

DERIVATIVE SPECTROPHOTOMETRIC DETERMINATION OF TRACE LEAD IN ALLOYS AND BIOLOGICAL SAMPLES AFTER SEPARATION AND PRECONCENTRATION WITH THE ION PAIR OF 2-(5-BROMO-2-PYRIDYLAZO)-5-DIETHYLAMINOPHENOL AND AMMONIUM TETRAPHENYLBORATE ON MICROCRYSTALLINE NAPHTHALENE OR BY COLUMN METHOD

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ABSTRACT. Lead is quantitatively retained on 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol-ammonium tetraphenylborate with microcrystalline naphthalene or by a column method in the pH range 4.0–6.0 from a large volume of aqueous solutions of various samples. After filtration, the solid mass consisting of the lead complex and naphthalene was dissolved with 5 mL of dimethylformamide and the metal was determined by third derivative spectrophotometry. Lead complex can alternatively be quantitatively adsorbed on ammonium tetraphenylborate-naphthalene adsorbent packed in a column and determined similarly. About 0.2 µg of lead can be concentrated in a column from 300 mL of aqueous sample, where its concentration is as low as 0.7 ng/mL. The interference of a large number of anions and cations has been studied and the optimized conditions developed have been utilized for the trace determination of lead in various samples.

KEY WORDS: Trace lead determination, Derivative spectrophotometry, 2-(5-Bromo-2-pyridylazo)-5-diethylaminophenol, Ammonium tetraphenylborate, Naphthalene

INTRODUCTION

Lead is the most important element, which affect the physical properties of steel, alloys and high purity metals. It is highly toxic to man, animals, and causes environmental disease when released in the atmosphere. Very low concentrations of this metal are normally present in various matrices such as plants, soils, food and water. Therefore, it is very important from an analytical point of view to develop sensitive, selective, rapid and economical methods for its quantitative determination when present in trace amounts. A survey of the literature reveals that lead may be determined spectrophotometrically after extraction of its complexes into various organic solvents [1, 2]. Although, these methods are simple and economical but are not sufficiently sensitive and selective. The preconcentration factor is much less as compared to the present method. Graphite furnace atomic absorption spectroscopy, neutron activation analysis, inductively coupled plasma-atomic emission spectroscopy, inductively coupled plasma-mass spectrometry and direct current plasma atomic emission spectrometry may be used for the determination of lead at trace level [3-8] but these instruments are expensive, day-to-day maintenance is high and they are not free from various types of inherent interferences [3-8].

Derivative spectrophotometry offers the advantages of increased selectivity and sensitivity compared with normal spectrophotometry [9-16]. Spectrophotometers equipped with suitable derivative units enable not only the derivative spectra of the first and second orders to be obtained but also higher orders.

The increased selectivity in derivative spectrophotometry results from the fact that bands, which overlap in normal absorption spectra, appear as separated bands in the derivative spectra. Derivative spectrophotometry can increase the sensitivity owing to the amplification of

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derivative signals and lowering of noise, improvements in selectivity and in sensitivity are easier to obtain in instances where the bands in the normal absorption spectra are fairly sharp [17, 18].

Sodium tetraphenylborate (TPB) and its derivatives have been used in the estimation of alkali and univalent metal ions [19-21]. It has also been used as a counter ion in the extraction and adsorption of some metal complexes into molten naphthalene [22-24] and microcrystalline naphthalene, respectively [25-27]. A survey of the literature reveals that metal ions may be preconcentrated on various adsorbents such as thiol cotton [28], silanized glass beads [29], silica gel [30], Amberlite XAD-4 resin [31], cellulose [32], green tea leaves [33] and polythioether foams [34]. Some of these adsorbents may be fairly effective for preconcentration of metal ions, but their methods of preparation are lengthy and involve rigid control of conditions. The desorption of the metal is carried out by the slow process of elution (the metal complex is probably held by the interior surfaces of the adsorbent and thus the adsorbed complex is not eluted easily), hence the procedure is time consuming. Solvent extraction is a simple and convenient technique for separating and concentrating metal ions, but it cannot be applied directly to metal ions, which form stable complexes with the chelating agents only at elevated temperature. This difficulty can be overcome by using naphthalene as the extractant [35] for thermally stable metal chelates [36]. Solid-liquid separation after adsorption of metal chelates on microcrystalline naphthalene is more rapid and convenient and can be applied to many types of metal complexes [25, 26]. The preconcentration of lead ion is also possible by passing its aqueous solution over naphthalene-NH₄-TPB adsorbent taken in a column. The microcrystalline naphthalene method is rapid but the column method gives a better preconcentration factor [14-16].

