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Nasir Khalid[a]; Shamim A. Chaudhri[a]; M. Mufazzal Saeed[a]; Jamil Ahmed[b]
[a] NUCLEAR CHEMISTRY DIVISION, PAKISTAN INSTITUTE OF NUCLEAR SCIENCE AND TECHNOLOGY, ISLAMABAD, PAKISTAN [b] DEPARTMENT OF CHEMISTRY, QUAID-I-AZAM UNIVERSITY, ISLAMABAD, PAKISTAN

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Separation and Preconcentration of Lead and Cadmium with 4-(4-Chlorophenyl)-2-phenyl-5-thiazoleacetic Acid and Its Application in Soil and Seawater

NASIR KHALID, SHAMIM A. CHAUDHRI,
and M. MUFAZZAL SAEED*
NUCLEAR CHEMISTRY DIVISION
PAKISTAN INSTITUTE OF NUCLEAR SCIENCE AND TECHNOLOGY
P.O. NILORE, ISLAMABAD, PAKISTAN

JAMIL AHMED
DEPARTMENT OF CHEMISTRY
QUAID-I-AZAM UNIVERSITY
ISLAMABAD, PAKISTAN

ABSTRACT

A simple and rapid extraction method for lead and cadmium with a new reagent 4-(4-chlorophenyl)-2-phenyl-5-thiazoleacetic acid (HCPTA) in *n*-butyl acetate and their subsequent determination by flame atomic absorption spectrometry has been investigated. The quantitative extraction was observed at pH 8.4. The stoichiometric composition of the extracted species was formulated as $M(CPTA)_2$, where M = Pb or Cd. The extraction constant ($\log K_{ex}$) of lead and cadmium were found to be -9.7 ± 0.11 and -10.44 ± 0.11, respectively. The effect of various anions and cations on the extraction of lead and cadmium has also been studied. The mutual separation of lead and cadmium has also been proposed. The developed procedure was applied to the determination of these metals in seawater, IAEA (SRM) of soil-7, and copepod-MA-A-1. Higher preconcentration factors can be achieved by using a higher aqueous-to-organic phase ratio.

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* To whom correspondence should be addressed.

INTRODUCTION

Lead and cadmium are toxic to human biosystems and can pose health hazards when present even at trace levels. The harmful effects of lead and cadmium have been well documented (1, 2). A significant increase of these metals in the environment is due to increased industrialization and urbanization. Determination of toxic metals in biotic and abiotic environmental samples is important to ascertain the degree of pollution. Atomic absorption spectrophotometry (AAS) has been particularly used for the determination of metals at trace levels due to its high specificity. However, the determination of trace levels of the metals in seawater is virtually impossible by the direct aspiration of the samples because of the interferences owing to light scattering and nebulizer clogging by the high salt contents (3, 4). To overcome these problems, the solvent extraction technique is generally employed for the separation and preconcentration of metal ions at trace or ultratrace levels.

Several chelating extractants like ammonium pyrrolidine dithiocarbamate (APDC), oxine, 2-thenoyltrifluoroacetone (HTTA), diphenylthiocarbazone, acetylacetone, and sodium diethyldithiocarbamate (NaDDC) are used for the separation and preconcentration of metals from different matrices (5–11). However, APDC and NaDDC are widely used in solvent extraction with certain disadvantages such as relative unstability and slow rate of formation of metal complexes (12).

In the present work an attempt is made to overcome these difficulties by using 4-(4-chlorophenyl)-2-phenyl-5-thiazoleacetic acid (HCPTA) as a new chelating extractant. The complexes of lead and cadmium formed with HCPTA in *n*-butyl acetate were used to determine these metals in Arabian Sea water, soil samples, and IAEA (SRM) of soil-7 and copepod-MA-A-1 using the AAS technique.

EXPERIMENTAL

Equipment

The absorbance measurements were made with a Hitachi Model Z-8000 Polarized Zeeman atomic absorption spectrophotometer coupled with a microprocessor-based data-handling facility and a printer. A water-cooled, premix, fish-tail type burner, having a 10 × 0.05 cm slot, was used for the air-acetylene flame. Hollow cathode lamps of lead and cadmium from Hitachi were used as radiation sources. All pH measurements were carried out with a Metrohm 605 pH meter.

Reagents

Stock solutions of lead and cadmium (1000 mg·L^{-1}) were prepared by dissolving 1 g Specpure metal in a minimum amount of distilled nitric acid (13). The resultant solutions were diluted to 1 L with water. Standard solutions were prepared by appropriate dilution of these stock solution. Fresh working standards were prepared immediately before use. Glassware was cleared by overnight soaking in nitric acid (1:1) followed by multiple rinses with water. Distilled and deionized water was used throughout.

