Atomic Absorption Spectrometric Determination of Lead after Extraction and Preconcentration with 5-Br-PADAP

Taher, Mohammad Ali
Department of Chemistry, Shahid Bahonar University, Kerman, I. R. Iran

ABSTRACT: *Lead is quantitatively retained on 2-(5-bromo-2-pyridylazo)-5-diethylammino-phenol (5-Br-PADAP) -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 with preconcentration factor of 60. 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 atomic absorption spectrometry. The calibration curve is linear in the range of 1.9-180 μg/mL in DMF with a relative standard deviation of 1.7%. The interference of a large number of anions and cations has been studied.*

KEY WORDS: *Trace lead determination, 2-(5-Bromo-2-pyridylazo)-5-diethylamminophenol, Atomic absorption spectrometry, Alloys and biological samples*

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 and animals and causes environmental disease when released in the atmosphere. Very low concentrations (about μg/mL) 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 method for its quantitative deter - mination when present in trace amounts. Spectrophoto - metric methods are simple and economical but are not sufficiently sensitive and selective [1,2]. Graphite furnace atomic absorption spectroscopy, neutron activation ana - lysis, inductively coupled plasma-atomic emission spec-troscopy, 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].

Sodium tetraphenylborate (TPB) and its derivatives have been used in the estimation of alkali and univalent

1021-9986/2001/1/1 8/$/2.80

metal ions [9-11]. It has also been used as a counter ion in the extraction and adsorption of some metal complexes into molten naphthalene [12-14] and microcrystalline naphthalene respectively [15-17]. A survey of the literature reveals that metal ions may be preconcentrated on various adsorbents such as thiol cotton [18], silanized glass beads [19], silica gel [20], Amberlite XAD-4 resin [21], cellulose [22], green tea leaves [23] and polythioether foams [24]. 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 can not be applied directly to metal ions which form stable complexes with the chelating agent only at elevated temperature. This difficulty can be overcome by using naphthalene as the extractant [25] for thermally stable metal chelates [26]. 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 [15-17]. The preconcentration of lead ion is also possible by passing its aqueous solution over naphthalene-NH_4-TPB adsorbent taken in a column. The microcrystalline naphthalene method is rapid but the column method gives a better preconcentration factor [27-29].

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 (NH_4^+) (TPB^-) ion pair supported on naphthalene. 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-T4PB). 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 atomic absorption spectrometry. The interference of a number of metal ions and anions on the estimation of lead has been studied in details 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 and reagents

A Zeiss Atomic-Absorption-Spectrometer FMD 3 (Germany) was used. All absorption measurements were performed under the following operating conditions: wavelength: 217.0 nm; slit setting: 0.3 mm; current: 15 mA; acetylene flow setting: 10 (pressure: 0.9 $kp.cm^{-2}$); air flow setting: 15.5 (pressure: ~1.2 $kp.cm^{-2}$). A Beckman pH meter was employed for pH measurements. A funnel-tipped glass tube (60 × 6 mm) was used as a column for preconcentration. It was plugged with polypropylene fibbers and then filled with the adsorbent to height of 1.0-1.2 cm after slightly pressing with a flat glass rod. All glassware and column were washed with mixture of concentrated sulfuric acid and concentrated nitric acid (1+1) before use. All reagents were of analytical reagent grade (Merck). A standard lead solution (1000 μg/mL Pb^{2+}) was prepared from $Pb(NO_3)_2$ in distilled water and standardized [30]. 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 di-potassium 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 mol L^{-1} ammonium acetate and 75 mL of 1 mol L^{-1} ammonia solution (pH 9.5), in a fast stream continuous flow with stirring at room temperature. 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.

Recommended procedure for the column method

An aliquot of the solution containing 9.5-900 μg of lead was taken in a 25 mL beaker and 2.0 mL of 0.01% alcoholic solution of 5-Br-PADAP and 2.0 mL of acetate buffer of pH 5 were added . The final volume in the beaker was made up to approximately 15 mL with water if required. The column loaded with the adsorbent NH^+_4-TPB^- -naphthalene was conditioned to pH 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 solution was aspirated into an air-acetylene flame and the absorbance measured at 217.0 nm against a reagent blank. The absorbances for standard amounts of lead were measured and a calibration curve was constructed against a reagent blank prepared in a similar manner.

