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Determination of Pb and Cd Ions in Contaminated Water using FAAS after Preconcentration by Dithizone-Modified Cellulose Acetate Polymeric Membranes

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ABSTRACT

This investigation proposes a new method for the determination of lead and cadmium ions in contaminated waters by dithizone-modified cellulose acetate polymeric membranes. This method is precise, cost-effective and eco-friendly. Quantitation of analytes was performed by flame atomic absorption spectrometry technique. The method is based on the retention of Pb and Cd by an adsorbent which its effective component is dithizone, a strong chelating ligand with lead and cadmium ions. Some important parameters affecting the analytical performance of the method such as pH, flow rate of the sample solution and eluent; concentration and volume of the eluent were optimized. Maximum adsorption capacities of adsorbent were 787 mg g^{-1} for Pb(II) and 195 mg g^{-1} for Cd(II). LODs ($3\sigma_b$) of 0.012 mg L^{-1} (Pb) and 0.001 mg L^{-1} (Cd) were obtained. Linear range of calibration curves were 0.044-1.047 and 0.006-0.113 mg L^{-1} for lead and cadmium ions, respectively. RSD% of the method in optimized conditions was below than 5% for lead (0.25 mg L^{-1}) and cadmium (0.025 mg L^{-1}) ions. Enrichment factors of the method were more than 19 and 17 for Pb and Cd ions, respectively.

Keywords: Lead; Cadmium; Cellulose acetate polymeric membranes; Dithizone; Determination

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INTRODUCTION

Clearly, heavy metals are toxic when present in natural water at hazardous levels. The pollution of heavy metals in aquatic systems has been attracting significant attention due to their capability to enter the food chain and bioaccumulate in living tissues. Toxic metals can probably cause mental retardation, reduction in hemoglobin production, damaging nervous system and even cancer. Strong exposure may cause acute effects on human bodies such as gastric pain, nausea and severe diarrhea [1]. Due to mentioned reasons, continuous monitoring of heavy metals by using accurate and precise determination is essential for environmentalists. Lead (Pb) and cadmium (Cd) are two such heavy metals discharge into the environment. The main ways to intake lead are food and edible water. Pb-based dyes, aerosols, combustion gases of fossil fuels, and battery manufacturing industries are other potential sources of exposure to Pb. Also, cadmium intake occurs via food and edible water. Phosphate fertilizers are the major sources of Cd pollution. Aerosols, dyes, Ni-Cd battery manufacturing industries, heating process systems like iron, and cement production are other sources of cadmium environmental pollution [1]. Various instrumental techniques such as inductively coupled plasma-optical emission spectrometry (ICP-OES) [2], inductively coupled plasma-mass spectrometry (ICP-MS) [3], graphite furnace atomic absorption spectrometry (GFAAS) [4] and flame atomic absorption spectrometry (FAAS) [5] are extensively used for trace determination of heavy metal ions. In compared to the other methods, FAAS appears to be an appropriate choice for the determination of lead and cadmium in water samples due to some reasons like easy maintenance and relatively low cost of analysis [6]. However, the direct determination of trace amounts of these ions in natural waters by FAAS is limited because its sensitivity is commonly insufficient. Therefore, applying a proportion separation and preconcentration process is often inevitable prior to analysis. There are many reported methodologies for the preconcentration step, such as ion exchange [7], cloud point extraction [8], liquid-liquid microextraction [9], membrane filtration [10] and coprecipitation [11]. The imperfections of most of the reported methods are high energy consumption, complicated operations and non-selectivity. Solid phase extraction (SPE) is thought to be the most effective and widely used method for preconcentration of pollutants in water samples. SPE has many advantages over the above mentioned sample pretreatment methods, including rapidity, low cost, minimal chemical usage and possibility of separation and preconcentration of analyte ions in the same step [12].

