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Solid phase extraction vis-à-vis coprecipitation preconcentration of cadmium and lead from soils onto 5,7-dibromoquinoline-8-ol embedded benzophenone and determination by FAAS

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Abstract

This article compares the solid phase extraction (SPE) and coprecipitative preconcentration of cadmium and lead from dilute aqueous solutions as a function of pH and weight of chelating agent. SPE enriches cadmium and lead over a wider pH range (6.0–8.0) and requires lower weight of DBQ chelate embedded benzophenone. Among the quinoline-8-ol and its dihaloderivatives, DBQ embedded benzophenone allows quantitative enrichment over a wide pH range (6.0–8.0) for both cadmium and lead unlike DCQ (~6.5 for Cd and 6.5–7.0 for Pb), DBQ was preferred. The calibration plots were rectilinear over the concentration range of 0.1–50 and 2.5–200 $\mu g\,l^{-1}$ of cadmium and lead with detection limits of 0.1 and 2.0 $\mu g\,l^{-1}$, respectively, which are 400 times lower than the direct FAAS method. The precision of the developed procedure is good as it provides relative standard deviation values of 2.20 and 2.45% during five replicate determinations of 2 and 25 $\mu g\,l^{-1}$ of cadmium and lead, respectively. The accuracy of the developed procedure was tested by analyzing certified reference materials (CRM's) of soil and marine sediment samples supplied by IAEA, Italy and NRC, Canada, respectively. Furthermore, the developed procedure has been successfully used for the speciative determination of cadmium and lead in soil samples collected from the vicinity of industries in India.

Keywords: Solid phase extraction; Coprecipitation; 5,7-Dibromoquinoline-8-ol; Benzophenone; Preconcentration; Soils; Chemical speciation; FAAS

1. Introduction

Heavy metal contamination presents a significant threat to the ecosystem and especially to people due to severe toxicological effects on living organisms. Cadmium is one of the toxic heavy metal elements for animals and humans even at low concentrations. Cadmium(II) is listed as the sixth most poisonous substance jeopardizing human health. Exposure to lower amounts of cadmium may cause gastrointestinal irritation, vomiting, abdominal pain and diarrohea. Acute exposure may affect kidneys resulting in tubular proteinosis and sometimes fatality. Lead ranks second in the list of prioritized hazardous substances issued by US Agency for Toxic substances and Disease Registry. Chronic lead poisoning in human beings (particularly in children) occurs at concentrations as low as 0.1 $\mu g\,ml^{-1}$. The principal target organ or organ systems of lead are the blood, brain, nervous system, kidney and reproductive system. Acute exposure may result in shock, severe anaemia, acute nervousness and irreversible brain damage. Through the food chain systems of soil–plant–animal–human, cadmium and lead are transferred into animals and human beings, causing severe contamination. Consequently, the development of reliable methods for the removal and determination of cadmium and lead in environmental samples is of particular significance.

Among the spectral methods, flame atomic absorption spectrometric (FAAS) and spectrophotometric methods are simple, rapid, reliable, low cost and present in almost all analytical laboratories. However, the latter method is beset with problems of lack of selectivity and sensitivity. On the other hand, FAAS is highly selective (as atomic lines are sharp) but not that sensitive compared to widely accepted and costlier ICP-MS, ICP-AES and GF-AAS. Hence, combining a preconcen-

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tration step prior to FAAS determination is often resorted to by various researchers. Of the various preconcentration techniques solid phase extraction (SPE) has come to the forefront in view of the several advantages it offers [1,2]. Table 1 lists the salient features of various coprecipitation and SPE procedures developed for cadmium and lead in conjunction with FAAS since 2003. In the present work, SPE technique is compared with coprecipitation for enrichment of cadmium and lead from dilute aqueous solutions. Again, the determination of total trace metal concentration is not adequate enough to evaluate the trace element partitioning between the different phases of soil. Various single and sequential extraction schemes are proposed to assess the bioavailable metal fraction (and related potential phytotoxic effects) and in the study of mobilization of trace metals from polluted soil, sludge or sediment used for landfill. A number of extraction methods have been proposed for this purpose, which are variants of Tessier et al. [13], Chester and Hughes [14] and Salomons and Forstner [15]. None of them have been developed into a commonly accepted procedure. In this context, to overcome difficulties in comparing results of different works, the Community Bureau of Reference (BCR, now Standards, Measurement and Testing Programme) started a programme in 1987 and arrived at one general sequential extraction scheme for the speciation of trace metals in soils and sediments. This sequential extraction procedure [16,17] is adopted in the present study to chemically speciate cadmium and lead in soil samples collected from the vicinity of industries (see Fig. 1 for such scheme). The fractions obtained on sequential extraction were subjected to preconcentration and FAAS determination after adjusting to desired pH in presence of ammonium acetate buffer.

