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FAAS DETERMINATION OF THALLIUM AFTER PRECONCENTRATION USING NITROSO-S AND TDBA ONTO BENZOPHENONE

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ABSTRACT. Thallium is quantitatively retained by 2-nitroso-1-naphthol-4-sulfonic acid (nitroso-S) and tetradecyldimethylbenzylammonium chloride (TDBA) onto benzophenone in the pH range 10.0-11.5 from large volumes of aqueous solutions of various samples. After filtration, each solid mass consisting of thallium complex and benzophenone is dissolved with 5 mL of dimethylformamide and the metal was determined by flame atomic absorption spectrophotometry (FAAS). Eight replicate determinations of 10.0 µg/mL of thallium in final dimethylformamide (DMF) solution gave a mean absorbance of 0.150 with a relative standard deviation of 1.9%. The sensitivity for 1% absorption was 0.293 µg/mL. The method of extraction and preconcentration is economical, rapid, sensitive, highly selective and satisfactory. The interference of a number of anions and cations has been studied and the optimized conditions developed were utilized for the trace determination of thallium in various samples.

KEY WORDS: Flame atomic absorption spectrophotometry, Thallium determination, Nitroso-S, Tetradecyldimethylbenzylammonium chloride (TDBA), Benzophenone

INTRODUCTION

2-Nitroso-1-naphthol-4-sulfonic acid (nitroso-S) was introduced by Hoffman [1] as a qualitative analytical reagent for cobalt, copper and iron and applied to the colorimetric determination of cobalt by Wise and Brandt [2]. The reagent form water-soluble chelate anion with metal ions, but the high absorption of the reagent blank at the measurement wavelength makes the nitroso-S procedure more troublesome. Motomizu and Toei reported the extraction of the Cu(II)-nitroso-S anion with TDBA cation [3] and Fe(II)-nitroso-S anion with azo dye cation in chloroform [4].

Solid-liquid separation after adsorption of metal chelates onto benzophenone is rapid and convenient and can be applied to many types of metal complexes. The only drawback is in the filtration and drying. A survey of the literature revealed that various adsorbents, such as thiol cotton [5], Sepiolite [6], C_{18}-bonded silica gel [7], Amberlite XAD-2 resin [8], cellulose [9], silica gel [10], green tea leaves [11] and polythioether foam [12] have been tried for the preconcentration of metal ions. Desorption of the metal is carried out by a slow process of elution (probably the metal complex may be held by interior surfaces of the adsorbent and hence is not eluted easily), so the procedure is time consuming.

In this paper, an efficient method for the preconcentration of thallium from large volumes of the aqueous solutions of various standard reference materials with nitroso-S-TDBA-benzophenone adsorbent is described. The method is economical (all reagents are cheap compared with many other reagents used recently [13-15]), rapid (the metal complex simply to adsorb onto benzophenone) and sensitive (the solid mass can be dissolved in 2-5 mL of an organic solvent, and the whole of the solution may be used for the absorbance measurement). The solid mass, consisting of the metal ion associated complex and benzophenone [Tl-(nitroso-S)-TDBA-benzophenone], can easily be dissolved with a suitable organic solvent such as dimethylformamide (DMF) and the thallium is then determined by flame atomic absorption spectrophotometry (FAAS). Various parameters for concentration measured by FAAS were

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evaluated, and optimized conditions were utilized for the trace determination of thallium in various complex samples.

EXPERIMENTAL

Apparatus

A Shimadzu AA-670 flame atomic absorption spectrophotometer was used in the following conditions: wavelength: 276.8 nm, lamp current: 3.0 mA, slit width: 0.5 nm, burner height: 6.0 mm, acetylene flow: 1.5 L min^{-1}, air flow: 8.0 L min^{-1}. A Beckman pH meter was employed for pH measurements. All glassware was washed with a mixture of concentrated sulfuric acid and concentrated nitric acid (1+1) before use.

