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ION PAIR-DISPERSIVE LIQUID-LIQUID MICROEXTRACTION OF TRACE AMOUNT OF RHODIUM ION IN WATER AND ROAD DUST SAMPLES PRIOR TO FLAME ATOMIC ABSORPTION SPECTROMETRY DETERMINATION

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A simple ion pair-dispersive liquid–liquid microextraction method was proposed for preconcentration trace amounts of rhodium. An ion association complex of $RhCl_4^-$ and tetradecyldimetylbenzylamonium was extracted into cholorobenzene. The volume and the type of extractive and dispersive solvents, the extraction time and the pH of the aqueous solutions were optimized. The calibration curve was linear in the range of 0.6-500 ng mL^{-1} of rhodium. The limit of detection was 0.10 ng mL^{-1} in initial solution and preconcentration factor was 40. The proposed method was successfully applied to the extraction and determination of rhodium in road dust and water samples.

Keywords: ion pair -microextraction; dispersive liquid-liquid; rhodium determination.

INTRODUCTION

It is an interest in the medical and industrial significance of platinum, and to a lesser extent palladium and rhodium, has been accompanied by an increasing interest in their determination at low levels. Rhodium has been introduced as catalytic converter. Since then, approximately 73% of the world production of rhodium is consumed in the production of autocatalysis.[1] Due to increasing in the applications of Rh, for example in automobile Pt-Rh catalysts, development of high sensitive analytical methods for this element has been a demand in environmental science. Most sensitive analytical techniques, such as graphite furnace atomic absorption spectrometry (GFAAS),[2] flame atomic absorption spectrometry (FAAS),[3] adsorptive stripping voltammetry (ASV),[4] inductively coupled plasma-atomic emission spectrometry (ICP-AES),[5] derivative spectrophotometry[6] and inductively coupled plasma-mass spectrometry (ICP-MS)[7] have been used for this purpose. However, all of these methods, except FAAS, are high cost methods with complex instrumentation. FAAS is a fast, low cost and relative simple method.[8] The detection of metal trace elements in aqueous samples is difficult due to various factors, particularly their low concentration and the matrix effects.[9] Because of low concentration of analytes and complex matrices, sample preparations such as extraction, clean-up and preconcentration before instrumental analysis are essential. Liquid–liquid extraction (LLE)[10] and solid-phase extraction (SPE)[11] are two of traditional pretreatment methods that are widely used for separation and preconcentration of rhodium ions.

In routine analysis, liquid-liquid extraction is the most widely used sample preparation technique, whose goal is cleanup, enrichment and signal enhancement. However, some shortcomings like the use of extensive amounts of hazardous organic solvents and sample volumes, the generation of large amounts of pollutants make this procedure time consuming, expensive, environmentally unfriendly, tedious laborious.[12] A special attention is nowadays focused on techniques, which are characterized by a considerable reduction of organic solvents that decrease the environmental pollution greatly throughout the analytical procedure.[13] Modern trends in analytical chemistry are towards the simplification and miniaturization of sample preparation procedures as they lead inherently to a minimum solvent and reagent consumption and drastic reduction of laboratory wastes.[14]

Recently, Rezaee *et al*.[15] proposed a microextraction technique, termed dispersive liquid-liquid microextraction (DLLME) based on ternary component solvent systems. An appropriate mixture of an extraction solvent and a disperser solvent, with high miscibility in both aqueous and organic phase, is rapidly injected into aqueous phase. The analyte is extracted into the fine dispersed droplets of extraction solvent.

The aim of the present study is developing of ion pair-dispersive liquid–liquid microextraction (IP-DLLME) method for separation and preconcentration trace amounts of rhodium ion.

