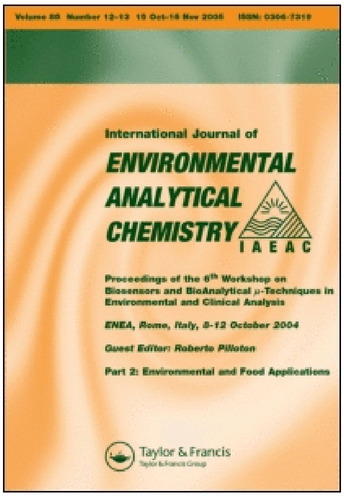

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Determination of Thallium in Natural Waters†

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KEY WORDS: Thallium, natural waters, sea water, atomic absorption spectroscopy, ion exchange.

A method is described for the determination of thallium in natural waters of low and high mineral salt contents. The sample is made 0.15 M in hydrobromic acid, filtered and after addition of bromine water it is passed through a column of the strongly basic anion exchange resin Dowex 1 on which thallium is adsorbed as the anionic thallium(III)-bromide complex. The thallium is eluted with an aqueous solution of sulphur dioxide and, after evaporation of the eluate, this element is determined by a.a.s. with an air-acetylene flame. The method was used successfully for the determination of thallium in waters suitable for drinking purposes, hydrothermal waters, sea-water and waters from oil-wells.

INTRODUCTION

The determination of thallium in natural waters is a difficult task on account of the low concentration of the element which even in mineral waters is several orders of magnitude lower than in rocks. Therefore, in most cases a preconcentration stage is essential before the element can be determined. For this purpose techniques based on anion exchange, solvent extraction and coprecipitation have been used.[1–4] Methods which have been employed to determine thallium in natural waters include anodic stripping voltammetry,[3,4] isotopic dilution using substoichiometric displacement[5] and emission spectrometry.[6]

The present paper reports a method for the atomic-absorption determination of thallium after its separation by anion exchange.

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EXPERIMENTAL

Solutions and reagents

Ion-exchange resin: The strongly basic anion-exchanger Dowex 1-X8 (Bio-Rad AG 1-X8; 100–200 mesh; chloride form) was used. Slurry the resin (4 g) with a few ml of 0.15 M hydrobromic acid; after ca. 30 min, pour into an ion-exchange column filled with the same acid. Subsequently pretreat the resin as mentioned in the procedure.

Standard solutions: From aliquots of a stock solution containing 200 μg of thallium per ml of 6 M hydrochloric acid, prepare dilute standard solutions of this element in 6 M hydrochloric acid.

1:1 Sulphurous acid: Dilute aqueous 5–6% solutions of SO_2 with an equal volume of water.

Apparatus

The separations of thallium were performed in ion-exchange columns of the type and dimensions described earlier.[7]

A Perkin–Elmer atomic-absorption spectrophotometer 303 (equipped with a Hitachi Perkin–Elmer Recorder connected to a read-out accessory) was used with the following instrumental settings:

Grating:	Ultraviolet
Wavelength:	276.8 nm
Scale expansion:	Up to 10X
Slit:	5 (3 mm; 2-nm band pass)
Source:	Hollow-cathode lamp
Lamp current:	20 mA
Burner:	Standard burner head
Acetylene pressure:	8 psig; 7.0 on flow meter (arbitrary scale)
Air-pressure:	30 psig; 9.0 on flow meter (arbitrary scale)
Noise suppression:	Up to 4

When the measurements are carried out in 6 M hydrochloric acid a sensitivity of 0.85 ppm of thallium is obtained for 1% absorption.

Procedure

Pretreatment and separation To the water sample add concentrated hydrobromic acid (20 ml per 1 litre of sample) and heat to boiling on a sand bath to remove carbon dioxide. Let cool to room temperature, filter into an amber bottle (or use a bottle wrapped in aluminium foil to exclude light) and add 10 ml of saturated bromine water (irrespective of the volume of the water sample always add this volume of oxidizing solution). Pass the resulting solution (=sorption solution) through an ion-exchange column containing 4 g of the anion exchanger (pretreated with 100 ml of 0.15 M hydrobromic acid to which 1.0 ml of saturated bromine water was added) at a flow-rate which corresponds to the back-pressure of the resin bed (about 0.7 ml · min^{-1}). Subsequently, wash the resin bed with 20 ml of 0.15 M hydrobromic acid containing 0.2 ml of saturated bromine water and elute thallium with 100 ml of 1:1 sulphurous acid (thallium eluate).

