were analysed after digestion with aqua regia (ISO 11466): light alluvial-deluvial meadow soil PS-1, COOMET No. 0001-1999 BG, SOD No. 310[a]-98 (Soil 1); light meadow cinnamonic soil PS-2, COOMET No. 0002-1999 BG, SOD No. 311[a]-98 (Soil 2); and light alluvial-deluvial meadow soil PS-3, COOMET No. 0003- 1999 BG, SOD No. 312[a]-98 (Soil 3). The results of analysis (Table 3) agree well with the certified values. The relative standard deviation (RSD) was lower than 3.1%.

Determination of iron in zinc concentrates

The content of iron in zinc sulfide concentrates is essential for the process of zinc production [17]. This content is typically in the range 3-18% [18], but if it exceeds 8% [19], about 10% of zinc passes into the zinc cake due to the obtaining of zinc ferrite, insoluble in dilute solutions of sulfuric acid.

Table 3. Determined and reference iron contents in soil samples (n = 3) and zinc sulfide concentrates* (n = 4).

Sample	Iron content, %			RSD %
	Certified	Sulphocyanate method	Proposed method	
Soil 1:PS-1, COOMET № 0001-1999 BG, SOD № 310a-98	2.78±0.17	-	2.7	3.1
Soil 2: PS-2, COOMET № 0002-1999 BG, SOD № 311a-98	2.88±0.12	-	2.9	2.4
Soil 3: PS-3, COOMET № 0003-1999 BG, SOD № 312a-98	3.19±0.13	-	3.1	2.0
Zinc concentrate 1	-	8.4±0.2	8.3	1.9
Zinc concentrate 2	-	12.4±0.3	12.7	1.4
Zinc concentrate 3	-	12.9±0.3	12.8	1.5

*Samples from KCM S.A.- Plovdiv (Non-ferrous metals smelter).

In this context, we used the developed procedure for determination of iron content in zinc sulfide concentrates. The results are shown in Table 3. They are statistically indistinguishable from these obtained by the sulfocyanate method [20] which is often preffered for routine analysis of such kind of samples.

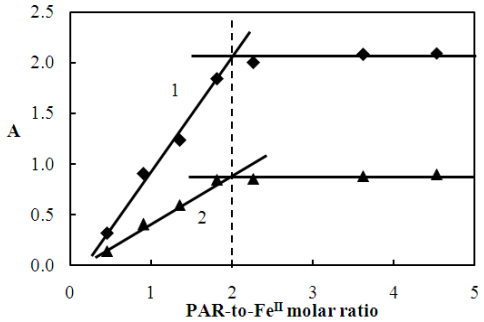

Figure 7. Determination of the PAR-to-Fe^{II} ratio by the molar ratio method. λ = 498 nm (1) and λ = 718 nm (2). The experimental conditions are given in Figure 3.

Composition of the complex

The molar PAR-to-Fe^{II} ratio was determined by the molar ratio method [21] (Figure 7) and the straight-line method of Asmus [22]. The results suggest a composition of 2:1 (PAR:Fe^{II}) which

corresponds to the formula $[Fe(HPAR)_2]$ [8, 10], where $HPAR^-$ is the monoprotonated form of PAR [12].

CONCLUSION

Fe^{II} forms a coloured complex with PAR which is appropriate for flotation separation and spectrophotometric determination of iron. In the present work we found conditions at which the analysis is inexpensive, fast, selective, sensitive, and precise. Many common sources of errors (e.g. addition of reagents for masking or formation of ternary/multicomponent complexes, high absorbance of the blank, narrow intervals of optimal reagents concentrations and pH, and application of additional separation steps), which can reduce the reliability of the determination, are avoided due to the simplicity of the proposed system based on a stable complex absorbing at a spectral region where the spectral interferences are limited.

ACKNOWLEDGEMENTS

This study was funded through the NP 05/2014 (Trakia University) and NI-15-HF001 (Plovdiv University "Paisii Hilendarski") projects. The authors are grateful to Eng. Irina Mincheva and Maria Patronova (from the Central Analytical Laboratory of KCM S.A. – Plovdiv) for their valuable assistance.

REFERENCES

1. Stefanova, T.S.; Simitchiev, K.K.; Gavazov, K.B. *Chem. Pap.* **2015**, 69, 495.
2. Nonova, D.; Evtimova, B. *J. Inorg. Nucl. Chem.* **1973**, 35, 3581.
3. Hoshino, H.; Yotsuyanagi, T. *Talanta* **1984**, 31, 525.
4. Dolezal, J.; Sommer, L. *Coll. Czech. Chem. Commun*. **1994**, 59, 2209.
5. Arya, S.P.; Mahajan, M.; Jain, P. *Anal. Chim. Acta* **2001**, 427, 245.
6. Tokalioglu, S.; Kartal, S. *Bull. Korean Chem. Soc*. **2006**, 27, 1293.
7. Ghasemi, J.; Peyman, H.; Meloun, M. *J. Chem. Eng. Data* **2007**, 52, 1171.
8. Karipcin, F.; Kabalcilar, E. *Acta Chim. Slov*. **2007**, 54, 242.
9. Pouretedal, H.R.; Sononi, P.; Keshavarz, M.H.; Semnani, A. *Chemistry* **2009**, 18, 22.
10. Gong, Z.-j.; Chen, G.-h.; Zhang. X.-s. *ICBBE 2009*, 11-13 June 2009, Beijing, DOI: 10.1109/icbbe.2009.5162862.
11. Susanto, D.; English, A.M.; Sharma, R.; Kwong, E. *J. Mass Spectrom*. **2011**, 46, 508.
12. Marić, L.; Široki, M. *Anal. Chim. Acta* **1996**, 318, 345.
13. Toncheva, G.K.; Gavazov, K.B. *Chem. J.* **2013**, 3, 122.
14. Marczenko, Z.; Balcerzak, M. *Separation, Preconcentration and Spectrophotometry in Inorganic Analysis*, Elsevier: Amsterdam; **2000**; p 228.
15. Ferreira, S.L.C.; Nano, R.M.W. *Talanta* **1994**, 41, 1937.
16. Shabazi, Z.; Dadfarnia, S.; Shabani, A.M.H.; Jafari, A.A. *J. Anal. Chem*. **2008**, 63, 446.
17. Boyanov, B.; Peltekov, A.; Petkova, V. *Thermochim. Acta* **2014**, 586, 9.
18. Loan, M.; Newman, O.M.G.; Cooper, R.M.G.; Farrow, J.B.; Parkinson, G.M. *Hydrometallurgy* **2006**, 81, 104.
19. Boyanov, B.; Sandalski, M.; Ivanov, K. *World Acad. Sci. Eng. Technol*. **2011**, 73, 326.
20. Umland, F.; Janssen, A.; Thierig, D.; Wünsch G. *Kompleksny'e Soedineniya v Analiticheskoi Khimii. Teoriya i Praktika Primeneniya (Complex Compounds in Analytical Chemistry)*, Mir: Moscow; **1975**; p 235.
21. Yoe, J.H.; Jones, A.L. *Ind. Eng. Chem. Anal*. Ed. **1944**, 16, 111.
22. Asmus, E. *Fresenius' J. Anal. Chem.* **1960**, 178, 104.