In this paper, a highly selective and sensitive preconcentration method has been developed, that uses 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol (5-Br-PADAP) as the complexing reagent and in addition to the (NH₄⁺) (TPB⁻) ion pair supported on naphthalene. The 5-Br-PADAP and its derivatives are highly selective for lead. The 5-Br-PADAP reacts with lead to form a water-soluble complex cation, but in the presence of the TPB anion, it forms a water-insoluble complex (Pb-5-Br-PADAP-TPB). Preliminary observations revealed that the Pb-5-Br-PADAP complex cation could be quantitatively retained on an ammonium tetraphenylborate adsorbent supported on naphthalene. The solid mass, consisting of the metal ion associated complex and naphthalene, can easily be dissolved with a suitable organic solvent such as dimethylformamide (DMF) and the lead is determined by third derivative spectrophotometry. The interference of a number of metal ions and anions on the estimation of lead has been studied in detail and the developed method is found to be highly sensitive and selective and has been employed for the estimation of lead in complex materials.

EXPERIMENTAL

Apparatus

A Shimadzu UV 160 spectrophotometer with 1.0 cm quartz cell was used. A Beckman pH meter was employed for pH measurements. A funnel-tipped glass tube (60 mm x 6 mm) was used as a column for preconcentration. It was plugged with polypropylene fibbers and then filled with the adsorbent to a height of 1.0–1.2 cm after pressing lightly with a flat glass rod. All atomic absorption measurements were made with an atomic absorption spectrometer (Shimadzu AA 670). All glassware was washed with a mixture of concentrated sulfuric and nitric acids (1+1) before use.

Reagents

All the reagents were of analytical reagent grade. A standard lead solution was prepared from $\text{Pb}(\text{NO}_3)_2$ in distilled water and standardized [37]. A 1.0 ppm solution was prepared by appropriate dilution of the standard solution. A 0.01% solution of 5-Br-PADAP in ethanol was prepared. Buffer solutions of pH 3–6, 6–8 and 8–11 were prepared by mixing appropriate ratios of a 0.5 M acetic acid and 0.5 M sodium acetate solution, 0.1 M sodium dihydrogen phosphate solution and 0.1 M dipotassium hydrogen phosphate solution, and 0.5 M ammonia solution and 0.5 M ammonium acetate solution, respectively. A 1% solution sodium tetraphenylborate (TPB) was prepared in distilled water. A 20% solution of naphthalene was prepared in acetone. Solutions of alkali metal salts (1%) and various metal salts (0.1%) were used for studying the interference of anions and cations, respectively.

Preparation of naphthalene- NH_4 -TPB adsorbent

A solution of naphthalene was prepared by dissolving 20 g of naphthalene in 40 mL of acetone on a hot-plate stirrer at 30–35 °C. This solution was transferred into 1500 mL of distilled water containing 25 mL of 1 M ammonium acetate and 75 mL of 1 M ammonia solution (pH 9.5), in a fast stream continues flow with continuous stirring at room temperature. Then, to this solution, 500 mL of an aqueous solution containing 1.7 g of TPB was added. The naphthalene coprecipitated with NH_4^+ and TPB^- . The solution was stirred for about 2 h and then allowed to stand for 2 h. The supernatant solution was decanted off and the remaining solid mass was washed twice with distilled water. The adsorbent in the form of a slurry was stored in a bottle for subsequent use.