Recently, much attention has been given towards use of urban and industrial wastes as novel sorbents for adsorption method. Cellulose acetate photography film tape is one of the considerable sources of wastes that has the capability to modify and use in analytical procedures. In order to enhance the adsorption capacity of cellulose acetate polymer chemical modification has been proposed as an appropriate option by scientists. Cellulose acetate derivatives like silver-loading cellulose acetate hollow fiber membrane [13], cellulose acetate/polyethyleneimine blend microfiltration membranes [14], epoxy functionalized poly (ether-sulfone) incorporated cellulose acetate ultrafiltration membrane [15] and cellulose acetate supported bimetallic Ni/Fe nanoparticles [16] have been applied to adsorb lethal compounds from water samples. An effective form of cellulose acetate that can be utilized in preconcentration of analytes is polymeric membrane-like structure. In recent years, polymeric membranes have been applied in various fields, such as microfiltration, ultrafiltration, reverse osmosis and gas separation. Polymeric membranes have been prepared by various chemical and physical techniques; the most common is phase separation [17]. Generally, phase separation comes from the difference in the solubility of polymeric compounds in two different miscible solvent, soluble in one solvent and insoluble in the other one. Phase separation is executable according to four methods including thermally induced phase separation, air-casting of a polymer solution, precipitation from the vapor phase and immersion-precipitation. Comparatively, in this study immersion-precipitation method was selected to prepare cellulose acetate polymeric membranes (CAPMs) in terms of its simplicity of operation and no more requirements to complicated instruments [18]. In this study, a simple and relatively rapid SPE procedure by using CAPMs modified with dithizone was developed in order to preconcentrate Pb and Cd ions in water prior to their determinations with FAAS. To the best of our knowledge, there is no any study for separation/preconcentration of the analytes by using this adsorbent. Before applying the method to real samples, analytical conditions for the quantitative recoveries of Pb and Cd ions, including pH of the solution, amount of adsorbent, concentration and volume of eluent; and flow rates of sample and eluent were experimented and optimized.

EXPERIMENTAL SECTION

Instruments

A Varian AA240FS Atomic Absorption Spectrophotometer (Australia) equipped with lead and cadmium hallow cathode lamps (Photron, Australia) at the wavelengths 283.3 and 228.8 nm was used for the determination of lead and cadmium ions in sample solutions, respectively. Scanning electron microscopy (SEM, Leo, 1455 VP, Germany) was performed to study the morphology of synthesized polymeric membranes. Structural analysis of modified cellulose acetate polymeric membranes was carried out by X-ray diffractometer (XRD, Brucker D8 Discover, Germany). An Orbital Shaker (IKA Works KS 130, Germany), a hotplate and stirrer (Jenway 1000, UK) and a pH meter (Metrohm 827, Switzerland) were used during the experiments.

Materials

All analytical solutions were prepared by deionized water with electric conductivity below 0.05 µS cm^{-1}. All the chemicals and standard solutions used were of analytical reagent grade. Diphenylthiocarbazone (Dithizone, Dz), alkyldimethylbenzylammonium chloride (Benzalkonium chloride, ADBAC), glacial acetic acid, sodium hydroxide, hydrochloric acid (37%, w/w) and suprapur® nitric acid (65%, w/w) were purchased from Merck (Darmstadt, Germany). Cellulose acetate (CA) was obtained from photographic film tape. Analytical solutions of lead and cadmium ions were prepared daily by stepwise dilution of 1000 mg L^{-1} standard solutions (Romil, UK) with water. The glassware used was acid washed by soaking overnight in HNO_3 1 M solution then washed with distilled water several times.

Sampling

The proposed method was applied to two different water samples including (i) Karoon river water (Ahvaz, Iran), (ii)tap water (Ahvaz, Iran). All the samples were filtered through a 0.45 µm cellulose acetate membrane filter and preserved at pH 2 with HNO_3 0.1 M. Before analysis, pH of the sample solutions was adjusted at 6 ± 1 by NaOH 0.1 M. All the separation, preconcentration and determination processes were performed on the samples according to proposed procedures in this study.