EXPERIMENTAL

Apparatus

A Varian SpectrAA 220 atomic absorption spectrometer was used for the measuring of Rh^{3+} in an air-acetylene flame. The operating conditions were as follows: wavelength, 343.5 nm; lamp current, 5.0 mA and slit width, 0.5 nm. The acetylene flow and the air flow were 1.5 and 3.5 L min^{-1}, respectively. The pH measurement was carried

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out using a pH meter (Metrohm 713) with a combined pH glass electrode calibrated against two standard buffer solutions at pH 4.0 and 7.0. The centrifuge (1EC Model HN-S) was used. All glassware and columns were washed with a mixture of concentrated hydrochloric acid and concentrated nitric acid (1:1) before application.

Reagents and materials

High purity reagents from Sigma (St. Louis, MO, USA) and Merck (Darmstadt, Germany) were used for preparation of all standard and sample solutions. Stock solution 1000.0 mg L^{-1}) of Rh were prepared from $RhCl_3$. $3H_2O$ (Merck, Germany) in hydrochloric acid. Double distilled water was used throughout the work.

Ion pair-dispersive liquid–liquid microextraction procedure

An aliquot of 10 mL sample solutions were placed in a screw cap glass test tube with conic bottom and then, 1 mL NaCl 5% (w/v) and 1 mL 0.05 mol L^{-1} of tetradecyldimethylbenzylammonium chloride (TDMBA) solution were sequentially added, pH was adjusted at 2 and completely mixed with the sample solutions. Then, 1.5 mL of ethanol (disperser solvent) containing 50.0 µL of chlorobenzene (extraction solvent) was injected rapidly into the sample solution. A cloudy solution (water, ethanol, and chlorobenzene) was formed in the test tube. In this step, an ion associate of $RhCl_4$-TDMBA is formed and extracted into the fine droplets of chlorobenzene. Then, the solution was centrifuged at 4000 rpm for 5 min, and the dispersed fine droplets of chlorobenzene that containing of $RhCl_4$-TDMBA was deposited at the bottom of conical test tube. The sediment phase was removed and then was added to it a mixture containing 0.2 mL of 0.1 mol L^{-1} HCl in ethanol. The final solution was aspirated directly into the FAAS.

RESULTS AND DISCUSSION

In order to reach the optimized experimental conditions for high enrichment factor and quantitative extraction of rhodium ions by IP-DLLME method, the influence of different parameters including concentration of NaCl, nature and volume of both extraction and disperser solvents and extraction time were investigated. Enrichment factor (EF) was calculated using ratio of the analyte concentration in the diluted organic phase (C_{do}) to the initial concentration of analyte (C_i) within the sample: $EF= C_{do/} C_i$

The analyte concentration in the diluted organic phase was calculated from the direct calibration after diluting the extractant by ethanol. The recovery of extraction (ER) was calculated according to: $ER=EF\times[V_{do}/V_{aq}]$

Here, V_{aq} was the initial volume (10 mL) and V_{do} was the final volume which introduced to nebulizer of flame atomic absorption spectrometry (250 µL).

Nature and volume of extraction solvent

The selection of an appropriate solvent is very important for the DLLME process. Organic solvents are selected based on their higher densities than water and their extraction efficiencies for the $RhCl_4$-TDMBA adduct. The ability of carbon tetrachloride, chloroform, and chlorobenzene with respective densities of 1.590, 1.492 and 1.106 g mL^{-3} for the extraction of $RhCl_4$-TDMBA by the proposed method were compared. A series of sample solutions of 50.0 ng mL^{-1} of rhodium were studied by using 1.5 mL of ethanol, as dispersing solvent, containing different volumes of the extraction solvent to achieve a final 50 µL volume of sedimented phase. The results were shown in Figure 1 and revealed that chlorobenzene has the highest extraction efficiency in comparison with other extraction solvent. Since chlorobenzene possesses a closer density to that of water and forms a very stable fine cloudy solution, it was selected as the best extraction solvent for the system.