All the reagents used were of Analar grade except 4-(4-chlorophenyl)-2-phenyl-5-thiazoleacetic acid (HCPTA) from Wyeth Laboratories Ltd., which was used as such. A 4% (w/v) solution of HCPTA was prepared in *n*-butyl acetate and was further diluted with *n*-butyl acetate as required. Buffer solutions of pH 1 to 10, having ionic strength 0.1 M, were prepared by mixing appropriate volumes of solutions of KCl and HCl (pH 1–3), CH_3COONa and CH_3 COOH (pH 4–6), NH_4Cl and NH_4OH (pH 6–7.5), and H_3BO_3, NaCl, and NaOH (pH 8–10).

The seawater was collected from the Arabian Sea about half a kilometer from the coast of Karachi. A 10-L sample was collected at a depth of 2 m using a peristaltic pump in a polypropylene container followed by the addition of 5 mL distilled HNO_3 and stored for further use.

Extraction Procedure

A metal solution (5.0 mg·L^{-1}) was prepared by appropriate dilution of the stock solution with buffer solutions of the desired pH in a 35-mL glass vial with a screwed polyethylene cap. Five milliliters of this buffer solution was equilibrated for 10 minutes with an equal volume of HCPTA solution in butyl acetate, using a wrist action Griffin & George shaker. The contents were centrifuged for 3 minutes for phase separation. The concentrations of the elements in the separated organic phase were determined by flame atomic absorption spectrophotometry under optimized instrumental conditions against appropriate standard solutions (Table 1). A blank solution without the metal was also prepared and treated under identical conditions. The signal evaluation was made by subtracting the absorbance of blank from the absorbance of sample. All experiments were conducted at an ambient temperature of 23 ± 1.0°C.

Analysis of Soil Samples

About 200 mg of the sample was slurried with 2 mL water in a 150-mL long stem beaker. Distilled HNO_3 (10 mL) was added and the mixture

TABLE 1
Optimized Instrumental Conditions of Lead and Cadmium in the Organic Phase after Extraction with HCPTA

Parameters	Lead		Cadmium
Lamp current (mA)	7.5		7.5
Resonance absorbance line (nm)	283.3		228.8
Width of slit (nm)	1.3		1.3
Type of burner		Standard[a]	
Burner height (mm)	7.5		7.5
Oxidant (air) pressure (kg·cm^{-2})	1.6		1.6
Fuel (C_2H_2) pressure (kg·cm^{-2})	0.30		0.25

[a] See the Experimental Section.

was heated at 70°C for 2 hours. The mixture was cooled, and 5 mL 30% H_2O_2 was added dropwise. Heating was resumed for another hour with intermittent stirring by gentle swirling of the beaker. The cooled contents were filtered and washed. The filtrate was transferred into a separating funnel. A few drops of cresol red indicator, 100 mg NaF, and 1 g citric acid were added, and the pH was adjusted with the dropwise addition of 1 M NaOH (the color of the indicator changed from yellow to violet). The contents were shaken with 10 mL of 4% HCPTA solution in *n*-butyl acetate. After phase separation the organic phase was aspirated in an air-acetylene flame of AAS for the estimation of lead and cadmium.

Analysis of Copepod-MA-A-1

About 300 mg of the sample was taken in a digestion flask fitted with an air condenser followed by 5 mL distilled HNO_3. The contents were heated at 60°C for 45 minutes, cooled, 2.5 ml concentrated $HClO_4$ was added, and heating was resumed at 280°C with occasional shaking until white fumes evolved. The clear solution was cooled, diluted up to 25 mL, and transferred into the separating funnel. A few drops of cresol red indicator, 100 mg NaF, and 50 mg citric acid were added. The pH (>8.2) was adjusted by the dropwise addition of 1.0 M NaOH until the color changed from yellow to violet. The contents were shaken vigorously for 20 minutes with 10 mL of 4% HCPTA solution. After phase separation, the organic phase was assayed by AAS for the estimation of lead and cadmium.