Preparation of Adsorbent

In order to prepare CA adsorbent, a simple experimental method was applied. Practically, the cellulose acetate photographic film tapes were previously treated with 5% sodium hypochlorite solution for several seconds in order to remove colored gelatinous layers. The transparent films were fragmented and washed by detergent solution and water several times. The cleaned discolored cellulose acetate films were dried in oven at 95°C for 1 hr. Finally, the fragmented cellulose acetate films were dissolved in glacial acetic acid. The prepared cellulose acetate solution (1 gr L^{-1} CA in acetic acid) was kept in an appropriate container prior to use. Cellulose acetate polymeric membranes (CAPMs) were prepared according to immersion-precipitation method. In order to make the 50 mg CAPMs, 50 mL of CA solution was injected rapidly in 700 mL water while stirring at 700 rpm. After injection, the CAPMs were immediately formed in the water. The prepared CAPMs were rinsed with water until the acetic acid in the solution was completely removed. To enhance the capability of CAPMs to adsorb the Pb(II) and Cd(II) a strong ligand like dithizone was applied. Direct coating of dithizone on CA surface was not effective because CA does not have sufficient strength to retain dithizone molecules. To fix this problem an intermediate compound was applied; ADBAC was selected as a desirable intermediate. In order to modify adsorbent surface with ADBAC, acetate groups of CA might be removed by a strong alkaline solution that allow ADBAC molecules to make a connection with cellulosic surface of CA through electrostatic forces between quaternary ammonium groups and OH groups. To accomplish this purpose, prepared CAPMs were poured in 500 mL KOH 5 M and kept on for 24 hours then washed with water several times. The alkalized CAPMs were remained in 1 L ADBAC surfactant solution (0.5%) for one night, then washed with sufficient water to clean up surplus ADBACs remained in the sphere of modified CAPMs. Finally, the modified CAPMs were poured in a solution of dithizone (0.80 g L^{-1} in ethanol) and held for one night. The dithizone-modified CAPMs (Dz@CAPMs) were washed with ethanol and deionized water several times. The prepared adsorbent was kept in water prior to use.

Procedure

The proposed extraction method in the continuous mode was experienced with model solutions prior to use to real samples. A polyethylene tube (5 cm length and 1 cm inner diameter) with a wide inlet and narrow outlet was used as column. The outlet of the column was fitted with the glass wool and no manipulation was done on the inlet. Before to use, it was filled with 10 mg Dz@CAPMs then washed with 50 mL HNO_3 1 M and sufficient water. 100 mL sample solutions containing 0.1 mg L^{-1} of Pb(II) and 0.05 mg L^{-1} of Cd(II) were passed through column. The pH of the solutions was adjusted to 6.0 with HNO_3 and NaOH 0.1 M as required. The flow of the sample and eluent solutions through the column was controlled at flow rates of 1.0 and 0.1 mL min^{-1} using a Thermo Scientific™ HyperSep™ vacuum manifold system connected to a vacuum pump, respectively. After being completed the passing of sample solution, the column was washed with 10 mL deionized water. Then, the retained metal ions were eluted with 5 mL HNO_3 1 M. Using 100 mL water with the same matrix to the samples was made the blank. Pb(II) and Cd(II) in the eluate solutions were determined by FAAS. The optimized method was applied to various real samples. First, the pH of water samples were adjusted to 6.0 and then the SPE procedure was applied. The analyte concentration in final solutions was determined by FAAS.

RESULTS AND DISCUSSION

Effect of pH

The pH of sample solutions in the SPE method is considered to be one of the critical parameters that mentioned for quantitative recoveries of the metal ions. The competition between metal ions and H^+ in the solution to adsorb on active sites of Dz@CAPMs is affected by pH variation. The effect of pH on the SPE efficiency of Pb(II) and Cd(II) was studied by varying pH in the range of 2.0-8.0 (vol. of sample 100 mL, vol. of eluent 5 mL, adsorbent amount 10 mg, Pb(II) 0.1 mg L^{-1}, Cd(II) 0.05 mg L^{-1}, flow rate of sample 1.0 mL $min.^{-1}$, flow rate of eluent 0.1 mL $min.^{-1}$ and 25 °C). At pH higher than 8.0, the lead and cadmium ions are removed from solution due to precipitation process that was undesirable in this study.

It was found that recovery increased by increasing pH, and at pH between 5.4-8.0, the recoveries were maximum at 95% for Pb(II) and 85% for Cd(II) (Figure 1). In all subsequent studies, pH of sample solutions was fixed at 7.0.

