Preconcentration of thallium with 2-nitroso-1-naphthol-4-sulphonic acid-tetradecyldimethylbenzylammonium chloride on microcrystalline naphthalene and its determination by DPP

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Thallium(I) is quantitatively retained as 2-nitroso-1-naphthol-4 -sulphonic acid-tetradecyldimethylbenzyl-ammonium chloride on microcrystalline naphthalene in the *p*H range 10-11.5 from its aqueous solution. After adsorption, the metal is desorbed with 10 ml of $1M$ HCl and determined by differential pulse polarography. The detection limit is 0.2 μg/ml (signal to noise ratio = 2) and the linearity is maintained in the concentration range 0.4-180 μg/10 ml of the final solution ($r = 0.9995$; rsd = 0.95%). The degree of reversibility has also been examined. Various parameters such as the effect of *p*H, concentrations of aqueous phase, HCl, reagent and naphthalene, shaking time and interference of a number of metal ions and anions on the determination of thallium (I) have been studied to optimize the conditions. The method has been successfully applied for estimation of Tl(I) in environmental and biological samples.

The reaction of 2-nitroso-1-naphthol-4-sulphonic acid (nitroso-S salt) with metal ions to form water-insoluble, colored chelate complexes has been applied widely in the liquid-liquid extraction spectrophotometric determination of several metal ions[1] . Several studies on the direct polarographic determination of metals after extraction of their metal complexes into organic solvents[2-5] have also

been reported. In addition to being time consuming and less reproducible these methods are not sensitive, since the extract has to be mixed with a solvent of high dielectric constant. Although methods involving anodic stripping voltammetry (ASV) and differential pulse anodic stripping voltammetry are fairly sensitive, they are time consuming because of prolonged deposition and stripping processes. These methods also suffer from poor reproducibility due to variation in the electrode area and the rate of formation of film on the surface of the electrode besides having limited selectivity [6,7].

In the present study, we have developed a simple, rapid and highly selective direct differential-pulse-polarographic method for direct determination of thallium(I) after adsorption of its nitroso-S-tetradecyldimethylbenzylammonium (TDBA$^+$) complex onto microcrystalline naphthalene. The developed procedure has been used for the determination of trace amounts of thallium(I) in various environmental and biological samples.

Experimental

Polarograms were recorded with a three-electrode Elico (model CL-90) polarographic analyzer fitted with a X-Y recorder (model LR-108). All atomic absorption measurements were made on a Varian AA (model 475) atomic absorption spectrometer. An Elico (model LI-120) *p*H meter was used for *p*H measurements.

Thallous nitrate solution was prepared by dissolving an analytical grade sample in doubly distilled water and standardized by known methods[8]. Solutions of tetradecyldimethylbenzyl-ammonium chloride (TDBA, 1 %) and 2-nitroso-1-naphthol-4-sulphonic acid (nitroso-S, 0.1 %) were prepared in distilled water. Solutions of naphthalene in acetone (20 %) and NaBH$_4$ in 0.2 M NaOH (4%) were also used. Solutions of alkali metal salts(1 %) and various metal salts (0.1 %) were used for studying the interference of anions and cations respectively. Sodium acetate-acetic acid (0.2 M) and aqueous ammonia-ammonium chloride

buffers were used for pH adjustments. Doubly distilled water was used for diluting the samples.

Solid environmental samples were dried in an oven at 200 °C for 2 hrs. A sample (1.0 g) of each was first decomposed with 50-60 ml of 6 M HCl, and then 3-5 ml hydrogen peroxide (30 %) was added [9]. The mixture was heated on a hot plate almost to dryness. The residue was then dissolved in 10 ml of 1 M HCl and diluted with 10 ml of distilled water and filtered.

To 100 ml of each liquid environmental sample, was added 5 ml of conc. HNO_3. The solution was heated almost to dryness on a hot plate and the residue dissolved in 5 ml of 1 M HCl [10].

A 0.1 g sample of each of the biological samples was dissolved in conc. nitric and perchloric acids[10] by heating and cooled. The solution was made up to 100 ml with distilled water in a calibrated volumetric flask. In the case of samples of unknown composition, thallium (I) was determined by the AAS method after preconcentration by the proposed method; in this case naphthalene was removed by filtration before aspirating the sample in a flame.

