Articles

Flame Atomic Absorption Spectrometric Determination of Ultra Traces of Thallium(I) ion after Solid Phase Extraction by Octadecyl Silica Membrane Disk Modified by a New Schiff Base

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A simple and reliable method has been developed to selectively separate and concentrate trace amounts of thallium ion from real samples for the subsequent measurement by flame atomic absorption spectrometry (FAAS). Thallium ions are absorbed quantitatively during passage of aqueous real samples through an octadecyl bonded silica membrane disk modified by 4-(4-Chloro-phenylazo)-2-[(4-hydroxy-phenylamino)-methyl]-phenol. The retained Tl$^+$ ions are then stripped from the disk quantitatively with a minimal amount of thiosulfate solution as eluent. The proposed method permitted large enrichment factors of about 130 and higher. The relative standard deviation for ten replicate extraction of thallium from 1 L samples containing 5 μg thallium is 1.2%. The break through volume for 5 μg thallium is 1000 mL. The limit of detection of the proposed method is 11.2 ng of Tl$^+$ per 1000 mL. The effects of various cationic interferences on the recovery of thallium in binary mixtures were studied. The method was applied to the recovery of Tl$^+$ ions from natural water and human hair samples.

Key Words : Solid phase extraction, Thallium, Octadecyl silica, Schiff base

Introduction

Thallium is widely distributed in the lithosphere and enters the environment primarily from coal burning and cements manufacture. Thallium can be complexed by organic matter and can be methylated, forming volatile compounds. The uptake of thallium by plants closely parallels the thallium content of the soil. Tobacco is relatively sensitive to thallium. High thallium hinders seed germination and affects both photosynthesis and transpiration. Thallium toxicity results in visual leaf chlorosis. The average human intake is estimated to be 1.5 to 2.0 μg/day; daily urinary excretion ranges from 0.0 to 9.0 μg/L. Thallium is moderately toxic and accumulates in different organs with age. Tachycardia and hypertension are the most common signs of thallium toxicity. Thallium may activate some enzymes, like pyruvate kinase.[1] Thus, the development of new methods for selective separation, concentration and determination of thallium in sub-micro levels in different industrial, biological and environmental samples is of continuing interest.

A large number of techniques have been employed for thallium analysis.[2] After suitable pretreatment procedures, determination has been carried out using spectrophotometry,[3] electrothermal atomic absorption spectrometry,[4,5] ion selective electrode,[6,7] RNNA method[8] and voltammetry.[9,10]

The low concentration of thallium in environmental and biological samples leads to the need for very large sample volumes to be processed. The transport of the samples to the laboratory and the storage until the analysis could induce problems. The addition of preservatives increases the risks for sample contamination because the distribution of the chemical forms could be altered.[11] A preconcentration step should be included in the analysis in order to achieve a final concentration level matching the detection limits accessible with the detection technique selected.[12] Solid phase extraction (SPE) techniques have been developed to replace many traditional liquid-liquid extraction methods for the determination of many organic and inorganic analytes in aqueous samples. SPE methods utilize bonded silica or resin solid sorbents packed into disposable plastic or glass cartridges or imbedded into Teflon or glass fiber disks. SPE techniques provide a means to process samples quickly, eliminate some of the glass ware necessary with liquid-liquid extraction procedures, consume much less solvent, isolate many analytes from large volumes of water with minimal or no evaporation losses, reduce exposure of analysts to organic solvents relative to traditional methods, and can provide more reproducible results.[13-15] In recent years, different trapped ligands on a variety of solid matrices have been successfully used for the preconcentration, separation and sensitive determination of trace metal ions.[16-22] Recently, SPE disks were successfully utilized for the extraction of several inorganic analytes.[18-22] There have been only limited reports on solid phase extraction of thallium in the literature.[5,23-25]

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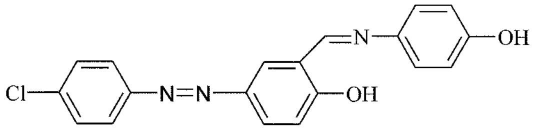

Figure 1. Structure of 4-(4-Chloro-phenylazo)-2-[(4-hydroxy-phenylamino)-methyl]-phenol Ligand (I).