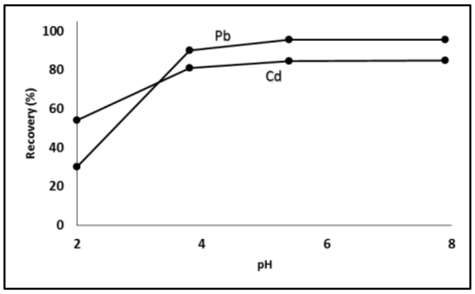

Figure 1: The effect of pH on the recoveries of Pb(II) and Cd(II) using Dz@CAPMs (vol. of sample 100 mL, vol. of eluent 5 mL, adsorbent amount 10 mg, Pb(II) 0.1 mg L^{-1}, Cd(II) 0.05 mg L^{-1}, flow rate of sample 1.0 mL min^{-1}, flow rate of eluent 0.1 mL min^{-1} and 25°C)

Effect of Adsorbent Amount

The effect of adsorbent quantity on preconcentration of Pb^{2+} and Cd^{2+} was investigated by varying its mass from 3 to 20 mg as shown in Figure 2 (vol. of sample 100 mL, vol. of eluent 5 mL, Pb(II) 0.1 mg L^{-1}, Cd(II) 0.05 mg L^{-1}, flow rate of sample 1.0 mL min^{-1}, flow rate of eluent 0.1 mL min^{-1}, 25°C and pH 7.0). As expected, it was found that recovery increased with the increasing amount of adsorbent. Maximum recovery efficiencies of Pb^{2+} (95.5%) and Cd^{2+} (85.0%) were observed when 10 mg of Dz@CAPMs was used.

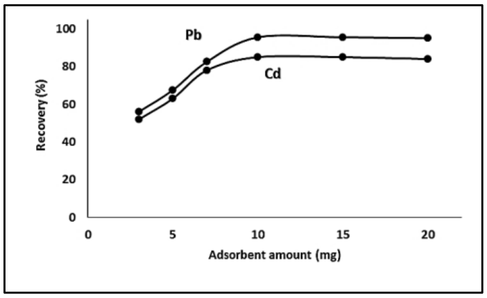

Figure 2: The effect of adsorbent amount on recoveries of Pb(II) and Cd(II) after SPE using Dz@CAPMs at 25°C (vol. of sample 100 mL, vol. of eluent 5 mL, Pb(II) 0.1 mg L^{-1}, Cd(II) 0.05 mg L^{-1}, flow rate of sample 1.0 mL min^{-1}, flow rate of eluent 0.1 mL min^{-1}, pH 7.0 and 25°C)

Effect of Sample and Eluent Amount

In order to recover the analytes adsorbed on the Dz@CAPMs quantitatively, diluted HNO_3 was used for elution of adsorbed ions from the adsorbent located in the column. Thus, different concentrations and volumes of HNO_3 solutions were investigated for the desorption process (vol. of sample 100 mL, adsorbent amount 10 mg, Pb(II) 0.1 mg L^{-1}, Cd(II) 0.05 mg L^{-1}, flow rate of sample 1.0 mL min.$^{-1}$, flow rate of eluent 0.1 mL min.$^{-1}$, 25°C and pH 7.0). As shown in Figures 3 and 4, it was found that 5 mL HNO_3 1 M was sufficient for simultaneous desorption of Pb^{2+} (95%) and Cd^{2+} (85%).

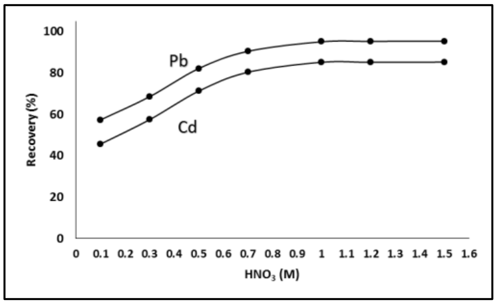

Figure 3: Study of varying concentration of HNO_3 as an eluent of Pb and Cd ions after preoconcentraion using Dz@CAPMs (vol. of sample 100 mL, vol of eluent 5 mL, adsorbent amount 10 mg, Pb(II) 0.1 mg L^{-1}, Cd(II) 0.05 mg L^{-1}, flow rate of sample 1.0 mL min^{-1}, flow rate of eluent 0.1 mL min^{-1}, pH 7.0 and 25°C)