General procedure

An aliquot of thallium (I) solution (containing 0.4-180 μg of the metal) was placed in a 100 ml Erlenmeyer flask with a tightly fitting stopper. To this, 2 ml of the reagent, (nitroso-S, 0.1%) and 2 ml of $TDBA^+$ (1%) were added and the mixture was diluted to 30-40 ml with water. The pH was adjusted to $\approx$ 11 with 2 ml of the buffer solution. After 2 min at room temperature, 2 ml of naphthalene in acetone (20%) was added to it with continuous shaking. The solid mass consisting of naphthalene and the metal complex was separated by filtration on a Whatman filter paper (No.1041). The residue was shaken vigorously with 9 ml of 1M HCl and 1 ml of 1M KCl and the solution was transferred to the polarographic cell. After passing N_2 gas for 5 min., the differential pulse polarogram was recorded (with E_p = -0.48 V versus SCE and i_p = 0.76 μA for 100 μg of thallium (I)).

Alternatively, dissolved O_2 from the solution could be removed by adding 3-5 ml of a solution of $NaBH_4$ (4 %) in NaOH. On removing the dissolved O_2 with $NaBH_4$ there was no need of adding KCl solution. Preliminary observations indicated that

$NaBH_4$ is quite effective in the removal of dissolved oxygen from the solution in a few seconds. Another advantage of using $NaBH_4$ solution was that it provided OH^- (since the solution of $NaBH_4$ was made in 0.2 M NaOH) and brought the pH in the desired range. Thus, it is helpful for adjusting the pH of the solution also. Many other supporting electrolytes like potassium chloride, and pyridinium chloride were also tried but had no advantage over HCl-NaCl.

Results and discussion

In the present work, differential pulse polarograms of thallium(I) in the HCl-NaCl medium as supporting electrolyte show a half-peak width of 90 $\pm$ 3 mV. The log plot method from the DC polarography gives a slope of $\approx$-59 mV (r = 0.9995, n = 5 where r is the correlation coefficient and n is the number of data points). The cyclic voltammograms, using a mercury pool as working electrode, under the same conditions show the difference between cathodic peak potential and anodic peak potential (ΔE_p) to be 65$\pm$2 mV and the ratio of anodic peak current (I_{pa}) and cathodic peak current (I_{pc}) to be $\approx$ 1. It is clearly established from these studies that thallium(I) is reduced reversibly involving a one-electron reduction.

The effect of pH was studied by varying pH, by adding a 4% $NaBH_4$ solution (or NaOH), while keeping the other variables constant. The shape of differential pulse polarograms and peak heights were found to be almost constant over the pH range 0.5-6.8. Adsorption measurements made at different pH values, keeping other variables constant, showed that the thallium(I) complex was quantitatively adsorbed on naphthalene in the pH range 10.0-11.5.

Preliminary observations indicated that the thallium(I) complex is desorbed completely with 10 ml of 0.1-4.0 M HCl; therefore 1 M HCl was used in all further experiments. Adsorptions were quantitative with 0.5-3.5 ml of 0.1% of the reagent, nitroso-S, and 0.75 - 5.0 ml of 1% TDBA. Peak height remained constant on the addition of 0.9-4.0 ml of 20% naphthalene solution. For all experiments, 2 ml of 20% naphthalene is recommended.

Table 1- Analysis of thallium(I) in biological and synthetic samples

Sample	Composition,µg/g	Thallium[†], µg/g	
		Cert.	Found
NIES[‡], No.1 Pepperbush	K,1.15±0.06; Mg,0.408±0.020; Ca,1.38 ± 0.07; Mn,2030 ± 170 Fe,205±17;Zn,340±20; Ba,165±10; Na,106±13; Rb,75±4; Ni,8.7±0.6; Sr,36±4; As, 2.3±0.3; Co,23±3; P,(1100); Cr(1.3); Cs,(1.2); Pb,5.5±0.8; Cd 6.7±0.5 Cu,12±1; Hg,(0.056)	0.13	0.128 ±0.003
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	8.0	7.95 ±0.12
Synthetic sample[b]	As, 60; Cd, 2.0; Cr, 130; Cu, 130; Pb, 30; Th, 25; Mn,500; Hg, 2.0; Ni, 100; Se,10; V, 210; Zn, 220, U, 12; Al, 69	4.0	3.94 ±0.06

[†]Average of five determinations ± std. dev.; 2 ml of 5% triethanolamine solution was added to mask Fe (III).
[‡]NIES: National Institute of Environmental Studies reference materials.
[a] corresponds to coal (NBS,SRM-1632)
[b] corresponds to coal fly ash (NBS,SRM-1633)

Table 2- Analysis of thallium(I) in environmental samples.

