

Original Paper

Solid-Phase Extraction with Slurry Injection of the Resin Into ETAAS for Trace Determination of Thallium in Natural Water

Isoshi Nukatsuka*, Hiroyuki Seitoh, and Kunio Ohzeki

Department of Materials Science and Technology, Faculty of Science and Technology, Hirosaki University, Hirosaki 036-8561, Japan

Received March 22, 2004; accepted August 12, 2004; published online November 26, 2004

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Abstract. Thallium in natural water samples was determined by electrothermal atomic absorption spectrometry after 1000-fold enrichment by mini solid-phase extraction from a 100-mL sample solution. A Tl-pyrrolidine-1-carbodithioate complex formed in a sample solution of pH 1.6 was extracted on fine particles of a cellulose nitrate resin dispersed in the sample solution. The cellulose nitrate resin was then collected on a membrane filter (25 mm^φ) by filtration under suction using a glass funnel with an effective filtration area of 0.64 cm². As a result, a circular thin layer of the resin phase with a diameter of 9 mm was obtained. Then the resin phase was carved out by an acrylate resin puncher with a 10-mm^φ hole to put it into a sample cup containing 100 μL of 10 mM HNO₃ containing 0.5 mM NaCl. The resin phase was suspended in the solution by ultrasonication. 1000-fold enrichment was thus attained within 15 min, and the suspension was delivered to electrothermal atomic absorption spectrometry. The linear calibration graph was obtained in the range of 0–4 ng of Tl in 100 mL of a sample solution. The detection limit obtained by 3σ method was 0.19 ng. The proposed method was applied to the determination of Tl in natural water samples. The results showed the concentration of Tl in seawater was 12.1 ± 1.8 pg mL⁻¹ for the calibration graph method and

12.6 ± 1.4 pg mL⁻¹ for the standard addition method. A snowmelt sample contained 20.7 ± 1.0 pg mL⁻¹ of Tl.

Key words: Thallium determination; solid-phase extraction; slurry injection; electrothermal atomic absorption spectrometry; seawater and natural water; ammonium pyrrolidine-1-carbodithioate.

The monitoring of aquatic environment for thallium and its speciation have drawn the attention of researchers due to its high toxicity [1–5]. The extremely low concentration of thallium in natural water samples (down to ng L⁻¹ level) requires an analytical method featuring high sensitivity and a low detection limit. Thallium in bottled water was determined by inductively coupled plasma-mass spectrometry (ICP-MS) [2, 3] and thallium in arctic snow and seawater was determined by electrothermal vaporization ICP-MS [6] and flow-injection hydride generation isotope dilution ICP-MS [7], respectively. Laser-excited atomic fluorescence spectrometry (LEAFS) is also highly sensitive to thallium and used for the analysis of snowmelt [8]. However, ICP-MS needs expensive instrumentation and incurs high running cost, and LEAFS is less frequently used.

Electrothermal atomic absorption spectrometry (ETAAS) has been used for the determination of thallium in aqueous sample solution in conjunction with enrichment techniques such as liquid–liquid extraction

* Author for correspondence. E-mail: nkt@cc.hirosaki-u.ac.jp

of the iodide complex [9] or the diethyldithiocarbamate complex [10], colloid precipitate flotation under the combined use of hydrated iron(III) oxide and the Fe(III)-pyrrolidine-1-carbodithioate complex [11], sorption on a Chelex-100 resin column [12], and solid-phase extraction (SPE) using a polyurethane foam [13] or cellulose nitrate resin (CNR) particles [14]. A critical drawback of these techniques was the need of large sample sizes (700–1000 mL) for the analysis of uncontaminated natural water samples. The treatment of large volumes of aqueous samples is time-consuming, requires a large amount of reagents, and would lead to the danger of contamination.