The aim of this study was to develop a rapid and sensitive enrichment procedure using an octadcyl silica membrane disk modified by 4-(4-Chloro-phenylazo)-2-[(4-hydroxy-phenylamino)-methyl]-phenol (I, Figure 1), for the determination of thallium in aqueous samples by flame atomic absorption spectrometry (FAAS). The influence of pH of sample solution, flow rates of eluent and sample solution, types and minimum amount of eluent for elution of Tl from disks were investigated.

Experimental Section

Reagents and materials. Unless stated otherwise all reagents were of analytical reagent grade. Glassware and plastic containers were cleaned by soaking in dilute nitric acid (1 + 9) and rinsed with distilled water prior to use. Stock solution of 100 ppm of Tl (I) was made by dissolving an appropriate of high purity thallium nitrate (Merck, Germany) in distilled water. Working solutions were prepared by appropriate dilution of the stock solution. Ligand I was synthesized and purified as described elsewhere.[26] Extractions were performed with 47-mm diameter × 0.5-mm thickness 3 M Empore^{TM} membrane disks containing octadecyl (C_{18})-bonded silica (8-μm particle size, 60-Å pore size) distributed by Varian. The disks were used in conjunction with a standard Sartorius 47-mm filtration apparatus.

Apparatus. An atomic absorption spectrometer, Varian Spectra (Australia) AA220, with an air-acetylene flame and a 50 mm burner slot was used in all measurements. A Varian Tl hollow cathode lamp was operated with a current of 6 mA and a wavelength 276.8 nm was used in the measurements. A deuterium hollow lamp was used for background correction.

General procedure. After placing the membrane disk in the filtration apparatus, it was washed with 10 mL methanol and 10 mL acetonitrile to remove all contaminants arising from the manufacturing process and the environment. After drying the disk by passing air through it for several minutes, it was dried inside an oven at 60 °C. Then a solution of 7 mg ligand I dissolved in 2-mL DMF was introduced to the reservoir of the apparatus and was washed with 25-mL water and then 5-mL methanol and finally dried by passing air through it. In this step membrane disk modified by the ligand I was ready for sample extraction.

The general procedure for the extraction of Tl^+ ions on the membrane disk was performed as follows: The modified disk was first washed with 2 mL methanol followed by washing with 25-mL water. This step pre-wets the surface of the disk prior to the extraction of Tl^+ ions from water. It is practically important to wet the surface of the disk with methanol during the extraction of thallium (I) ions was underway. Then 100-500 mL of the sample solutions containing mg amounts of Tl^+ was passed through the membrane at a flow rate of 20 mL/min. With this procedure, Tl^+ ions in water samples was quantitatively adsorbed on the modified disk and consequently were eluted by two 5.0-mL portions of 0.2 M thiosulfate solution at a flow rate of 10 mL/min. Each portion was collected in a 5-mL volumetric flask and diluted to the mark with water (if necessary) and the amount of thallium (I) was then determined by FAAS.

Samples of waste water and river water were collected from the Sarcheshme (near the copper mine the Sarcheshme) and Karoun river. Recovery experiments were also conducted by spiking the samples with appropriate amounts of thallium, and its thallium content determined by this method.

Hair samples were washed with acetone and distilled water to remove the surface contamination and dryashed in a muffle furnace at 450 °C. The residue was dissolved in nitric acid and evaporated to dryness at low heating rate. The residue dissolved in 20 mL of water and filtered. The clear solution was quantitatively transferred into a 50-mL volumetric flask and diluted to mark with water. Working solutions were prepared by taking a suitable aliquot of the sample and its thallium content determined by this method and by FAAS.

Results and Discussion

The effects of several experimental parameters on the preconcentration and determination of Tl^+ was studied by spiking 50 mL of distilled water with 5 µg of thallium and using the procedure described in general procedure. These parameters comprise, amount of ligand I, the nature and concentration of eluent, sample and eluent flow rate, pH of sample, and sample volume.