Analysis of Seawater

Seawater (1 L) was taken in a 2-L beaker. To this solution was added 1 mL cresol red indicator solution, 1 g NaF, 50 mg citric acid, and known amounts of lead and cadmium carrier solution. They were mixed thoroughly. The pH was adjusted by adding 1 M NaOH solution dropwise until the color of the indicator changed from yellow to violet. Then about 500 mL of this solution was transferred into a 1-L separating funnel and 40 mL of 4% HCPTA solution in *n*-butyl acetate was added. The contents were shaken on a reciprocating action shaker for 20 minutes. The aqueous phase was drained out after phase separation, and the remaining solution was transferred to the separating funnel and shaken for a further 20 minutes. When the two phases were separated, the organic phase was directly aspirated into the flame of AAS for the determination of Pb and Cd.

RESULTS AND DISCUSSION

The extraction of lead and cadmium with HCPTA and their subsequent determinations with the flame atomic absorption spectrophotometric technique has been investigated in detail. The solubility of the reagent was checked in various water-immiscible organic solvents, and it was observed that the reagent was soluble in polar solvents only. The chlorinated solvents are not suitable for atomic absorption spectrophotometry due to the formation of phosgene. On the basis of above considerations, *n*-butyl acetate and MIBK were found to be the most suitable solvents for the extraction of metals and subsequent measurements with atomic absorption spectrophotometry. Of these two solvents, *n*-butyl acetate was preferred because the distribution coefficients of Pb and Cd were higher compared to MIBK.

Lead and cadmium were extracted with 4% HCPTA solution in *n*-butyl acetate from aqueous solutions of pH 1–10. Figure 1 shows that no HCPTA–metal chelate is formed below pH 6.0, and quantitative extraction was found to be at pH 8.2 and above. A pH of 8.4 was therefore selected for further investigation. The extraction was found to be completed within 10 minutes. The effect of reagent concentration (0.1 to 0.5%) on the extraction of 5 mg·L^{-1} metal solution was checked at pH 8.4. The optimum reagents concentration was found to be 0.2% (6.07×10^{-2} M).

The stoichiometric compositions of the adducts were established by the slope analysis method (14). The possible reaction is

$$M^{+m} + (m + n)\text{HCPTA} \xleftrightarrow{K_{ex}} \text{M(CPTA)}_m\cdot n\text{HCPTA} + m\text{H}^+$$

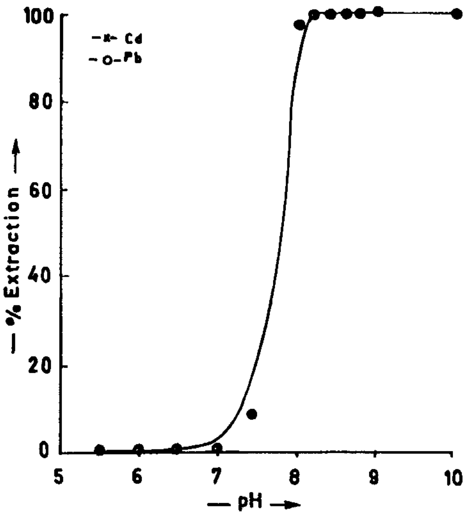

FIG. 1 Effect of pH on the extraction of lead and cadmium with HCPTA.

and in logarithm form:

$$\log K_{ex} = \log D - m\text{pH} - (m + n)\log[\text{HCPTA}] \qquad (1)$$

The plot of log D vs log [HCPTA] in Fig. 2 gives the value of $(m + n)$ which is 1.93 ± 0.06 and 2.13 ± 0.10 for lead and cadmium, respectively. This shows that no free ligand is attached to the central metal atom and that the numerical value of $n = 0$. The data also indicate that the number of chelating ligand attached to the metal ion is equivalent to the charge of the central metal ion. Hence, the stoichiometric composition of the extractable complex is $M(CPTA)_2$, where M = Pb or Cd. The equilibrium constants (log K_{ex}) from the intercepts of Fig. 2 and using Eq. (1) were found to be −9.7 ± 0.11 and −10.44 ± 0.11 for lead and cadmium, respectively.

The effect of different masking agents on the extraction of lead and cadmium was checked under the optimized extraction conditions and are tabulated in Table 2. The data show that EDTA masked the extraction of both lead and cadmium completely due to the formation of more stable metal complexes as compared to HCPTA. Moreover, only lead was completely masked in ascorbate or phosphate media, and it could be easily separated from cadmium.

