Trace-level Lead Analysis in Environmental Water and Whitening Cosmetics Based on Solid-Phase Extraction Followed by Flame Atomic Absorption Spectrometry Determination

Hong-Li Sun, Yi-Wei Wu*, Yang Yu, and Shuai-Hua Zhu

Department of Chemistry and Chemical Engineering,

Hubei Key Laboratory of Pollutant Analysis and Reuse Technique, Hubei Normal University, Huangshi 435002, P.R. China

INTRODUCTION

Lead is considered one of the most toxic environmental pollutants because of its bioaccumulation and is thus extremely dangerous for all biological organisms, and humans in particular (1). Its effects include not only blood enzyme changes, anaemia, hyperactivity, and neurological disorders, but also pathophysiological changes in several organs (2,3). The World Health Organisation (WHO) recommended a limit of $10 \mu\text{g L}^{-1}$ as the guideline tolerable value for lead in drinking water (4). In addition, Pb is also often added to whitening cosmetics owing to its whitening effect. Therefore, highly sensitive determination methods of trace Pb in environmental samples and whitening cosmetics need to be established.

A separation and preconcentration step is usually necessary prior to the determination of Pb due to the low levels and the complex matrix. Many preconcentration techniques have been reported, including ion exchange (5), coprecipitation (6), electrodeposition (7), membrane filtration (8), flotation (9), dispersive liquid-liquid microextraction (10), cloud point extraction (11), and solid phase extraction (SPE) (12, 13). Among these techniques, SPE has been frequently used for pharmaceutical (14), fine chemicals (15), biological medicine (16), and environmental analysis (12,13) due to its simplic-

ABSTRACT

Zirconia and alumina doped with silicon material ($\text{ZrO}_2\text{-Al}_2\text{O}_3\text{-SiO}_2$) was synthesized by a sol-gel method. A simple and selective method of flow injection (FI) using a micro-column packed with $\text{ZrO}_2\text{-Al}_2\text{O}_3\text{-SiO}_2$ as solid phase extractant has been developed for the preconcentration and separation of trace amounts of Pb in environmental water and whitening cosmetics prior to the determination by flame atomic absorption spectrometry (FAAS). At pH 4.0–6.0, the doped material was selective towards Pb, and the retained Pb could be desorbed quantitatively with 4.0 mL of 0.3 mol L^{-1} HCl. Under the optimum conditions, the detection limit of Pb was 1.69 ng mL^{-1} with an enrichment factor of 50. The relative standard deviation (RSD) was 1.09 % ($n=9$, $C=2 \text{ ng mL}^{-1}$). The proposed method has been successfully applied to the determination of Pb in environmental water and whitening cosmetics samples, and the recoveries for Pb were 98.4–109.6%. In order to validate the developed procedure, a GSB-07-1183-2000 certified reference (environmental water) was analyzed, and the results were in good agreement with the certified values.

ity, speed, and ability to provide high enrichment factors.

In the SPE technique, selection of an appropriate sorbent is an important strategy in the elaboration of an analytical procedure, and doped inorganic materials have

proved to be especially effective as a result of its high mechanical property, numerous active sites, large surface area, strong adsorption ability, and stability (17). The doped inorganic materials originate in the sol-gel process and usually exhibit specific properties that are not achieved by the individual components (18). Silica-based materials doped with other metallic ions have been widely used in analytical chemistry (19). An SPE-FAAS method using $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-L}$ as the adsorbent for the determination of Pb, Cd, and Cu in water, food, and biological samples has been reported with satisfactory results (20). Farahmand et al. (21) also successfully developed a simple and accurate SPE-FAAS method for the determination of beryllium in aqueous samples using silica gel micro-particles doped with alumina as the adsorbent.

The aim of this work is to prepare alumina and zirconia doped with silicon material ($\text{ZrO}_2\text{-Al}_2\text{O}_3\text{-SiO}_2$) by the sol-gel method and explore the possibility of using it as an adsorbent for the extraction of lead prior to its determination by FAAS. Factors affecting $\text{ZrO}_2\text{-Al}_2\text{O}_3\text{-SiO}_2$ SPE were investigated in detail. The developed method was applied to the determination of lead in environmental water and whitening cosmetics.

