Flame Atomic Absorption Spectrometric Determination of Trace Amounts of Thallium after Solid-Liquid Extraction and Preconcentration with Use of 1,10-Phenanthroline onto Benzophenone

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Thallium is quantitatively retained by 1,10-phenanthroline and tetraphenylborate onto benzophenone in the pH range 0-11 from a large volumes of aqueous solutions of various samples. After filtration, the solid mass consisting of thallium complex and benzophenone is dissolved with 5 mL of dimethylformamide and the metal was determined by flame atomic absorption spectrometric. About 0.4 μg of thallium can be concentrated from 400 mL of aqueous sample, where its concentration is as low as 1.0 ng/mL. Eight replicate determinations of 8.0 μg/mL of thallium in final dimethylformamide solution gave a mean absorbance of 0.160 with a relative standard deviation of 1.7%. The sensitivity for 1% absorption was 0.22 μg/mL. 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 various alloys and biological samples.

Key Words : Benzophenone adsorption, 1,10-Phenanthroline, Solid-liquid extraction of thallium

Introduction

Solid-liquid extraction 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,[1] Sepiolite,[2] C_{18}-bonded silica gel,[3] Amberlite XAD-2 resin,[4] cellulose,[5] silicagel,[6] green tea leaves[7] and polythioether foam[8] have been tried for the preconcentration of metal ions. The 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 a large volume of the aqueous solutions of various standard reference materials with 1,10-phenanthroline – tetraphenylborate (TPB)-benzophenone adsorbent is described. The method is economical (all reagents are cheap compared with many other reagents used recently[9-11]), 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-1,10-phenanthroline – (TPB)-benzophenone], can easily, be dissolved with a suitable organic solvent such as dimethylformamide (DMF) and the thallium is determined by flame atomic absorption spectrophotometer (FAAS). A number of parameters have been evaluated and the developed method has been applied to the trace determination of thallium in various standard alloys and biological samples.

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Experimental Section

Apparatus. A Shimadzu AA-670 flame atomic absorption spectrophotometer was used in 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.[12] A 0.2% solution of 1,10-phenanthroline in distilled water 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.

General procedure. An aliquot of thallium solution (containing 1.5-175 μg) was placed in a 100 mL of an Erlenmeyer flask with tightly fitting stopper. Then 2 mL of 0.2% of the reagent (1,10-phenanthroline) was added to it and the mixture was diluted to 30-40 mL with water. The pH was adjusted to 3.5 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 few seconds. Then, 0.2 g benzophenone was added as a solid solvent. This solution was

stirred for 4 minutes to adsorb quantitatively Tl-1,10-phenanthroline 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 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 measured at 276.8 nm. A calibration graph was prepared by taking various known amounts of thallium under the conditions given above.

Results and Discussions

Reaction Conditions. Reaction conditions were established with the use of 40 μg of thallium. The adsorption of thallium on the adsorbent was found to be maximum in the pH range 0-11 (Fig. 1). In subsequent studies, the pH was maintained at pH ~3.5. Addition of 0.5-15.0 mL of the buffer (pH ~3.5) did not affect the retention of thallium and therefore use of 2.0 mL was recommended. Thallium was quantitatively adsorbed over the range 1.0-6.0 mL of the reagent (Fig. 2). Therefore, 2.0 mL of the reagent is recommended in the present study.

Various amounts of benzophenone were added to the sample solutions keeping other variables constant. It was observed that the signal height remained constant with the addition of 0.05-0.4 g of benzophenone (Fig. 3). 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.

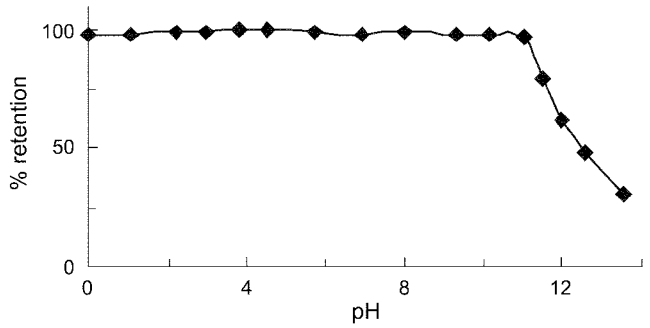

Figure 1. Effect of pH. Tl, 40.0 μg; 1,10-phenanthroline, 2.0 mL (0.2%); TPB, 2.0 mL (1%); benzophenone, 0.2 g; solvent, 5.0 mL DMF.