2. Experimental

2.1. Reagents and materials

Quinoline-8-ol, 5,7-dichloroquinoline-8-ol (DCQ), 5,7-dibromoquinoline-8-ol (DBQ), 5,7-diiodoquinoline-8-ol (DIQ) and benzophenone were obtained from Aldrich, USA. Stock solutions (1000 μg ml^{-1}) of cadmium and lead were prepared by dissolving 0.5708 g of cadmium sulphate ($3CdSO_4{\cdot}8H_2O$) and 0.3998 g of lead nitrate [$Pb(NO_3)_2$], respectively (purchased from E Merck, India) in 250 ml of deionized water. A pH 7.0 ammonium acetate solution was prepared to maintain the pH of the aqueous phase during solid phase extraction (SPE) and coprecipitation preconcentration experiments.

2.2. Instrumentation

A Perkin-Elmer® AAnalyst^{TM} 100 flame atomic absorption spectrometer (Perkin-Elmer, Life and Analytical Sciences, Shelton, CT, USA) was used for monitoring SPE and coprecipitative preconcentration studies. Perkin-Elmer Lumina® cadmium and lead hollow cathode lamps were used. The instrumental settings are as per instructions of the manufacturer.

Table 1
Salient feature of coprecipitation and SPE preconcentration procedures for cadmium and lead in conjunction with FAAS since 2003

Sl. no.	Metal ion	Preconcentration reagent	Solid phase material/ coprecipitant	pH	Calibration range (μg/ml)	Detection limit (μg/ml)	Enrichment factor	Application	Reference
Coprecipitation									
1	Pb	Methyl thymol blue	Napthalene	–	10–200	4.5	100	River and waste water	[3]
2	Pb	NaOH	Erbium hydroxide	0.05 M NaOH			25	Urine, soil, sediment and natural waters	[4]
Solid phase extraction									
3	Cd	Diazoamino-benzene (DAAB)	Poly Cd(11) DAAB-V Presin	–	0.093–30	0.093	200	Rap and river water	[5]
4	Pb	Aminopoly-carboxylicacid	Cellulose	2.5–5.5		0.5	200	Water	[6]
5	Pb	Thioglycollic acid	Cellulose	>5.0				Table salt and water	[7]
6	Pb	Quioline-8-ol	Chromosorb-103	5.0–8.0	20–100		200	Bovine liver CRM	[8]
7	Pb	Phthallic acid	Amberlite XAD-16	5.0–8.0		5.8	850		[9]
8	Pb	Brilliant Cresyl blue	Diaion HP-2MG	8.0		3.7	50	Water, tea, soil and dust	[10]
9	Cd and Pb	Bathocuprio-indislphonic acid	Chromosorb-108	8.0–10.0	0.5-10	0.6	80	Tap and river water, red wine, rice, black tea and honey	[11]
10	Cd and Pb	1-(2-Pyridylazo)-2-naphthol	Chromosorb-106	8.0–9.0		0.19, 0.32	100	Natural waters and salts	[12]
11	Cd and Pb	5,7-Dibromo-quinoline-8-ol	Benzophenone	6.0–8.0	0.01–50, 2.5–200	0.1, 2.0	200	CRMs and real samples of soils, sea water waste water	Present method

LI-120 digital pHmeter (ELICO, India) was used for pH measurements.

2.3. Coprecipitative preconcentration procedure

The sample solutions (1000 ml) containing 0–50 and 0–200 μg of cadmium and lead, respectively, were transferred to a 2 l beaker. Their pH was adjusted to 7.0 ± 0.2 after adding 10 ml of 1.0 M of ammonium acetate buffer. 0.5 g of benzophenone and 0.005 g of DBQ were dissolved in 5 ml of acetone solution and added to above solution drop-wise while stirring for 5 min. The residue collected on the filter paper during filtration using buchner funnel was dissolved in 2.5 ml of DMF and subjected to FAAS analysis.