EXPERIMENTAL

Instrumentation

The Pb determination was performed using a Model Shimadzu 6200 atomic absorption spectrometry.

* Corresponding author.
E-mail: chemwuyiwei@163.com

ter (Kyoto, Japan) equipped with deuterium lamp background correction. The operating conditions for Pb are listed in Table I.

An HL-2 peristaltic pump (Shanghai Qingpu Instrument Factory, P.R. China) and a home-made polytetrafluoroethylene (PTFE) micro-column (20 mm×3.0 mm i.d.) were used in the extraction process. A minimum length of PTFE tubing (0.5 mm i.d.) was used for flow injection (FI).

The reported pH of the solution was carefully measured with a PHS-3 C pH-meter (Shanghai Precision & Scientific Instrumental, Shanghai, P.R. China).

Scanning electron micrography (SEM) of $\text{ZrO}_2\text{-Al}_2\text{O}_3\text{-SiO}_2$ was performed with a Model S-3400N scanning electron microscope (Hitachi, Tokyo, Japan).

Fourier-transform infrared spectroscopy of $\text{ZrO}_2\text{-Al}_2\text{O}_3\text{-SiO}_2$ was performed with a Model 5700 FT-IR (Niconet, USA).

Standard Solution and Reagents

Stock standard solutions (1 mg mL^{-1}) were prepared by dissolving $\text{Pb}(\text{NO}_3)_2$ (Beijing Hengyeyuanzhong Chemical Reagent Corporation, Beijing, P.R. China) in 1% (v/v) HNO_3 . The standards were further diluted with doubly distilled water (DDW) to prepare working solutions. All reagents were of analytical reagent grade.

For pH adjustment, a series of Britton-Robison (B-R) buffer solutions were used containing phosphoric acid, acetic acid, and boric acid (Tianjin Kermel Chemical Reagents Development Center, Tianjin, P.R. China), each with concentrations at 0.04 mol L^{-1} .

Preparation of $\text{ZrO}_2\text{-Al}_2\text{O}_3\text{-SiO}_2$

$\text{ZrO}_2\text{-Al}_2\text{O}_3\text{-SiO}_2$ was prepared using Pluronic F127 (EO106PO70 EO106, $M_w=12,600$) as template

TABLE I
FAAS Operating Conditions
for the Determination of Pb

Wavelength	217.0 nm
Lamp Current	6.0 mA
Spectral Band Pass	0.7 nm
Burner Height	8.0 mm
Flow Rate of C_2H_2	2.0 mL min^{-1}
Flow Rate of Air	8.0 mL min^{-1}

along with $\text{ZrClO}_4 \cdot 8\text{H}_2\text{O}$, tetraethylorthosilicate (TEOS) and $\text{Al}(\text{OiPr})_3$ (aluminum isopropoxide) as Zr, Si, and Al sources, respectively. The detailed experimental procedure used is similar to reference (22). A quantity of 2.3 g F127 was dissolved in a mixture of 15 mL ethanol, 0.1 mL acetic acid, and 1.0 mL 35% hydrochloric acid (HCl). Then, 2.5 mmol $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ and 5.0 mmol TEOS were sequentially added to the mixed solution with vigorous stirring for 2 hours. Finally, 2.5 mmol $\text{Al}(\text{OiPr})_3$ was added to the mixture and stirred for another 8 hours at room temperature. The resulting solution was evaporated at 313–323K for 24 hours, and then calcined at 673 K for 6 hours in order to obtain the doped material of $\text{ZrO}_2\text{-Al}_2\text{O}_3\text{-SiO}_2$.

SPE Column Preparation

The PTFE micro-column was filled with a total of 90.0 mg $\text{ZrO}_2\text{-Al}_2\text{O}_3\text{-SiO}_2$ and both ends were plugged with a small portion of skimmed cotton. The column was conditioned to the desired pH with B-R buffer solution.

Sample Preparation

Preparation of Environmental Water Samples

Environmental water samples (tertiary water treatment from Daye Lake and pond water) were collected and filtered through a $0.45 \mu\text{m}$ membrane (Shanghai Xingyajinghua Instrument Factory, Shanghai, P.R. China). Then the

samples were acidified to the proper pH with B-R buffer prior to their SPE-FAAS analysis.

