Simultaneous separation and determination of Tl(I) and Tl(III) by IC-ICP-OES and IC-ICP-MS

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Abstract

A new hyphenated method was developed for the speciation of Tl. In this method, Tl(III) was complexed with DTPA to form a Tl(III)-DTPA anionic complex. Tl(I) did not form a complex with DTPA. The two species were separated simultaneously by means of ion chromatography using a Dionex cation exchange guard column, CG12A, and 15 mmol/ℓ nitric acid as eluant. When ICP-OES was used as detector the detection limits for both species were 0.8 mg/ℓ for an inert V-groove nebuliser and 0.1 mg/ℓ for an ultrasonic nebuliser. No spectral interference was observed but high concentrations of metals such as Fe and Al could lead to broadening of the Tl(I) peak. It was demonstrated that the same chromatographic method can be used with ICP-MS detection. Detection limits were then reduced to 25 ng/ℓ for Tl(I) and 70 ng/ℓ for Tl(III).

Introduction

Tl and its compounds are used in various industrial applications such as semiconductors, nuclear medicine, catalysts, dyes and pigments, thereby increasing the risk of occupational poisoning and environmental pollution (Asami, 1996). It is also a byproduct in mercury mining. It is present in flue dust from coal-fired power stations and thus is being distributed in the environment. It is known that thallium is more toxic than Hg, Pb or Cd and is one of 13 priority metal pollutants listed by the USAEPA. Tl poisoning is therefore a recognised industrial hazard (Lin and Nriagu, 1999; Shabalina and Spiridonova, 1979), although not wide spread. Some unique applications of Tl are stimulating Tl related research in diverse fields ranging from toxicology (Borgmann, et al., 1998) and biology (Lepp and Logan, 1983) to chemistry (Kocovsky and Baines, 1993, Lin and Nriagu, 1999), and environmental monitoring. In these research fields the determination of the Tl(I) and Tl(III) species is important. In recent work in the environmental field (Lin and Nriagu, 1999), Tl(III), the more reactive form of Tl, was found to be the dominant Tl species in polluted waters of the Huron river. One must therefore assume that Tl(III) can be stabilised through complexation with ligands present in polluted river waters. Tl(III) forms very stable complexes with dicarboxylic acids and β-ketones. Depending on the application, the concentration levels at which the analysis must be performed span a wide range and can vary from mg/ℓ in chemical research to ng/ℓ in environmental monitoring.

During the last decade many analytical methods for Tl determination were developed, most of them focused on low level determinations in natural waters. Atomic absorption spectrometry (Ivanova et al, 1997), in particular ETA-AAS is widely used for the determination of Tl, due to its high sensitivity. Electrochemical methods (Bohrer and Schwedt, 1998; Kahlert et al, 1996 and Diewald et al, 1994), as well as spectrophotometric methods (Vartak and Shinde, 1998; Namboothiri et al, 1991; Mihajlovic and Stafilov, 1996 and Hafez et al, 1996) have also been used for Tl determination. In addition, fluorimetric methods (Perez-Ruiz et al, 1996), liquid scintillation counting (Rajesh and Subramanian,

1992 and 1994), and isotope dilution mass spectrometry (Oliver and Klaus, 1999) have been reported for Tl determination. However, these methods can determine only one of the two Tl species at a time (Lin and Nriagu, 1999 and Perez-Ruiz et al, 1996). Typically, one Tl species is measured, followed by the determination of total Tl concentration after oxidation or reduction. The other species concentration is then obtained by subtraction. Interference from other metals is a common problem in many published methods.

The aim of this work was to develop a quick, interference-free method for the simultaneous separation and determination of the two Tl species, Tl(I) and Tl(III). A hyphenated technique, IC-ICP-OES, i.e. ion chromatography (IC) coupled with inductively coupled plasma optical emission spectrometry (ICP-OES), or IC-ICP-MS, ion chromatography coupled with inductively coupled plasma mass spectrometry (ICP-MS) was developed for this purpose. This is the first useful IC-ICP-OES/MS method for the simultaneous online determination of Tl(I) and Tl(III) species.