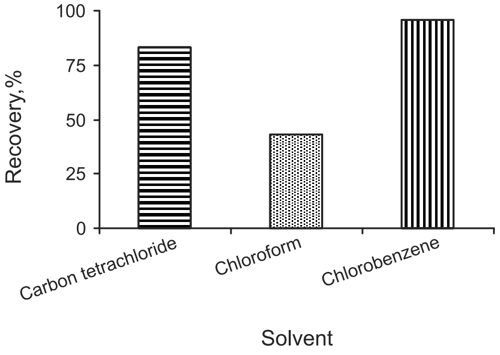

Figure 1. Selection of extraction solvent type. Conditions: Rh(III), 500.0 ng; pH, 2; NaCl 5%; 1 mL; TDMBA, 0.05 mol L^{-1}, 1 mL; ethanol (disperser solvent) 1.5 mL; extraction solvent volume, 50.0 µL

In order to evaluate the effect of extraction solvent volume, solutions containing different volumes of chlorobenzene were examined with the same DLLME procedures. The experimental conditions are fixed and include the use of 1.5 mL ethanol containing different volumes of chlorobenzene (i.e., 25.0, 40.0, 50.0, 60.0 and 75.0 µL). The results are illustrated in Figure 2 and showed that the extraction recovery is almost quantitative in the case of higher than 50.0 µL solvent volumes, which emphasizes the high distribution coefficient of $RhCl_4$-TDMBA in chlorobenzene under the experimental conditions used. Thus, 50.0 µL of chlorobenzene was selected as the optimum volume of extraction solvent.

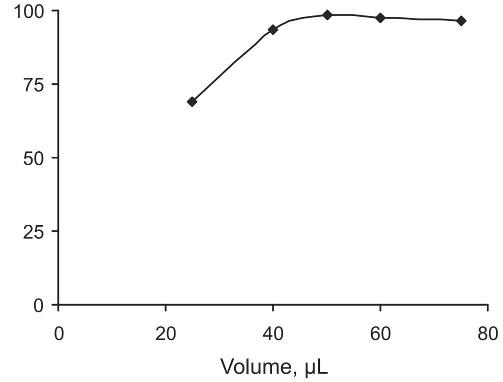

Figure 2. Effect of extraction solvent volume on the recovery of Rh(III). Conditions were same as Figure 1 except extraction solvent volume

Nature and volume of disperser solvent

The mutual miscibility of disperser solvent in organic phase (extraction solvent) and aqueous phase (sample solution) is the most important point for the selection of a disperser solvent.

Thereby, acetone, methanol and ethanol, which possess these abilities, were tested as potential disperser solvents. Thus, under the same experimental conditions, a series of sample solutions of 50.0 ng mL^{-1} of rhodium were studied by using 1.5 mL of each disperser solvent containing 50.0 µL of chlorobenzene and following the recommended procedure. The results showed that the variations in rhodium recovery by using ethanol (98.9), acetone (96.86) and methanol (98.7) are not remarkable; thus, ethanol was selected as disperser solvent due to its lower toxicity and cost. Since the variation in volume of ethanol caused a change in the volume of sedimented phase, it was necessary to optimize the volume of disperser solvent. It was found that, at low volumes of ethanol, the cloudy solution was not formed completely while, at high ethanol volume, the solubility of chlorobenzene in aqueous solution was increased. Therefore, it was important to consider the influence of the volume of ethanol on the extraction efficiency. In order to achieve a constant volume of sedimented phase, the volumes of ethanol were changed while the volume of the sedimented phase remained more or less constant at 50.0 µL. The extraction efficiency increases with increasing volume of ethanol until a volume of 1.5 mL is reached; a further increase in volume of ethanol will result in decreased efficiency of the extraction process (Figure 3).