2.4. Preparation of SPE material

DBQ (0.25 g) and 25 g of benzophenone were dissolved in minimum amount of acetone and poured as a fine stream into 500 ml of deionized water while stirring. Stirring was continued for further 30 min. After filtration, the residue was dried at 40 °C in hot air oven for 2–3 h. The resulting DBQ embedded benzophenone SPE material was stored in an Amber coloured bottle.

2.5. SPE preconcentration procedure

The sample solution (1000 ml) containing 0–50 and 0–200 μg of cadmium and lead, respectively, were transferred to a 2 l beaker. The pH was adjusted to 7.0 ± 1.0 after addition of 10 ml of 1.0 M ammonium acetate buffer. 0.5 g of SPE material (prepared as described in Section 2.4) was added to above solution and stirred for 5 min. Metal enriched SPE material obtained on filtration was dissolved in 2.5 ml of DMF and subjected to FAAS analysis.

2.6. Analysis of soil samples

Soil samples were collected from the areas neighbouring to industrial sites in India. These samples were subjected to the sequential extraction procedure (see Fig. 1). The pH of the fractions 1–4 was adjusted to 7.0 ± 1.0 and were subjected to SPE preconcentration procedure descried in Section 2.5 and then analysed by FAAS.

2.7. Analysis of lead acid battery effluent

The samples collected from lead acid battery effluent (after treatment) and pond (where the treated effluents are discharged)

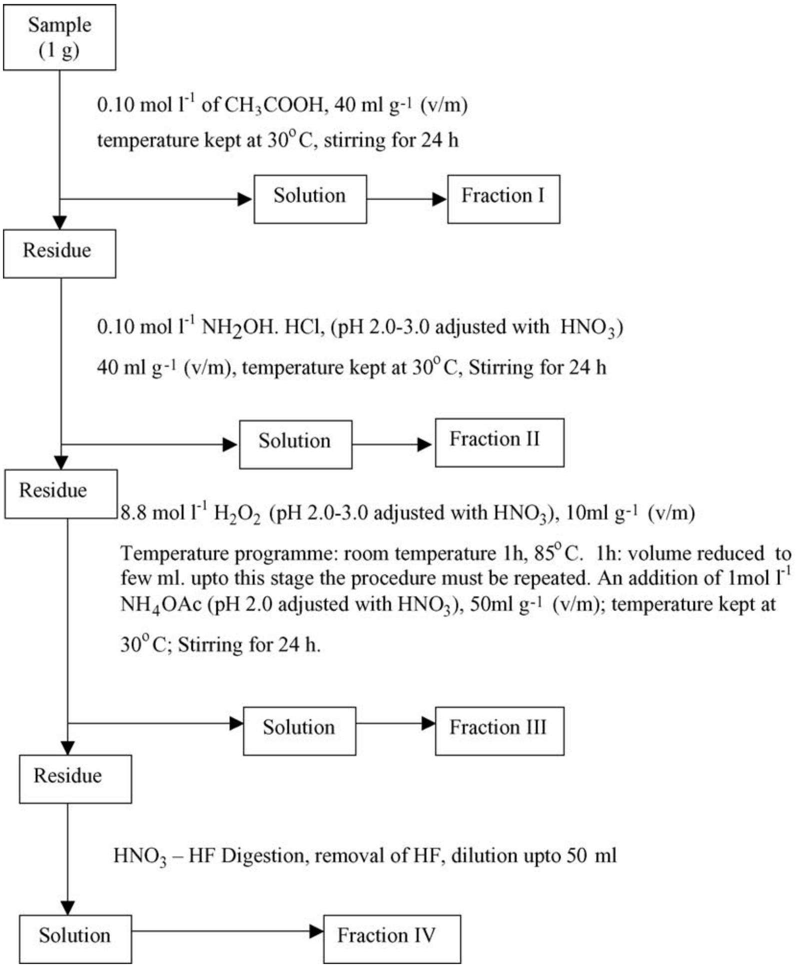

Fig. 1. Scheme of the sequential extraction procedure prior to the determination of cadmium and lead in soil by FAAS.

were subjected to SPE preconcentration and determination for cadmium and lead by following the procedure described in Section 2.5.