The effect of other cations on the extraction of lead and cadmium was also studied, and the results are reproduced in Table 3. It was observed

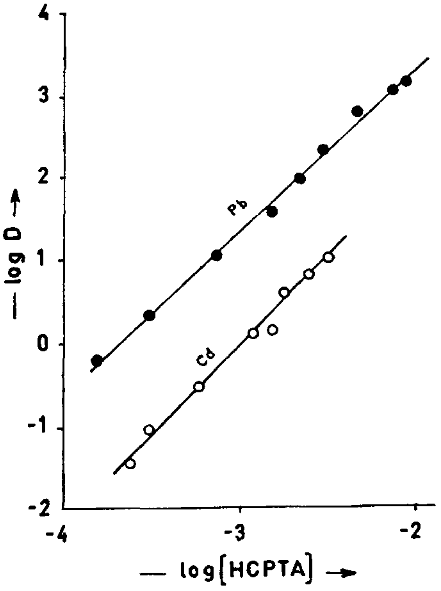

FIG. 2 Distribution ratio of lead and cadmium as a function of log[HCPTA] at pH 8.4.

TABLE 2
Effect of Anions on the Extraction of Lead and Cadmium (5 mg·L^{-1})

Anion	Compound added	Concentration × 10^2 M	Extraction (%)	
			Lead	Cadmium
Nil	—	—	100.00	100.00
Perchlorate	$NaClO_4$	7.12	100.00	96.53
Fluoride	NaF	23.80	99.20	98.25
Chloride	KCl	13.41	94.92	98.71
Bromide	KBr	8.41	98.44	99.23
Iodide	KI	6.02	97.20	100.00
Nitrate	KNO_3	9.89	96.80	99.31
Bicarbonate	$NaHCO_3$	11.90	100.00	100.00
Acetate	$CH_3COONa{\cdot}3H_2O$	7.35	96.26	96.36
Sulfate	Na_2SO_4	7.04	96.16	100.00
Phosphate	$Na_2HPO_4{\cdot}2H_2O$	5.62	3.11	100.00
Thiocyanate	NaSCN	12.33	96.06	100.00
Oxalate	$C_2H_2O_4{\cdot}2H_2O$	7.90	93.05	100.00
Citrate	$Na_3C_6H_5O_7{\cdot}2H_2O$	3.40	95.12	98.87
Ascorbate	$C_6H_8O_6$	5.68	8.51	100.00
Tartrate	$C_4H_6O_6$	6.66	98.65	96.65
EDTA	$Na_2C_{10}H_{14}N_2O_8{\cdot}2H_2O$	2.69	4.04	00.60
Thiourea	H_2NCSNH_2	13.14	97.09	100.00
Cyanide	NaCN	20.40	97.92	100.00

TABLE 3
Effect of Cations on the Extraction of Lead and Cadmium (5 mg·L^{-1})

Cation	Compound added	Concentration of cation (mg·L^{-1})	Extraction (%)	
			Lead	Cadmium
Nil	—	—	100.00	100.00
Lithium	LiCl	100	96.73	100.00
Potassium	KBr	100	95.03	98.83
Cesium	$CsNO_3$	100	99.35	100.00
Magnesium	$MgCl_2$	100	99.08	100.00
Calcium	$CaCl_2$	100	93.07	100.00
Strontium	$Sr(NO_3)_2$	100	100.00	96.39
Vanadium	VCl_5	100	65.23	100.00
Chromium	$K_2Cr_2O_7$	100	93.20	100.00
Manganese	$Mn(NO_3)_2 \cdot 6H_2O$	100	100.00	100.00
Iron	$Fe_2(SO_4)_3 \cdot 7H_2O$	100	28.10	94.20
Cobalt	$CoSO_4$	100	100.00	100.00
Nickel	$NiCl_2$	100	100.00	100.00
Copper	$CuSO_4 \cdot 5H_2O$	100	100.00	100.00
Zinc	$ZnCl_2$	100	96.73	100.00
Paladium	$PdCl_2$	100	62.22	76.20
Platinum	H_2PtCl_6	100	95.00	99.22
Gold	$HAuCl_4$	100	69.28	100.00
Molybdenum	$(NH_4)_6Mo_7O_{24} \cdot 4H_2O$	100	48.37	100.00
Cadmium	$CdSO_4 \cdot 8H_2O$	100	88.23	—
Mercury	$Hg(NO_3)_2$	100	81.31	100.00
Arsenic	$As_2(SO_4)_3$	100	84.97	98.38
Selenium	Na_2SeO_3	100	83.66	97.71
Lead	$Pb(NO_3)_2$	100	—	99.97
Aluminum	$Al_2(SO_4)_3 \cdot H_2O$	25	71.11	85.61
Silver	$AgNO_3$	100	97.00	100.00

that up to 10 mg/L cation concentration of metals show no depression in the absorption signals of lead and cadmium. Further, it is true for lead that even up to a 100 mg/L concentration of these elements there was no significant variation in the absorption signal except for V, Fe, Pd, Au, Mo, and Al. However, Pd and Al depressed the absorption signals of cadmium up to 24 and 15%, respectively, at higher concentration of these metal ions. This is probably due to the hydrolysis of these cations and the adsorption of metal ions on these precipitates.