Some preliminary experiments were carried out in order to investigate the quantitative retention of Tl^+ ions by the membrane disks in the absence and presence of ligand I. It was found, that, while the plain membrane disk itself does not show any tendency for the extraction of thallium ions, the ligand I modified disks are capable to retain Tl^+ ions in the sample solution quantitatively. The optimum amount of ligand must be adsorbed on the C_{18} membrane disks for the quantitative recovery of 1-100 µg thallium from aqueous sample solutions was found to be approximately 7 mg. At higher loadings lower efficiencies were observed. This behavior was basically attributed to the heterogeneity of the surface of the membrane disk. At loadings higher than 7 mg, leakage of the immobilized ligand I to the sample solution was taking place, thus indicating the maximum disk capacity for entrapping the specific ligand (I).

From the various eluents used, the highest recovery was achieved with thiosulfate solution. Incomplete stripping of Tl^+ ions was observed for all the other solutions (Table 1). From the data given in Table 1 it is immediately obvious that, the concentration of thiosulfate solution which gave the

Table 1. Percent recovery of thallium from the modified membrane disk as a function of stripping solutions and volume of eluent[a]

Stripping agent	Percentage of recovery				
	first 5 mL	second 5 mL	third 5 mL	forth 5 mL	total
KSCN (0.1 M)	35	15	8	6	64 (±1)
NH_4SCN (0.1 M)	12	6	4	4	26 (±1)
HNO_3 (0.1 M)	25	14	7	2	48 (±2)
EDTA (0.1 M)	46	19	5	3	73 (±1)
$Na_2S_2O_3$ (0.05 M)	46	24	6.5	4	80.5 (±0.5)
$Na_2S_2O_3$ (0.1 M)	54	23.5	19.5	3	100.0 (±0.8)
$Na_2S_2O_3$ (0.5 M)	63	36.5	0.5	–	100.0 (±0.7)
$Na_2S_2O_3$ (1.0 M)	64	36.0	0.4	–	100.4 (±0.8)

[a]Initial samples containing 5 μg Tl^+ ion in 500-mL water.

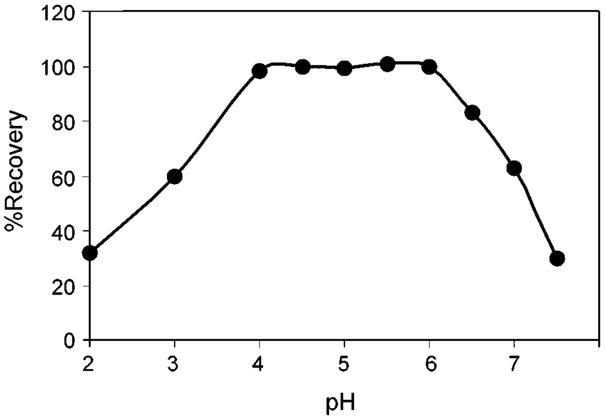

Figure 2. Effect of flow rate of sample solution on the recovery of Tl^+ ion, each sample containing 5 μg Tl^+ in 500 mL aqueous sample at pH ~5.

highest stripping with lower volume was 0.5 M or higher.

The sample's pH is one of the critical variables for the formation of Tl-Ligand I complex, and its adsorption on the modified disk surface. The influence of the pH of test solutions on the recovery of 5 μg Tl^+ from 500 mL solutions was studied in the pH range 2.0-7.5. The pH was adjusted by using 0.1 M nitric acid or 0.01 M NaOH. The results shown in Figure 2 indicate that the Tl^+ ion can be retained quantitatively in the pH range 4.0-6.0. The optimum pH range found to be inside to the range of the standard batch method.[27] The decrease of the efficiency at lower pH values is due to the protonation of ligand I in acid solution, and not to the function of the octadecyl silica membrane disk material, which is very resistant to any acidic solution. However, decreased in the Tl^+ recovery in solutions of higher pH values (>6) are due to the hydrolysis of Tl^+.

The effect of flow rates of sample and stripping solutions from the modified membrane disk on the retention and recovery of Tl^+ ion was studied. The effect of sample flow rate (5 μg Tl^+ in 50 mL) is shown in Figure 3. It can be seen that retention of the Ag^+ ion was independent of flow rate from 5 to 20 mL min^{-1}. The effect of the eluent flow rate on recovery is also investigated and the maximum recovery was achieved for flow rates between 2-10 mL min^{-1}. At higher flow rates, quantitative stripping of thallium needed larger volumes of 0.5 M thiosulfate solution.