Experimental

Apparatus

The IC-ICP-OES system consisted of a Dionex analytical pump (2000i), a Dionex cation exchange guard column, CG12A, and a Varian Liberty 110 ICP-OES spectrometer with V-groove nebuliser. The effluent from the column was fed directly into the nebuliser of the ICP-OES system. An ultrasonic nebuliser (Cetac, U-5000AT+) was used to enhance detection limits. The analog signal from the spectrometer was digitised and analysed using Varian Star Chromatography software (Version 4.0).

The IC-ICP-MS system consisted of a Waters Alliance 2690D high performance liquid chromatograph, a Dionex cation exchange guard column, CG12A, and a Micromass Platform ICP-MS (collision cell) with a V-groove nebuliser. Masslynx 3.4 software was used to control the instrument, to acquire, and to process data.

Reagents

A 1 000 mg/ℓ Tl(I) stock solution was prepared by dissolving an appropriate amount of TlNO$_3$ (Seelze-Hannover) in deionised H$_2$O (18 MΩ). A 1 000 mg/ℓ Tl(III) stock solution was prepared by

| TABLE 1 |
| Optimised ICP-OES conditions |

Parameter	Value
Emission wavelength	351.924 nm
Viewing height	12 mm
Search window	0.04 nm
Filter	6
Order	1
Photomultiplier voltage	700 V
Power	1.00 kW
Plasma gas flow rate	18.0 ℓ/min
Auxiliary gas flow rage	1.5 ℓ/min
Nebuliser pressure	200 kPa

TABLE 2
Optimised conditions for the ICP-MS

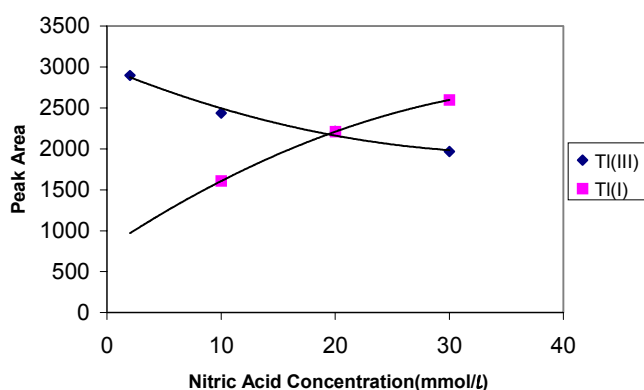| ICP		Hexapole		Quadruple/Detector	
Nebuliser:	0.80 ℓ/min	Hex Exit:	355 V	LM Res:	12.5
Intermediate:	1.2 ℓ/min	Ion Focus:	400 V	HM Res:	12.5
Coolant:	13.5 ℓ/min	Hex Bias:	0.0 V	Ion Energy:	1.0 V
Power:	1200 W	He Flow:	5.2 mℓ/min	Multiplier:	450 V
		H_2 Flow:	5.1 mℓ/min		

Figure 1
The change in peak area vs HNO_3 concentration for a sample containing 20 mg/ℓ each of Tl(I) and Tl(III). Flow rate 2 mℓ/min. Sample volume 50 $\mu\ell$.

dissolving an appropriate amount of $Tl(NO_3)_3 \cdot 3H_2O$ (Sigma-Aldrich) in 10 mmol/ℓ HNO_3 and 5 mmol/ℓ DTPA (diethylene-triaminepentaacetic acid, Merck). A mixture of 1 mmol/ℓ DTPA and 10 mmol/ℓ nitric acid (Suprapure, Merck) was used as diluent for all samples containing Tl(III). All solutions were filtered with 0.22 micron membrane filters before use.

Results and discussion

The stabilisation of Tl(III)

Tl(I) is stable in aqueous media but Tl(III) is reactive and can be hydrolysed in alkaline or neutral solutions and reduced by common reducing agents. It can, however, be stabilised by complexation. In this study a chelating reagent, DTPA was utilised to prevent hydrolysis and reduction of Tl(III) and to stabilise it in aqueous solutions. Tl(III) forms a very stable complex, $[Tl(DTPA)]^{2-}$, with DTPA with stability constant of $logK = 46$ (Inczedy, 1976). A Tl(I)-DTPA complex is not formed. After the stabilisation of Tl(III), the two species exist as Tl^+ and $[Tl(DTPA)]^{2-}$, and can in principle, be separated by either an anion exchange column or a cation exchange column. In practice, however, the use of an anion exchange column is not useful, because the alkaline eluant normally used with this column, could cause the hydrolysis of Tl(III). A cation exchange guard column, CG12A, was therefore used to

separate the two species using HNO_3 as eluant. The anionic Tl(III)-DTPA complex had no retention on the cation exchange column and eluted from the column with the eluant front, followed by Tl^+.

