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Determination of palladium by on-line flow-injection direct spectrophotometry in environmental samples using 2,2′-furyldioxime as a chelator

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ABSTRACT

A new, sensitive, and accurate on-line spectrophotometric method for the determination of palladium was developed. The method is based on the reaction between Pd(II) and 2,2′-furyldioxime in nitric acid medium. The absorbance of the complex is spectrophotometrically measured at 410 nm with a diode-array detector. Several factors that influence the analytical performance of the method such as acidity, flow rates of the reagent and sample solutions, concentration of the reagent, and effect of interfering ions were investigated. The calibration curve was obtained in the range of 0.01–10.0 mg L^{-1} Pd(II). The detection limit was 0.1 μg L^{-1} while the relative standard deviation of the method was found to be 1.2% ($n=13$) at 4.0 mg L^{-1} Pd(II) level. The sample throughput was 275 h^{-1}. The method was successfully applied to the determination of palladium in catalytic converter, anodic slime, road sediment, ore, and water samples.

1. Introduction

Noble metals have low crustal abundance (approximately 1 ng g^{-1}), yet they are components of different geological samples such as rocks, ores, concentrates, minerals, soils, and sediments. In the earth's crust, Pd usually occurs in its native form associated with one or more of the other platinum group elements (PGEs) along with gold, iron, copper, nickel, and chromium [1]. Palladium is an element of increasing importance in today's industries. The annual production of palladium is estimated to be 195 t; the majority of this is used in autocatalysts (55%), with other uses including electronics (16%), jewelry (11%), dental medicine (8%), investment (5%), the chemical industry (4%) and in the purification of hydrogen gas [2,3].

The low concentration of Pd, together with the high concentration of interfering matrix components, often requires a preconcentration step combined with a matrix separation; this allows an accurate and precise determination of Pd in samples with very low analyte content, such as airborne particulate matter and water. Furthermore, it enables the distinguishing of contaminated from background levels [4].

Recently, on-line solid phase extraction techniques have been described for the separation and preconcentration of Pd and Pt using polyamine Metalfix-Chelamine resin [5], and Pd using Amberlite XAD-16 resin functionalized with 2-[2-(5-thiol-1,3,4-thiadiazolyl)]-azonaphthol (TTAN) reagent [6]. Si et al. used 2-(2-quinolylazo)-5-dimethylaminoaniline as a chromogenic reagent [7] and Kumar et al. reported the use of 2-hydroxy-3-methoxy benzaldehyde thiosemicarbazone for the spectrophotometric determination of palladium [8]. Dimitrova et al. described a flow-injection on-line separation/preconcentration technique and ETAAS detection of palladium in a tunnel dust matrix utilizing a cyclic polyether, 18-crown-6 [9]. Shah and Devi synthesized a poly (vinylpyridine)-based chelating resin anchored with dithizone for the separation and preconcentration of palladium(II) and platinum (IV) from gold(III) and nickel(II).

Fire-assay [10], coprecipitation [11], sorption and ion exchange [12], liquid–liquid extraction [13,14], solid-phase extraction [15,16], dispersive liquid–liquid microextraction [17], and cloud point extraction [18,19] techniques have been developed and applied for the preconcentration/separation of palladium prior to its detection. However, many preconcentration approaches involve tedious procedures with multiple steps.

Many analytical techniques, such as flame atomic absorption spectroscopy [20–23], electrothermal atomic absorption spectroscopy [24–25], inductively coupled plasma–atomic emission spectroscopy [26], inductively coupled plasma–mass spectrometry [27], and voltammetry [28], are actually available to determine palladium in various samples.

From a practical point of view, for application in the in-situ analysis of various environmental samples and natural waters, a method must be rapid, simple and without preconcentration step.

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In the case of palladium, we usually find that concentrations below 5–10 $\mu g\ L^{-1}$ and detection limits of about 1–5 $\mu g\ L^{-1}$ are required. This sensitivity may be reached only with a preconcentration step. Therefore, the preconcentration step is not easily applicable to *in-situ* analysis; consequently, the above mentioned methods are not suitable for practical environmentalists [4–8,29–35].

Actually, there is no direct method with the required sensitivity, and though the flow-injection spectrophotometric determination of palladium has received much attention, the detection limits are normally found at around $\mu g\ L^{-1}$ levels [13].