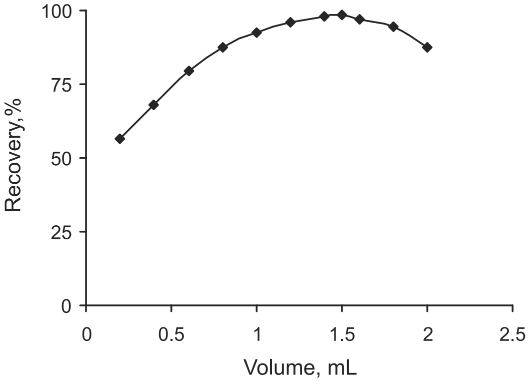

Figure 3. *Effect of disperser solvent volume on the recovery of Rh(III). Conditions were same as Figure 1 except disperser solvent volume*

The observed decrease in the extraction efficiency at lower ethanol volumes than 1.5 mL seems to be due to incomplete formation of cloudy state. While at higher ethanol volumes, the decreased extraction efficiency is due to the increased solubility of $RhCl_4$–TDMBA adduct in water, which results in diminished distribution coefficient and extraction recovery of rhodium. According to these results, a volume of 1.5 mL ethanol was chosen as the optimum disperser volume.

Effect of the extraction time

In DLLME, the extraction time is considered as the time interval between the injection moment of the disperser/extraction solvent mixture and the moment of starting the centrifugation process. In order to reach the optimum extraction time, under the same experimental conditions, the extraction procedure was carried out at different time intervals in the range of 0-3 min with the constant experimental conditions. The results clearly revealed that the proposed extraction method is fast so that the extraction time has no measurable effect on the extraction efficiency. Therefore, the DLLME method was time-independent, which was the most important advantage of this technique.

Effect of NaCl concentration

The concentration of NaCl is one of the most important variables influencing the formation of ion associate of $RhCl_4$-TDMBA and its subsequent extraction. Thus, the influence of the NaCl concentration (in the range of 0.0-10%) in test solutions on the extraction of 50.0 ng mL^{-1} of Rh(III) from 10 mL aqueous solution by the proposed method was studied. The results are shown in Figure 4.

According to the results, the recovery was increased by increasing concentration of NaCl up to 5%, and remained more or less constant upon further increase in NaCl concentration. Thereby, a 5% concentration of NaCl for quantitative extraction of $RhCl_4$-TDMBA was selected for further studies.

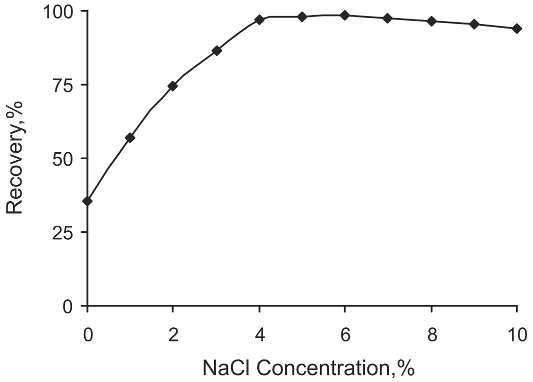

Figure 4. *Effect of NaCl concentration on the recovery of Rh(III) . Conditions were same as Figure 1 except NaCl concentration*

Effect of the sample pH

The influences of pH of the aqueous solution on the recovery of rhodium ions were investigated at range of 0.5-6 while keeping other parameter constant. As can be seen in Figure 5, the results showed that the recovery increases with the increase of pH up to 1.5; thereafter, the recovery is almost constant up to pH 3. In this method, the extraction was carried out using a sample solution adjusted to pH 2.