Recommended procedure for microcrystalline naphthalene

An aliquot of lead solution (containing 9.5-900 μg) was placed in a 100 mL of an Erlenmeyer flask with tightly fitting stopper. Then 2 mL of 0.01% of the reagent (5-Br-PADAP) was added to it, and the mixture was diluted to 30-40 mL with water. The pH was adjusted to 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 for 1 min. 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). The solution was aspirated into an air-acetylene flame and the absorbance measured at 217.0 nm against a reagent blank solution prepared in the same way. A calibration graph was prepared by taking various known amounts of lead under the conditions given above.

RESULTS AND DISCUSSION

Retention characteristics of NH_4^+ -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. Also reacts with ammonium salts to form water-insoluble precipitates. The TPB^- forms a weakly bonded ion-pair with NH_4^+ in aqueous solution and coprecipitates with microcrystalline naphthalene as follows:

$$NH_4^+ + TPB \rightleftharpoons (NH_4^+)(TPB^-)\ (s)$$

From the experimental observation, the NH_4 - 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. However, the NH_4 - TPB ion-pair prepared in buffer of pH 9.5 is highly stable and TPB^- is not desorbed even on washing with water or the buffer of pH 5. The adsorbent shows excellent adsorption characteristics for various cationic metal complexes such as $Fe(1,10\text{-}Phen)_3^{2+}$. In this work, TPB has been selected as the counter-ion because of its purity and moderated price.

Reaction conditions

These were established by using 100 μg lead. The surface 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. 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 1.0-3.0 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) was added to the sample solution keeping other variables constant. It was observed that the signal height remained constant by 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 indicates that the signal height remaines 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 used in all experiments.

The volume of the aqueous phase was varied in the range of 10-700 mL under the optimum condition; 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 was 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 atomic absorption spectrometric measurements. The solid material is insoluble in ordinary organic solvents such as toluene, 1,2-dichloroetane, 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 absorbent. It was found that the surplus water caused the absorbance to decrease by 10-12%. 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 addition of 500 μg of lead, 2 mL of the buffer (pH 5), a suitable amount of reagent 5-Br-PADAP to and 40 mL of water in a beaker. This solution was transferred into a separatory funnel and then a suitable amount of the adsorbent naphthalene-NH^+_4-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 by AAS. The solid mass on the filter paper was dried in an oven, kept in a desiccator, and then weighed to determine the mass of the adsorbent. The maximum amount of lead retained was 3.5 mg/g of the adsorbent.

Calibration and sensitivity

On the basis of the optimum conditions developed above, a calibration graph (after preconcentration of lead) was constructed according to the standard procedure. It was linear over the concentration range 9.5-900 μg of lead in 5 mL DMF solution, $A = 3.24\times10^{-3}\ [Pb]_{ppm} + 3.14\times10^{-4}$ with correlation coefficient, $r = 0.9998$ with $n = 8$. The detection limit was 0.6 μg/mL of lead in final DMF solution. Eight replicate determinations of 100 μg of lead in 5 mL DMF solution gave a mean absorbance of 0.065 with a relative standard deviation of 1.7%. The sensitivity for 1% absorption was 1.35 μg/mL.

Effect of diverse ions

Various salts and metal ions were added individually to a solution containing 100 μg of lead and the recommended procedure was applied. The tolerance limit was set as the diverse ion required to cause ±3% error in the determination of lead. The results obtained are given in Table 1. Among the anions examined, large amounts of chloride, bromide, nitrate, acetate, carbonate and sulphate could be tolerated. Citrate, oxalate, orthophosphate, tartrate and EDTA interfered. Except EDTA, a relatively low amount of these anions could be tolerated. Obviously the stability constants of Pb-EDTA complex must be

higher than Pb-5-Br-PADAP complex. Of the metal ions examined, many did not interfere up to mg levels except Fe(III),Cu(II) and Ni(II). Fe(III) was masked with 3 mL of 5% NaF solution, Cu(II) with 3 mL of 1% $Na_2S_2O_3$ solution and Ni(II) with 5 mL 0.1% of dimethylglyoxime solution. Thus the proposed method is selective and can be used to determine lead in standard alloys and biological samples without any prior separation.