Reagents

All reagents were of analytical reagent grade. Thallium nitrate was prepared in distilled water and then diluted to 1000 mL with distilled water in a standard flask and standardized by established method [16]. Buffer solutions of pH 3-6, pH 6-8 and pH 8-11 were prepared by mixing an appropriate ratio of 0.5 M acetic acid and 0.5 M ammonium acetate, 0.1 M disodium hydrogen phosphate and 0.1 M sodium dihydrogen phosphate and 0.5 M aqueous ammonia and 0.5 M ammonium acetate, respectively. A 1% solution of tetradecyldimethylbenzylammonium chloride (TDBA) (Merck) and 0.1% 2-nitroso-1-naphthol-4-sulfonic acid (nitroso-S) (Fluka, Switzerland) were prepared in distilled water. Solutions of alkali metal salts (1%) and various metal salts (0.1%) were used for studying the interference of anions and cations, respectively.

General procedure

An aliquot of thallium solution (containing 2.0-250 μg) was placed in a 100 mL of an Erlenmeyer flask with tightly fitting stopper. Then, 2 mL of 0.1% of the reagent (nitroso-S) was added to it and the mixture was diluted to 30-40 mL with water. The pH was adjusted to 11 with 2 mL of the buffer and then 2 mL of 1% TDBA solution was added. The solution was mixed well and allowed to stand for few seconds. Then 0.2 g benzophenone was added as a solid solvent. This solution was stirred for 4 min to adsorb quantitatively Tl-nitroso-S complex onto benzophenone. The solid mass consisting of benzophenone and metal complex was separated by filtration on a Whatman filter paper. The residue was dried at the room temperature in the folds of a filter paper and transferred to the Erlenmeyer flask. The solid mass consisting of the metal complex along with benzophenone was dissolved with 5 mL of dimethylformamide (DMF). The solution was aspirated into an air-acetylene flame and the absorbance was measured at 276.8 nm. A calibration graph was prepared by taking various known amounts of thallium under the conditions given above.

RESULTS AND DISCUSSION

Reaction conditions

Reaction conditions were established with the use of 50 μg of thallium. The adsorption of thallium on the adsorbent was found to be maximum in the pH range 10.0-11.5. In a subsequent study, the pH was maintained at ~11. Addition of 0.5-15.0 mL of the buffer (pH ~11) did not affect the retention of thallium and use of 2.0 mL was recommended. Thallium was quantitatively adsorbed over the range 1.0-6.0 mL of the 0.1% of nitroso-S solution. Therefore, 2.0 mL of the reagent is recommended in the present study.

Various amounts of benzophenone were added to the sample solutions while keeping other variables constant. It was observed that the signal height remained constant with the addition of 0.05-0.4 g of benzophenone. Therefore, 0.2 g of benzophenone was used in subsequent studies. The effect of shaking time on the adsorption indicated that the signal height remained constant over a range of 2.0-9.0 min. Therefore, 4.0 min of shaking time was maintained in the present work.

The volume of the aqueous phase was varied in the range of 10-700 mL under the optimum conditions, while keeping the other variables constant. It was observed that the signal height was almost constant up to 400 mL (preconcentration factor of 80). However, for convenience, all the experiments were carried out with 40 mL of the aqueous phase.

Choice of solvent

A number of solvents were tried for dissolving the Tl-nitroso-S-TDBA-benzophenone. As it was desired to dissolve the solid mass in a small volume (3-5 mL) of solvent, it was essential to select a solvent in which the chelate is highly soluble in order to achieve a high sensitivity for the atomic absorption spectrometry. The solid mass was found to be insoluble in ordinary organic solvents, such as n-hexane, but is soluble in dimethyl sulfoxide, toluene, ethanol, chloroform, dioxane, acetone and DMF. DMF was preferred owing to the high solubility and stability of the metal complex on benzophenone. It was found that 3-5 mL of this solvent was sufficient to dissolve the mixture thus enhancing the sensitivity of the method. As only a small volume (3-5 mL) of the solvent was used to dissolve the complex and benzophenone.

