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ORIGINAL ARTICLE



Enrichment-separation and determinations of cadmium(II) and lead(II)-1-phenyl-1H-tetrazole-5thiol chelates on Diaion SP-207 by solid phase extraction-flame atomic absorption spectrometry

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KEYWORDS

1-Phenyl-1H-tetrazole-5thiol: Diaion SP-207; Preconcentration; Solid phase extraction; Determination

Abstract A separation-enrichment system based on adsorption of cadmium(II) and lead(II) ions as their 1-phenyl-1H-tetrazole-5-thiol chelates on Diaion SP-207 polymeric resin has been established. Flame atomic absorption spectrometry was used for the determination of cadmium and lead. Analytes were recovered (>95%) on 0.5 g Diaion SP-207 at pH 6.5 and 4.5 mg of 1-phenyl-1H-tetrazole-5-thiol at 1.5 ml min⁻¹ flow rate. Cadmium and lead were desorbed by 10 ml of 1 M CH₃COOH. The influences of some 1A and 2A group metals, transition metals on the recoveries of analyte were also investigated. Addition/recovery tests were performed. The accuracy was checked by the analysis of TMDA 54.4 fortified lake water certified reference material. The proposed procedure was applied for the analysis of analyte in real samples with successful results. © 2012 Production and hosting by Elsevier B.V. on behalf of King Saud University.

1. Introduction

Metals at trace levels still represent a group of dangerous pollutants, to which close attention is paid (Dogan et al., 2002; Babula et al., 2008; Massanyi et al., 2001; Daka et al., 2008). Cadmium and lead are problematic elements for plants, ani-

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ELSEVIER Production and hosting by Elsevier mals and humans. Cadmium and lead are toxic at trace levels due to disrupting enzyme functions, replacing essential metals in pigments or producing reactive oxygen species (Babula et al., 2008; Massanyi et al., 2001; Daka et al., 2008). In the determination of trace metals by instrumental analytical techniques, lower analyte levels than the quantification limits of instrument and the interference of saline components are generally two main limitations (Babula et al., 2008; Massanyi et al., 2001; Aksuner et al., 2011; Khan et al., 2011). To solve these limitations, separation-enrichment procedures like solvent extraction (Helena et al., 1999; Nishimoto and Wagatsuma, 2009), electro deposition (Kanchi et al., 2011; Zhao et al., 2010; Liu and Dai, 2010), cloud point extraction (Ojeda et al., 2010; Borkowska-Burnecka et al., 2010; Baig et al., 2010),

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membrane filtration (Soylak et al., 2007; Itoh et al., 1996), coprecipitation (Aydin and Soylak, 2007; Doner and Ege, 2005), microextraction (Gharehbaghi and Shemirani, 2010; Shirkhanloo et al., 2010; Salahinejad and Aflaki, 2011) etc are continuously used by analytical chemists around the world.

Solid phase extraction is also used for this purpose (Elci et al., 2000; Soylak et al., 2004; Oral et al., 2011; Armagan et al., 2002; Al-Fifi et al., 2009). It is one of the important enrichment/separation methodologies for the trace heavy metal ions (Soylak et al., 1996a,b; Escudero et al., 2010; Soleimani and Khani, 2010). Natural and synthetic solid phase extractors that have high surface area and adsorption capacity, stable for acidic and basic media are preferred for solid phase extraction of metal ions. Zeolites, wool and diatom soils are natural materials and polymeric resins like Amberlite XAD, Ambersorb, and Diaion are also some artificial materials. Diaion SP-207 is brominated styrene–divinylbenzene polymers, and has relatively hydrophobic nature. Its mesh size, surface area, and pore size are 20–60 mesh, 650 m² g⁻¹, and 105 Å, respectively (http://www.sigmaaldrich.com).

1-phenyl-1*H*-tetrazole-5-thiol was used as chelating agent for presented work. It was used for accurate spectrophotometric determinations of palladium and bismuth ions at trace levels (http://www.sigmaaldrich.com). According to our literature scanning, until now, 1-phenyl-1*H*-tetrazole-5-thiol and Diaion SP-207 resin combination is not used for the solid phase extraction studies.

In this work, a simple and accurate procedure for cadmium(II) and lead(II) ions that is based on solid phase extraction of cadmium(II) and lead(II) as their 1-phenyl-1*H*-tetrazole-5-thiol on Diaion SP-207 resin.

2. Experimental

2.1. Reagents and solutions

High purity reagents from Merck, Darmstadt were used. Stock solutions containing 1000 mg l^{-1} analyte were prepared from nitrate salts of cadmium and lead ions in 1% of HNO₃. Diluted standard solutions and model solutions were daily prepared from the stock standard solutions. Diaion SP-207 is purchased from Sigma, St. Louis, USA (Supelco no: 13623-U). It was washed successively with NaOH, water, 3 mol l⁻¹



Figure 1 The influences of the pH on the recoveries of cadmium(II) and lead(II) ions (N = 3).