General procedure for the column method

Sample solution (up to 300 mL) containing 0.2–40 μg of lead was taken in a beaker and 2.0 mL of 0.01% alcoholic solution of 5-Br-PADAP and 2.0 mL of acetate buffer of pH 5.5 were added to it. The column loaded with the adsorbent NH_4 -TPB-naphthalene was conditioned to pH 5.5 by passing 2–5 mL of the acetate buffer solution at a flow rate of 1 mL min^{-1} . The lead sample solution prepared above was then passed at a flow rate of 1 mL min^{-1} . The packing in the column was washed with a few milliliters of distilled water and then aspirated strongly for 2–3 min, pushing down the solid mass in the column with a glass rod in order to eliminate the excess water attached to the adsorbent. The metal complex was dissolved out of the column along with naphthalene with 5 mL of DMF. The third derivative absorption spectra in the range 500–650 nm were recorded against a blank solution prepared in the same way. The signal was measured between $\lambda_1 = 629$ nm and $\lambda_2 = 597$ nm. A calibration curve was prepared by taking various known amounts of lead under the conditions given above.

General procedure for microcrystalline naphthalene

Sample solution (up to 100 mL) containing 0.2–40 μg of lead solution was placed in an Erlenmeyer flask with tightly fitting stopper. Then 2 mL of 0.01% of the reagent (5-Br-PADAP) was added to it. The pH was adjusted to 5.5 with 2 mL of the buffer, and then 2 mL of 1% TPB solution was added. The solution was mixed well and allowed to stand for a few seconds. Then, 2 mL of a 20% solution of naphthalene in acetone was added to it with continuous shaking. The solid mass so formed consisting of naphthalene and metal complex was separated by filtration on a Whatman filter paper (No.1041). The residue was dried in the folds of a filter paper and transferred to the Erlenmeyer flask. The solid mass consisting of the metal complex along with naphthalene was dissolved with 5 mL of dimethylformamide (DMF). Finally, the third

derivative absorption spectra were recorded in the range 500–650 nm against a blank solution prepared in the same way.

RESULTS AND DISCUSSION

Spectrophotometric measurements

The zero order (normal spectrophotometric) and third order derivative spectra of the complex are shown in Figure 1. As can be seen, the longer wavelength peaks of the third derivative spectra are more significant. The sensitivity of the third order derivative is much higher than for zero (normal), first and second orders. Third derivatization leads to sharper zero order bands (normal spectrophotometric bands) and gives higher signals on the resulting spectra. The characteristics of derivative spectra, such as peak height and noise level, depend on the choice of parameters such as order of derivative, scan speed and integration time during recording of the spectra. The optimum parameters were chosen from preliminary experiments. The best results were obtained from third derivative spectra due to high signals at $\lambda_1 = 629$ nm, $\lambda_2 = 597$ nm, with a wavelength interval of 9 nm. Lead could be determined by measuring the signal between the baseline and the corresponding peaks. It could also be determined from the signal between λ_1 and λ_2 . In the present work, a peak-to-peak method between λ_1 and λ_2 was applied.

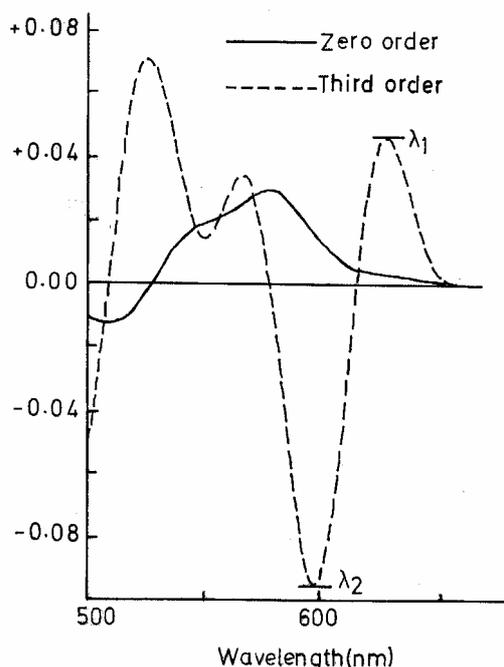
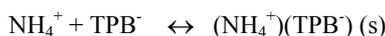


Figure 1. Zero and third order spectra of the naphthalene-Pb-(5-Br-PADAP)-TPB complex. Pb, 2 μ g; buffer, 2 mL; pH, 5.5; 5-Br-PADAP, 2.0 mL (0.01%); solvent, 5 mL DMF; reference, reagent blank.