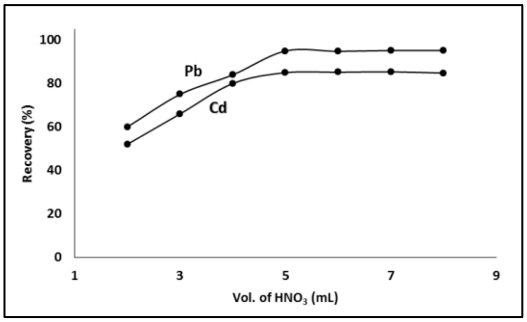

Figure 4: The effect of volume of eluent on recovery efficiencies of Pb(II) and Cd(II) after SPE using Dz@CAPMs (vol. of sample 100 mL, adsorbent amount 10 mg, Pb(II) 0.1 mg L^{-1}, Cd(II) 0.05 mg L^{-1}, flow rate of sample 1.0 mL min^{-1}, flow rate of eluent 0.1 mL min^{-1}, pH 7.0 and 25°C). Effect of sample and eluent flow rate

The effect of flow rate of sample solution and eluent on recovery of analytes was studied by varying the flow rate in the range of 0.5-3.0 mL min^{-1} and 0.05-1.00 mL min^{-1}, respectively (vol. of sample 100 mL, vol. of eluent 5 mL, adsorbent amount 10 mg, Pb(II) 0.1 mg L^{-1}, Cd(II) 0.05 mg L^{-1}, 25°C and pH 7.0). The results (Figures 5 and 6) showed that the recovery yields decreased by increasing the flow rate of sample and eluent. The quantitative recoveries (Pb^{2+} 95%, Cd^{2+} 85%) were achieved when the flow rates of sample and eluent were reduced to less than 1.0 and 0.1 mL min^{-1}, respectively. The maximum adsorption capacity of Dz@CAPMs was studied by using 5 mg of adsorbent added to 50 mL solutions (Pb^{2+} 500 mg L^{-1}, Cd^{2+} 100 mg L^{-1}, pH 7.0, 25°C) in a batch mode. The solutions were stirred for 24 hours at 300 rpm. Then, Pb^{2+} and Cd^{2+} amounts were determined before and after adsoprtion process by FAAS. Appropriate dilution of analysis solutions was performed to fix the concentration of analytes in the linear range of calibration curve. The loading capacities were found to be 787 mg g^{-1} for Pb^{2+} and 195 mg $g^{-1}$for Cd^{2+}.

Analytical Performance

In order to determine limit of detection (LOD) of the proposed method, IUPAC definition which defined as the calculation based on three times of the standard deviation of 11 runs of the blank solution was applied. For making blank solution, 100 mL of distilled water adjusted to pH 7.0 was passed through the column following by passing 5 mL HNO_3 1 M. Measuring the absorption of acidic solution was used to determine LOD. In the calculation of LODs, the 20-fold preconcentration factor was taken into consideration. The preconcentration factor was calculated as ratio of the sample volume (100 mL) to the volume after recovery (5 mL) and found to be 20 for the metal ions studied. The LODs were found to be 0.012 and 0.001 mg L^{-1} for Pb(II) and Cd(II), respectively. The precision of the method under the controlled conditions (vol. of sample 100 mL, vol. of eluent 5 mL, adsorbent amount 10 mg, flow rate of sample 1.0 mL min^{-1}, flow rate of eluent 0.1 mL min^{-1}, 25°C and pH 7.0) was determined by using successive five extraction and recovery periods at definite concentration levels of metal ions followed by FAAS measurement. The relative standard deviations for Pb^{2+} and Cd^{2+} were found to be 4.5% (0.250 mg L^{-1}) and 4.1% (0.025 mg L^{-1}), respectively. Under the optimal conditions, the calibration curves related to the proposed method for the preconcentration and determination of Pb^{2+} and Cd^{2+} were constructed. After applying the proposed method, it was found that calibration graphs were linear for Pb^{2+} concentrations in 0.044–1.047 mg L^{-1} range (y=0.2744x+0.0046, r^2=0.996), and for Cd^{2+} concentrations in 0.005–0.113 mg L^{-1} range (y=2.7256x+0.0036, r^2=0.997).