HNO₃ and water, sequentially. 0.3% (m/V) solution of 1phenyl-1*H*-tetrazole-5-thiol (Sigma Chem. Co., St. Louis) was prepared by dissolving in ethanol. The buffer solutions given in the Literature (Soylak et al., 1996a,b) were used in the presented work. TMDA 54.4 fortified lake water certified standard reference material was supplied by National Water Research Institute, Environment Canada (Burlington, ON, Canada). Synthetic seawater was prepared according to the literature (http://www.thelabrat.com/protocols/SyntheticSea Water.shtml).

2.2. Instrument

A Perkin-Elmer Model 3110 atomic absorption spectrophotometer equipped with a 10-cm air-acetylene burner was used for the determination of the metal ions. All instrumental settings were those recommended in the manufacturer's manual book. The samples were introduced to nebulizer of the AAS by using micro injection system (Berndt and Jackwerth, 1975; Soylak et al., 2008). A pH meter, Sartorius PT-10 Model glass-electrode was employed for measuring pH values in the aqueous phase. A column (15.0 cm in length and 1.0 cm in diameter), packed with 0.5 g of Diaion SP-207 was used.

2.3. Procedure

Twenty five milliliters of reverse osmosis water containing 5–20 g of analytes was placed in a beaker. Five milliliters of



Figure 2 Effects of amounts of 1-phenyl-1*H*-tetrazole-5-thiol on the recoveries of cadmium(II) and lead(II) ions (N = 3).



Figure 3 Relations between sample volume and recoveries (N = 3).

Table 1 Effects of various eluents on the recoveries of analyte ions (N = 3).

Eluent type	Recovery, (%)	
	Cd	Pb
1 mol l ⁻¹ CH ₃ COOH	99 ± 2	98 ± 1
2 mol l ⁻¹ CH ₃ COOH	99 ± 2	89 ± 1
3 mol l ⁻¹ CH ₃ COOH	100 ± 2	76 ± 3
$1 \text{ mol } 1^{-1} \text{ HNO}_3$	99 ± 0	95 ± 3
$2 \text{ mol } l^{-1} \text{ HNO}_3$	92 ± 2	77 ± 1
$3 \text{ mol } l^{-1} \text{ HNO}_3$	92 ± 2	74 ± 2
1 mol l ⁻¹ HCl	100 ± 1	99 ± 1
$2 \text{ mol } l^{-1} \text{ HCl}$	89 ± 1	75 ± 2
$3 \text{ mol } l^{-1} \text{ HCl}$	90 ± 3	$89~\pm~1$

buffer solution to give the desired pH between 3-8 and 1-phenyl-1*H*-tetrazole-5-thiol solution was added. After 10 min, the solution was passed through to Diaion SP-207 column. The adsorption of metal chelates is performed. Then adsorbed analytes on the resin were desorbed by 10 ml of 1 mol 1^{-1} CH₃COOH. The eluent content was evaporated to 2 ml. Hundred microliters of the solution was introduced to the nebulizer of the flame AAS by micro injection system to determine analyte elements (Berndt and Jackwerth, 1975; Soylak et al., 2008).

2.4. Analysis of water samples

The method was also applied to TMDA-54.4 fortified lake water certified reference materials. The separation-preconcentration procedure given above was applied to 10.0 ml of TMDA-54.4 fortified lake water sample.

Natural waters were collected in prewashed polyethylene bottles. The pH of 75 ml of the sample was adjusted to 6.5 with buffer. Then the separation–enrichment procedure given above was applied to the final solutions. Then analyte element contents were determined by flame AAS.

3. Results and discussion

3.1. Influences of pH

At the big ratio metal chelates are used and metal chelates generally occurred at the buffered pH medium (Soylak et al., 2011, 1999; Bouariche et al., 2010; Baig et al., 2009; Ghaedi et al., 2009a,b; Chang et al., 2010), the effects of pH of the aqueous medium were investigated for recoveries of cadmium(II) and lead(II)-1-phenyl-1*H*-tetrazole-5-thiol chelates on Diaion SP-207 resin at the pH range of 3.0-8.0 by using model solutions containing 5 µg of cadmium(II) and 20 µg of lead(II). The results are depicted in Fig. 1. Quantitative recovery values were obtained at the pH range of 6.0-7.0. All other works were done at pH 6.5 by using phosphate buffer.