Retention characteristics of NH₄-TPB

Sodium tetraphenylborate (TPB⁻) is soluble in water, it forms water-insoluble precipitates with some alkali metal ions such as K⁺, Rb⁺, Cs⁺ (but not Li⁺, Na⁺), and univalent metal ions such as Ag⁺, Tl⁺, and Cu⁺, but does not form precipitates with multivalent metal ions. It has been used as a gravimetric and volumetric reagent. Furthermore, it also reacts with ammonium salts such as NH₄⁺ and its derivatives to form water-insoluble precipitates. The TPB⁻ forms a weakly bonded ion-pair with NH₄⁺ in aqueous solution and coprecipitates with microcrystalline naphthalene as follows:



From the experimental observation, the NH₄-TPB ion-pair, produced from TPB⁻ and ammonium acetate in aqueous solution, when supported on naphthalene was unstable and partly desorbed from the surface of the naphthalene in the column on passage of the buffer of pH 5.5. However, the NH₄-TPB ion-pair prepared in acetate buffer of pH 9.5 is highly stable and TPB⁻ is not desorbed even on washing with water or the buffer of pH 5.5. The adsorbent shows excellent absorption characteristics for various cationic metal complexes such as Fe(1,10-Phen)₃²⁺. In this work, TPB⁻ has been selected as the counter-ion because of its purity and moderated price.

Reaction conditions

These were established with the use of 2 µg lead. The adsorption of lead on this adsorbent was found to be a maximum in the pH range 4.0–6.0. In subsequent studies, the pH was maintained at approximately 5.5. Addition of 0.5–5 mL of the buffer did not affect the retention of lead and the use of 2 mL is recommended. Various amounts of 0.01% alcoholic solution of 5-Br-PADAP were tried. Lead was quantitatively adsorbed on the adsorbent over the range 0.6–3.0 mL of the reagent. Therefore, 2.0 mL of the reagent is recommended in the present study.

Various amounts of naphthalene (20% solution of naphthalene in acetone) were added to the sample solutions keeping other variables constant. It was observed that the signal height remained constant with the addition of 1.0–4.0 mL of 20% naphthalene solution. Therefore, 2.0 mL of 20% naphthalene solution was used in subsequent studies. The effect of shaking time on the adsorption indicated that the signal height remained constant over a range of 0.5–5.0 min. Therefore, 1.0 min of shaking time was maintained in the present work.

In the case of column method, the flow rate was varied from 0.2 to 8 mL/min. It was found that a flow rate of 0.2–5.0 mL/min did not affect adsorption. A flow rate of 1 mL/min was recommended in all experiments.

The volume of the aqueous phase was varied in the range of 10–700 mL under the optimum conditions, keeping other variables constant. It was observed that the signal height was almost constant up to 100 mL (preconcentration factor of 20). However, for convenience, all the experiments were carried out with 40 mL of the aqueous phase. Whereas, in the case of column method, signal height was almost constant up to an aqueous phase volume of 300 mL. Therefore, a preconcentration factor of 60 can be achieved by the column.

Choice of solvent

A number of solvents were tried to dissolve the metal complex along with naphthalene. Since the solid mass is dissolved in a small volume (3–5 mL) of solvent, it is essential to select a solvent in which the chelate is highly soluble and also sensitive for UV-Vis spectrophotometric measurements. The solid material is insoluble in ordinary organic solvents such as toluene, 1,2-dichloroethane, n-hexane, nitrobenzene, isoamyl alcohol, n-amyl alcohol, ethyl acetate, methyl

isobutyl ketone, chloroform and dioxane, but soluble in dimethyl sulfoxide, DMF, and propylene carbonate. DMF was preferred because of the high solubility and stability of metal complex on naphthalene. It was found that 2-3 mL of this solvent was sufficient to dissolve the entire mixture, thus further enhancing the sensitivity of the method. Since only a small volume (3–5 mL) of the solvent is required to dissolve the solid mass, it was essential to study the effect of the surplus water attached to the adsorbent. It was found that the surplus water caused the absorbance to decrease by 10-12% and led to an error in the determination. Thus, it was necessary to eliminate the water attached to naphthalene in the column completely by aspirating the column for 2–3 min.