3. Results and discussion

Batch “static” preconcentration studies were carried out by taking 1000 ml of sample solution containing 2 μg of cadmium and 25 μg of lead and adjusting the pH to around 7.0 after the addition of 10 ml of 1.0 M ammonium acetate buffer. 0.5 g of benzophenone and 5 mg of chelating agent dissolved in minimum amount of acetone were added during coprecipitation experiments. In SPE studies, 0.5 g of chelate embedded benzophenone material was added during SPE preconcentration studies. The resulting solutions were stirred for 5 min, filtered and the residue was dissolved in 2.5 ml of DMF and subjected to FAAS determination.

3.1. Nature of chelating agent

The percent enrichment of cadmium and lead using coprecipitative/SPE preconcentration method was determined with quinoline-8-ol and its dihaloderivates. The results obtained are shown in Table 2 from which it is clear that DCQ and DBQ chelates gave quantitative recoveries of both cadmium and lead by coprecipitation and SPE preconcentration methods. Hence, these two chelates were chosen for further studies.

3.2. Effect of pH

The effect of pH on enrichment of cadmium and lead was studied by adjusting the dilute aqueous solutions in the range 5.0–10.0 by both coprecipitation and SPE methods. Fig. 2(a and b) show the results obtained using DBQ and DCQ chelates, respectively. It is clear from the figure that with DCQ chelate, the percent enrichment of lead is quantitative in the pH range 6.0–7.0 by both coprecipitation and SPE methods. However, the percent enrichment of cadmium is non-quantitative in the entire pH range with coprecipitation and quantitative at a pH of ~6.5 only with SPE method. Again, DBQ chelate offers quantitative enrichment of cadmium (pH ~ 7.0) and lead (pH 6.0–7.0) by using coprecipitation method. On the other hand, SPE using DBQ chelate offers quantitative enrichment in the pH range 6.0–8.0 for both cadmium and lead. Hence, DBQ was chosen in subsequent preconcentration studies.

Table 2
Comparison of percent enrichment of cadmium and lead using coprecipitative/SPE preconcentration methods with quinoline-8-ol or its derivatives

Sl. no.	Chelating agent	Percent enrichment			
		Coprecipitation		SPE	
		Cadmium	Lead	Cadmium	Lead
1	Quinoline-8-ol	72.3	16.2	12.7	7.7
2	5,7-Dichloroquinoline-8-ol	>99.5	>99.5	>99.9	>99.5
3	5,7-Dibromoquinoline-8-ol	>99.5	>99.5	>99.9	>99.5
4	5,7-Diiodoquinoline-8-ol	60.8	71.5	48.4	89.2

3.3. Effect of weight of DBQ

SPE materials with 1–10 mg of DBQ per 0.5 g of benzophenone were prepared and used for percent enrichment studies of cadmium and lead. The results obtained are shown in Fig. 3(a) from which it is clear that as low as 1 and 5 mg of chelate is enough for quantitative preconcentration of cadmium and lead, respectively. On the other hand, the results obtained on similar studies conducted with coprecipitative preconcentration are shown in the Fig. 3(b). As seen from the figure, a minimum of 2 and 5 mg of DBQ chelate is necessary for quantitative enrichment of cadmium and lead, respectively. Hence, SPE preconcentration method was chosen for subsequent studies using 0.5 g of 1% DBQ embedded benzophenone material.

3.4. Effect of preconcentration time

The preconcentration time was varied from 5 to 60 min during enrichment of cadmium and lead using 0.5 g of DBQ embedded benzophenone as SPE material. The results obtained are shown in Table 3 from which it is clear that as low as 5 min of stirring time was enough for quantitative enrichment of cadmium and lead.

3.5. Effect of aqueous phase volume

The effect of aqueous phase volume on the SPE preconcentration of cadmium and lead from dilute aqueous solutions was studied in the range 10–1000 ml. The results obtained (see Table 3) indicate that quantitative preconcentration of cadmium and lead was possible even with 1000 ml. Subsequent studies were carried out using 1000 ml of sample solution.