Calibration and sensitivity

Since it is possible to retain 0.5 μg of thallium from 400 mL of solution, the dissolution with 5.0 mL DMF gives a detection limit of 1.25 ng/mL for thallium at the optimum conditions. The linearity was maintained in the concentration range of 5 ng/mL to 25 μg/mL thallium in aqueous solution or 0.4 to 50 μg/mL thallium in final DMF solution with a correlation factor of 0.9995. Eight replicate determinations of 50.0 μg of thallium in final 5 mL DMF solution gave a mean absorbance of 0.150 with a relative standard deviation of 1.9%. The sensitivity for 1% absorption was 0.293 μg/mL in final DMF solution. The limit of detection (LOD) of thallium was calculated 0.2 μg/mL in final DMF solution.

Effect of diverse ions

Various salts and metal ions were added individually to a solution containing 50 μg of thallium and the general procedure was applied. The tolerance limit (error < 3%) is given in Table 1. Among the salts examined, many did not interfere even at the g-mg level. Among the metal ions studied, most did not interfere at the milligram level, except Fe(III) and Pb(II). However, these could be easily masked with addition of 2 mL of 5% triethanolamine solution for Fe(III) and 0.4 mg of EDTA for Pb(II). Thus the method is highly selective and may safely be applied for the determination of thallium in various environmental and biological samples.

Table 1. Effect of different salts and metal ions.

Salt or ion	Tolerance limit
$CH_3COONa.3H_2O$, KNO_3	1 g
NaCl, K_2CO_3, NH_4Br	75 mg
$(NH_4)_2SO_4$, NaF, KI	50 mg
Sodium potassium tartrate	70 mg
KSCN	80 mg
Trisodium citrate	35 mg
Sodium oxalate	30 mg
Disodium-EDTA	500 µg
Mo(VI), Zn(II)	55 mg
Mn(II)	45 mg
Cr(III), Ti(IV), Al(III)	25 mg
Se(VI), Ga(III)	17 mg
U(VI), V(V), Te(IV)	5.5 mg
Bi(III)	5.0 mg
Fe(III)	150 µg, 3.0 mg*
Ru(III), Cd(II), Rh(III)	2.5 mg
Pd(II), Os(VIII)	1.5 mg
Co(II), Ni(II), Sb(III)	1.0 mg
Sn(II),Cu(II), Cr(VI)	800 µg
Pb(II)	70 µg, 600 µg**

*After masking with 2 mL of 5% triethanolamine solution. **After masking with 0.4 mg of EDTA.

Analysis of thallium in biological samples

The accuracy and applicability of the proposed method has been applied to the determination of thallium in National Institute for Environmental Studies (NIES) No. 1 Pepperbush; NIES, No.3 Chlorella; NIES, No.5 Human Hair; NIES, No.7 Tea Leaves. A 0.1-0.5 g sample was taken in a beaker with an appropriate amount of thallium from the standard sample and dissolved in concentrated nitric acid (~10 mL) with heating. The solution was cooled, diluted and filtered. The filtrate was made to 100 mL with distilled water in a calibrated flask. NIES, No.8 Vehicle Exhaust Particulates (1 g) along with an appropriate amount of thallium from the standard sample 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. Aliquots between 10 and 50 mL of the sample solution were taken individually and thallium was determined by the general procedure. The results are given in Table 2.

Analysis of thallium in synthetic and real samples

The accuracy and applicability of the proposed method was evaluated by its application on various synthetic samples corresponding to coal (N.B.S., SRM-1632) and coal fly ash (N.B.S., SRM-1633) and environmental samples. Synthetic sample was prepared from appropriate amounts from various ions aqueous solution in 10 mL of concentrated hydrochloric acid and nitric acid (1+1) by heating on a hot plate in the presence of 3-5 mL of 30% hydrogen peroxide. The excess of peroxide was decomposed by heating the sample on a hot plate for a few minutes. The solution was cooled, filtered if needed, and the volume was made to 100 mL in a standard flask. An aliquot of the pre-treated sample solution was taken [17] and analyzed by the general procedure. The results are given in Tables 3 and 4.

Table 2. Analysis of thallium in biological samples.