Retention capacity of the adsorbent

The retention capacity of adsorbent was determined by a batch method. The experiment was performed by adding 500 µg of lead, 2 mL of the buffer (pH 5.5), a suitable amount of reagent 5-Br-PADAP to 40 mL of water in a beaker. This solution was transferred into a separatory funnel and then a suitable amount of the adsorbent naphthalene-NH₄-TPB added to it. The separatory funnel was vigorously shaken on a mechanical shaker for 5 min. The solid mass was separated by filtration and lead was determined from the filtrate. The solid mass on the filter paper was dried in an oven, kept in a dessicator, and then weighed to determine the mass of the adsorbent. The maximum amount of lead retained was 6.5 mg/g of the adsorbent.

Calibration, sensitivity, precision and stability

Considering that it is possible to retain 0.1 µg of lead from 300 mL of solution passing through the column, the dissolution with 5.0 mL DMF gives a detection limit of 0.3 ng/mL for lead at the minimum instrumental settings. The linearity was maintained in the concentration range of 0.7 ng/mL to 4.0 µg/mL lead in aqueous solution or 0.04 to 8.0 µg/mL lead in final DMF solution with a correlation factor of 0.9998. Eight replicate determinations of 2 µg of lead in 5 mL DMF solution gave a mean intensity in the third derivative spectrum, measured from the peak-to-peak signal between λ_1 and λ_2 , of 0.142 with a relative standard deviation of $\pm 1.2\%$. The sensitivity was 0.355 (d³A/dnm³)mL/µg from the slope of the calibration curve. The solution was stable for over 6 days.

Effect of foreign ions

Various salts and metal ions were added individually to a solution containing 2 µg of lead in 40 mL of the aqueous phase and the general procedure was applied. The tolerance limit (error <3%) is given in Table 1. Among the salts examined, most did not interfere at the g-mg level, only EDTA interfered seriously due to the high formation constant of this metal-EDTA complex than the 5-Br-PADAP. Among the metal ions studied, many did not interfere even at the milligram level. Thus, the method is highly selective without the use of masking agents. The proposed procedure has therefore been applied to the determination of lead in alloys and biological samples without any prior separations.

Table 1. Effect of foreign salts and ions.

Salt or ion	Tolerance limit
CH ₃ COONa.3H ₂ O, NaCl, KNO ₃	1 g
NH ₄ Br, (NH ₄) ₂ SO ₄	300 mg
K ₂ CO ₃	100 mg
Sodium potassium tartrate	90 mg
Potassium thiocyanate	60 mg
Trisodium citrate, sodium oxalate	35 mg
Na ₂ EDTA	80 µg
Zn(II)	25 mg
Mn(II), Mo(VI)	20 mg
Cr(III), Al(III), Fe(III)	15 mg
Ti(VI), Se(VI), Ga(III), Cd(II)	10 mg
Ni(II), Cu(II), Co(II), In(I)	9.5 mg
U(VI), V(V), Te(IV), Sn(II)	8.5 mg
Rh(III), Pd(II), Os(VIII), Ru(III), Sb(III)	6.0 mg

Analysis of lead in standard alloys

The proposed method was applied to the determination of lead in Nippon Keikin-zoku Kogyo (NKK) CRM No. 916 and No. 920 Aluminum Alloy and NKK No. 1021, Al, Si, Cu, Zn Alloy. A 0.1 g sample of the standard aluminum alloy was completely dissolved in 6–14 mL of hydrochloric acid (1+1) by heating on a water-bath and then 1 mL of 30% (v/v) hydrogen peroxide was added to it. The excess of peroxide was decomposed by heating the sample on the water-bath. The solution was cooled, filtered if needed and diluted to 100 mL with distilled water in a standard flask. An aliquot (1–2 mL) of this sample was taken in a 20 mL beaker and the general procedure was applied. The results obtained are given in Table 2. These results are in agreement with the certified values.