Solid-phase spectrometric assays are integrated analytical systems. The analyte is extracted on a suitable solid phase, *e.g.* fine particles of ion exchange resin or other sorbent, and unlike common enrichment procedures the measurement is carried out on the solid phase without elution of the desired element. Elimination of the desorption step simplifies the procedure and makes it highly sensitive [15]. For resin suspension injection (RSI) ETAAS, fine particles holding the analyte were suspended in a small volume of aqueous solution, usually 1 mL, and the resulting suspension was introduced into a graphite tube for determination of the desired element [14, 16, 17]. The enrichment factor can be adjusted by modifying the volume of the suspension. The smaller the volume of suspension, the greater the enrichment factor attained. However, some difficulties arising from handling a sub-mL level solution must be overcome. For example, the fine particles dispersed in a 100-mL sample solution must be transferred to 100 μ L of suspension with reasonable accuracy and reproducibility within acceptable time.

In sequential injection-bead injection-lab-on-valve schemes, a minute amount of sorbent beads was successfully manipulated automatically, and the desired element collected on the sorbent was introduced into ETAAS along with the sorbent beads or after elution. However, the enrichment factors attained were limited to 7–70 [18].

The aim of this work is to develop a “mini” SPE system that enables 1000-fold enrichment from a 100-mL sample solution containing thallium. In the proposed method, thallium is extracted on a minute amount of fine CNR particle as a pyrrolidine-1-carbodithioate complex and introduced into ETAAS along with CNR without elution. A high enrichment factor can be attained because the dilution resulting from the elution of the desired ion is avoided.

Experimental

Apparatus

Atomic absorption of Tl was measured by a model AA-6800 atomic absorption spectrophotometer equipped with a D₂ background corrector, a model GFA-EX7 graphite furnace atomizer with an optical temperature controller, and a model ASC-6100 auto sampler (Shimadzu Corporation, Kyoto, Japan). A pyrolytically coated graphite tube with a pyrolytic graphite platform was used. A hollow cathode lamp obtained from Hitachi (Tokyo, Japan) was operated at 6 mA and at a wavelength of 276.8 nm with a 0.5 nm slit width. Integrated absorbance with a read time of 5 s was recorded. The temperature program was set as described previously and consisted of the 10 following steps [17]: the drying steps are No. 1–5. The temperature was raised gradually to avoid sudden expansion of the water held in CNR and splashing of CNR particles in the graphite tube, No. 1 (80 °C, 10 s, ramp), No. 2 (95 °C, 10 s, ramp), No. 3 (95 °C, 10 s, hold), No. 4 (110 °C, 10 s, ramp), and No. 5 (140 °C, 15 s, ramp). The pyrolysis steps are No. 6 (300 °C, 25 s, ramp), No. 7 (700 °C, 20 s, ramp), and No. 8 (700 °C, 30 s, hold). The atomization step is No. 9 (2200 °C, 5 s, step). The cleaning step is No. 10 (2400 °C, 4 s, step). The argon flow was stopped during atomization and set at 1.00 L min⁻¹ in the other steps. For the collection of CNR particles on a membrane filter, membrane filtration under suction was carried out using a mixed cellulose ester membrane filter (Advantec, Tokyo, Japan), with a 25 mm diameter and a 0.45 μ m pore size, sandwiched between a glass funnel (model KGS-04) and filter base for 25 mm ϕ filter (model KGS-13AA) from Advantec as shown in Fig. 1. The diameter of the throat of the funnel was expanded from 4 mm to 9 mm by filing away the inner wall. A custom-made acrylate resin puncher consisted of two acrylate resin plates (130 \times 60 \times 3 mm) with a 10-mm ϕ hole and a 10-mm ϕ glass tube with a sharp edge (Fig. 1). An A-3S aspirator (Tokyo Rikakikai, Tokyo, Japan) was used for filtration under suction.