This work describes a rapid, sensitive, and cost-effective flow-injection method for the determination of palladium based on the spectrophotometric detection of the intense yellow complex which is formed by the reaction between Pd(II) and 2,2′-furyldioxime in 3 mol L^{-1} HNO_3 medium. To the best of our knowledge, a direct spectrophotometric flow-injection method for the determination of palladium in various samples is not yet available in the literature.

2. Experimental

2.1. Instrument

The absorption spectrum was recorded on a Hitachi model 150-20 UV–vis spectrophotometer (Hitachi, Ltd., Japan).

A peristaltic pump (Ismatec SA, Glattbrugg, Switzerland) was used for the flow-injection manifold. The sample solution was injected via a two-way valve with a 50 μL sample loop (7125 Cotat, California, Rheodyne). Tygon tubings (0.64 mm i.d.) were used as the flow lines for nitric acid and 2,2′-furyldioxime solutions, and Y-shaped connectors for merging the reagent streams. A home-made mixing coil with optimized length was prepared from PTFE tubing. The analytical signals were acquired by using a photo diode array detector (DAD) equipped with a chart recorder (D-2500 Chromato-Integrator, Merck Germany). The home-made FI manifold used is shown schematically in Fig. 1.

2.2. Reagents and standard solutions

All chemicals were of analytical reagent grade and used without further purification. The palladium standard solution (1000 mg L^{-1}) was purchased from BDH Spectrosol (England). Working solutions were prepared by diluting the stock solutions with deionized water. A 0.1% (w/v) solution of 2,2′-furyldioxime (Fluka, Germany) was prepared by dissolving 0.1 g of the reagent in ethanol and diluting to 100 mL with 3 mol L^{-1} HNO_3. In order to ensure the accuracy of the recommended procedure, a certified reference material, (CDN-PGMS-10, CDN Resource Laboratories Ltd., British Columbia, Canada), which contains platinum group metals was analyzed. Its certified values are: 10.99 ± 0.73 mg kg^{-1} for Pd, 0.307 ± 0.044 mg kg^{-1} for Au, and 2.93 ± 0.20 mg kg^{-1} for Pt. All laboratory glassware was cleaned by using a nitric acid solution, and then rinsing several times with deionized water.

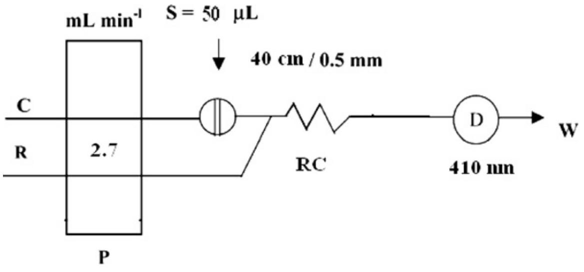

Fig. 1. Schematic diagram of direct spectrophotometric flow-injection determination of palladium(II). P: Peristaltic pump (at flow rate of each stream, 2.7 mL min^{-1}), C: Carrier (3 mol L^{-1} HNO_3), R: Reagent (0.1% 2,2′-furyldioxime, w/v), RC: Mixing coil (40 cm), S: Sample injection valve (injection loop, 50 μL), D: Diode array detector, W: Waste, Number of injection cycle: 275 h^{-1}, Injection cycle time: 13 s.

2.3. Recommended procedure

The flow-injection system consists of the carrier stream (nitric acid, C) and the reagent (2,2′-furyldioxime, R) streams, and they merge with each other after the sample injection valve. 50 μL of the sample solution, containing 0.01 mg L^{-1} to 10 mg L^{-1} Pd(II), is injected directly into the carrier stream. The water-soluble complex (λ_{max} at 410 nm) was formed during the passage of the mixture through a 40-cm reaction coil (RC). The cycle time was about 13 s for one run. Therefore, approximately 275 injections are possible in 1 h. The transient signal from the detector was recorded as the peak area, which was proportional to the palladium concentration in the sample, and this was used for all the measurements. The recorded peaks were sharp and the baseline was stable. Five replicate injections per sample were made in all instances. The signal was measured by the DAD detector at 410 nm and recorded on the chart recorder. The flow-injection on-line system with a two-channel peristaltic pump is illustrated in Fig. 1.