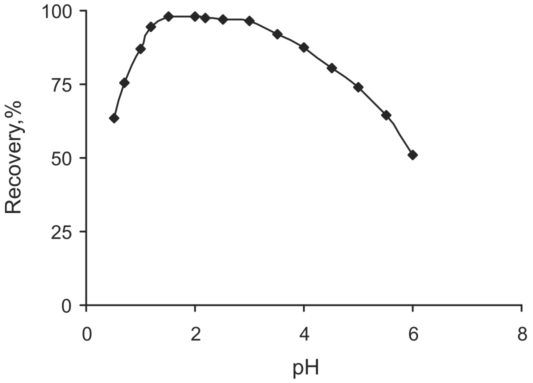

Figure 5. *Effect of pH on the recovery of Rh(III). Conditions were same as Figure 1 except pH*

Interferences

The interference of coexisting ions in binary mixtures of Rh(III) with foreign ions on the percent recovery of rhodium (50.0 ng mL^{-1}) were studied. After introducing the binary solution, the recommended procedure was followed. A relative error of ± 5% was considered tolerable. Considering the selectivity provided by the extraction and flame atomic absorption spectrometry, the effects of several cations were evaluated. The effect of foreign ions on the extraction and determination of rhodium was investigated. Among the tested ions; Al^{3+}, Mg^{2+}, Ca^{2+} did not show any interference at a concentration of 300 times higher than rhodium concentration. However, Pd^{2+}, Fe^{3+}, Cu^{2+}, Ag^{+}, Ir^{3+}, Co^{2+}, Cr^{3+}, Zn^{2+}, Mn^{2+}, Pb^{2+}, Cd^{2+}, Ni^{2+}, Sb^{3+}, As^{3+} showed interferences at a concentration of 40 times higher than rhodium concentration and Au^{3+}, Hg^{2+}, Bi^{3+}, Mo^{6+}, V^{5+}, showed interference at a 24 times higher than rhodium concentration.

Figures of merit

A calibration curve was constructed by pre-concentrating 10 mL of sample standard solution. Under the optimum experimental conditions, the calibration curve for Rh(III) was linear from 0.6 to 500 ng mL^{-1} with a regression coefficient of 0.9984. The enrichment factor for the proposed method is 40. The limit of detection (LOD) and limit of quantification (LOQ) were calculated using the relation KSb where, Sb is the standard deviation of the blank measurements (10 replicates) and K is a confidence factor equal to 3 and 10 for LOD and LOQ respectively. The LOD and LOQ of Rh(III) achieved using the proposed method were 0.1 and 0.33 ng mL^{-1} respectively. The relative standard deviation for the 10 replicate recoveries of 50.0 ng mL^{-1} Rh(III) from 10 mL of aqueous solutions was found to be ± 2.5%.

Analysis of a platinum-iridium alloy

In order to test the applicability of the proposed method for the analysis of real samples, one platinum-iridium alloy was analyzed. To 1.0 mg of the alloy with known composition, 3 mL of aqua regia was added and the solution was evaporated. Five mL of concentrated hydrochloric acid was added to it and the solution was warmed, transferred to a 100 mL volumetric flask, and made up to the mark with distilled water. An aliquot of this solution was taken and rhodium was determined by the general procedure. Six determinations were made, and the results were shown that the recovery for rhodium in platinum-iridium alloy was 97.57%. It was found that there is no significant difference between results obtained by the proposed method and the certified results. These results indicate the applicability of the developed procedure for rhodium separation.

Analysis of rhodium in water samples

In order to test the applicability and reliability of the proposed method, sea water, well water, river water and wastewater samples were analyzed. For this purpose, 10.0 mL of each sample was preconcentrated in accordance to the proposed method. The results are shown in Table 1. In all cases the spiked recoveries confirmed the reliability of the proposed method. The results showed that good recoveries were achieved for analyzed samples.

Table 1. Determination of rhodium in the real and spiked water samples

Sample	Spiked (ng mL^{-1})	Found (ng mL^{-1}) [a]	Recovery (%)
Well water (Kerman University)	0.0	N.D. [a]	
	2.0	1.97±0.03	98.5
River water (Shoor, Shahdad)	0.0	N.D	
	4.0	3.93±0.09	98.25
Sea water (Persian Gulf)	0.0	B.L.R. [c]	
	5.0	5.31±0.14	106.2
Wastewater (Copper factory)	0.0	B.L.R.	
	5.0	5.46±0.16	109.2

[a] Mean± Standard deviation (*n* =6). [b] N.D.: Not detected. [c] B.L.R.: Below of linear range.