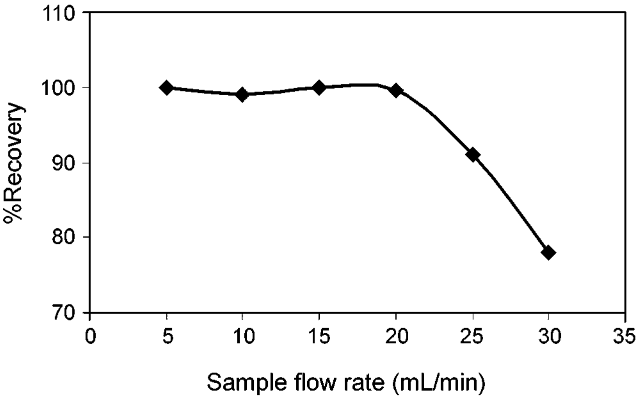

Figure 3. Effect of pH on recovery of thallium (I) ion from membrane disks modified with 7 mg ligand I. Initial sample containing 5 μg Tl in 100 mL aqueous sample.

The reuse of a modified disk was tested for its ability to perform the SPE for more than one sample. It was found that the use of the same disk modified with 7 mg ligand I for at least ten times resulted in no change in the recovery of Tl^+ ion. For the SPE of trace amounts of thallium ions from real samples, it is recommended to use a new modified disk for every sample to protect the samples from possible contaminations. Although, the use of an old disk for real samples might not cause any problems. Therefore this method is practically useful.

The maximum capacity of the membrane disk modified with 7 mg ligand I was determined by passing various volumes of an aqueous solution containing 500 ppb Tl at pH ~5, followed by the determination of retained metal ions using AAS. The results are shown, the maximum capacity of the membrane disk was found to be 100 ± 5 μg of Tl^+ ion on the disk.

The break through volume in solid phase extraction is the maximum volume of sample contains a fixed amount of the analyte, until the recovery is quantitative. The break through volume of sample solutions was investigated by dissolving

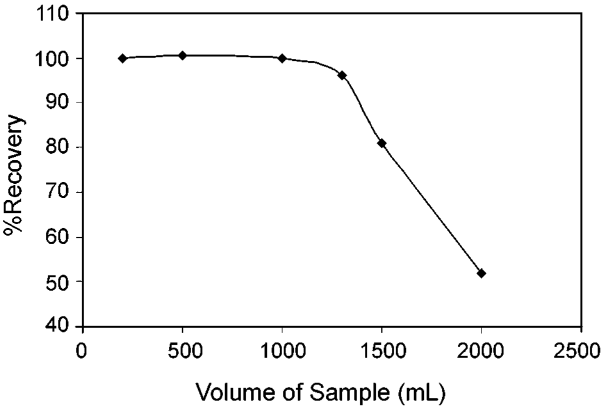

Figure 4. Effect of sample volume on the recovery of thallium (I) ion, each sample containing 5 μg Tl at pH ~5.

Table 2. Separation of thallium from binary mixtures[a]

Diverse Ion	Amount of diverse ion taken (mg)	% Found (diverse ion)	% Recovery of Tl^+ ion
Co^{2+}	10	NADP[b]	101.1 (1.1)[c]
Na^+	100	NADP	99.8 (0.8)
Cd^{2+}	10	NADP	99.5 (1.2)
Ag^+	0.5	15	99.4 (0.7)
Zn^{2+}	10	NADP	99.0 (0.8)
Mn^{2+}	10	NADP	98.5 (0.8)
Ca^{2+}	100	NADP	96.6 (1.1)
Ni^{2+}	5	4.2	97.5 (1.3)
Fe^{3+}	8	7.6	95.8 (1.3)
Pb^{2+}	10	7.3	101.2 (1.1)
Hg^{2+}	10	NADP	100.2 (1.5)
Cu^{2+}	0.5	10	99.8 (1.2)

[a] Initial samples containing 5 μg Tl^+ and different amounts of divers ions in 500-mL water. [b] No adsorption passes through disk. [c] Values in parentheses are RSDs based on four replicate analyses.