3.6. Choice of solvent

DBQ embedded benzophenone SPE material was found to be soluble in various water miscible solvents, viz., acetone, ace-

Table 3
Influence of various parameters on the percent enrichment of cadmium and lead via SPE (0.50 g of DBQ embedded benzophenone, pH 7.0 ± 1.0)

Sl. no.	Parameter	Percent enrichment	
		Cadmium	Lead
1	Preconcentration time (min)		
	5	>99.9	>99.5
	15	>99.9	>99.5
	30	>99.9	>99.5
	60	>99.9	>99.5
2	Aqueous phase volume (ml)		
	10	>99.9	>99.5
	100	>99.9	>99.5
	1000	>99.9	>99.5
		>99.9	>99.5

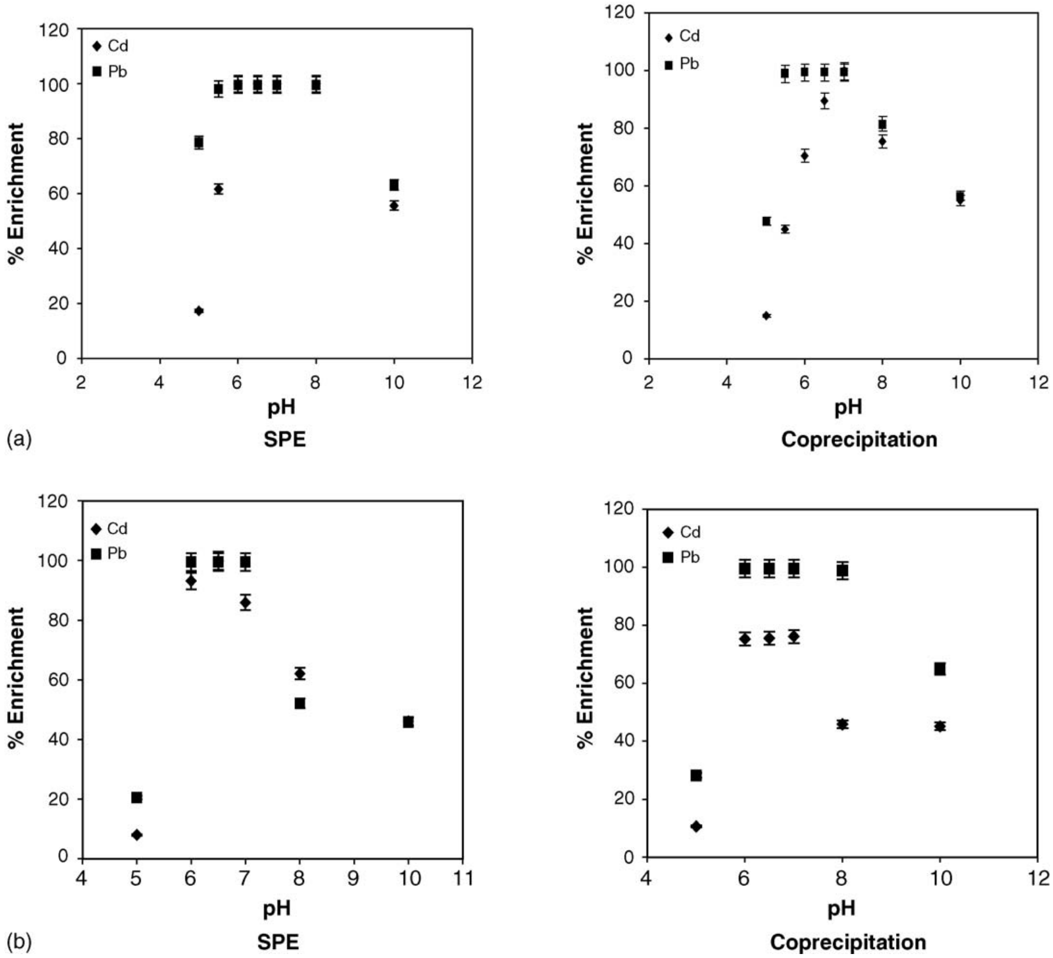

Fig. 2. Effect of pH on the SPE/coprecipitation preconcentration of cadmium and lead using DBQ (a) or DCQ (b) chelates.

tonitrile, DMSO or DMF thus eliminating the need of eluent. The SPE material (0.5 g) after preconcentration was dissolved in various volumes of above mentioned solvents and found that as low as 0.7, 0.7, 0.8 and 0.5 ml, respectively, are required for their complete dissolution. As solubility with DMF is more, 2.5 ml of this solvent was chosen in subsequent studies for dissolution of preconcentrated SPE material prior to FAAS determination resulting in an enrichment factor of ∼400.