3.2. Amounts of ligand

The influences of amounts of 1-phenyl-1*H*-tetrazole-5-thiol on the retentions of Cd(II) and Pb(II) on Diaion SP-207 resin were also studied. The results for analyte ions are depicted in Fig. 2. The recoveries of both ions were quantitative (>95%) after 4.5 mg of 1-phenyl-1*H*-tetrazole-5-thiol. 4.5 mg of 1-phenyl-1*H*-tetrazole-5-thiol was used for all other experiments. (See Fig. 3).

3.3. Eluent type

The influences of various eluents given in Table 1 were examined for desorption of adsorbed metal ion chelates from Diaion SP-207 resin. Quantitative results (95%) were obtained for both cadmium and lead with $1 \mod 1^{-1}$ acetic acid, $1 \mod 1^{-1}$ HNO₃ and $1 \mod 1^{-1}$ HCl. Ten microliters of $1 \mod 1^{-1}$ acetic acid was selected. (See Table 2).

3.4. Flow rates

Because the flow rates of sample solution and eluent solutions are two important parameters for the quantitative retention of analytes on the solid phase extraction works (Soylak et al., 1997; Ghaedi et al., 2005; Soylak, 2004; Kamau et al., 2011), the effects of sample and eluent flow rates on the recoveries of Cd(II) and Pb(II)-1-phenyl-1*H*-tetrazole-5-thiol chelates in the range of 1.5-6.0 ml min⁻¹. The recoveries of Cd(II) and Pb(II) were quantitative till 2.0 ml min⁻¹. For all further studies for sample and eluent flow rates, 1.5 ml min⁻¹ were used.

3.5. Sample volume

The effect of the sample volume on the recoveries of cadmium and lead ions as 1-phenyl-1*H*-tetrazole-5-thiol on Diaion SP-207 resin was examined in the sample volume range of 50– 300 ml (Fig. 2). While the recoveries of cadmium ions were quantitative till 200 ml, lead ions were recovered quantitatively

Table 2 Effect of some matrix ions on the recoveries of the analytes (N = 3)

Ion	Added as	Concentration ($\mu g m l^{-1}$)	Recovery, (%)		
			Cd	Pb	
Na ⁺	NaCl	10,000	96 ± 2	102 ± 3	
Mg ⁺²	$Mg(NO_3)_2$	500	96 ± 2	97 ± 2	
Ca ⁺²	CaCl ₂	2000	98 ± 1	103 ± 1	
K ⁺	KCl	10,000	97 ± 3	95 ± 2	
SO_4^{-2}	Na_2SO_4	2500	98 ± 3	97 ± 2	
Cl	NaCl	10,000	96 ± 2	100 ± 2	
Pb ⁺²	$Pb(NO_3)_2$	5	98 ± 2	-	
Cd ⁺²	$Cd(NO_3)_2$	1	_	100 ± 2	
Fe ⁺³	Fe(NO ₃) ₃ ·9H ₂ O	5	98 ± 2	102 ± 3	
Ni ⁺²	Ni (NO ₃) ₂ ·6H ₂ O	5	97 ± 1	100 ± 0	

Table 3 Addition-recovery tests for some water samples as application of presented method (N = 3).

	Added (µg)	Tap water		Bottled Mineral W	Bottled Mineral Water	
		Found (µg)	Recovery, (%)	Found (µg)	Recovery, (%)	
Cd	0	BDL		BDL		
	2,5	2.4 ± 0.1	97	2.6 ± 0.2	102	
	5	5.0 ± 0.0	100	5.0 ± 0.2	100	
	10	9.9 ± 2.0	99	9.8 ± 0.5	98	
Pb	0	BDL		BDL		
	2,5	2.5 ± 0.1	100	2.4 ± 0.1	98	
	5	5.0 ± 0.1	100	4.8 ± 0.1	97	
	10	$10.0~\pm~0.2$	100	10.1 ± 0.1	101	
		Added (µg)	Synthetic	seawater		
			Found (µg	g)	Recovery, (%)	
Cd		0	BDL			
		10	10.2 ± 0.0	1	102	
		20	20.0 ± 0.6	j	103	
Pb		0	BDL			
		10	10.4 ± 0.0		104	
		20	19.4 ± 0.0		98	

till 75 ml. Due to the quantitative recovery values (>95%) were obtained at 75 ml for both analyte ions, the preconcentration factor is calculated by the ratio of the highest sample volume for both analyte ions (75 ml) and the lowest final volume (2.0 ml). In the present study to achieve the highest possible preconcentration the factor was 37.5.