Determination of thallium

Evaporate the thallium eluate on a steam-bath, dilute the residual 1–2 drops of sulphuric acid with 5 ml of 6 M hydrochloric acid, add 1–2 drops of hydrogen peroxide solution (30%) and heat on the steam bath until effervescence ceases. Dilute the solution to 10 ml with 6 M hydrochloric acid and carry out the atomic-absorption measurements with an air-acetylene flame. Construct calibration curves by aspirating suitable standard solutions of thallium before and after each batch of samples.

RESULTS AND DISCUSSION

Pretreatment, separation and determination

Removal of carbon dioxide by boiling the acidified water sample is always necessary in particular when larger amounts of bicarbonates and/or carbonates are present as is the case for example with mineral waters. If this pretreatment step is omitted a portion of the carbon dioxide will form gas bubbles not only in the sorption solution but also within the resin bed so that serious interferences are observed when the anion exchange enrichment of thallium is attempted under these conditions.

Elemental bromine must be present in the sorption solution as well as in the 0.15 M hydrobromic acid solutions used for the pretreatment and washing of the resin to ensure that thallium is in the trivalent state; thallium(I) is not retained by the anion-exchange resin.[1] However, the amount of bromine to be added to the sample solution should not exceed that contained in 10 ml of saturated bromine water irrespective of the volume of the water sample subjected to analysis. If much more of it is present the bromine which is adsorbed on the resin will occupy a larger zone and eventually may prevent the complete retention of thallium by the anion exchanger. On the other hand bromine may lose its effectiveness as an oxidant in the presence of dust and light. Therefore, the sample solution is kept in an amber bottle or in a vessel wrapped in aluminium

TABLE I

Effect of volume, acidity and sulphate concentration on thallium recovery from water samples. (In all cases 100 μg of thallium were added to the samples before application of the procedure.)

A. *Effect of volume*

Volume of water[a] sample used litres)	μg Thallium recovered
1	103.2
2	100.0
3	97.5
4	98.8
5	105.2
10	100.6

B. *Effect of acidity*

Sample (1 litre)	Overall acidity of sample	μg Tl recovered
Vöslauer mineral water	0.015 M HBr	78.2
	0.15 M HBr	97.7
	1.50 M HBr	106.8
Vienna drinking water	0.015 M HBr	95.4
	0.15 M HBr	96.7
	1.50 M HBr	92.8
Sea-water	0.015 M HBr	97.7
	0.15 M HBr	102.1
	1.50 M HBr	99.9

C. *Effect of sulphate concentration*

Sulphate concentration (grams of Na_2SO_4 dissolved in 1 litre water[b])	Overall acidity of sample	μg Tl recovered
1	0.015 M HBr	99.6
1	0.15 M HBr	100.8
1	1.50 M HBr	94.7
5	0.015 M HBr	101.2
5	0.15 M HBr	100.7
5	1.50 M HBr	96.0
10	0.015 M HBr	102.9
10	0.15 M HBr	100.8
10	1.50 M HBr	97.1
25	0.015 M HBr	102.7
25	0.15 M HBr	102.9
25	1.50 M HBr	93.1
50	0.015 M HBr	100.8
50	0.15 M HBr	103.0
50	1.50 M HBr	96.4

[a] Vöslauer mineral water.

[b] Vienna drinking water.

foil and furthermore the sorption process is carried out in a relatively dark room.

Under the conditions employed i.e. in 0.15 M hydrobromic acid containing bromine a weight distribution coefficient of 17×10^3 was measured for thallium so that quantitative separation from practically all major, minor and trace constituents of natural waters such as calcium, magnesium, iron, and copper is readily achieved. These elements have distribution coefficients which are less than unity.[8] Adsorbed together with the thallium are lead ($Kd = 3.4 \times 10^3$),[8,9] cadmium ($Kd > 10^3$)[8,10] and bismuth ($Kd > 10^3$)[8] which however do not interfere with the adsorption or determination of thallium because in natural waters these elements are present in trace quantities only.

Studies with respect to the effects on thallium recovery by the volume of the water sample as well as by its acidity and concentration in sulphate ion gave the results presented in Table I. From the results shown in Section A of Table I it is seen that in the range investigated, the volume of mineral water sample has no effect on the recovery of thallium which was isolated quantitatively in all cases. Similar results were obtained when analysing tap- and sea-water samples of varying volumes. This behaviour is due to the fact that the adsorption of thallium on the anion-exchanger is extremely high from 0.15 M hydrobromic acid containing bromine (see above). That adsorption of thallium from samples made 0.015 M or 1.5 M in hydrobromic acid is also possible is shown by the results listed in Section B of Table I. However, quantitative retention of thallium by the resin is best achieved from 0.15 M hydrobromic acid media.