Backextraction of lead and cadmium were checked from 0.05 to 1.0 M HCl, HNO_3, H_2SO_4, and $HClO_4$ acid solutions. The results indicate that this concentration range of all the acids is effective for the complete stripping of these metals into the acidic layer.

All the reported data regarding the optimization of extraction conditions were cross-checked by measuring the metal contents in the aqueous acidic

TABLE 4
Determination of Lead and Cadmium in IAEA Standard Reference Materials

		IAEA value (ppm)	Our value (ppm)
Soil-7	Lead	60.0 ± 7.8	60.34 ± 2.63
	Cadmium	1.3 ± 1.1	1.08 ± 0.11
Copepod-IAEA-MA-A-1	Lead	2.10 ± 0.29	1.94 ± 0.17
	Cadmium	0.75 ± 0.03	0.77 ± 0.09

phase after backstripping in 0.5 M HNO_3 against aqueous standards in 0.5 M HNO_3.

For the quantitative estimation of lead and cadmium using AAS, known amounts of these metals were extracted in *n*-butyl acetate under the optimum extraction conditions. These organic extracts were then aspirated into an air-acetylene flame to optimize the instrumental conditions for the direct measurement of these metals in the organic solvent. The sensitivity, expressed as the concentration of metal which produces 1% absorption, was found to be 6.0 and 1.6 $\mu g \cdot L^{-1}$ of lead and cadmium, respectively. The detection limit (15) was determined to be 2.0 $\mu g \cdot L^{-1}$ for lead and 1.0 $\mu g \cdot L^{-1}$ for cadmium. These values are comparable to the reported values for APDC (16), APDC + DDDC (17), dithizone (18), and azoquinolinol (19).

TABLE 5
Determination of Lead and Cadmium in Seawater by Spiking Method

Element	Amount added ($\mu g \cdot L^{-1}$)	Amount found ($\mu g \cdot L^{-1}$)	Difference
Lead	—	3.1 ± 1.7	—
	4.0	8.8 ± 1.3	4.8
	6.0	11.4 ± 1.1	5.4
	8.0	13.2 ± 0.5	5.2
	10.0	15.0 ± 0.6	5.0
			$\bar{X}$ = 5.10 ± 0.26
Cadmium	—	1.8 ± 1.2	—
	4.0	5.8 ± 1.1	1.6
	6.0	8.2 ± 0.7	2.2
	8.0	9.9 ± 0.4	1.9
	10.0	12.1 ± 0.5	2.3
			$\bar{X}$ = 2.0 ± 0.3

TABLE 6
Concentration of Lead and Cadmium in Local Soil Sample

No.	Lead (μg/g)	Cadmium (ng/g)
1	37.33	261
2	36.69	253
3	37.33	274
4	38.08	289
5	38.81	259
6	39.79	248
Mean	38.00 ± 1.14	264 ± 15

The developed procedure was applied on IAEA (SRM) to check the reliability and accuracy of the method. The results of triplicate determinations of lead and cadmium in IAEA soil-7 and copepod-MA-A-1 are given in Table 4, and they are in good agreement with the reported values. This shows that lead and cadmium can easily be measured in the organic phase at ppb levels by this method. It was observed during experimentation that when the ratio of the organic to aqueous phases was less than one, a third phase was formed due to Ca and Fe precipitation. This was removed by the addition of fluoride and citrate ions to the aqueous phase before preconcentration/extraction. The amount of these masking agents added depends upon the concentrations of Ca and Fe in the analyte solution.

The developed procedure was also applied on environmental samples of seawater and local soil samples, and the results are shown in Tables 5 and 6. The results of the five determinations of lead and cadmium in seawater are tabulated in Table 5. Due to the low concentration of lead and cadmium in seawater, the spiking method was applied for their estimation. The difference between the added and found concentrations of the metal ions was the actual concentration of these metal ions in seawater. The precision of cadmium was low as compared to lead due to its very low concentration. The results of six replicate determinations of a local soil sample, used as standard for this laboratory, are tabulated in Table 6. They show good precision with a relative standard deviation of 2.99 and 5.71% for lead and cadmium, respectively.

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