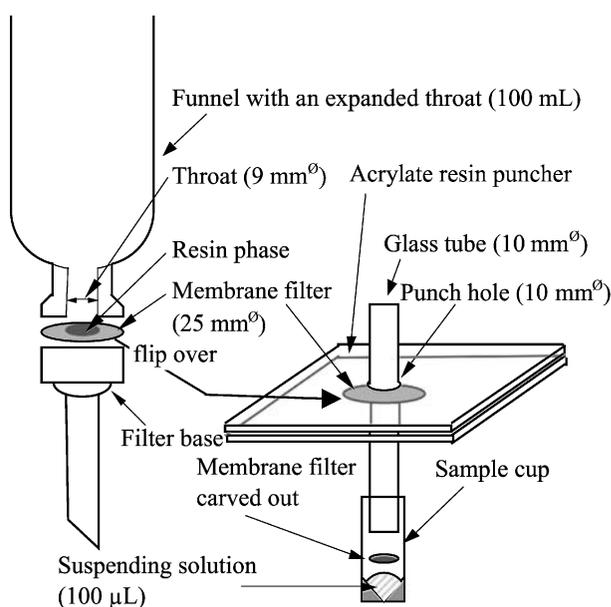


Fig. 1. Filtration apparatus and a purpose-built acrylate resin puncher

Reagents

Water was purified by an Auto Pure WQ500 (Yamato Kagaku, Tokyo) equipped with a Q-Pak (Millipore, MA, USA). Hydrochloric acid, nitric acid (Super Special Grade), and bromine water (content, 2–3% (w/v)) were purchased from Wako (Osaka, Japan). A 1000 mg L^{-1} Tl(I) stock standard solution was purchased from Wako. An 0.1 mg L^{-1} Tl(I) working standard solution was obtained by diluting the stock standard solution maintaining the HNO_3 concentration at 0.1 M and preparing it freshly every day. Ammonium pyrrolidine-1-carbodithioate (APDC) from Wako (for AAS) was dissolved in water to prepare a 30 mM solution. The APDC solution was prepared freshly every week.

A CNR particle suspension was prepared by a method reported earlier [14, 17]. The method consists of the two following steps: (1) *the preparation of an oil-in-water (o/w) emulsion*. A 1 L portion of water containing 7.4 g of benzalkonium chloride (Nacalai Tesque, Kyoto, Japan) was placed in a 3-L beaker and warmed to about 30°C on a hot plate under stirring (900–1000 rpm). A 1-g amount of CNR (12 wt% N, Sigma-Aldrich, Milwaukee, WI, USA) was placed into a 300-mL beaker and dissolved in 50 mL of tetrahydrofuran. A 100-mL portion of dichloromethane was added to make the solution immiscible in water. This solution was poured slowly into the benzalkonium chloride solution to obtain an o/w emulsion. (2) *The formation of CNR particle in water and the concentration of the suspension*. The temperature of the emulsion was raised gradually to 98°C until tetrahydrofuran and dichloromethane had been removed completely by volatilization. The resulting CNR particles were separated by centrifugation (3000 rpm), washed twice with water, and suspended in 100 mL of water.

General Procedure

A 100-mL portion of sample solution containing up to 4 ng of thallium was placed into a 100-mL Pyrex beaker. To the sample solution, 2.9 g of NaCl was added to facilitate filtration and to match the matrix in seawater. The acidity was adjusted to pH 1.6 by adding HCl. Next, 4 mg of CNR and 100 μL of bromine water were added. Tl(I) is oxidized to Tl(III) by bromine. After stirring for 2 min with a magnetic stirrer, 1.5 mL of the APDC solution was added and the solution was stirred for another 3 min. During this period, Tl(III) reacts with APDC and is extracted on the CNR as a hydrophobic complex. Then, the CNR extracting thallium was collected on a membrane filter (25 mm ϕ in diameter) by filtration under suction using a glass funnel with the expanded throat (Fig. 1). After completion of the filtration, the funnel was washed with 3 mL of 0.025 M hydrochloric acid. Then it was detached, and the CNR and the membrane filter were washed again while the suction was continued. The membrane filter holding the thin layer of CNR was then detached from the filter holder, transferred, and placed on an acrylate resin puncher as the resin phase was fitted into the 10-mm ϕ hole of the lower plate. The resin thin layer was carved out with a glass tube to put it into a sample cup containing 100 μL of 10 mM HNO_3 and 0.5 mM NaCl as shown in Fig. 1. In the previous study [17], it was found that a variation in NaCl concentration in a suspension results in a variation in atomic absorption of Tl, and the addition of 0.5 mM NaCl is effective to suppress such variation without loss of sensitivity. The solution was subjected to ultrasonication for 1 min to disperse the CNR particles on the membrane filter and prepare the suspension of CNR. At this stage, 1000-fold enrichment is attained. Finally, after the membrane filter was taken out with ceramic forceps, a 20- μL aliquot of the suspension was delivered to ETAAS measurement by the autosampler.