2.4. Sample preparation

To PTFE beakers which contained 0.1 g portions of the CDN-PGMS-10 certified reference material were added 10 mL of concentrated HNO_3 and 3 mL of concentrated H_2O_2. The mixture was heated until the solution became transparent, and heating continued to near dryness. The residue was dissolved in 25 mL of 3 mol L^{-1} HNO_3, and then the procedure was applied to these aqueous samples [3,6,17,32].

A 0.1 g crushed and ground portion of the converter, and 1.0 g portions of anode slime, ore, and road sediment samples were weighed into 100 mL beakers. In order to facilitate decomposition, 20 mL of *aqua regia* was added to the beaker and the mixture was heated to near dryness. Then, 10 mL of *aqua regia* was again added to the moist residue and the mixture was evaporated to dryness. The volume of the filtrate was completed to 25 mL with 3 mol L^{-1} HNO_3 and used for the determination of Pd(II) [3,6,17,32]. Blank determinations were carried out in the same way. The determination of Pd(II) ions in the final measurement solutions was performed by the proposed flow-injection spectrophotometric method.

Tap water samples were analyzed without pre-treatment. All the other water samples were filtered through Whatman no. 41 filter paper and subsequently analyzed by the proposed method.

3. Results and discussion

3.1. Formation and absorption spectra of the Pd(II)–2,2′-furyldioxime complex

Pd(II) reacts with 2,2′–furyldioxime and forms a yellow-colored complex in 3 mol L^{-1} HNO_3 medium. Stopped-flow experiments showed that the completion of the complex-formation was realized within a few seconds. The complex exhibits maximum absorbance at around 410 nm. At this wavelength, the reagent blank has practically negligible absorbance (≈0.002). The sensitivity increased at least 10-fold in the FI system due to the distribution of the complex compared with the direct measurement. The absorption spectra of the complex which formed between palladium(II) and 2,2′–furyldioxime were recorded on a Hitachi model

150-20 UV–vis spectrophotometer in the wavelength range 200 nm to 700 nm. In order to achieve the greatest sensitivity, the measurements were made at 410 nm in further studies.

3.2. *Effect of acidity*

The acidity of the sample solution plays a unique role in metal-chelate formation. So, in order to evaluate the effect of acidity on the determination of Pd(II) (0.5 mg L^{-1}), sample solutions were acidified with 0.01 mol L^{-1} to 4 mol L^{-1} HNO_3, H_2SO_4 and/or HCl, and processed according to the recommended procedure. As can be seen from Fig. 2, the results showed that the absorbances are kept almost constant by increasing acidity, i.e., from 0.01 to 2 mol L^{-1} HNO_3. In 3 mol L^{-1} HNO_3 medium the maximum absorbance was observed and then a decrease in absorbance occurred. Consequently, 3 mol L^{-1} HNO_3 was selected for the optimum acidity for further experiments. The results, obtained with H_2SO_4 were lower with respect to HNO_3. Also, the HCl medium gave low results probably due to the formation of stable Pd(II)-chloro complexes. This is because the dissociation constant of the chloropalladite anion, $PdCl_4^{2-}$, is 6×10^{-14} [36]. Consequently, the formation constant of the $PdCl_4^{2-}$ complex is probably higher than that of the Pd(II)-2,2′-furyldioxime complex.

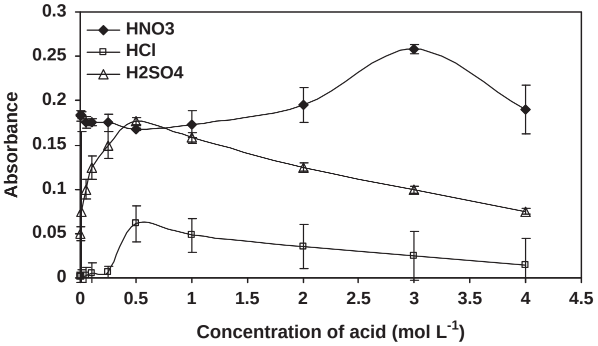

Fig. 2. Effect of acidity of the sample solution on the Pd(II) signals.