Table 2. Analysis of lead in standard alloys.

Sample	Composition (%)	Concentration (%)	
		Certified value	Found ^a
NKK No. 916 Aluminum Alloy	Si, 0.41; Fe, 0.54; Mg, 0.10; Cr, 0.05; Ni, 0.06; Ti, 0.10; Sn, 0.05; Zn, 0.30; Sb, 0.01; B, 0.0006; Zr, 0.05; Bi, 0.03; Co, 0.03; Mn, 0.11; Cu, 0.27; V, 0.02	0.04	0.039±0.002 ^a
NKK No. 1021 Al, Si, Cu, Zn, Alloy	Si, 5.56; Fe, 0.99; Mg, 0.29; Cr, 0.03; Ni, 0.14; Ti, 0.04; Sn, 0.10; Zn, 1.76; Sb, 0.01; Zr, 0.01; Bi, 0.01; V, 0.007; Ca, 0.004; Mn, 0.11; Cu, 2.72	0.18	0.177±0.008 ^a
NKK No. 920 Aluminum Alloy	Si, 0.78; Fe, 0.72; Mg, 0.46; Cr, 0.27; Ni, 0.29; Ti, 0.15; Sn, 0.20; Zn, 0.80; Sb, 0.10; Bi, 0.06; Ga, 0.05; Ca, 0.03; Co, 0.10; Mn, 0.20; Cu, 0.71; V, 0.15	0.10	0.103±0.004 ^b

*Average of five determinations ± standard deviation. ^aColumn method was applied. ^bMicrocrystalline naphthalene method was applied.

Table 3. Analysis of lead in biological samples.

Sample	Composition	Concentration ($\mu\text{g g}^{-1}$)	
		Certified value	Found ^{*,†}
NIES, No.1 Pepperbush	K, 1.51±0.06; Mn, 0.203±0.107; Mg, 0.408±0.020; Ca, 1.38±0.07%; Cd, 6.7±0.5; Cu, 12±1 Fe, 205±17; Co, 23±3; Zn, 340±20; Ni, 8.7±0.6; Rb, 75±4; Ba, 165±10; Na, 106±13; Sr, 36±4; As, 2.3±0.3; P, (1100); Cr, (1.3); Cs, (1.2); Tl, (0.13); Hg, (0.056) $\mu\text{g g}^{-1}$	5.5±0.8	5.43±0.07 ^a
NIES, No.5 Human Hair	Zn, 169; Cd, 0.20; Sb, 0.07; Ni, 1.8; Al, 240; Fe, 225; Mg, 208; Hg, 4.4; K, 34; Rb, 0.19; Sc, 0.05; Se, 1.4; Na, 26; Sr, 2.3; Ti, 3.2; Ca, 728; Cr, 1.4; Ba, 2.2; Cu, 16.3; Co, 0.10 $\mu\text{g g}^{-1}$	6.0	5.9±0.1 ^a
NIES, No.7 Tea Leaves	Zn, 33; Cd, 0.030; Sb, 0.014; Ni, 6.5; Cr, 0.15; Al, 775; Mg, 1530; Ba, 5.7; K, 18600; Sc, 0.011; Na, 15.5; Sr, 3.7; Ca, 3200; Cs, 0.221; Co, 0.12; Mn, 7.00; Cu, 7.0 $\mu\text{g g}^{-1}$	0.80	0.76±0.04 ^b
NIES, No. 8 Vehicle Exhaust Particulates	K, 0.115±0.008; Ca, 0.53±0.02; Mg, 0.101±0.005; Al, 0.33±0.02; Na, 0.92±0.008; Zn, 0.104±0.005%; Sr, 89±3; Co, 3.3±0.3; Cu, 67±3.5; Cd, 1.1±0.1; As, 2.6±0.2; Cr, 25.5±1.5; V, 17±2; Sb, 6.0±0.4; Ni, 18.5±1.5; Cs, (0.24); Rb, (4.6); Sc, (0.055); La, (1.2); Br, (56); Ag, (0.2); Se, (1.3); Mo, (6.4); Ce, (3.1); Th, (0.35); Sm, (0.20); Eu, (0.05); Lu, (0.02) $\mu\text{g g}^{-1}$	219±9	215±7 ^b
NIES, No. 3 Chlorella	K, 1.24±0.06; Ca, 0.49±0.03; Fe, 0.185±0.010; Mg, 0.33±0.02; P, (1.7)%; Mn, 69±5; Sr, 40±3; Co, 0.87±0.05; Cu, 3.5±0.3; Zn, 20.5±1.0; Cd, (0.026); Sc, (0.013) $\mu\text{g g}^{-1}$	0.60	0.58±0.02 ^a
NIES, No. 6 Mussels	Na, 1.00±0.03; K, 0.54±0.02; Ca, 0.13±0.01; Mg, 0.21±0.01; P, (0.77)%; Mn, 16.3±1.2; Fe, 158±8; As, 9.2±0.5; Cu, 4.9±0.3; Ni, 0.93±0.06; Cr, 0.63±0.07; Ag, 0.027±0.003; Zn, 106±6; Cd, 0.82±0.03; Al, (220); Sr, (17); Se, (1.5); Co, (0.37); Hg, (0.05) $\mu\text{g g}^{-1}$	0.91±0.04	0.92±0.03 ^b
NIES, No.2 Pond Sediment	Fe, 6.53±0.35; Al, 10.6±0.5; Ca, 0.81; K, 0.68; Na, 0.57% Zn, 343; Cu, 210; Cr, 75; Ni, 40; Cd, 0.82; Co, 27; As, 12 $\mu\text{g g}^{-1}$	105	108±4 ^a