Preparation of Whitening Cosmetics Samples

An amount of 5.0 g whitening cosmetic was dissolved in 50 mL 1:1 (v/v) HNO_3 , homogenized, and heated in a boiling water bath for 2 hours. The mixture was then heated (200°C) in the furnace until the solution was nearly dry. After cooling, the solution was dissolved in 50 mL B-R buffer prior to SPE-FAAS analysis.

General Procedure

Real-world samples or standard solutions at the proper pH were passed through the $\text{ZrO}_2\text{-Al}_2\text{O}_3\text{-SiO}_2$ micro-column at an optimum flow rate. The analyte trapped in the column was subsequently stripped with the eluent and then determined by FAAS.

RESULTS AND DISCUSSION

FT-IR Analysis

To characterize the structural formation of $\text{ZrO}_2\text{-Al}_2\text{O}_3\text{-SiO}_2$, Fourier-transform infrared (FTIR) spectroscopy was performed with a Nicolet 5700 FT-IR instrument. As shown in Figure 1, the peaks at 3430 and 1640 cm^{-1} correspond to the surface adsorbed water molecules and surface $-\text{OH}$ groups, respectively. The absorbance peaks at 1080 cm^{-1} , 475 cm^{-1} , and 1390 cm^{-1} represent the stretching vibration of Si-O-Si , Zr-O-Zr , and Al-O bonds, respectively (23,24).

SEM Image Analysis

The adsorption characteristic of silicon material is related to its physical morphology. Thus, the surface morphology of $\text{ZrO}_2\text{-Al}_2\text{O}_3\text{-SiO}_2$ is an important factor affecting its performance. Figure 2 shows the morphology of the $\text{ZrO}_2\text{-Al}_2\text{O}_3\text{-SiO}_2$ characterized by SEM at different magnifications. As seen in Figure 2,

the micrograph of $\text{ZrO}_2\text{-Al}_2\text{O}_3\text{-SiO}_2$ displays a roughened and porous structure.

Effect of pH

The pH value plays an important role in the adsorption of different ions on $\text{ZrO}_2\text{-Al}_2\text{O}_3\text{-SiO}_2$. To characterize the selectivity of $\text{ZrO}_2\text{-Al}_2\text{O}_3\text{-SiO}_2$, a number of metal ions (Cr, Cu, Cd, and Pb) were tested at varying pH, and the experimental results are shown in Figure 3. As seen, Pb can be quantitatively adsorbed while Cr, Cu, and Cd cannot. A quantitative adsorptive rate ($> 90\%$) was found for Pb in the pH range of 4.5–6.0. As a result, $\text{ZrO}_2\text{-Al}_2\text{O}_3\text{-SiO}_2$ exhibited good selectivity towards Pb, and the pH of 4.5 was selected for the preconcentration and separation of Pb.

Effect of Sample Flow Rate

The retention of an analyte on the adsorbent depends on the flow rate of the sample solution. In order to improve the analysis efficiency, it was examined under the optimal pH with flow rates varying from 0.2 to 5.0 mL min^{-1} . Quantitative recoveries of Pb were obtained at flow rates of less than 4.0 mL min^{-1} . Thus, a flow rate of 4.0 mL min^{-1} was employed as the optimum.

Effect of Elution Conditions

With respect to stripping Pb from $\text{ZrO}_2\text{-Al}_2\text{O}_3\text{-SiO}_2$, a series of concentrations ($0.1\text{--}2.0 \text{ mol L}^{-1}$) of HCl were studied. The results in Figure 4 show that Pb was completely desorbed quantitatively ($> 90\%$) with $0.1\text{--}2.0 \text{ mol L}^{-1}$ HCl. Thus, 0.3 mol L^{-1} HCl was selected to strip the analyte.

To obtain a significant enrichment factor, the volume of the eluent should be as small as possible. By keeping the HCl concentration at 0.3 mol L^{-1} , the effect of eluent volume on the recoveries of Pb was investigated. The results showed that 4.0 mL of 0.3 mol L^{-1} HCl was sufficient to quantitatively recover Pb.