Analysis of rhodium in road dust samples

The road dust samples were collected from different roadsides in the Kerman Province. The samples were dried at 100 °C for 2 h, ground, passed through a sieve of 200 meshes and homogenized. 2.50 g of each sample was weighed into a 100 mL of beaker. In order to decompose it, 10 mL of aqua regia was added to the beaker and the mixture was heated almost to dryness. Then, 10 mL of aqua regia was added again to the residue and the mixture was evaporated to dryness. The insoluble part was filtered through a filter paper (blue band) and washed with de-ionized water. The pH was adjusted to 2 and the total volume was made up to 10.0 mL with de-ionized water in calibrated flaks. An aliquot of this solution was taken and then, the proposed IP-DLLME procedure was applied for preconcentration of rhodium in the road dust samples prior FAAS determination. The results were given in Table 2. The recovery of rhodium from the road dust samples spiked with the known amounts of rhodium ions was also studied. The results were shown in Table 2.

Table 2. Determination of rhodium in road dust samples

Sample	Spiked (μg g^{-1})	Found (μg g^{-1})[a]	Recovery (%)
Street dust (Kerman)	0.00	0.14±0.02	-
	0.20	0.35±0.05	105
Street dust (Sirjan)	0.00	0.09±0.02	-
	0.20	0.28±0.04	95
Street dust (Mahan)	0.00	0.06±0.01	-
	0. 20	0.27±0.03	105

[a] Mean ± Standard deviation (*n* =6).

According to these results, the added rhodium ions can be quantitatively recovered from the road dust samples by the IP-DLLME procedure. These results were demonstrated the applicability of the IP-DLLME procedure for rhodium determination in the road dust samples.

Comparison of IP-DLLME-FAAS with other methods

In Table 3 are compared the main analytical characteristics (i.e., LR, ER and LOD) of the proposed IP-DLLME–FAAS method for the determination of Rh(III) with those of some of the

Table 3. Comparison of the IP-DLLME with other methods for preconcentration and determination of rhodium

Determination technique	Preconcentration method	Enrichment factor	Detection limit (ng mL^{-1})	Linear range (ng mL^{-1})	Ref.
FAAS	SPE	120	0.010	0.16-25000	3
Spectrophotometry	SLS [a]	40	14.4	30-2500	6
ICP-OES	LLE	66.1	7.0	-	10
Spectrophotometry	SPE	-	20	40-7500	11
FIA-FAAS	SPE	-	3-8	-	16
ETAAS	IEM [b]	20	0.3	0.9-50	17
DPP [c]	SPE	-	60	250-7500	18
LI-TLS [d]	CPE	450	0.06	0.5-50	19
FAAS	CPE	50	0.052	0.16-1.5	20
FAAS	IP-DLLME	40	0.10	0.6-500	This work

[a] SLS: Solid liquid separation. [b] IEM: Ion exchange microcolumn. [c] DPP: Differential pulse polarography. [d] LI-TLS: Laser induced-thermal lens spectrometry.

best previously reported methods for this purpose including SPE-spectrophotometry,[6,11] FIA–FAAS, where Rh (III) is adsorbed on a cross-linked polystyrene sorbent,[16] ETAAS after separation, using Dowex 1×8-200,[17] differential pulse polarography, after preconcentration onto microcrystalline naphthalene,[18] laser induced-thermal lens spectrometry after cloud point extraction,[19] FAAS determination after preconcentration onto carbon nanotube,[3] FAAS determination after cloud point extraction[20] and liquid-liquid extraction prior inductively coupled plasma optimal emission spectrometer determination (ICP-OES)[10].