Sample	Tl [†]	
	Present method	AAS[†]
Fly ash near Indraprastha (IP) power station, New Delhi, India.	94 ± 4	96 ± 3
Soil near Indraprastha (IP,) power station, New Delhi, India.	4.28 ± 0.05	4.30 ± 0.08
Water, Okhla Canal, Near industrial area,New Delhi, India.	2.82 ± 0.05	2.80 ± 0.07
Water,Yamuna River near Indraprastha power station, New Delhi, India.	3.73 ± 0.06	3.80 ± 0.05

[†]Average of five determinations, ± std. dev. ; µg/g for solid samples and µg/ml for liquid samples.
[‡]After preconcentration by the present method, 2 ml of 5% triethanolamaine solution added as masking reagent.

The adsorption remained unaffected so long as the volume of the aqueous phase did not exceed 150 ml. For convenience, in all the experiments, the use of 40 ml of the aqueous phase was maintained.

A calibration curve for the determination of thallium(I) was prepared according to the general procedure. The detection limit was 0.2 ppm at minimum instrumental settings (signal-to-noise ratio = 2) and linearity was maintained in the concentration range of 0.04-18.0 ppm (r = 0.9995 and rsd = ± 0.95 %, n = 5).

Effect of foreign ions

The effect of various salts of anions and cations on adsorption and subsequently on the differential pulse polarographic determination of 100 µg of thallium (I) was studied. The tolerance limit was set at error < 3. The following (the amounts shown in parentheses) did not interfere: sodium acetate, potassium nitrate (1 g each), sodium chloride (75 mg), ammonium sulphate (50 mg), ammonium bromide, potassium carbonate and sodium potassium tartrate (70 mg each), potassium thiocyanate (80 mg), sodium citrate and sodium oxalate (30 mg each), sodium fluoride and potassium iodide (40 mg each), disodium EDTA(500 µg), Mo(VI) (50 mg), Zn(II) (45 mg), Mn(II) (35 mg), Cr(III) and Ti(IV) (20 mg each), Al(III), Se(VI) and Ga (III) (17 mg each), U(VI) and V(V) (4 mg each), Te(IV) (3 mg), Bi(III) (5mg), Fe(III) (2 mg after masking with 5 ml of 5% triethanolamine), Rh(III) (1.5 mg), Ru(III) and Cd(II) (1.7 mg each), Pd(II) (1.0 mg), Os(VIII) (1.1 mg), Co(II) (700 µg), Ni(II) and Sb(III) (500 µg each), Sn(II) and Cu(II) (400 µg each), Cr(VI) (300 µg) and Pb(II) (200 µg after masking with 0.4 mg of EDTA).

Determination of thallium(I) 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. An aliquot of the pre-treated sample solution was taken [9-11] and analyzed by the general procedure after masking iron(III) with triethanolamine and lead(II) with disodium EDTA solution. The results are given in Tables 1 and 2.

References

1. De A K, Chalmers R A & Khopkar S M , *Solvent extraction of metals*, (Van Nostrand Reinhold, London) 1970

2. Nagaosa Y & Sato N, *Bunseki Kagaku*, (1987) 36, 877.

3. Odshima T, Kawate Y & Ishii H, *Bunseki Kagaku*, (1988) 37, 439.

4. Nagaosa Y & Kobayashi K, *Talanta*, (1984) 31, 593.

5. Fujinaga T & Nagaosa Y, *Chem Lett*, (1987) 6, 587.

6. Locatelli C, Vasca E, Bighi C, Fagioli F, Garai T, *Electroanalysis*, (1996) 8, 165.

7. Samuel B O and Pablo F, *Electroanalysis*, (1995) 7, 750.

8. Vogel A I, *Text book of quantitative inorganic analysis*, (Longmans, London) IV edn,(1978).

9. Goulden P D, *Environmental pollution analysis*, (Heyden & Son, London)1978, pp 2-5.

10. Usami S, Yamada S, Puri B K & Satake M, *Mikrochim Acta*, (1989) I, 263.

11. Puri B K, Abdul Wasey and Mohan Katyal, *Mikrochim Acta*, (1989)III, 17.