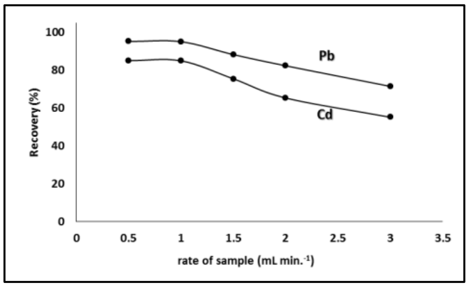

Figure 5: Variation of recoveries of Pb and Cd ions with respect to flow rate of sample solution after preconcentraion using Dz@CAPMs (vol. of sample 100 mL, vol. of eluent 5 mL, adsorbent amount 10 mg, Pb(II) 0.1 mg L^{-1}, Cd(II) 0.05 mg L^{-1}, flow rate of eluent 0.1 mL min^{-1}, pH 7.0 and 25°C)

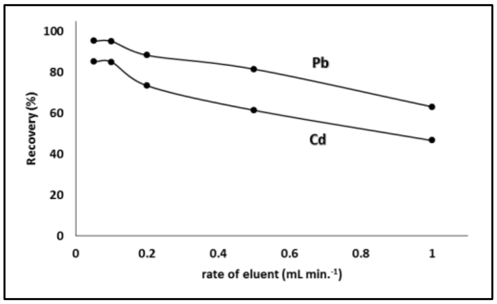

Figure 6: Variation of recoveries of Pb and Cd ions with respect to flow rate of eluent after preconcentraion using Dz@CAPMs (vol. of sample 100 mL, vol. of eluent 5 mL, adsorbent amount 10 mg, Pb(II) 0.1 mg L^{-1}, Cd(II) 0.05 mg L^{-1}, flow rate of sample 1.0 mL min^{-1}, pH 7.0 and 25°C)

Real Samples

The proposed method was used for the determination of lead and cadmium ions in different water samples. To specify the usability and accuracy of the method, several 100 mL of water samples which have been spiked by Pb^{2+} (0.05 and 0.10 mg L^{-1}) and Cd^{2+} (0.01 and 0.10 mg L^{-1}) were prepared. Then, the preconcentration and determination processes were carried out under optimum condition (vol. of eluent 5 mL, adsorbent amount 10 mg, flow rate of sample 1.0 mL min^{-1}, flow rate of eluent 0.1 mL min^{-1}, 25°C and pH 7.0). A good agreement was observed between the added and found quantities of metal ions (Table 1). The best obtained enrichment factors for Pb and Cd ions were found to be more than 19 and 17, respectively. The recovery values calculated were between 85-98%, thus verifying the accuracy of the proposed procedure and its independence from the complicated matrix effects. As a result, the obtained results confirm the accuracy of the proposed SPE method.

Table 1: Determination of spiked lead and cadmium ions at different concentrations in aqueous solutions after preconcentration using Dz@CAPMs (vol. of sample 100 mL, vol. of eluent 5 mL, adsorbent amount 10 mg, Pb(II) 0.1 mg L^{-1}, Cd(II) 0.05 mg L^{-1}, flow rate of sample 1.0 mL min^{-1}, flow rate of eluent 0.1 mL min^{-1}, pH 7.0 and 25°C). (E.F.: Enrichment factor)

		Added (mg L-1)	**found (mg L-1)**	**E.F**	**Recovery(%)**
Karoon river water	Pb	0.05	0.0470 ± 0.0040	19	94
		0.1	0.0970 ± 0.0005	19.4	97
	Cd	0.01	0.0085 ± 0.0004	17	85
		0.1	0.0885 ± 0.0006	17.7	88
Tap water	Pb	0.05	0.0472 ± 0.0050	19	94
		0.1	0.0980 ± 0.0004	19.6	98
	Cd	0.01	0.0090 ± 0.0003	18	90
		0.1	0.0910 ± 0.0004	18.2	91

CONCLUSION

A simple, cost-effective and eco-friendly SPE method has been successfully developed for the preconcentration and determination of lead and cadmium ions in water samples with dithizone-modified cellulose acetate polymeric membranes. The adsorbent could be manufactured by a simple procedure according to immersion-precipitation method and exhibited high adsorption capacity for the determination of Pb and Cd ions at trace levels by using FAAS. The obtained enrichment factors for Pb and Cd ions determination were more than 19 and 17, respectively. The RSD of the proposed method was below than 5%. The Dz@CAPMs adsorbent may also be useful for the determination of other toxic metal ions in water samples. Therefore, the proposed method is potentially a good method for the determination of lead, cadmium and even other heavy metal ions at trace levels and can be easily applied for real sample analysis.

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