3.7. *Effect of neutral electrolytes*

The effect of neutral electrolytes, viz., NaCl, $NaNO_3$, Na_2SO_4, KCl, NH_4Cl, $CaCl_2$ and $MgCl_2$ on the percent enrichment of cadmium and lead prior to FAAS determination was carried out and the results obtained are shown in Table 4. From the table it is clear that excepting Na_2SO_4 (for lead) none of the electrolytes at 0.1 M and NaCl, $NaNO_3$, Na_2SO_4, KCl and

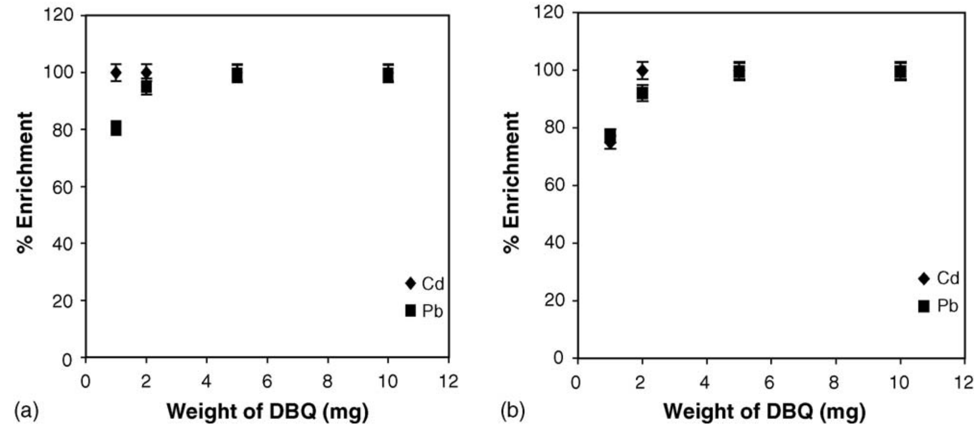

Fig. 3. Effect of weight of DBQ on the percent enrichment of cadmium and lead by SPE (a) and coprecipitation (b) methods.

Table 4
Effect of neutral electrolytes on the percent enrichment of cadmium and lead via SPE prior to FAAS determination (0.5 g of DBQ embedded benzophenone, pH 7.0 ± 1.0)

Sl. no.	Electrolyte (mol l^{-1})	Percent enrichment	
		Cadmium	Lead
1	NaCl		
	0.1	>99.9	>99.5
	1.0	>99.9	29.7
2	$NaNO_3$		
	0.1	>99.9	>99.5
	1.0	>99.9	83.2
3	Na_2SO_4		
	0.1	>99.9	<0.5
	1.0	>99.9	<0.5
4	KCl		
	0.1	>99.9	>99.5
	1.0	>99.9	25.0
5	NH_4Cl		
	0.1	>99.9	>99.5
	1.0	>99.9	67.2
6	$CaCl_2$		
	0.1	>99.9	>99.5
	1.0	63.0	26.0
7	$MgCl_2$		
	0.1	>99.9	>99.5
	1.0	65.3	24.0

NH_4Cl at 1.0 M (for Cd) were found to have deleterious effect on the recovery of cadmium and lead.

3.8. Retention capacity

The amount of cadmium/lead taken during the retention capacity experiments was varied from 1 to 12 mg per 100 ml of aqueous solution with 0.5 g of DBQ embedded benzophenone SPE material. The results obtained are shown in Fig. 4 from which it is clear that the retention capacity increases with increasing amount of cadmium/lead taken initially and reaches a plateau at 10.60 and 11.90 mg g^{-1} of SPE material.

3.9. Statistical and calibration parameters

Under the optimum conditions described in Section 2, the calibration curves were found to be linear over the concentration range of 0–50 and 0–200 μg of cadmium or lead in 1000 ml of solution. The linear equation with regression is as follows:

$$A_{\mathrm{Cd}} = -0.005 + 0.045 \times C$$

$$A_{\mathrm{Pb}} = 0.001 + 0.002 \times C$$

where A is the absorbance and C the amount of cadmium or lead in μg l^{-1} of aqueous solution. The correlation coefficients were 0.9999 and 0.9999 for cadmium and lead, respectively. Five replicate determinations of 2 or 25 μg of cadmium or lead present in 1000 ml of solution gave a mean absorbance of 0.088 and 0.055, respectively, with a relative standard deviation of 2.20 and 2.45%. The detection limit corresponding to 1% absorption (or 0.0044 absorbance units) was found to be 0.1 and 2.0 μg l^{-1} for cadmium and lead, respectively.