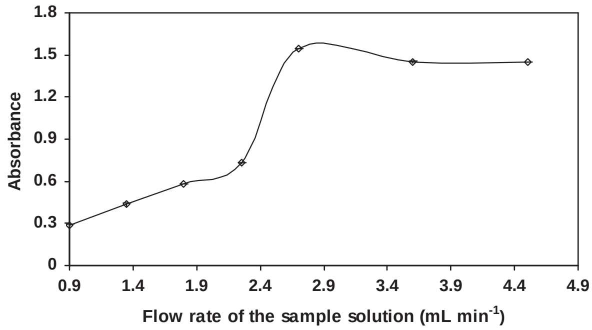

Fig. 3. Effect of the flow rate of the sample solution on the Pd(II) signals ($n=5$).

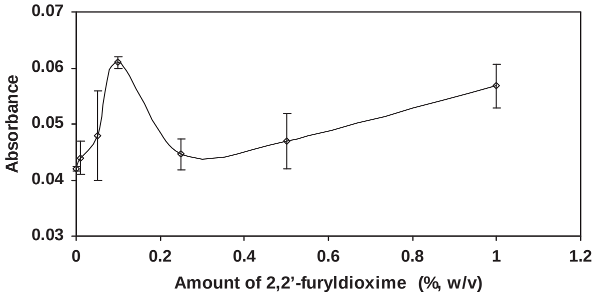

Fig. 4. Effect of the concentration of 2,2′-furyldioxime on the Pd(II) signals ($n=5$).

3.3. *Flow rate of sample solution*

Flow rate of the sample solution plays an important role in the determination of Pd(II) by the flow-injection system. The analyte signals increased with the increasing flow rate of the sample solution up to 2.7 mL min^{-1}; thereafter the analytical signals were almost constant. Thus, the optimum flow rate for the sample solution was chosen as 2.7 mL min^{-1} for the further experiments (Fig. 3).

3.4. *Effect of 2,2′-furyldioxime concentration*

The effect of various concentrations of 2,2′-furyldioxime solutions (0.001–0.02%, w/v) on the absorbance signals (as peak area) of the palladium–2,2′-furyldioxime complex was examined. As can be seen from Fig. 4, the best results were obtained with a 0.1% solution of 2,2′-furyldioxime. After from this point, the absorbance first decreased and then increased gradually again, but low repeatability was observed. For this reason, this concentration of the reagent was chosen as optimum.

3.5. *Effect of mixing coil length*

The studies were carried out with various lengths of mixing coil changing between 0 and 60 cm. The influence of mixing coil

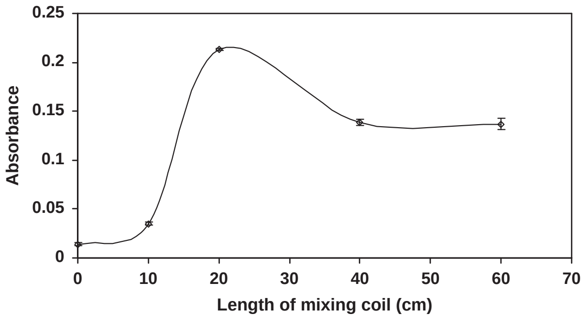

Fig. 5. Effect of the length of the mixing coil ($n=5$).

Table 1
Effect of foreign ions on the determination of 0.5 mg L^{-1} Pd(II) using the proposed direct on-line system ($n=5$).

Ions	Added as	Concentration (mg L^{-1})	Recovery (%)
Na^+	$NaNO_3$	20,000	100 ± 1
K^+	KNO_3	4000	98 ± 1
Ca^{2+}	$Ca(NO_3)_2 \cdot 4H_2O$	3000	97 ± 1
Mg^{2+}	$Mg(NO_3)_2 \cdot 6H_2O$	2500	98 ± 1
Zn^{2+}	$Zn(NO_3)_2$	100	98 ± 1
Fe^{3+}	$Fe(NO_3)_3 \cdot 6H_2O$	100	99 ± 2
Cu^{2+}	$Cu(NO_3)_2.4H_2O$	100	100 ± 1
Ni^{2+}	$Ni(NO_3)_2 \cdot 6H_2O$	100	100 ± 1
Co^{2+}	$Co(NO_3)_2$	100	98 ± 1
Pb^{2+}	$Pb(NO_3)_2$	100	99 ± 1
Pt^{2+}	$Pt(NO_3)_2$	100	98 ± 1
Au^{3+}	$Au(NO_3)_2$	100	99 ± 2
Cr^{3+}	$Cr(NO_3)_3$	100	99 ± 1
Cd^{2+}	$Cd(NO_3)_2$	100	100 ± 1
Mn^{2+}	$Mn(NO_3)_2$	100	100 ± 1
Cl^-	NaCl	8000	96 ± 1
$SO_4{}^{2-}$	Na_2SO_4	2500	98 ± 1
$PO_4{}^{3-}$	H_3PO_4	3000	100 ± 2