3.6. Interferences

On the spectroscopic determination of metals, highly saline solutions are affected by the analyte levels, this is known as "Matrix Effect" (Soylak et al., 1996a,b; Ghaedi, 2006; Soylak and Tuzen, 2006; Soylak et al., 2003; Divrikli et al., 2003; Munagapati et al., 2010; Ghaedi et al., 2010; Soylak and Yilmaz, 2011). The influences of the alkaline, alkaline earth and transition metal ions were examined. The results are given in Table 1. The limit of tolerance for analytes is defined as the ion concentration causing a relative error smaller than $\pm 5\%$ related to the enrichment, separation and determination of analytes.

3.7. Figure of merits

The calibration curves were linear in the range of $0.02-1.5 \,\mu\text{g ml}^{-1}$ for cadmium and $0.5-8.0 \,\mu\text{g ml}^{-1}$ for lead. The regression equations were A = 0.140C + 0.002 ($R^2 = 0.999$) for cadmium and A = 0.009C-0.001 ($R^2 = 0.999$) for lead. The detection limits for cadmium(II) and lead(II) were calculated after presented solid phase extraction procedure was applied to the blank solutions. The limits of detection for

Table 4 Application of the presented method to TMDA 54.4 fortified lake water certified reference material (N = 3).

Element	Found ($\mu g l^{-1}$)	Certified value ($\mu g l^{-1}$)	Recovery, (%)
Pb	493.5 ± 0	514	96
Cd	164 ± 4	158	104

cadmium and lead (k = 3, N = 10) were $1.1 \ \mu g \ l^{-1}$ and $48 \ \mu g \ l^{-1}$, respectively.

Various amounts of cadmium and lead ions were spiked to various water samples given in Table 3. The presence of natural waters has no significant influences on the recovery of cadmium and lead ions on Diaion SP-207 resin.

3.8. Application of the method

The accuracy of methodology was checked by certified reference material. As shown in Table 4, good and quantitative recoveries are obtained. This is an important point for the application of the presented method to natural water samples. The presented solid phase extraction method was applied to some water samples from Kayseri Turkey. The results are given in Table 5.

4. Conclusion

A new simple, precise and accurate solid phase extraction method has been established in the presented work. The effect of some analytical parameters like pH, amounts of reagents and concomitant ions are tolerable. The presented procedure was successfully applied to natural water samples from Kayseri Turkey to determine the level of lead and cadmium in these

Table	5	The	level	of	Cd	and	Pb	in	water	samples	from
Kayse	ri T	urkey	<i>.</i>								

Sample	Concentration ($\mu g l^{-1}$)			
	Cd	Pb		
Tap water from Kayseri city	BDL	BDL		
Bottled mineral water	BDL	BDL		
Waste water from a factory	27.4 ± 0.0	530 ± 56		
Waste pool water	26.5 ± 1.9	$53.0~\pm~0.0$		
BDI : Below the detection limit				

Table 6 Comparison methods for preconcentration of cadmium and lead.							
Instrument	Conditions	LOD, $\mu g l^{-1}$	Ref.				
FAAS	рН 7	Cd:6, Pb: 16	Doner and Ege (2005)				
FAAS	pH 8	Cd: 1.4, Pb: 2.8	Ghaedi et al. (2009b)				
ICP-OES	рН 6	Cd: 0.8	Salahinejad and Aflaki (2011)				
FAAS	рН 9	Cd: 0.08, Pb: 0.93	Soylak et al. (2007)				
FAAS	pH 6.5; Eluent: 1 mol l^{-1} acetic acid	Cd: 1.1, Pb: 48	Presented work				
	r preconcent Instrument FAAS FAAS ICP-OES FAAS FAAS	r preconcentration of cadmium and lead.InstrumentConditionsFAASpH 7FAASpH 8ICP-OESpH 6FAASpH 9FAASpH 6.5; Eluent: 1 mol 1 ⁻¹ acetic acid	Instrument Conditions LOD, μg l ⁻¹ FAAS pH 7 Cd:6, Pb: 16 FAAS pH 8 Cd: 1.4, Pb: 2.8 ICP-OES pH 6 Cd: 0.8 FAAS pH 9 Cd: 0.08, Pb: 0.93 FAAS pH 6.5; Eluent: 1 mol l ⁻¹ acetic acid Cd: 1.1, Pb: 48				

FAAS: Flame atomic absorption spectrometry; ICP-OES: Inductively coupled plasma optical emission spectrometry; CoP: Coprecipitation; CPE: Cloud point extraction; DLLME: Dispersive liquid–liquid microextraction; MF: Membrane filtration; LOD: Limit of detection.

samples. The performance of this work was compared with some enrichment works in Table 6. The detection limit of this work is better than some of them in Table 6. Lower detection limits of some other works are related with higher sensitivity of the instrument used in these studies. The presented method is also comparable to other methods described in the literature based on high tolerance to matrix ions.

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