Results and Discussion

Mini SPE System

Miniaturized membrane filtration was reported using a 4-mm ϕ [19] or 5-mm ϕ membrane filter [20]. The sample volume was, however, restricted to 5–20 mL, because a small effective filtration area required an excessively long filtration time: it took 35 min for 15–20 mL of sample solution using a funnel with 0.03 cm 2 of the filtration area [20]. In our mini SPE system (Fig. 1), the funnel has an effective filtration area of 0.64 cm 2 , and it takes only 7 min to complete filtration of 100 mL of sample solution. Furthermore, the use of a sample cup with a tapered bottom face made it possible to suspend the CNR resin in 100 μL of the solution. Thus, 1000-fold enrichment from 100 mL of sample solution was attained.

In Table 1, mini SPE/RSI-ETAAS is compared with RSI-ETAAS using a conventional membrane filtration apparatus with an effective filtration area of 2.26 cm 2 (throat diameter of 17 mm). Mini SPE/RSI-ETAAS was optimized as shown later, and the conventional one was optimized similarly (data not shown). The results shown in Table 1 indicate that the filtration time is inversely proportional to the effective filtration area. Therefore, it is important to keep the effective filtration

Table 1. Comparison of RSI-ETAAS following mini and conventional SPE for 1000-fold enrichment

	Mini	Conventional ^a
<i>Membrane filtration</i>		
Effective filtration area/cm 2	0.64	2.26
Sample size/mL	100	1000
Final solution/mL	0.1	1
Filtration time/min	7	20
<i>Amounts of reagent required</i>		
30 mM APDC/mL	1.5	15
Bromine water/mL	0.1	0.1
CNR/mg	4	15
<i>Calibration graph</i>		
Range/ pg mL^{-1}	0–40	0–30
Slope/ mL pg^{-1}	3.59×10^{-3}	3.91×10^{-3}
Standard deviation/ mL pg^{-1}	0.07×10^{-3}	0.07×10^{-3}
Correlation factor	0.999	0.999
Detection limit/ $\text{pg mL}^{-1\text{b}}$	1.9	1.3

^a A filtration apparatus with a 17 mm throat diameter for a 25 mm ϕ membrane filter.

^b Calculated by the equation $3 \times s_{y/x}/b$, where b is the slope of the calibration graph and $s_{y/x}$ is the estimate of the standard deviation of the blank given by regression analysis of the calibration graph.

area as large as possible for rapid filtration. The volume of 30 mM APDC solution added in mini SPE was even 1/10 of the conventional one, although the amounts of CNR were not. It was suspected that part of the CNR particles had dug into the pore of the membrane filter during filtration and were not released into the suspension. Therefore, the amounts of CNR added should be in large excess of those trapped in the pore of the membrane filter and be proportional to the effective filtration area. In this study, bromine water was added in excess.

The calibration graphs were prepared in the range of 0–40 pg mL⁻¹ for mini SPE and 0–30 pg mL⁻¹ for conventional SPE. The regression analysis of the calibration graphs indicated that the two methods were comparable in terms of sensitivity, reproducibility, and detection limit as shown in Table 1.