Table 1: Effect of diverse salts and metal ions in the determination of 0.1mg of lead

Salt or ion	Tolerance limit
$CH_3COONa.3H_2O$, KNO_3	1 g
K_2SO_4	250 mg
KI, NaF	200 mg
Thiourea	150 mg
NH_4Cl, $Na_3PO_4.12H_2O$, K_2CO_3	120 mg
$Na_2S_2O_3$	100 mg
Sodium potassium tartrate	20 mg
KSCN	15 mg
Sodium oxalate	11 mg
Trisodium citrate	10 mg
Dimethylglyoxime	9 mg
Na_2EDTA	50 µg
Mg(II)	200 mg
Ca(II)	80 mg
Zn(II)	8.0 mg
Cd(II)	6.0 mg
Sb(III)	5.0 mg
Ag(I)	2.0 mg
Cu(II)	40 µg, 1.0 mg[a]
Mn(II), Ti(IV)	4.0 mg
Cr(VI), Cr(III)	2.0 mg
Se(VI), Ga(III)	1.5 mg
U(VI), Al(III)	1.0 mg
Mo(VI)	1.1 mg
Pd(II), Te(IV)	0.9 mg
Fe(III)	60 µg, 0.7 mg[b]
Ni(II)	70 µg, 1.0 mg[c]
Os(VIII)	0.7 mg
Bi(III)	0.6 mg
Rh(III), V(V)	0.5 mg
Co(II), Ru(III)	0.4 mg
Hg(II)	0.3 mg

a) Masked with 3 mL of 1% $Na_2S_2O_3$ solution

b) Masked with 3 mL of 5% NaF solution

c) Masked with 5 mL of 0.1% dimethylglyoxime solution

Analysis of lead in standard alloys

The proposed method was applied to the determination of lead in Nippo Keikinzoku Kogyo (NNK) CRM 916 and No. 920 Aluminium Alloy and NKK No. 1021, Al, Si, Cu, Zn Alloy. A 0.1 g sample of the standard aluminium 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 recommended procedure was applied. The results obtained are given in Table 2. These results are in agreement with the certified values.

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) by 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 recommended 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 complex samples using 5-Br-PADAP as the complexing agent. This reagent is fairly sensitive and selective for lead, but by the preconcentration step and using atomic absorption

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	0.04±0.01[b]
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	0.18±0.01[b]
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	0.10±0.01[c]

a) Average of five determinations, ±standard deviation

b) Column method was applied.

c) Microcrystalline naphthalene method was applied.

3 mL of 5% NaF solution, 5 mL of 0.1% dimethylglyoxime solution and 3 mL of 1% $Na_2S_2O_3$ solution were added as masking reagents.

spectrometry its sensitivity and selectivity has been further improved. Since 5-Br-PADAP reacts with many metal ions, therefore, similar procedure may also be developed for other metal ions and simultaneous determination of lead with other metal ions . It is not possible to develop selective methods for metal ions using this adsorbent in spectrophotometry since many metal-5-Br-PADAP complexes absorb at close wave-lengths. However, by using AAS this could be easily overcome.

Acknowledgment

Sincere thanks of the author are due to International High Technology (Mahan, Kerman, Iran), Payame Noor University and Jahad Daneshgahi for their assistance.

Received: 16th, October 1999; Accepted: 24th , April 2000

REFERENCES

[1] Stanley ,J.B. and Jaselskis, B., *Analyst,* **116**, 1059 (1991).

[2] Alizadeh , N. and Shamsipur, M., *Talanta,* **40**, 503 (1993).

[3] Tian, Y. H., Pipalnik, R. and Fanger, H. V., *J. Radioanal. Nucl. Chem.*, **139**, 43(1990).

[4] Jackson , K. W. and Mahmood, T.M., *Anal. Chem.*, 66, 252(1994).

[5] Sumitani, H., Suekane, S., Nakatani , A. and Ktatsuka, K., *J. AOAC Int.*, **76**, 1374(1993).