[a] Average ± standard deviation.

length on the absorbance signals was recorded by injecting 50 μL portions of 0.5 mg L^{-1} Pd(II). It was shown that the highest analytical signals were obtained when the length of the mixing coil was 20 cm. Afterwards, the signals decreased gradually up to 60 cm. These results indicate that the maximum concentration of the complex occurs when the length was about 20 cm. The optimum length, therefore, was chosen as 20 cm for subsequent studies (Fig. 5).

3.6. *Interferences*

The influences of some alkali and alkaline earth elements, as well as some cations and anions, on the determination of Pd(II) by the presented system were investigated. Interference was due to the competition of other metal ions for the reagent. In these experiments, solutions containing 0.5 mg L^{-1} Pd and the interfering species (in the range 100 mg L^{-1} to 20,000 mg L^{-1}) were treated under the optimized conditions with the proposed FI procedure. The tolerance limits of the coexisting ions, defined as the largest amount making the recovery of Pd(II) less than 95%, are given in Table 1. Large amounts of alkaline and alkaline earth metal ions had no interferences on the determination of Pd(II) ion, probably due to the low stabilities of their 2,2′-furyldioxime complexes. The other metal ions and anions (Zn^{2+}, Fe^{3+}, Cu^{2+}, Ni^{2+}, Co^{2+}, Pb^{2+}, Pt^{2+}, Au^{3+}, Cr^{3+}, Cd^{2+}, Mn^{2+}, Cl^{-}, $SO_4{}^{2-}$, $PO_4{}^{3-}$) did not show any interfering effect at the studied levels under the optimum conditions.

Table 2
The determination of Pd(II) in catalytic converter, ore, tap water and sea water samples after the application of the presented procedure ($n=3$).

Sample	Added	Found	Recovery (%)
Catalytic converter (μg g^{-1})	–	1148 ± 28 [a]	–
	1000	2144 ± 18	99 ± 2
Ore (μg g^{-1})	–	1.03 ± 0.04	
	5.0	6.02 ± 0.03	99 ± 1
Tap water (mg L^{-1})	–	–	–
	5.0	4.98 ± 0.01	100 ± 1
Sea water (mg L^{-1})	–	–	–
	5.0	4.97 ± 0.07	99 ± 1

[a] Average ± standard deviation.

Table 3
The concentration of Pd(II) contents in various environmental samples ($n=3$).

Sample	Pd content (μg g^{-1})	
	Presented method	Reference method [17]
Catalytic converter 1	3130 ± 38 [a]	3280 ± 51
Catalytic converter 2	3420 ± 35	3413 ± 47
Catalytic converter 3	1148 ± 27	1150 ± 13
Anode slime	3.05 ± 0.20	1.98 ± 0.01
Road sediment 1	0.29 ± 0.01	0.25 ± 0.01
Road sediment 2	0.75 ± 0.01	0.66 ± 0.01
Ore 1	10.2 ± 0.8	–
Ore 2	1.03 ± 0.04	–
Ore 3	61.9 ± 1.3	–
Ore 4	69.5 ± 1.1	–

[a] Average ± standard deviation.

3.7. *Analytical characteristics*

For the purpose of quantitative determination, a calibration curve for Pd(II) was constructed by injecting the working standards into 3 mol L^{-1} HNO_3 acid stream under the optimum conditions. The equation of the calibration curve, which was obtained after applying the proposed procedure, was $A=0.018\ C_{Pd}+0.011$; A is the absorbance and C_{Pd} is the concentration of palladium. Linearity was observed over the range of 0.01–10 mg L^{-1} with a determination coefficient (r^2) of 0.9998. The limit of detection (LOD), based on 3 s, was 0.1 μg L^{-1}. The precision of the method was found to be 1.2% as the relative standard deviation by analyzing ore samples ($n=8$).