It was found that mini SPE has the advantages of economy in sample volume, filtration time, and reagents compared to conventional SPE. In mini SPE, only 100 mL of sample solution is required for 1000-fold enrichment, and this is effective to eliminate the danger of contamination arising from the treatment of large sample solutions.

Optimization

Since 0.8 mg of CNR is introduced into the graphite furnace, the drying temperature recommended by the

ETAAS manufacturer (80 °C, 10 s, ramp; 140 °C, 30 s ramp) led to incomplete drying and a sudden expansion of water held in CNR. It caused splashing of CNR in the graphite tube and the deterioration of the repeatability. Therefore, the temperature was gradually increased in the furnace temperature program. The background absorption increased with decreasing pyrolysis temperature lower than 500 °C. Atomization was not completed within 5 s at an atomization temperature lower than 1800 °C. Therefore, the pyrolysis and the atomization temperatures were set at 700 °C and 2200 °C, respectively. The introduction of the CNR particles into the graphite furnace seems to have no adverse effect on the lifetime of the tube, since we were able to use it up to 1000 times the firing time.

To establish the optimum enrichment conditions, the effect of pH, the amounts of CNR, the volume of the APDC solution and bromine water, and the reaction time after the addition of bromine water and APDC solution were examined. The effect of pH was studied by adding various volumes of 35% HCl to adjust the pH of the sample solution in the range of 0–2. The results showed that the optimum pH range was 0.5–2. The effect of the amounts of CNR was studied by adding various amounts of CNR in the range of 0–5 mg, and it was found that maximum and constant absorbance was obtained in the range of 3–5 mg. The optimum range of the

Table 2. Effect of foreign ions^a

Species	Added as	Ratio	Error (%)	Species	Added as	Ratio	Error (%)
Ag(I)	AgNO ₃	100	-3.3	Li(I)	LiNO ₃	2 × 10 ⁴	-2.0
Al(III)	Al(NO ₃) ₃	50	-1.7	Mg(II)	Mg(NO ₃) ₂	2 × 10 ⁸	-3.6
As(III)	H ₃ AsO ₃	0.5	2.2	Mn(II)	Mn(NO ₃) ₂	50	0.8
As(V)	H ₃ AsO ₄	200	-0.1	Mo(VI)	(NH ₄) ₆ Mo ₇ O ₂₄	2000	-2.7
B(III)	H ₃ BO ₃	7 × 10 ⁵	-4.6	Ni(II)	Ni(NO ₃) ₂	50	-0.3
Ba(II)	BaCl ₂	2000	3.0	P(V)	NaH ₂ PO ₄	9 × 10 ⁴	-2.2
Ca(II)	CaCl ₂	5 × 10 ⁷	-3.7	Pb(II)	Pb(NO ₃) ₂	100	0.3
Cd(II)	Cd(NO ₃) ₂	100	4.4	Rb(I)	RbNO ₃	2 × 10 ⁴	-1.4
Co(II)	Co(NO ₃) ₂	50	-0.3	S(VI)	Na ₂ SO ₄	7 × 10 ⁷	-16.1
Cr(III)	Cr(NO ₃) ₃	100	3.1			7 × 10 ⁷	0.1 ^b
Cr(VI)	K ₂ Cr ₂ O ₇	100	1.6	Si(IV)	Na ₂ SiO ₃	4.4 × 10 ⁵	1.8
Cs(I)	CsNO ₃	100	0.8	Sr(II)	Sr(NO ₃) ₂	1.3 × 10 ⁶	1.1
Cu(II)	Cu(NO ₃) ₂	100	-3.3	Ti(IV)	Ti(SO ₄) ₂	100	0.7
Fe(III)	Fe(NO ₃) ₃	100	-4.3	U(VI)	UO ₂ (CH ₃ COO) ₂	500	3.8
Ga(III)	Ga(NO ₃) ₃	100	2.9	V(V)	NH ₄ VO ₃	100	0.6
Ge(IV)	GeO ₂	100	4.4	W(VI)	Na ₂ WO ₄	100	-1.5
I ⁻	KI	100	0.3	Zn(II)	Zn(NO ₃) ₂	100	1.4
I(V)	KIO ₃	5000	3.1	Zr(IV)	ZrO(NO ₃) ₂	50	2.4
La(III)	La(NO ₃) ₃	100	-3.3				

^a TI, 30 pg mL⁻¹.