Investigations with respect to the influence of sulphate, which is one of the major anions present in natural waters, gave the results presented in Section C of Table I. From these it is seen that the sulphate ion concentration has no effect on the recovery of thallium except at the high overall concentration of 1.50 M hydrobromic acid. Similar experiments were carried out at varying concentrations of sodium chloride to study the effect of chloride ion on the recovery of thallium at these three acidities. The results showed that quantitative recovery of thallium was achieved not only at the lower overall acidities but also from 1.50 M hydrobromic acid solutions. This is not surprising because chloride ion enhances the formation of anionic chloride complexes of thallium(III) which are also strongly retained by the anion exchange resin.[11] Therefore thallium can also be isolated quantitatively from highly saline waters such as sea-water and waters from oil fields (oil-well brines) (see Table II).

Application to natural waters

Table II gives the results when this procedure was applied to the analysis

TABLE II

Results of thallium determinations in various natural waters (A = Results obtained after application of the procedure. B = As under A, but in presence of 100 μg of thallium which were added to the samples before application of the procedure.)

A. *Bottled mineral waters*

Sample	μg Thallium/litre	
	A	B
Karlsbader Michlbrunn	3.5	102.4
Donat	3.2	98.8
Radenska	2.9	105.0
Hunyedi	2.5	100.2
Gasteiner	1.9	103.1
Römerquelle	1.6	97.9
Alpquell	~1.3	105.0
Severinquelle	~1.2	99.1
Peterquelle	~1.2	97.3
Güssinger	~1.2	99.7
Preblauer (Ebriach)	~0.9	96.4
Juvina	~0.6	98.2
Ausseer Heilquelle	<0.6	97.9
Gleichenberger Johannisbrunnen	<0.6	103.1
Badener Peregrini	<0.6	98.5
Franz Josef Bitterquelle	<0.6	104.1
Vöslauer	<0.6	103.2

B. *Hydrothermal waters*

Sample	μg Thallium/litre	
	A	B
Oberlaa, Thermalschwefelquelle	<0.6	96.6
Eisenkappel	<0.6	101.4
Badner Marienquelle	<0.6	98.8

C. *Oilfield Waters*

Sample Nr.	μg Thallium/litre	
	A	B
65085	16.2	117
69061	442.0	540
70004	70.0	172
70027	63.7	165
70049	103.0	201
70052	467.0	565
70063	660.0	754
71015	531.0	635
71019	672.0	770
74001	13.0	115
74002	138.0	240
74003	166.0	260
74004	12.9	113

of bottled mineral waters, hydrothermal waters and waters from U.S. oilfields. Comparison of the thallium results listed in columns A and B of Table II shows that the added amounts of thallium were recovered quantitatively in all cases, i.e. thallium is not lost during the separation and evaporation procedures.

While the thallium contents of the mineral waters and hydrothermal waters are within the concentration ranges that may be expected for such waters, the thallium contents in the oil-field waters (see Section C of Table II) were found to be sensationally high. The reason for this is not known. Similar large enrichments of thallium are observed in marine manganese nodules as compared to other marine sediments or terrestrial rocks.[11]

Thallium contents of natural waters so far reported in the literature are the following: 13.0 ± 1.4 ng Tl/litre in sea-water samples from Australian waters,[4] 10.1 ± 0.6 ng Tl/litre and 18.7 ± 0.9 ng Tl/litre from sea-water from the Bay of Biscay and the Irish Sea respectively,[12,13] 3.7 ± 1.0 ng Tl/litre in water from a freshwater catchement area,[4] 14 μg Tl/litre in water from Mercuryville, California,[2] 40 μg Tl/litre and 82 ± 8 μg Tl/litre in unidentified mineral waters[6] and in a hydrothermal water[5] respectively.

No attempt has been made in the present work to determine the actual thallium contents of tap- and sea-water which contain extremely low concentrations of this element (see above) but to show that the developed method can be applied to the quantitative isolation and determination of thallium in waters containing μg/litre amounts of this element which may have toxic effects on the environment. Pollution of this kind may occur when discharging oil-field waters into rivers, lakes or other water bodies such as the world's oceans.

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