Sample	Certified composition of the sample Thallium added (μg)	Thallium found[*+] (μg)	Recovery (%)
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; Ni, 8.7±0.6; Fe, 205±17; Co, 23±3; Pb, 5.5±0.8; Zn, 340±20; Rb, 75±4; Ba, 165±10; Na, 106±13; Sr, 36±4; As, 2.3±0.3; Cu, 12±1; Cr, (1.3); Cs, (1.2); P, (1100); Tl, (0.13); Hg, (0.056) μg/g	0.13±0.01	100.0
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) %; Zn, 20.5±1.0; Sr, 40±3; Cu, 3.5±0.3; Co, 0.87±0.05; Mn, 69±5; Cd, (0.026); Pb, (0.60); Sc, (0.013) μg/g Tl[#] added 1.50 μg	1.45±0.07	96.7
NIES, No.5 Human Hair	Pb, 6.0; Cd, 0.20; Cu, 16.3; Sb, 0.07; Zn, 169; Fe, 225; Mg, 208; Hg, 4.4; Al, 240; K, 34; Rb, 0.19; Se, 1.4; Na, 26; Sr, 2.3; Sc, 0.05; Ti, 3.2; Ca, 728; Ba, 2.2; Cr, 1.4; Ni, 1.8 μg/g Tl[#] added 0.40 μg	0.41±0.02	102.5
NIES, No.7 Tea Leaves	Pb, 0.80; Cd, 0.030; Sb, 0.014; Zn, 33; 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; Ni, 6.5 μg/g Tl[#] added 0.70 μg	0.67±0.06	95.7
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; Zn, 0.104±0.005; Na, 0.92±0.008%; Sr, 89±3; Co, 3.3±0.3; Cu, 67±3; Ni, 18.5±1.5; Cd, 1.1±0.1; Pb, 219±9; As, 2.6±0.2; Cr, 25.5±1.5; V, 17±2; Sb, 6.0±0.4; 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) μg/g Tl[#] added 0.15 μg	0.146±0.008	97.3

[*] Average ±standard deviation of five determinations using standard addition method.

[+] 2 mL of 5% triethanolamine solution and 0.4 mg EDTA were added as masking reagents.

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

NIES: National Institute of Environmental Studies reference materials.

NIES, No. 1, No. 3 and No. 8 (values in parentheses were approximate and not certified).

Table 3. Analysis of thallium in synthetic samples.

Sample	Composition (μg/g)	Thallium found[*+] (μg/g)	Recovery (%)
Synthetic sample[a]	As, 6.0; Cd, 0.25; Cr, 20.5; Cu, 15; Pb, 15; Mn, 80; Hg, 12; Ni, 115; Se, 3; V, 35; Zn, 100; Al, 98.25; Tl, 8.0	7.90±0.15	98.7
Synthetic sample[b]	As, 6.0; Cd, 2.0; Cr, 130; Cu, 130; Pb, 30; Mn, 500; Th, 25; Hg, 2.0; Ni, 100; Se, 10; V, 210; Zn, 220; Al, 69; U, 12; Tl, 4.0	3.92±0.09	98.0

[*] Average ±standard deviation of five determinations using standard addition method.

[+] 2 mL of 5% triethanolamine solution and 0.4 mg EDTA were added as masking reagents.

[a] Corresponds to coal (N.B.S., SRM-1632). [b] Corresponds to coal fly ash (N.B.S., SRM-1633).

Table 4. Analysis of thallium in environmental samples.

Sample	Thallium found[*+] (μg/mL)
Water, industrial copper area, Sarchashmeh, Kerman, Iran	1.20±0.07
Water, near industrial area, Rafsanjan, Kerman, Iran	0.35±0.02
Water, near industrial area, Zarand, Kerman, Iran	0.28±0.01

[*] Average ±standard deviation of five determinations using standard addition method.
[+] 2 mL of 5% triethanolamine solution and 0.4 mg EDTA were added as masking reagents.

CONCLUSIONS

A simple, economical and highly selective adsorbent has been generated simply by mixing the aqueous solutions of nitroso-S salt and $TDBA^+Cl^-$ with benzophenone for the preconcentration of thallium from the large volume of the aqueous solution of alloys, biological and environmental samples. Since nitroso-S reacts with many metal ions, therefore similar procedure may also be developed for other metal ions too. The method of extraction and preconcentration is economical, rapid, sensitive, highly selective and satisfactory.

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