^b 0.12 M MgCl₂ was added.

volume of APDC solution was 0.5–4 mL ($1-8 \times 10^5$ fold to Tl in molar concentration). Because Tl(I) is not extracted on CNR under the conditions employed, only Tl(III) can react with APDC, and Tl(I) has to be oxidized to Tl(III) by bromine [14]. The addition of a 25- μ L portion of bromine water (ca. 2×10^4 fold to Tl) was enough to oxidize Tl(I) to Tl(III), and up to 200 μ L of bromine water did not interfere with the determination. The reaction times required after addition of bromine water (for the oxidation of Tl(I)) and APDC solution (for the complexation and the extraction) were studied in the range of 0–10 min. It was found that the reaction times required were 2 min and 3 min, respectively.

The general procedure was developed under the optimized analytical conditions described above. The relative standard deviation obtained from five repeated measurements of 3 ng of Tl was 6.1%.

Effect of Foreign Ions

To confirm the reliability of the proposed method, the effect of foreign ions was studied by adding each of 36 chemical species to the test solution containing 30 pg mL^{-1} of Tl. The ratio of the foreign ions to Tl was set higher than in natural seawater [21]. The results are tabulated in Table 2. Among the foreign ions tested, only sulfate ions interfered with the determination, causing a negative error. Since the CNR particles have positive charges on their surface due to the benzalkonium ions, the sulfate ions may adsorb on the surface, be introduced in the resin suspension, and interfere with the atomic absorption measurements. We attempted to eliminate the interference by adding a masking agent. It was found that addition of 0.12 M MgCl_2 could effectively suppress the interference. A rough estimation using the equilibrium constants revealed that about half the sulfate species exist in the form of an ion-association complex with a magnesium ion. Therefore, the suppression of interference seemed to be attributed to the formation of the ion-association complex and the decrease in adsorption.

Determination of Thallium in Natural Water Samples

The coastal surface seawater sample was taken from Fukaura, Aomori, Japan. The fresh snow sample was taken from the residential block of the suburb of

Table 3. Determination of thallium in natural water samples^a

Sample	Taken/mL	Tl added/ng	Found/ng	Recovery (%)
Seawater	100 ^b		1.26 \pm 0.13	
	100		1.21 \pm 0.18	
	100	2.5	3.60 \pm 0.20	95.5
Snowmelt	100		2.07 \pm 0.10	
	60 ^c	2.5	3.87 \pm 0.29	105

^a 0.12 M MgCl_2 was added. n = 5–7.

^b Standard addition method.

^c The final volume was adjusted to 100 mL.

Hirosaki city and thawed in the laboratory. These water samples were then filtered through a membrane filter of 0.45 μm pore size using a polysulfone filter holder and acidified to pH 2 by addition of 35% HCl. The concentration of Tl was determined as described under General Procedure. The results are summarized in Table 3. The concentrations of Tl in seawater obtained by the standard addition method and the calibration graph method were $12.6 \pm 1.4 \text{ pg mL}^{-1}$ (n = 5) and $12.1 \pm 1.8 \text{ pg mL}^{-1}$ (n = 7), respectively. The concentration of Tl in snowmelt obtained by the calibration graph method was $20.7 \pm 1.0 \text{ pg mL}^{-1}$ (n = 5). The recovery test was carried out using a 100-mL portion of seawater sample and a 60-mL portion of snowmelt sample spiked with 2.5 ng of Tl. The recoveries obtained were 95.5% and 105%, respectively.

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