The recovery studies for palladium(II) were performed in tap water, sea water, ore, and catalytic converter samples. Known amounts of palladium were spiked to the sample solutions in order to estimate the accuracy of the presented procedure (Table 2). Good agreement was obtained between the added and obtained analyte contents by using the recommended procedure.

3.8. *Accuracy of the method*

To verify the accuracy of the proposed method, the Pd content of the certified reference material (CDN-PGMS-10: 10.99 ± 0.73 μg g^{-1}) was determined by the proposed method. The palladium content of the reference material was found to be 10.9 ± 0.2 μg g^{-1}, which seems harmonious with each other with a recovery of 99 ± 1%, or which indicates that the result is in good agreement with the reference value.

The proposed method was successfully applied to the determination for Pd(II) in catalytic converter, anode slime, ore, and road sediment samples (see Table 3).

Table 4
Comparison of the results of the proposed method with the other published works for the determination of palladium.

Preconcentration method	Samples	Technique	LOD (μg L^{-1})	RSD (%)	PF	Reference
Solidified floating organic drop microextraction	Water samples, synthetic samples	FAAS	0.6	2	49.9	[5]
SF-EX-FIA	Airborne particulate matter, automobile catalysts	Spectrophotometry	7	< 3.5	–	[13]
CPE	Mine stone	ICP-OES	0.3	< 5	20	[18]
DLLME	Alloy, road dust sample	FAAS	1.4	1.5	–	[20]
SPE	Geological sample, anode slime, nickel alloy	FI-FAAS	26	2	–	[21]
DLLME	Water samples	GFAAS	2400	4.3	156	[24]
DLLME	Water samples	FAAS	90	0.7 ($n=5$)	45.7	[35]
SPE	Real samples	FI-FAAS	200	0.3	–	[40]
SPE	Spiked natural waters	ICP-OES	0.2	3.2	100	[41]
M-CIAME	Sea water, tea and biological samples	Spectrophotometry	0.2	1.7	97	[42]
DLLME	Real and synthetic samples	FO-LADS	0.25	< 4	162	[43]
Direct FI	Converter, anode slime, road sediment, mine ore, water sample	FI- Spectrophotometry	0.1	1.2	–	This work

4. Conclusion

The proposed flow-injection on-line spectrophotometric method is simple, rapid, selective and sensitive for the determination of palladium. In addition, the method is directly applicable to aqueous samples without separation/preconcentration steps. The calibration graph is valid in a wide range of Pd(II) concentrations from 0.01 mg L^{-1} to 10 mg L^{-1}. The detection limit of the proposed method was more reasonable than those of previously reported methods (Table 4), i.e., spectrophotometric [13], electrochemical [28], chromatography [37–39] and flow-injection [31–40]. The method developed is economical and provides a good sample frequency of 275 h^{-1}, and is especially suitable for routine analysis.