Optimisation of spectrometer conditions

The optimum ICP-OES and ICP-MS conditions were determined experimentally and are listed in Table 1 and 2, respectively.

The optimisation of IC conditions

The choice of eluant
HNO_3 was selected as eluent because among the common strong acids, HNO_3, H_2SO_4 and HCl, HCl cannot be used as eluant because it can form a precipitate (TlCl) with Tl(I). H_2SO_4 is also not suitable, because in real samples common cations such as Ba^{2+}, Ca^{2+} or Pb^{2+} may be present, which will precipitate with SO_4^{2-} and cause column blockage.

Optimising eluant concentration and composition
Figure 1 shows the change in peak area for the chromatographic peaks obtained after separating 20 mg/ℓ Tl(I) and 20 mg/ℓ Tl(III) using different HNO_3 concentrations. Clearly an inverse relationship of peak area (or sensitivity) vs HNO_3 concentration exists for the two Tl species. Optimum sensitivity is achieved at HNO_3 concentrations of between 15 and 20 m mol/ℓ. Baseline resolution was achieved at HNO_3 concentration < 20 m mol/ℓ The trend for peak height is the same. An acceptable compromise between sensitivity and resolution, was obtained by selecting an eluent concentration of 15 mmol/ℓ HNO_3.

To determine whether it was necessary to add DTPA to the eluant to ensure the stability of the Tl(III) DTPA complex, a set of eluants containing 15 mmol/ℓ HNO_3 and different DTPA concentrations were tested. It was found that the addition of DTPA to the eluant does not significantly change the chromatographic parameters, resolution, retention time, peak area and peak height. DTPA was therefore, not added to the eluant in subsequent analyses.

The optimisation of eluant flow rate
The effect of eluant flow rate on resolution, peak area, peak height and retention time was evaluated experimentally, and the results are shown in Table 3.

From the Table 3, it can be seen that even at high flow rates, good resolution was obtained. Flow rate did, however, as expected, affect the retention time and peak area. Both decreased with the

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TABLE 3

The effect of flow rate on resolution, peak area, peak height and retention time.Sample: 20 mg/ℓ Tl(III), 20 mg/ℓ Tl(I) in 1 mmol/ℓ DTPA and 10 mmol/ℓ HNO₃. Injection volume: 50 $\mu\ell$

Flow rate (mℓ/ℓ)	Reso-lution	Retention time (min)	Tl(III)		Tl(I)	
			Peak area	Peak height	Peak area	Peak height
1.0	2.34	1.67	2706	236	2856	189
1.4	2.21	1.20	3361	251	2735	210
1.8	2.18	0.96	2598	262	2328	228
2.2	2.21	0.80	1942	253	1773	220
2.6	1.97	0.67	1787	247	1616	222
3.0	1.93	0.58	1648	251	1489	228
3.4	1.89	0.52	1450	256	1223	234

TABLE 4
The optimised chromatographic conditions for Tl speciation

Column	CG12A cation exchange guard column
Eluant	15 mmol/ℓ HNO₃
Flow rate	2 mℓ/min.
Sample size	100 $\mu\ell$
Sample pretreatment	The mixture of 1 mmol/ℓ DTPA and 10 mmol/ℓ HNO₃ as diluent.

increase in flow rate. The best sensitivities can be achieved at low flow rates but this will result in longer retention times for the Tl(I) species. To keep analysis time below 1 min per sample, a flow rate of 2 mℓ/min was chosen.

Optimising sample size
Sample sizes between 20 and 100 $\mu\ell$ were tested. The results show that retention time of Tl(I) and resolution were not influenced significantly by changes in sample volume. As expected, peak area and peak height increased linearly with increasing sample size. In order to obtain maximum sensitivity, the maximum sample size of 100 $\mu\ell$, was chosen for further analysis. This relatively large sample size did not cause column overload. Optimised chromatographic conditions for the separation of the two Tl species are summarised in Table 4.

