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Flame Atomic Absorption Spectrometric Determination of Trace Amounts of Thallium in Natural Waters and Standard Pepperbush after Solid-phase Extraction on to Amberlite XAD-2 Resin Modified with 2-(5-Bromo-2-pyridylazo)-5-diethylaminophenol

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A procedure for separation and preconcentration of trace amounts of thallium has been proposed. It is based on the adsorption of thallium(I) ions solution on to a column of Amberlite XAD-2 resin loaded with 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol. Thallium is quantitatively retained on the column in the pH range of 8.5–12.0 at a flow rate of 15 mL min^{-1}. The retained analyte on the resin recovered with 5.0 mL of 4% ascorbic acid and thallium is determined by flame atomic absorption spectrometry. In this case, 0.18 μg of thallium can be concentrated in the column from 1200 mL of aqueous sample, where its concentration is as low as 0.15 ppb. Eight replicate determinations of 2.0 ppm of thallium gave a mean absorbance of 0.044 in final ascorbic acid solution with a relative standard deviation of ±1.68%. The interference of a large number of anions and cations has been studied and the optimized conditions developed were utilized for the trace determination of thallium in natural waters and various standard samples.

Key Words: Atomic absorption spectrometry, Solid-phase extraction, Amberlite XAD-2-(5-bromo-2-pyridylazo)-5-diethylaminophenol.

INTRODUCTION

Thallium is a rare element in the earth's crust. Both the element and its compounds are extremely toxic; skin-contact, ingestion and inhalation are all dangerous. The determination of thallium in environmental samples is of interest because of the high toxicity of its compounds. Due to new concerns regarding the toxicity of thallium, there are growing needs for improved analytical methods for monitoring this metal[1]. Several methods extensively used for preconcentration include liquid-liquid extraction, ion exchange, solid-phase extraction and chelating materials. However, solvent extraction suffers with problems like handling of large sample volume, slow attainment of equilibrium, mutual solubility of two phases, poor selectivity and emulsion formation. The multistage extraction is required several times for quantitative recovery. Consequently, in the last two decades use of chelating resins for metal enrichment has increased very significantly[2–5]. Their advantages include good selectivity, preconcentration factor, binding energy and mechanical stability, easy regeneration for multiple sorption-desorption cycles and good reproducibility in the sorption characteristics. Thallium determination in the environmental samples is a very difficult task because of its low concentration levels and interference effects[6–8]. Existing analytical techniques applicable to thallium determinations in environmental and industrial samples include laser-induced fluorescence[9], atomic absorption spectrometry[10], graphite furnace atomic absorption spectrometry[11], anodic stripping voltammetry[12–14] and cathodic stripping voltammetry[1].

In the present communication, a flame atomic absorption spectrometry (FAAS) method for the trace determination of thallium(I) after adsorption of its 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol (5-Br-PADAP) complex on Amberlite XAD-2 resin and subsequent desorption with 5.0 mL of 4% ascorbic acid, has been developed. Amberlite XAD-2 (polystyrene-divinylbenzene polymer) is a much used resin in preconcentration procedures, due to its good physical and chemical properties such as porosity, high surface area, durability and purity[15]. The interference of a number of metal ions and anions on the estimation of thallium has been studied in detail. The developed method is found to be highly sensitive and selective, and has been employed for the estimation of thallium in various samples.