The effect of the desorption flow rate of 0.3 mol L^{-1} HCl was

further studied at a range of $0.2\text{--}2.5 \text{ mL min}^{-1}$ fixing the eluent volume at 4.0 mL . The results in Figure 5 show that the recoveries of Pb strongly depend on the eluent flow rate. The higher the flow rate of HCl, the lower the recovery of Pb. When the flow rate was less than 1.5 mL min^{-1} , the recoveries of Pb were over 90% . Thus, 1.0 mL min^{-1} was selected as the optimum.

Effect of Sample Volume

To explore the possibility of enriching low concentrations of the analyte from a large volume, the effect of sample volume on the Pb recovery was investigated. For this purpose, $10.0\text{--}250.0 \text{ mL}$ of sample solutions containing $5.0 \mu\text{g mL}^{-1}$ Pb were passed through the micro-column at the optimum conditions. Up to a sample volume of 200.0 mL .

Fig. 2. SEM image of $\text{ZrO}_2\text{-Al}_2\text{O}_3\text{-SiO}_2$ at (A) $2000\times$ and (B) $1000\times$ magnification.

Fig. 1. FT-IR spectra of $\text{ZrO}_2\text{-Al}_2\text{O}_3\text{-SiO}_2$.

Fig. 3. Effect of pH on the adsorption of $5.0 \mu\text{g mL}^{-1}$ Pb, $2.0 \mu\text{g mL}^{-1}$ Cd, $2.0 \mu\text{g mL}^{-1}$ Cr and $1.0 \mu\text{g mL}^{-1}$ Cu on $\text{ZrO}_2\text{-Al}_2\text{O}_3\text{-SiO}_2$.

quantitative recovery (>90%) was obtained. As described previously, 4.0 mL of 0.3 mol L⁻¹ HCl was sufficient to elute the analyte retained on ZrO₂-Al₂O₃-SiO₂. An enrichment factor of 50 was achieved for Pb by this method. In our procedure, sample volumes of 200 mL and 50 mL were ultimately chosen for environmental water and the whitening cosmetic, respectively.

Adsorptive Capacity

The adsorptive capacity is an important factor to evaluate the adsorption performance of ZrO₂-Al₂O₃-SiO₂, because it determines how much ZrO₂-Al₂O₃-SiO₂ is required to quantitatively concentrate Pb from a given solution.

Static Adsorptive Capacity

Using a pH 4.5 and a 10-minute stirring time as the adsorptive conditions, a 20-mg portion of ZrO₂-Al₂O₃-SiO₂ was shaken with 100 mL

aqueous solution containing 0.1–10.0 µg mL⁻¹ of Pb. After the distribution equilibrium was reached, the concentration of Pb in solution was determined. The results showed that the static adsorptive capacity of the doped material for Pb was 15.0 mg g⁻¹.

Dynamic Adsorptive Capacity

Under optimum conditions, the determination of the dynamic adsorptive capacity of Pb was performed, and 100 mL of a series of Pb concentrations (0.1–10.0 µg mL⁻¹) was investigated. The results showed that the micro-column was saturated at 100 mL of 10.0 µg mL⁻¹ of Pb, and the dynamic adsorption capacity of ZrO₂-Al₂O₃-SiO₂ for Pb was 11.1 mg g⁻¹.

Interferences

The effects of common coexisting cations and anions as commonly expected in environmental water

or whitening cosmetics on Pb extraction by ZrO₂-Al₂O₃-SiO₂ were examined. Solutions of 5.0 µg mL⁻¹ Pb containing the added interfering ions were treated according to the recommended procedure. The results are listed in Table II. The effect expresses the recovery in the presence of interfering ions relative to the interference-free response. As seen, 5.0 mg mL⁻¹ Na⁺, 10.0 mg mL⁻¹ K⁺, 15.0 mg mL⁻¹ Ca²⁺, Mg²⁺, 1.0 mg mL⁻¹ Al³⁺, 9.2 mg mL⁻¹ Cl⁻, 10.4 mg mL⁻¹ SO₄²⁻, and 6.89 mg mL⁻¹ NO₃⁻ have no obvious influence on the separation or determination of Pb under the selected conditions.