As can be seen the LOD of the proposed IP-DLLME-FAAS method, with a sample volume of only 10. 0 mL, is lower than some of the previously proposed methods[6,10,11,16-18] and higher than some of the other methods.[3,19,20] While, the extraction time is very shorter than all of the mention methods because no need any Rh-ligand complex formation, which indicates the fact that IP-DLLME is a very sensitive and rapid technique that can be used for the pre-concentration and determination of Rh(III) from real samples.

CONCLUSION

In this paper we introduced a new IP-DLLME-FAAS method for the analysis of trace amounts of Rh(III) in different samples. The important features of IP-DLLME method are rapidity, low cost, use of minimized toxic organic solvents, simplicity of operation, high enrichment factor and high sensitivity and selectivity. This study demonstrated the separation and preconcentration of rhodium without application of ligand. The complex formation of Rh-ligand needed to heat and it increased the time of separation[21] while in this work the time is very short because no need any Rh-ligand complex formation.

REFERENCES

1. Manzick, L.; *Precious metals recovery and refining*, Historial Publications: Texas, 1990.
2. Tsogas, G. Z; Giokas, D. L.; Vlessidis, A. G.; Evmiridis, N. P.; *Talanta* **2008**, *76*, 635.
3. Ghaseminezhad, S.; Afzali, D.; Taher, M. A.; *Talanta* **2009**, *80*, 168.
4. Georgieva, M.; Pihlar, B.; *Fresenius J. Anal. Chem.* **1997**, *357*, 874.
5. Kovacheva, P.; Djingova, R.; *Anal. Chim. Acta* **2002**, *464*, 7.
6. Pancras, J. P.; Puri, B. K.; *Anal. Sci.* **1999**, *15*, 575.
7. Motelica-Heino, M.; Rauch, S.; Morrison, G. M.; Donard, O. F. X.; *Anal. Chim. Acta* **2001**, *436*, 233.
8. Carasek, E.; Tonjes, J. W.; Scharf, M.; *Talanta* **2002**, *56*, 185.
9. Chena, J.; Xiao, S.; Wu, X.; Fang, K.; Liu, W.; *Talanta* **2005**, *67*, 992.
10. Lee, J. Y.; Kumar, J. R.; Kim, J. S.; Park, H. K.; Yoon, H. S.; *J. Hazard. Mater*. **2009**, *168*, 424.
11. Taher, M. A.; *Anal. Chim. Acta* **1999**, *382***,** 339.
12. Psillakis, E.; Kalogerakis, N.; *TrAC, Trends Anal. Chem.* **2003**, *22*, 565.
13. Liu, H. G.; Dasgupta, P. K.; *Anal. Chem.* **1996**, *68*, 1817.
14. Jeannot, M. A.; Cantwell, F. F.; *Anal. Chem.* **1996**, *68*, 2236.
15. Rezaee, M.; Assadi, Y.; Hosseini, M. R. M.; Aghaee, E.; Ahmadi, F.; Berijani, S.; *J. Chromatogr., A* **2006**, *1116*, 1.
16. Kovalev, I. A.; Bogacheva, L. V.; Tsysin, G. I.; Formanovsky, A. A.; Zolotov, Y. A.; *Talanta* **2000**, *52*, 39.
17. Rojas, F. S.; Ojada, C. B.; Pavon, J. M. C.; *Talanta* **2004**, *64*, 230.
18. Dubey, R. K.; Bhalotra, A.; Gupta, M. K.; Puri, B. K.; *Microchem. J.* **1998**, *58*, 117.
19. Shokoufi, N.; Shemirani, F.; *Talanta* **2007**, *73*, 662.
20. Suvardhan, K.; Kumar, K. S.; Rekha, D.; Subrahmanyam, P.; Kiran, K.; Jayaraj, B.; Ramanaiah, S.; Janardhanam, K.; Chiranjeevi, P.; *Microchim. Acta* **2007**, *157*, 237.
21. Stokley, J. R; Jacobs, W. D.; *Anal. Chem.* **1963**, *35*, 149.