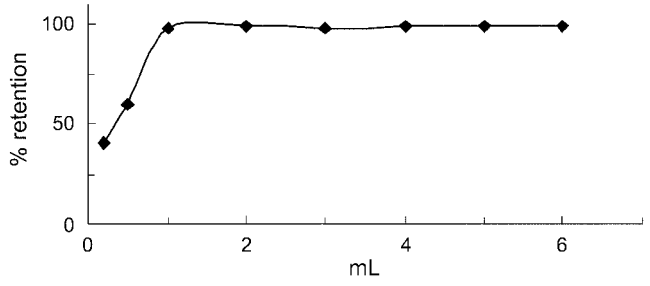

Figure 2. Effect of volume of 0.2% of 1,10-phenanthroline. For conditions, see Figure 1.

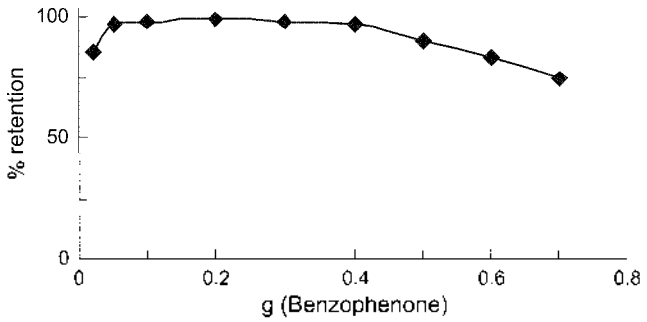

Figure 3. Effect of amounts of benzophenone. For conditions, see Fig. 1.

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, keeping 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-1,10-phenanthroline – TPB-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 material was found to be insoluble in ordinary organic solvents such as, *n*-hexane, but soluble in dimethyl sulfoxide, toluene, ethanol, chloroform, dioxane, acetone and dimethylformamide (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. Considering that it is possible to retain 0.40 μg of thallium from 400 mL of solution, the dissolution with 5.0 mL DMF gives a detection limit of 1.0 ng/mL for thallium at the optimum conditions. The linearity was maintained in the concentration range of 3.75 ng/mL to 17.5 μg/mL thallium in aqueous solution or 0.3 to 35 μg/mL thallium in final DMF solution with a correlation factor of 0.9994. Eight replicate determinations of 40 μg of thallium in final 5 mL DMF solution gave a mean absorbance of 0.160 with a relative standard deviation of 1.7%. The sensitivity for 1% absorption was 0.22 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. Thus the method is highly selective and may safely be applied for the determination of thallium in various standard alloys and biological samples.

Table 1. Effect of foreign salts and metal ions

Salt or ion	Tolerance limit
$CH_3COONa.3H2O$, KNO_3, NaCl	1 g
K_2CO_3, NH_4Br	700 mg
$(NH4)_2SO_4$, NaF, KI	650 mg
Sodium Potassium tartrate	400 mg
KSCN, Sodium oxalate	150 mg
Trisodium citrate	300 mg
Disodium-EDTA	60 mg
Ca(II), Mo(II), Zn(II), Pb(II), Ni(II)	90 mg
Mn(II), Al(III), Cr(VI),W(VI), Cr(III)	55 mg
Ti(IV) ,V(V), Co(II), Cu(I), Cu(II)	40 mg
Se(VI),Ga(III), ,Cd(II)	17 mg
U(VI), Te(IV), Bi(III), Sn(II)	10 mg
Ru(III), Rh(III)	5.0 mg
Pd(II), Os(VIII), Sb(III)	4.0 mg
La(III), Au(III), Cs(I), Pt(II)	3.5 mg
Fe(III), Hg(II)	2.0 mg