EXPERIMENTAL

A Varian model Spectra AA 220 flame atomic absorption spectrophotometer was used in the following conditions: wavelength: 276.8 nm, lamp current: 10.0 mA, slit width: 0.5 nm, acetylene flow: 1.5 L min^{-1}, air flow: 3.5 L min^{-1}. A Beckman pH-meter was employed for pH measurements. A funnel-tipped glass tube (60 × 6 mm) was used as a column for preconcentration. All glassware and columns were washed with a mixture of concentrated hydrochloric acid and concentrated nitric acid (1 : 1) before use. All reagents were of analytical reagent grade. A standard thallium solution was prepared from thallium(I) nitrate in a minimum volume of concentrated nitric acid and then diluted to 1000 mL with distilled water in a standard flask and standardized by known methods[16]. 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 disodium hydrogen phosphate solution, and 0.5 M ammonia solution and 0.5 M ammonium acetate solution, respectively. 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 Amberlite XAD-2 column loaded with 5-Br-PADAP: Amberlite XAD-2 was treated with an ethanol : hydrochloric acid : water (2 : 1 : 1) solution overnight. Then, resin was rinsed with deionized water until supernatant water pH got neutral. Packing of the column must be done using ethanol as eluent since water makes resin beads float. The resin was saturated with the reagent by passing 2.5 mL of a 0.01% 5-Br-PADAP solution in ethanol at a flow rate of 1 mL min^{-1}. Afterwards, it was washed with water until reagent excess was eliminated from the resin. All experiments were done in a funnel-tipped glass tube (60 × 6 mm) which was used as a column for preconcentration. It was plugged with polypropylene fibres and then filled with XAD-2. Before sample loading the column must be preconditioned by passing a buffer solution. Then, the column could be used repeatedly for ten times at least.

Procedure for the sorption of thallium(I) on the column: An aliquot of thallium solution (containing 0.5 to 75 μg) was placed in a 100 mL beaker and to it was added 5.0 mL of buffer solution of pH 10.0, then diluted to *ca.* 30 mL with distilled water. This solution was passed through the column at a flow rate of 15.0 mL min^{-1}. After passing this solution, the column was eluted with 10 mL of deionized water. The adsorbed thallium(I) on the column was eluted with 5.0 mL of 4% ascorbic acid solution at a flow rate of 2.0 mL min^{-1}. The eluent was collected in a 5 mL volumetric flask and thallium was determined by flame atomic absorption spectrometry.

RESULTS AND DISCUSSION

Reaction conditions: The reaction conditions were investigated with 10 μg of thallium. The sorption of thallium(I) on the column was found to be a maximum in the pH range of 8.5–12.0. In subsequent studies, the pH was maintained at approximately 10.0. The flow rate was varied from 0.1–20 mL min^{-1}. It was found that a flow rate of 0.1–15 mL min^{-1} did not affect adsorption. Thus, a flow rate of 15.0 mL min^{-1} was recommended in all experiments.

The volume of the aqueous phase was varied in the range of 10–1500 mL under the optimum conditions, keeping the other variables constant. It was observed that the absorption was almost constant up to 1200 mL. However, for convenience, all the experiments were carried out with 30 mL of the aqueous phase. Preliminary observations indicated that thallium(I) was desorbed completely with 5.0 mL of 4% ascorbic acid. Therefore, 5.0 mL of 4% ascorbic acid was used in the present work.

Sorption capacity of resin for ligand and thallium: The sorption capacity of the Amberlite XAD-2 resin for ligand and thallium was also evaluated. The resin had a sorption capacity of 0.8 mg and 0.27 mg per g of XAD-2 resin for ligand and thallium, respectively.

Calibration and sensitivity: Since, it is possible to retain 0.18 μg of thallium from 1200 mL of solution passing through the column, the dissolution with 5.0 mL ascorbic acid gives a detection limit of 0.15 ppb for thallium. The linearity was maintained in the concentration range of 0.1 to 15 ppm thallium in final aqueous solution with a correlation factor of 0.9991. Eight replicate determinations of 10 μg of thallium in 5.0 mL ascorbic acid solution gave a mean absorbance of 0.044 with a relative standard deviation of ±1.68%.

Effect of diverse ions: Various salts and metal ions were added individually to a solution containing 10 μg of thallium and the general procedure was applied. The tolerance limit was set as the concentration of the diverse ions required to cause ±3% error in the determination of thallium. The results obtained are given in Table-1. Among the salts examined, most could be tolerated up to gram or milligram levels except EDTA. Of the metal ions examined, many did not interfere up to mg levels except Fe(III), which was masked with 2 mL of 5% NaF solution. Thus, the proposed method is relatively selective and can be used for the determination of thallium in alloys and biological samples without any prior separation.