[6] Arpadjan, S., Vuchkova, L. and Kostadinova, E., *Analyst,* **122**, 243(1997).

[7] Kantipuly, C. J. and Westland, A. D., *Talanta,* **35**, 1

Table 3: Analysis of lead in biological samples

Sample	Composition	Concentration ($\mu g\ g^{-1}$) Certified value	Found[a,b]
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)$\mu g\ g^{-1}$	5.5±0.8	5.4±0.1[c]
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 $\mu g\ g^{-1}$	6.0	6.1±0.2[c]
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 $\mu g\ g^{-1}$	0.80	0.78±0.03[d]
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) $\mu g\ g^{-1}$	219±9	216±5[d]
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) $\mu g\ g^{-1}$	0.60	0.61±0.02[c]
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) $\mu g\ g^{-1}$	0.91±0.04	0.89±0.03[d]
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 $\mu g\ g^{-1}$	105	103±2[c]

a) Average of five determinations, ± standard deviation,
b) Standard addition method was applied.
NIES: National Institute of Environmental Studies reference materials.
NIES, No. 1, 3, 6 & No. 8 (Values in parentheses were approximate and not certified).
3 mL of 5% NaF solution, 5 mL of 0.1% dimethylglyoxime solution and 3 mL of 1% $Na_2S_2O_3$ solution were added as masking reagents.
c) Column method was applied.
d) Microcrystalline naphthalene method was applied.

(1988).

[8] Ramesh, A., Krishanamacharayulu, J., Rayindranath, L. K. and Rao, S. B., *Analyst,* **117**,1037 (1992).

[9] Barnard, Jr., A. J., *Chemist-Analyst,* **44**, 104(1955). **109**, 31(1984).

[10] Bernard, Jr., A. J., *Chemist-Analyst,* **47**, 46(1958).

[11] Reilly, C. N., "Advances in Analytical Chemistry", Vol, 1, Interscience, New York(1960).

[12] Satake, M., Naghairo, T. and Puri, B. K., *Analyst,* **109**, 31(1984).

[13] Nagahiro, T., Uesugi, K., Satake, M. and Puri, B. K., *Bull, Chem. Soc. Jpn.,* **85**, 1115(1985).

[14] Chang, L. F., Satake, M., Kuwamoto, T. and Puri, B. K., *Microchem. J.,* **33**, 46(1986).

[15] Nagahiro, T., Satake, M., Lin, J. L. and Puri, B. K., *Analyst,* **109**, 163(1984).

[16] Lin, J. L., Satake, M. and Puri, B. K., *Analyst,* **110**, 1351(1985).

[17] Mehra, M. C., Nagahiro, T. and Satake, M., *Micro-Chem. J.,* **33**, 198(1986).

[18] Quig, Y. M. and Quin, L. G., *Talanta,* **30**, 265 (1983).

[19] Taguchi, S., Yal, T., Shimada, Y. and Goto, K., *Talanta,* **30**, 169(1983).

[20] Bota, M., Matseemoto, K. and Terada, T., *Anal. Sci.,* **3**, 45(1987).

[21] Sakai, Y. and Mori, N., *Talanta,* **33**, 161(1986).

[22] Burba, P. and Willmer, P.G., *Talanta,* **30**, 381 (1983).

[23] Kimura, M., Yamashita, H. and Komada, J., *Bunseki Kagaku,* **35**, 400(1986).

[24] Khan, A. S. and Chow, A., *Talanta,* **33**, 182(1986).

[25] Wasey, A., Bansal, R. K., Puri , B. K. and Rao, A. L. J., *Talanta,* **31**, 205(1984).

[26] Satake, M., Kano, G., Usami , S.and Puri, B. K., *Indian, J. Chem.,* **27A**, 265(1988).

[27] Taher, M. A. and Puri, B. K., *Analyst,* **120**, 1589 (1995).

[28] Taher, M. A., Puri, S., Bhalotra, A. and Puri, B. K., *Quim. Ana. (Spain),* **18**, 181(1999).

[29] Taher , M. A. and Puri, B. K., *Talanta,* **48**, 355 (1999).

[30] Vogel, A. I., "Text Book of Quantitative Inorganic Analysis", Longman, London (1989).