Analytical parameters for ICP-OES

Evaluating peak area and peak height as response functions
Tl species can be quantified by using either peak area or peak height. To determine which function is the most effective for the quantitative determination of Tl, a set of standards was measured under the optimum conditions shown in Table 1 and Table 4. The respective calibration curves are given in Figs. 2 and 3.

For Tl(III), the difference between the relative standard deviations for peak area and peak height determinations and the correlation coefficient for the calibration graphs was insignificant. Sensitivity was significantly better for peak area measurements, as can be seen from the following equations for Tl(III) calibration curves:

Peak area: $y = 162.18x + 103.37$
Peak height: $y = 18.96x - 29.40$

For Tl(I), the calibration curve was non-linear (See Fig.3) for peak height determinations, possibly because of peak broadening. Peak area was, therefore, chosen for the quantitative determination of Tl(I) and Tl(III).

Detection limits and working range
 Detection limits were calculated as that concentration equivalent to a signal of three times the standard deviation of the calibration line obtained by the successive dilution of standards. The detection
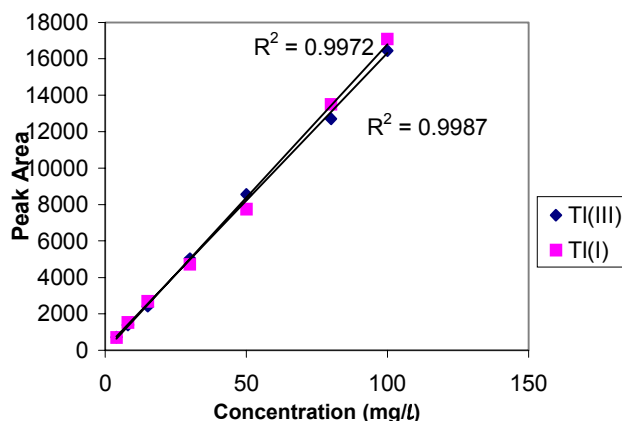

Figure 2
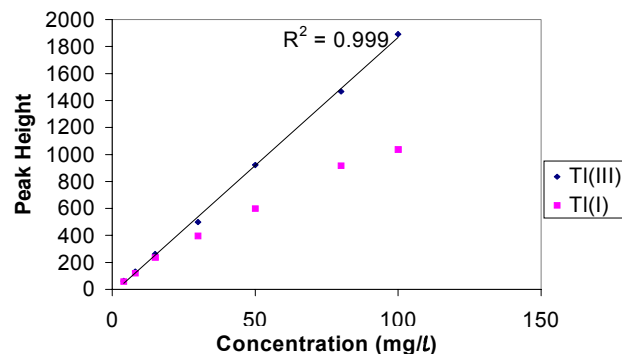*Tl(I) and (III) calibration curves using peak area as response function*

Figure 3
Calibration curves for Tl(I) and Tl(III) using peak height as response function

limits for both species were 0.8 mg/ℓ using an inert V-groove nebuliser and 0.1 mg/ℓ for the ultrasonic nebuliser.

The linear range for Tl measurement by this method can span up to three orders of magnitude.

Interference study: IC-ICP-OES

Common anions
In samples containing precipitating ions, such as I^-, Tl(I) will be precipitated out of the solution as TlI and would not be determinable. Experimental results, show that no interference from the common anions, F^-, Cl^-, Br^-, SO_4^{2-}, and HPO_4^{2-}, was observed for the determination of Tl.