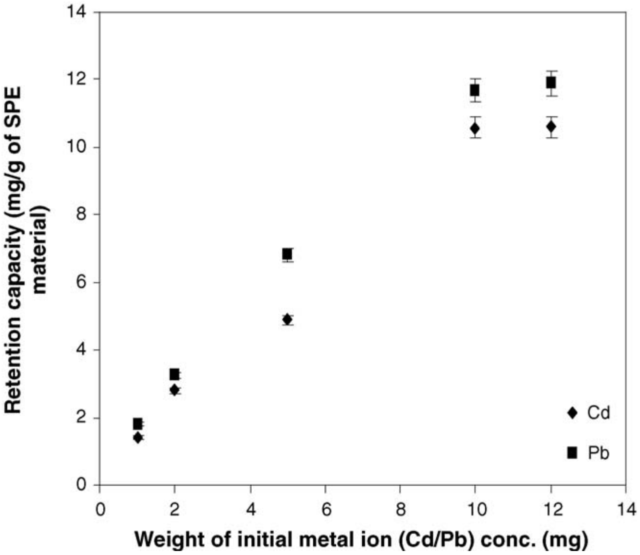

Fig. 4. Effect of initial concentration of cadmium and lead on the retention capacities of DBQ embedded benzophenone.

3.10. Recovery of cadmium and lead from synthetic sea water solutions

Table 5 shows the results obtained on the analysis of synthetic sea water solutions of open sea, deep sea and great salt lake water composition [18,19] spiked with 2 and 25 μg of cadmium and lead. From the recoveries, it is clear that the developed procedure is suitable for selective enrichment of cadmium and lead from a variety of seawater samples in addition to dilute aqueous solutions.

Table 5
Analysis of synthetic sea water solutions (Cd = 2 μg, Pb = 25 μg, pH 7.0 ± 1.0)

Sl. no.	Composition of synthetic sample (%)	Aliquot taken (ml)	Recovery (%)	
			Cadmium	Lead
1	None	1000	>99.9	>99.5
2	Sea water			
	Na (1.05), K (0.04)	500	>99.9	>99.5
	Mg (0.13), Ca (0.04), Cl (1.89)	1000	99.8	99.0
3	Deep sea water			
	Na (3.2), K (0.64)	500	99.8	99.5
	Mg (3.67), Ca (1.30), Cl (17.0)	1000	99.5	99.0
4	Great salt lake water			
	Na (3.2), K (0.34)	500	99.5	98.5
	Mg (0.56), Ca (0.03), Cl (11.2)	1000	99.0	98.0

Table 6
Analysis of certified reference materials

Sl. no.	CRM	Metal added ($\mu g\ g^{-1}$)		Metal found ($\mu g\ g^{-1}$)				Recovery (%)	
		Cd	Pb	Present method*		Certified value		Cd	Pb
				Cd	Pb	Cd	Pb		
1	IAEA	–	–	–	60.5	–	–	–	–
	Soil-7	0.1	30	0.10	91.0	–	60[a]	100	102
		0.2	60	0.19	120.0			95.0	99
2	MESS-3	–	–	0.25	21.0	0.24 ± 0.01	21.1 ± 0.7	–	–
		0.20	20.0	0.45	41.0			100	100
		0.40	40.0	0.65	82.0			100	102

* Average of three determinations.

[a] 95% confidence interval = 55–71 $\mu g\ g^{-1}$.

3.11. Analysis of lead acid battery effluents

The treated effluent and lake water (into which treated effluents are discharged) samples (1000 ml) from a lead acid battery industry located at Tirupati, India, were subjected to preconcentration and determination of cadmium and lead by following the procedure described in Section 2. The cadmium and lead contents were found to be below the detection limit of the developed procedure. However, the recoveries of spiked cadmium and lead to above samples were found to be good indicating the possible application of the developed procedure for routine pollution monitoring of lead acid battery effluents for cadmium and lead.