*Average of five determinations ± standard deviation. †Standard addition method was applied. NIES: National Institute of Environmental Studies reference materials. NIES, No. 1, 3, 6 and 8 (values in parentheses were approximate and not certified). ^aColumn method was applied. ^bMicrocrystalline naphthalene method was applied.

Analysis of lead in biological samples

The accuracy and applicability of the proposed method has been applied to the determination of lead in National Institute for Environmental Studies (NIES) No.1 Pepperbush; NIES, No.5 Human Hair; NIES, No.7 Tea Leaves; NIES, No. 3, Chlorella; NIES, No. 6, Mussels and NIES, No.2, Pond Sediment. A 0.1 g sample was taken in a beaker and dissolved in concentrated nitric acid (~5 mL) with heating. The solution was cooled, diluted and filtered. The filtrate was made to 100 mL with water in a calibrated flask. NIES, No.8 Vehicle Exhaust Particulates (1 g) was dissolved in 18 mL of concentrated nitric acid, 18 mL of concentrated perchloric acid and 2 mL of concentrated hydrofluoric acid in a 100 mL Teflon beaker, evaporated to a small volume, filtered through a filter paper and made up to 100 mL with distilled water. An aliquot (10–50 mL) of the sample solution was taken individually and lead was determined by the general procedure. The results are given in Table 3 which are in good agreement with the certified values.

CONCLUSION

A solid ion-pair compound produced from NH_4^+ and TPB^- naphthalene provides a simple and economical method for the preconcentration of lead from large volumes of alloys and biological samples using 5-Br-PADAP as the complexing agent. This reagent is fairly sensitive and selective for lead but with the preconcentration step and the use of derivative spectrophotometry, its sensitivity and selectivity have been further improved. Thus, the developed method can be used safely for the estimation of lead in a number of complex materials. Since the adsorbent provides TBP^- as the counter anion, the adsorbent may therefore be used for the preconcentration of various types of cationic metal complexes. Although the metal may be estimated by atomic absorption spectrometry (AAS) after the preconcentration step. AAS is a relatively expensive instrument, and day-to-day expenses and maintenance are high. Another, cheaper, technique is differential pulse polarography, which could be tried for the estimation of lead after the preconcentration step. As a whole the proposed method is highly sensitive, selective, simple and highly economical (it requires simple glassware, and a small volume of the organic solvent to dissolve the solid mass from the column) for the estimation of lead.

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