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TABLE 5
Analysis of water samples with different Tl(I) and Tl(III) concentrations using the V-groove nebuliser

Sample No.		Tl(III) (mg/ℓ)			Tl(I) (mg/ℓ)	
	Known	Measured	Recovery	Known	Measured	Recovery
1	4	4.8 ± 1	120%	4	4.5 ± 0.4	113%
2	8	8.5 ± 0.9	107%	8	9.4 ± 1.3	118%
3	15	15.3 ± 0.9	102%	15	16.3 ± 2.3	109%
4	30	27.9 ± 1.2	93%	30	28.3 ± 2.5	94%
5	50	50.1 ± 3.8	100%	50	46.3 ± 9.9	93%
6	80	78.9 ± 9.5	99%	80	80.4 ± 9.1	100%
7	100	101.2 ± 9.6	101%	100	101.6 ± 3.7	102%

TABLE 6
Comparing known concentrations with measured concentrations for various Tl(III) to Tl(I) ratios using the V-groove nebuliser

Sample No.	Ratio		Tl(III)			Tl(I)	
		Known (mg/ℓ)	Measured (mg/ℓ)	Recovery	Known (mg/ℓ)	Measured (mg/ℓ)	Recovery
1	1:20	5	4.8 ± 0.4	95%	100	102.1 ± 6.1	102%
2	1:8	10	10.0 ± 0.5	100%	80	81.1 ± 1.0	101%
3	2:3	30	30.9 ± 2.2	103%	60	59.0 ± 2.5	98%
4	5:4	50	49.0 ± 1.0	98%	40	38.9 ± 1.2	97%
5	4:1	80	80.1 ± 1.3	100%	20	20.0 ± 0.5	100%
6	10:1	100	100.2 ± 1.4	100%	10	10.9 ± 0.7	110%

TABLE 7
Comparing known concentrations with measured concentrations using the ultrasonic nebuliser

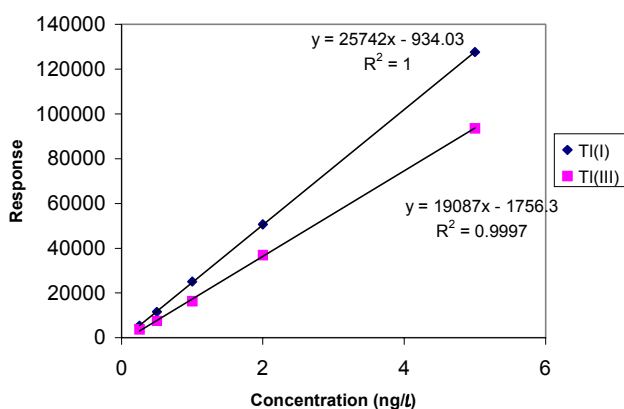| Sample No.		Tl(III)			Tl(I)	
	Known (mg/ℓ)	Measured (mg/ℓ)	Recovery	Known (mg/ℓ)	Measured (mg/ℓ)	Recovery
1	2	1.98 ± 0.17	99%	2	1.99 ± 0.15	100%
2	3	3.04 ± 0.10	101%	4	4.03 ± 0.12	101%
3	4	3.96 ± 0.10	99%	6	5.96 ± 0.07	99%
4	5	5.00 ± 0.12	100%	8	8.01 ± 0.12	100%
5	2	1.90 ± 0.10	95%	8	7.88 ± 0.17	98%

Figure 4
Calibration curves of the two Tl species by means of HPLC-ICP-MS

Cations

Spectral interference at the 351.924 nm Tl line may come from spectral lines of the following elements: Ce (351.908 nm), Th (351.890 nm) and Zr (351.960 nm). Ce and Th are very rare elements in the nature and they are not expected in most samples. To investigate if Zr interferes with the measurement of Tl at the chosen conditions, four samples containing 30 mg/ℓ Tl(III) and 30 mg/ℓ Tl(I) with different Zr concentrations were analysed.

The measured results were in agreement with the known value, indicating that Zr did not interfere with the measurement of Tl. Fe(III) and Al(III) can form complexes with DTPA and may elute with Tl(III)-DTPA. They are not expected to cause spectral interference. It was, however, found that they do slightly affect the peak shapes. The Tl(I) peak was found to be slightly broadened and the Tl(III) peak slightly narrower.

The ratio of Tl(I) and Tl(III)

When low concentrations of one species were to be determined together with high concentrations of the other species, the detection of the species at low concentration becomes difficult. The concentration ratio of the two species therefore, can affect the measurement. This is especially true for low concentrations of Tl(I) because of peak broadening.

The effect of concentration ratios on the reliability of the measurement was studied for the working range 4 to 100 mg/ℓ. When low concentrations of Tl(III) were to be determined in the presence of high Tl(I) concentrations, Tl(I) / Tl(III) ratios of up to 25 could be analysed without difficulty. When low concentrations of Tl(I) were to be determined in the presence of high Tl(III) concentrations, the Tl(I) values are impaired at concentration ratios of Tl(III) / Tl(I) below 12.