Regeneration and Stability of ZrO₂-Al₂O₃-SiO₂

To test the stability and potential regeneration of the adsorbent, it must be subjected to successive adsorption and elution cycles at optimum conditions. The results

TABLE II
Effects of Interfering Ions on Determining of 5.0 µg mL⁻¹ Pb

Interfering Ions	K ⁺	Na ⁺	Ca ²⁺	Mg ²⁺	Al ³⁺	Cl ⁻	SO ₄ ²⁻	NO ₃ ⁻
Permit ratio ^a	2000	1000	3000	3000	200	1846	2087	1378
Recovery ^b (%)	90.50	90.37	93.55	94.33	90.11	90.50	90.37	90.11

^a Concentration ratio of the interfering ions to the analyte.

^b Recovery of the analyte.

Fig. 4. Effect of HCl concentration on the desorption of Pb on ZrO₂-Al₂O₃-SiO₂.

Fig. 5. Effect of desorption flow rate of HCl on the recoveries of Pb on ZrO₂-Al₂O₃-SiO₂.

showed that $\text{ZrO}_2\text{-Al}_2\text{O}_3\text{-SiO}_2$ can be re-used after regeneration with 10 mL of distilled water and is stable for up to 10 times adsorption-elution cycles without obvious decrease in the recoveries of Pb.

Analytical Performance

Under the optimized experimental conditions, the detection limit (LOD, calculated as the concentration corresponding to three times the standard deviation of 9 runs of the blank samples) of the method for Pb with an enrichment factor of 50 was 1.69 ng mL^{-1} , and the relative standard deviation (RSD) was 1.09% ($n=9$, $C=2 \text{ ng mL}^{-1}$). A com-

parison of the proposed method to some recent papers on Pb determination by SPE is given in Table III. As seen, the obtained LOD is lower than in the studies by Ungoren et al. (27) and Ghaedi et al. (20), and close to the reports by Al-qadami et al. (2) and Wang et al. (28).

Analytical Application

The proposed method was applied to the determination of Pb in pond water, tertiary treatment water from Daye Lake, and whitening cosmetic samples. The real-world samples and their spiked recoveries were treated as in the Sample Preparation section. The

analytical results, listed in Tables IV and V, show that the recoveries of Pb were 98.4–109.6%, indicating that the proposed method is suitable and acceptable.

In order to establish the validity of the proposed procedure, the method was applied to the determination of Pb in certified reference material GSB 07-1183-2000 Environmental Water (Beijing Haotian Wing Tai Technology Co., Ltd., P.R. China). The content of Pb was determined according to the recommended procedure. The analytical result (0.384 ± 0.017) showed that it was in good agreement with the certified value (0.378 ± 0.017).

TABLE III
Comparison of Proposed Method with Earlier Reported Methods

Matrix	Analytes	Extraction Solvents	Technique	LODs	EF ^a	Ref.
Rice Flour and Tea	Pb(II)	Halloysite nanotubes -N-2-Pyridylsuccinamic acid	ICP-OES	0.32 ng mL^{-1}	67	(25)
Milk and Yogurt	Pb(II) and Ni(II)	Aminothiazole-containing sulfonamide resin	FAAS	0.15 (Pb) and 0.75 (Ni) ng mL^{-1}	Pb 350 Ni 50	(26)
Seawater	Mn(II), Co(II), Ni(II), Zn(II), and Pb(II)	2,4-Dioxobutyl-chelating resin	FAAS	3.8(Co), 3.7(Mn), 1.8(Ni), 6.1(Pb), 0.5(Zn) ng mL^{-1}	Co 50 Mn 50 Ni 100 Pb 100 Zn 100	(27)
Whitening Cosmetics	As, Bi, Cd, Pb, Hg and Ti	Multiwalled carbon nanotubes	ICP-AES	2.4(As), 4.08(Bi) 0.3(Cd), 2.1(Pb), 1.8(Hg) and 1.8(Ti) ng mL^{-1}		(2)
Water, Food and Biological samples	Pb(II), Cd(II), and Cu(II)	$\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{L}$	FAAS	0.14(Pb), 0.19(Cd), and 0.12(Cu) ng mL^{-1}	87	(20)
Environmental Water	Pb(II)	Carbon nanostructures,	FAAS	0.61 ng mL^{-1}	125	(28)
Tap and Wastewater	Pb(II)	Ground eucalyptus stem	FAAS	4.5 ng mL^{-1}	50	(29)
Fruit and Leaves	Fe(III), Pb(II), Ni(II) and Zn(II)	Sodium dodecyl sulfate (SDS)-coated alumina	FAAS	1.6(Zn), 2.6(Fe), 2.8(Pb) and 2.1(Ni) ng mL^{-1}	63	(30)
Water and Food	Cu(II), Cd(II), Pb(II) and Ni(II),	Sepabeads SP-207 resin	FAAS	0.18(Cu), 0.17(Cd), 0.55(Pb) and 1.67 (Ni) ng mL^{-1}	50	(31)
Water and Whitening	Pb(II)	$\text{ZrO}_2/\text{Al}_2\text{O}_3/\text{SiO}_2$	FAAS	1.69 ng mL^{-1}	50	This work