Analysis of Thallium in Standard Alloys and Steel Samples. The proposed method was applied to the determination of thallium in Nippon Keikinzoku Kogyo (NKK) CRM 916 and No. 920 Aluminum Alloy and NKK No. 1021. Al. Si. Cu. Zn Alloy and Japanese Standards of iron and Steel (JSS) CRM 651-7 and 653-7 Stainless Steel. A 0.1 g sample of the standard aluminum alloy or steel was completely dissolved in 6-14 mL of hydrochloric acid (1+1) by heating on a water-bath in the presence of a known amount of thallium added from the standard solution and then 1 mL of 30% (v/v) hydrogen peroxide was added to it. The excess of peroxide was decomposed by heating the sample at 90 ℃ on the water-bath. The solution was cooled, filtered if needed and diluted to 100 mL with distilled water in a standard flask. Aliquots between 5 and 10 mL of this sample were taken in a 20 mL beaker and the general procedure was applied. The results obtained are given in Table 2.

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.

Table 2. Analysis of thallium in standard alloys

Sample	Certified composition of the sample (%) Thallium added (%)	Thallium found* (%)	Recovery (%)
JSS 651-7 Stainless Steel	C, 0.047; Si, 0.072; P, 0.028; Cr, 18.60; S, 0.0063; Mo, 0.84; Al, 0.002; N, 0.0312; Co, 0.22; Mn, 1.72; Ni, 9.20; Cu, 0.082; Tl# added 0.23%	0.22 ± 0.01	95.6
JSS 653-7 Stainless Steel	C, 0.068; Si, 0.63; Cr, 22.53; Co, 0.35; Mn, 1.72; Ni, 13.91; N, 0.0276; Cu, 0.030; Tl# added 0.38%	0.36 ± 0.03	94.7
NKK No. 916 Aluminum Alloy	Si, 0.41; Fe, 0.54; Mg, 0.10; Cr, 0.05; Zn, 0.30; Ti, 0.10; Sn, 0.05; Pb, 0.04; Sb, 0.01; B, 0.0006; Zr, 0.05; Bi, 0.03; Co, 0.03; Mn, 0.11; Ni, 0.06; V, 0.02; Cu, 0.27; Tl# added 0.43%	0.44 ± 0.02	102.3
NKK No. 1021 Al, Si, Cu, Zn, Alloy	Si, 5.56; Fe, 0.99; Mg, 0.29; Cr, 0.03; Zn, 1.76; Ti, 0.04; Sn, 0.10; Pb, 0.18; Sb, 0.01; Zr, 0.01; Bi, 0.01; V, 0.007; Ca, 0.004; Mn, 0.11; Ni, 0.14; Cu, 2.72; Tl# added 0.56%	0.55 ± 0.02	98.2
NKK No. 920 Aluminum Alloy	Si, 0.78; Fe, 0.72; Mg, 0.46; Cr, 0.27; Zn, 0.80; Ti, 0.15; Sn, 0.20; Pb, 0.10; Sb, 0.10; Bi, 0.06; Ga, 0.05; Ca, 0.03; Co, 0.10; Mn, 0.20; Ni, 0.29; V, 0.15; Cu, 0.71; Tl# added 0.14%	0.13 ± 0.01	92.8

*Average of five determinations. #No thallium was present in these standard samples. Therefore, thallium was added from the standard solution in each case. = standard deviation.

Table 3. 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 28 μg	27 ± 1	96.4
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 46 μg	45 ± 2	97.8
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 62 μg	63 ± 2	101.6
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 78 μg	76±3	97.4

*Average of five determinations, ± standard deviation. #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 & No. 8 (Values in parentheses were approximate and not certified).

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 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 3.

Conclusions

A simple, economical and highly selective adsorbent has been generated simply by mixing the aqueous solutions of 1,10-phenanthroline and TPB with benzophenone for the preconcentration of thallium from the large volume of the aqueous solution of alloys and biological samples. Since 1,10-phenanthroline reacts with many metal ions, therefore, similar procedure may also be developed for other metal ions too. It is not possible to develop selective methods for metal ions using this adsorbent in spectrophotometry, since many metal-1,10-phenanthroline complexes absorb at close wavelengths. However, with the use of AAS this problem can be easily solved.

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