References

[1] B. Godlewska-Zyłkiewicz, Microchim. Acta 147 (2004) 189–210.
[2] J. Banham, Annual Report and Accounts, Johnson Matthey, 2008, pp.19–20. Available at.
[3] B. Dimitrova, K. Benkhedda, E. Ivanova, F. Adams, Can. J. Anal. Sci. Spectrosc. 49 (2004) 347–352.
[4] X. Dong, Y. Han, Q. Hu, J. Chen, G. Yang, J. Braz, Chem. Soc. 17 (2006) 189–193.
[5] M. Muzikar, C. Fontas, M. Hidalgo, J. Havel, V. Salvado, Talanta 70 (2006) 1081–1086.
[6] Ş. Saçmacı, S. Şahan, M. Saçmacı, U. Şahin, A. Ülgen, Ş. Kartal, Intern. J. Environ. Anal. Chem. http://dx.doi.org/10.1080/03067319.2012.727809, in press.
[7] Y. Si, Q. Hu, Z. Huang, G. Yang, J. Yin, Turk. J. Chem. 29 (2005) 135–140.
[8] A. Praveen Kumar, P. Raveendra Reddy, V. Krishna Reddy, Y.I. Lee, Anal. Lett. 42 (2009) 84–93.
[9] B. Dimitrova, K. Benkhedda, E. Ivanova, F. Adams, Can. J. Anal. Sci. Spectrosc. 49 (2004) 346–352.
[10] M. Gros, J.P. Lorand, A. Luguet, Chem. Geol. 185 (2002) 179–190.
[11] M.B. Gòmez, M.M. Gòmez, M.A. Palacios, J. Anal. At. Spectrom. 18 (2003) 80–83.
[12] J.D. Whiteley, F. Murray, Sci. Total Environ. 317 (2003) 121–135.
[13] A.N. Anthemidis, D.G. Themelis, J.A. Stratis, Talanta 54 (2001) 37–43.
[14] L. Pan, Y.C. Qin, B. Hu, Z.C. Jiang, Chem. Res. Chin. Univ. 23 (2007) 399–403.
[15] K. Pyrzynska, Talanta 47 (1998) 841–848.
[16] B. Godlewska-Zylkiewicz, Spectrochim. Acta Part B 58 (2003) 1531–1540.
[17] Ş. Saçmacı, Ş. Kartal, S. Dural, J. Braz, Chem. Soc. 23 (2012) 1033–1040.
[18] M.A.M. da Silva, V.L.A. Frescura, A.J. Curtius, Spectrochim. Acta B 56 (2001) 1941–1949.
[19] L. Tavakoli, Y. Yamini, H. Ebrahimzadeh, A. Nezhadali, S. Shariati, F. Nourmohammadian, J. Hazard. Mater. 152 (2008) 737–743.
[20] S.Z. Mohammadi, D. Afzali, M.A. Taher, Y.M. Baghelan, Microchim. Acta 168 (2010) 123–128.
[21] Q. Pu, P. Liu, Q. Sun, Z. Su, Microchim. Acta 143 (2003) 45–51.
[22] M. Mohamadi, A. Mostafavi, Talanta 81 (2010) 309–313.
[23] T.A. Kokya, K. Farhadi, J. Hazard. Mater. 169 (2009) 726–733.
[24] P. Liang, E. Zhao, F. Li, Talanta 77 (2009) 1854–1857.
[25] K.S. Patel, P.C. Sharma, P. Hoffmann, Fresenius' J. Anal. Chem. 367 (2000) 738–741.
[26] P. Kovacheva, R. Djingova, Anal. Chim. Acta 464 (2002) 7–13.
[27] M.V.B. Krishna, M. Ranjit, K. Chandrasekaran, G. Venkateswarlu, D. Karunasagar, Talanta 79 (2009) 1454–1463.
[28] Q. Sun, C. Wang, L. Li, H. Li, Fresenius' J. Anal. Chem. 363 (1999) 114–117.
[29] E. Helmers, M. Schwarzer, M. Schuster, Environ. Sci. Pollut. Res. 5 (1998) 44–50.
[30] J. Tilch, M. Schuster, M. Schwarzer, Fresenius' J. Anal. Chem 367 (2000) 450–453.
[31] K. Boch, M. Schuster, G. Risse, M. Schwarzer, Anal. Chim. Acta 459 (2002) 257–265.
[32] P. Kovacheva, R. Djingova, Anal. Chim. Acta 464 (2002) 7–13.
[33] K. Ravindra, L. Bencs, R. Van Grieken, Sci. Total Environ 318 (2004) 1–43.
[34] W.G. Van Ketel, C. Ntebber, Contact Dermatitis 7 (1981) 331–357.
[35] S. Dadfarnia, A.M.H. Shabani, Anal. Chim. Acta 658 (2010) 107–119.
[36] D.H. Templeton, G.W. Watt, C.L. Garner, J. Am. Chem. Soc. 65 (1943) 1608–1612.
[37] M.C. Bruzzoniti, S. Cavalli, A. Mangia, C. Mucchino, C. Sarzanini, E. Tarasco, J. Chromatogr. A 997 (2003) 51–63.
[38] S. Hoshi, K. Higashihara, M. Suzuki, Y. Sakurada, Talanta 44 (1997) 571–576.
[39] H. Wang, H.S. Zhang, J.K. Cheng, Talanta 48 (1999) 1–7.
[40] P. Liu, Q. Pu, Z. Su, J. Anal. Chem. 60 (2005) 1023–1029.
[41] E. Birinci, M. Gülfen, A.O. Aydın, Hydrometallurgy 95 (2009) 15–21.
[42] M. Vaezzadeh, F. Shemirani, B. Majidi, Food Chem. Toxicol. 48 (2010) 1455–1460.
[43] N. Shokoufi, F. Shemirani, Y. Assadi, Anal. Chim. Acta 597 (2007) 349–356.