3.11.1. Analysis of certified reference materials

The accuracy of the developed preconcentration procedure was tested by analyzing certified reference materials (CRMs) of soil (IAEA soil-7, supplied by International Atomic Energy Agency, IAEA, Vienna) and marine sediment (MESS-3, supplied by National Research Council, Canada). The soil and sediment samples were brought into solution by treating 0.5 g of sample with 5 ml of HF and 1 ml of conc. HNO_3 at 150 °C. The process was repeated thrice. The residue was cooled, dissolved in 50 ml of water and diluted to 100 ml. Preconcentration and determination were carried out by following the procedure described in Section 2. The results obtained are shown in Table 6, from which it is clear that the amounts of cadmium and lead in IAEA soil sand MESS-3 determined by present method agree well with certified values. Furthermore, the recoveries of cadmium and lead added to CRM's prior to dissolution, preconcentration and determination were found to be good indicating the suitability of the developed preconcentration/enrichment procedure for the determination of cadmium and lead in soil and sediment samples.

3.11.2. Analysis of soil samples

Four soil samples were collected from the vicinity of various industries located in India. The speciation of above soil samples was carried out by subjecting to sequential extraction procedure presented in Fig. 1. Preconcentrated cadmium and lead contents were determined using FAAS as described in Section 2. The results obtained are given in Table 7. In the soil samples collected from Madhu industries, Spartek Ceramics and Amara Raja Batteries, the total amount of cadmium is ranging from 4.25 to 7.98 $\mu g\ g^{-1}$. In case of Madhu industries, cadmium appears in fraction III, indicating that cadmium is bound to organic matter and released under oxidizing conditions. Similarly lead is essentially bound to organic matter in case of Madhu industries, Spartek ceremics and S.V. Sugar industries. On the other hand, in case of soil sample collected

Table 7
Results of analysis of soil samples ($\mu g\ g^{-1}$ of soil)[a]

Sl. no.	Sample description	Acetic acid fraction (I)		Hydroxylamine hydrochloride fraction (II)		H_2O_2 fraction (III)		HF–HNO_3 fraction (IV)		Total metal	
		Cd	Pb	Cd	Pb	Cd	Pb	Cd	Pb	Cd	Pb
1	Madhu Industries, Agarala	0.48 ± 0.02	0.6 ± 0.4	<0.02	<0.4	3.80 ± 0.02	83.8 ± 4.0	<0.02	<0.4	4.25 ± 0.03	84.3 ± 4.0
2	Spartek Ceramics, Mangapuram	0.24 ± 0.02	0.6 ± 0.4	<0.02	0.6 ± 0.4	1.92 ± 0.02	82.2 ± 0.4	3.89 ± 0.03	<0.4	6.05 ± 0.04	84.0 ± 4.0
3	Amara Raja Batteries, Tirupati	0.48 ± 0.02	0.6 ± 0.4	<0.02	0.6 ± 0.4	0.96 ± 0.02	1.9 ± 0.4	6.67 ± 0.04	1750 ± 50	7.98 ± 0.04	1750 ± 50
4	S.V. Sugars, Gajulamandyam	<0.02	<0.4	<0.02	<0.4	<0.02	1.9 ± 0.4	<0.02	<0.4	<0.02	1.9

[a] Average of three determinations.

in the proximity of Amara Raja Battery Industry, cadmium and lead are present in higher amount compared to other soil samples due to the large scale production of lead acid batteries in this industry. As cadmium and lead are extracted only in fraction IV, these are not likely to be released spontaneously to the environment.

4. Conclusions

DBQ embedded benzophenone SPE material enriches cadmium and lead from 1000 ml of aqueous solutions with enrichment factors of ∼400. This SPE material enriches cadmium and lead over a wider pH range (6.0–8.0) compared to narrow pH range with DCQ and non-quantitative enrichment for quinoline-8-ol and DIQ. Again, the SPE preconcentration procedure is preferred to coprecipitation on the basis of wider optimal pH range and lower amount of chelating agent embedded in benzophenone required for quantitative enrichment. The DBQ embedded SPE gave quantitative enrichment of cadmium and lead with as low as 5 min of stirring and that too from 1000 ml of sample solution. In addition to verifying the accuracy of developed preconcentration procedure by analyzing soil and marine sediment reference materials, the feasibility of the present method was established unequivocally by a successful chemical speciative determination of cadmium and lead in real soil samples collected from the vicinity of four industries.

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