TABLE-1
EFFECT OF DIVERSE SALTS AND METAL IONS

Salt or ion	Tolerance limit
$CH_3COONa\cdot3H_2O$, KNO_3	1 g
K_2SO_4	195 mg
KI, NaF	200 mg
NH_4Cl, K_2CO_3	85 mg
Sodium potassium tartrate	35 mg
Thiourea, KSCN	25 mg
Na_2 EDTA	85 mg
Mg(II)	145 mg
Ca(II)	95 mg
Cd(II), Pb(II)	40 mg
Sb(III)	15 mg
Zn(II), Ni(II)	2 mg
Bi(III), Co(II)	5 mg
Mn(II), Mo(VI), AS(III)	8 mg
Hg(II)	0.7 mg
Fe(III)	70 μg, 1 mg[a]

[a] Masked with 2 mL of 5% NaF solution

Analysis of thallium in pepperbush: The accuracy and applicability of the proposed method has been applied to the determination of thallium in National Institute for Evironment Studies (NIES) No. 1 pepperbush. 5.0 g of sample was taken in a beaker and dissolved in concentrated nitric acid (*ca.* 30 mL) with heating. The solution was cooled, diluted and filtered. The filtrate was made to 100 mL with water in a calibrated flask. An aliquot of the sample solution was taken individually and thallium was determined by the general procedure. The results are given in Table-2 which are in good agreement with the certified value.

TABLE-2
ANALYSIS OF THALLIUM IN PEPPERBUSH

Sample	Composition	Found*
NIES, No. 1	K, 1.51 ± 0.06; Mn, 0.203 ± 0.17;	0.129 ± 0.003
Pepperbush	Mg, 0.408 ± 0.020; Ca, 1.38 ± 0.07%	
	Cd, 6.7 ± 0.5; Ni, 8.7 ± 0.6;	
	Fe, 205 ± 17; Co, 23 ± 3;	
	Pb, 5.5 ± 0.8; Cu, 12 ± 1;	
	Zn, 340 ± 20; Ba, 165 ± 10;	
	Na, 106 ± 13; Rb, 75 ± 4;	
	Sr, 36 ± 4; As, 2.3 ± 0.3;	
	P, 1100; Cr, 1.3; Cs, 1.2;	
	Tl, 0.13; Hg, 0.05 $\mu g\ g^{-1}$	

NIES: National Institute of Enviromental studies reference materials.

*Average of five determinations, ± standard deviation

Analysis of thallium in water samples: The method has been employed for the determination of thallium in hot spring, river, lake and drinking water samples. All samples (500 mL) were adjusted to pH 1.5 with nitric acid, filtered to remove suspended material. Since, there is no sample containing thallium, an experiment was conducted by adding a known amount of thallium to the samples and thallium was determined Table-3.

TABLE-3
ANALYSIS OF THALLIUM IN WATER SAMPLES

Sample	Thallium added[a] (μg)	Thallium found[b] (μg)
Spring water	30.0	29.9 ± 0.2
River water	50.0	49.7 ± 0.9
Lake water	10.0	9.95 ± 0.08
Drinking water 1	25.0	24.8 ± 0.4
Drinking water 2	30.0	30.1 ± 0.5

[a] No thallium was present in these samples. Therefore, thallium was added from the standard solution in each case.

[b] Average of five determinations, ± standard deviation.

Conclusion

The main advantages of this procedure are: (i) the preparation of the extractor system is simple and fast; (ii) during thallium desorption the 5-Br-PADAP reagent remains in the resin, which allows using the column several times; (iii) a good enrichment factor can be achieved. 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 wavelengths. However, with the use of atomic absorption spectrophotometer this problem can be easily solved.

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