^a Enrichment Factor.

CONCLUSION

ZrO₂-Al₂O₃-SiO₂ silicon material was prepared simply by the sol-gel method, and its adsorptive performance for metallic ions was investigated. ZrO₂-Al₂O₃-SiO₂ micro-column extraction, resulting in a 50-fold enrichment factor, was utilized for improving the selectivity and sensitivity of FAAS in the determination of Pb. A simple, selective, and sensitive method was therefore developed for the determination of Pb in environmental water and whitening cosmetics samples by using ZrO₂-Al₂O₃-SiO₂ as the extraction adsorbent. In comparison to some of the previously published works on the same subject, the obtained LOD was lower than that of some other works.

ACKNOWLEDGMENTS

This project was financially supported by the National Nature Science Foundation of China (No. 20975031, 21075030), Education Committee of Hubei Province (D20132501), Hubei Key Laboratory of Pollutant Analysis and Reuse Technique (Hubei Normal University) (KL2013M06), Young and Middle-Aged Elitists' Scientific and the Technological Innovation Team Project of Hubei Education Department of China under Grant (T201007).

Received November 23, 2013.

TABLE IV
Analytical Results of Pb in Environmental Water
by ZrO₂-Al₂O₃-SiO₂ Micro-Column SPE-FAAS

Samples	Added ($\mu\text{g mL}^{-1}$)	Found ^a ($\mu\text{g mL}^{-1}$)	Recovery (%)
Tertiary Water Treatment from Daye	0	ND ^b	—
	1	1.096±0.018	109.6
	5	5.11±0.00032	102.2
Pond Water	0	0.27±0.018	—
	1	1.249±0.011	98.5
	5	5.185±0.012	98.4

^a For three parallel samples.

^b Not detected.

TABLE V
Analytical Results of Pb in Whitening Cosmetics
by ZrO₂-Al₂O₃-SiO₂ Micro-column SPE-FAAS

Samples	Added ($\mu\text{g mL}^{-1}$)	Found ^a ($\mu\text{g mL}^{-1}$)	Recovery (%)
Sample 1	0	0.3001±0.035	—
	1	1.296±0.018	99.6
	5	5.3063±0.0044	100.1
Sample 2	0	ND ^b	—
	1	0.9941±0.0099	99.7
	5	5.014±0.0041	100.3

^a For three parallel samples.

^b Not detected.

Samples 1 and 2: Whitening cosmetics (from different companies).