Table 3. Recovery of Tl^+ from 200 mL water samples based on four replicate analysis at pH ~5

Sample	Tl^+ spiked (μg)	Tl^+ detected (μg)[a]	%Recovery
Blank	5.0	4.9 (0.3)	98.0 (0.7)
Tap water	5.0	5.1 (0.4)	102.0 (1.2)
river water	5.0	5.1 (0.4)	101.7 (1.1)
Sarcheshmeh water	5.0	4.9 (0.4)	98.0 (0.9)
Synthetic water (1)[b]	5.0	5.2 (0.3)	104.0 (1.2)
Synthetic water (2)[c]	4.0	4.1 (0.3)	102.5 (1.1)

[a] Values in parentheses are RSDs based on four replicate analyses. [b] Synthetic water containing (Cd^{2+}, Co^{2+}, Ni^{2+}, Ca^{2+}, Na^+, and Zn^{2+}, 5 mg of each). [c] Synthetic water containing (Ag^+, Hg^{2+}, Cu^{2+} and Fe^{3+}, 2 mg of each)

Table 4. Recovery of Tl^+ from human hair samples

Sample	Tl^+ spiked (μg/g)	Tl^+ detected (μg/g)[a]	%Recovery
Hair sample 1	1.50	1.52 (0.08)	101.3 (1.1)
Hair sample 2	1.20	1.21 (0.07)	100.8 (1.0)
Hair sample 3	4.25	4.20 (0.06)	98.8 (0.9)

[a] Values in parentheses are RSDs based on four replicate analyses.

5.0 mg of thallium in 100, 200, 500, 1000, 1300, 1500 and 2000 mL water and the proposed procedure was followed. The Tl^+ ions were quantitatively retained from 1000 mL and smaller volumes (Figure 4). Thus, the break through volume for the proposed SPE method was 1000 mL. Since, the final volume of elution solution is 10 mL and the sample solution volume is 1000 mL (the break through volume) hence, an enrichment factor of 100 was easily achievable.

The limit of detection (LOD) of the method for the determination of thallium was studied under the optimal experimental conditions. The LOD obtained from 3s of blank[28] ($C_{LOD} = K_bS_b/m$, where K_b is a numerical factor of 3, S_b is the S.D. of ten replicate blank measurement and m is the slope of calibration graph) is 0.1 ng/mL. The relative standard deviation for the ten replicate recoveries of 5 μg Tl^+ from 100 ml aqueous solutions was found to be ± 1.2%.

In order to study the selective separation and determination of Tl^+ ion from its binary mixtures with diverse metal ions, an aliquot of aqueous solutions (500 mL) containing 5 mg Tl^+ and excess amounts of diverse cations was taken and the proposed procedure was followed. The results are summarized in Table 2. The results clearly indicate that the Tl^+ ions in the binary mixtures are retained almost completely by the modified membrane disk, even in the presence of up to mg amounts of diverse ions. Meanwhile, the retention of other cations by the modified disk, with the exception of Cu^{2+} and Ag^+, is quite low and most of them can be separated almost completely from the Tl^+ ion.

In order to test the accuracy and applicability of the proposed method to the analysis of the real samples, with different matrices, it was applied to the separation and recovery of Tl^+ ions from two synthetic samples. The result, as the average of four separate determinations is shown in Table 3. In view of the application of the method to the determination of thallium in water, standard solutions containing Tl^+ were added to tap water, river water and Sarcheshme water. The results are summarized in Table 3 and show that, in all cases, the thallium recovery is almost quantitative.

The analytical system was used for thallium determination in human hair samples. The results are indicated in Table 4. As can be seen recovery obtained by the proposed method proved that the developed procedure is not affected by matrix interferences and can be applied satisfactorily for real samples.

Conclusion

The proposed SPE method based on octadecyl silica membrane disk modified with a new Schiff base 4-(4-Chlorophenylazo)-2-[(4-hydroxy-phenylamino)-methyl]-phenol is a simple, rapid, selective and reproducible method for the separation, concentration and determination of thallium ions in real samples. The method can be successfully applied to the separation and determination of Tl (I) in water and real samples.

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