Better resolution and correspondingly higher ratios could be achieved by using two guard columns in series or guard column plus the analytical column CS12.

Application of IC-ICP-OES for Tl speciation

The proposed method was used to analyse water samples with known concentrations of the Tl species. The measured concentrations and recoveries are summarised in Table 5 and 6 for the V-groove nebuliser, and Table 7 for the ultrasonic nebuliser. The confidence intervals are based on three replicate measurements (t = 4.30) and a confidence level of 95%.

Application of IC-ICP-MS for Tl speciation in environmental samples

For the determination of Tl species in environmental samples, the IC-ICP-OES method does not have sufficient sensitivity. However,

it was demonstrated in this study that ICP-MS detection can be used without modification of the chromatographic conditions. In doing so, detection limits were improved dramatically, thereby making it possible to apply the method for the analysis of environmental samples. The detection limits for Tl(I) and Tl(III) were 25 ng/ℓ and 70 ng/ℓ, respectively, by using the V-groove nebuliser. Calibration curves for Tl(I) and Tl(III) are shown in Fig. 4 . Excellent linearity was obtained for both calibration curves. To determine the reliability of the method, several samples with very low known concentrations were measured. The measured results and recoveries are summarised in Table 8.

Tap water samples spiked with 0.5 µg/ℓ Tl(I) and 0.5 µg/ℓ Tl(III) and 1 mmol/ℓ DTPA were determined by HPLC-ICP-MS. The results are listed in Table 9.

Excellent consistency of the measured concentrations with the known concentrations has been achieved by means of the IC-ICP-MS. These results show that the IC-ICP-MS can be used in the measurement of Tl species at levels appropriate for environmental samples.

The measurement of Tl at mass 205 is practically interference free since no other stable isotopes occur at this mass number. Interference from adjacent peaks could, however, be possible if large quantities of lead (^{206}Pb) and mercury (^{204}Hg) are present. It was beyond the scope of this paper to include a comprehensive interference study.

TABLE 8
Analysis of water samples with known Tl concentrations using IC-ICP-MS

Sample No.	Tl(III)			Tl(I)		
	Known (µg/ℓ)	Measured (µg/ℓ)	Recovery	Known (µg/ℓ)	Measured (µg/ℓ)	Recovery
1	0.25	0.26	104%	0.25	0.23	92%
2	0.50	0.46	92%	0.50	0.48	96%
3	1.00	0.93	93%	1.00	1.01	101%
4	2.00	2.01	100%	2.00	2.00	100%
5	5.00	5.01	100%	5.00	5.01	100%

TABLE 9
The measurement of tap waters spiked with 0.5 µg/ℓ Tl(I) and 0.5 µg/ℓ Tl(III) and 1 mmol/ℓ DTPA by means of HPLC-ICP-MS

Sample No.	Tl(III)		T(I)	
	Spiked conc. (µg/ℓ)	Measured conc. (µg/ℓ)	Spiked conc. (µg/ℓ)	Measured conc. (µg/ℓ)
1	0.50	0.58	0.50	0.52
2	0.50	0.55	0.50	0.54
3	0.50	0.56	0.50	0.52
4	0.50	0.59	0.50	0.52

Conclusion

The main objective of this work was to demonstrate that the simultaneous separation and determination of Tl species was possible using a hyphenated analytical technique such as IC-ICP-OES and IC-ICP-MS.

The proposed method is the first for the simultaneous separation and determination of both Tl species. The method is fast, simple, accurate and interference-free. It has been used successfully for the determination of Tl in self-prepared samples. The disadvantage of the IC-ICP-OES method is its poor detection limit which is inherent to the ICP-OES detector for this element. The method using ICP-OES detection can find application in the determination of both Tl species in industrial samples, or in chemical and biological research.

For application in environmental trace analysis, it was demonstrated that the same chromatographic conditions can be used for the separation of the two Tl species and that in conjunction with ICP-MS detection, analysis could be performed with the appropriate sensitivity.

Acknowledgements

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