REFERENCES

1. A.M.L. Marzo, J. Pons, D. A. Blake and A. Merkoć, *Biosens Bioelectron* 47, 190 (2013).
2. A.A. ALqadami, M. A. Abdalla, Z. A. ALOthman and Kamal Omer, *Int. J. Environ. Res. Public Health* 10, 361 (2013).
3. X.S. Wei, A. M. Yu, M. X. Han, J. Zhang, H. L. Zhang and Y. W. Wu, *At. Spectrosc.* 33, 67 (2012).
4. World Health Organization, *Health Criteria and Other Supporting Information* (1996).
5. P. N. Nomngongo, J. C. Ngila, J. N. Kamau, T. A.M. Msagati, L. Marjanovic and B. Moodley, *Anal. Chim. Acta* 787, 78 (2013).
6. J. X. Qiao, X. L. Hou and P. Roos, *Anal. Chem.* 85, 1889 (2013).
7. R. Moradkhani, A. Rouhollahi, H. Shirkhanloob and J. B. Ghasemia, *J. Chin. Chem. Soc.* 60, 481 (2013).
8. C. H. Yin, J. Iqbal, H. L. Hu, B. X. Liu, L. Zhang, B. L. Zhu and Y. P. Du, *J. Hazard Mater.* 233, 207 (2013).
9. M. Shamsipur, R. Davarkhah, R. Hassani and A. R. Khanchi, *Sep. Sci. Technol.* 45, 1340 (2010).
10. I. L. Garc, Y. V. Martinez and M. H. Cordoba, *Talanta* 110, 46 (2013).
11. J. B. Burnecka, A. S. Madej and W. Zyrnicki, *J. Hazard Mater.* 182, 477 (2010).
12. Y. Date, A. Aota, S. Terakado, K. Sasaki, N. Matsumoto, Y. Watanabe, T. Matsue and N. Ohmura, *Anal. Chem.* 85, 434 (2013).
13. Y. B. Zhu and K. Chiba, *Talanta* 90, 57 (2012).
14. N. Gilart, R. M. Marcé, N. Fontanals and F. Borrull, *Talanta* 110, 196 (2013).
15. M.C. P. Blancoa, Y. M. Martinez and P. C. Falcó, *J. Chromatogr. A* 1297, 226 (2013).
16. M. Shekarchia, M. Pourfarzib, B. A. Adergania, A. Mehramizic, M. Javanbakhtd and R. Dinarvand, *J. Chromatogr. B* 931, 50 (2013).
17. M. M. Rahman, S. B. Khan, H. M. Marwani, A. M. Asiri and K. A. Alamry, *Chem. Cent. J.* 6, 158 (2012).
18. K. Shiba1, M. Tagaya, R. D. Tilley and N. Hanagata, *Sci. Technol. Adv. Mater.* 14, 1 (2013).
19. H.G. Lin, T. Gan and K. B. Wu, *Food Chem.* 113, 701 (2009).
20. H. Bagheri, A. Afkhami, M. S. Tehrani and H. Khoshshafar, *Talanta* 97, 87 (2012).
21. A. R. Farahmand, S. R. Yousefi, N. S. Fumani, S. Mirza, M. Shamsipur and J. Hassan, *Microchim. Acta* 166, 89 (2009).
22. N. Pal, M. M. Seikh and A. Bhaumik, *J. Solid State Chem.* 198, 114 (2013).
23. L. Sowntharya, R. C. Gundakaram, K.R.C. SomaRaju and R. Subasri, *Ceram. Int.*, 39, 4245 (2013).
24. G. Y. Fang, H. Li, L. Cao and F. Shan, *Mater. Chem. Phys.*, 137, 558 (2012).
25. Q. He, D. Yang, X. L. Deng, Q. Wu, R. J. Li, Y. H. Zhai and L. J. Zhang, *Water Research* 47, 3976 (2013).
26. C. Er, B. F. Senkal and M. Yaman, *Food Chem.* 137, 55 (2013).
27. S. H. Ungoren and S. Kartal, *J. Appl. Polym. Sci.* 2414 (2013).
28. Y. K. Wang, S. T. Gao, X. H. Zang, J. C. Li and J. J. Ma, *Anal Chim. Acta* 716, 112 (2012).
29. H. Z. Mousavi, B. A. Esfahani and A. Arjmandi, *J. Chin. Chem. Soc-Taip* 56, 974 (2009).
30. M. Ghaedi, H. Tavallali, A. Shokrollahi, M. Zahedi, M. Montazerzohoria and M. Soylak, *J. Hazard Mater.* 166, 1441 (2009).
31. D. Mendil, T. Kiris, M. Tuzen and Mustafa Soylak, *Int. J. Food Sci. Tech.* 48, 1201 (2013).