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Thallium (III) determination in the Baltic seawater samples by ICP MS after preconcentration on SGX C18 modified with DDTC

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ABSTRACT

The main difficulty of speciation analysis of thallium lies in extremely low concentrations of Tl(III) in comparison to Tl(I), which is the dominating form of thallium in environmental samples. In this study, a sensitive method is presented for separation of trace amounts of Tl(III) from Tl(I) and preconcentration of Tl(III) using octadecyl silica gel modified with diethyldithiocarbamate (DDTC). Under optimal conditions, only Tl(III) is retained on the sorbent, and then eluted with 96% ethanol. After chemical decomposition of Tl(III)–DDTC complex, thallium is determined by inductively coupled plasma mass spectrometry. High performance liquid chromatography with ICP MS detection was used to control the correctness of the obtained results. Parameters affecting solid phase extraction (SPE) such as pH, type, concentration and volume of eluent, breakthrough volume, and the impact of sample salinity (chlorides) and other interfering ions (Cd(II), Zn(II), Pb(II), Cu(II), Sn(II)) were investigated. The limit of detection (LOD), evaluated for 2 mL of sample solution, was 0.10 ng for Tl(I) and 0.43 ng for Tl(III). The method was applied to the determination of Tl(I) and Tl(III) in the Baltic seawater samples enriched in both thallium species.

1. Introduction

Thallium is an element scattered in the environment. It occurs in small amounts in sulfide ores (Fe, Zn, Cu, Pb) and selenite ores (Cu, Ag). Extensive sulphide ore mining, flotation treatment and smelting are the major sources of anthropogenic dispersion of thallium, especially in the vicinity of the zinc–lead smelters. The areas of high content of that metal are in Poland [1], Spain [2], Turkey [3] and China [4]. Thallium belongs to the group of very toxic elements. It occurs in the environment in two redox states: Tl (I) and Tl(III). The well-known mechanism of Tl(I) ion toxicity is related to the interference with the vital potassium-dependent processes. Tl(I) can pass across cell membranes and accumulate in cells [5]. Experimental data show that Tl(I) is the dominant but not the only one form of Tl existing in the environment. Other species found in environmental samples are dimethylthallium in the Atlantic Ocean [6], Tl(III) in river waters [7] and two unidentified forms other than Tl(I) [8], as well as trivalent form extractable with DTPA, in plants [9]. Considering chemical properties of Tl(III) and equilibria taking place in aqueous solutions containing complexing ions, seawater, which is rich in chlorides, seems to be a medium in which Tl(III) could occur.

Monovalent thallium had received much more attention than Tl (III), but both forms are toxic to humans, plants and animals and the redox state can markedly affect Tl toxicity. As evaluated for microorganisms: *Daphnia magna* [10] and *Chlorella* [11], trivalent thallo-compounds (nitrate, chloride and acetate) are approximately several thousand times more toxic than Tl(I), Cd(II), Cu(II) and Ni(II), and similar to Hg(II) [11]. Therefore, determination of chemical species of thallium in the aquatic environment is important and the interest in it has increased considerably during the last few years. Methods of the speciation analysis are based on the differences in physical and chemical properties of the species. In comparison to Tl(III), Tl(I) is thermodynamically more stable and less reactive. In the aquatic environment dissolved thallium is present as Tl(I). The ligands of importance are carbonate, sulphate and phosphate species, and their complexes with Tl^+ are relatively weak (log K in the range 1.0–3.4) [12]. Also hydrolysis is quite insignificant for Tl(I), in contrast to Tl(III). The reduction potential of Tl(III) to Tl(I) is +1.26 V, and this value is affected by pH and the presence of complexing agents. Chlorides lower the reduction potential (+0.77 V), because of forming a strong complex of $TlCl_4^-$ (log K = 18.0) [13]. Even more stable complexes are formed by Tl(III) with organic ligands such as EDTA (log K = 22.5), DTPA (log K = 46) and DDTC. Dithiocarbamates have found considerable use in inorganic analysis for heavy metals determination. Tl(III) precipitates with DDTC even in the presence of some complexing ions [14,15].

Determination of total Tl content can be performed using ICP MS. In case of Tl there are no significant spectral interferences and the detection limit enables carrying determinations at trace levels. Speciation analysis can be performed with LC ICP MS, using either

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cation exchange [16], anion exchange [17], reversed phase [18] or size exclusion column [19]. Electrochemical methods could also be used both for total Tl determination and distinguishing between Tl (I) and Tl(III) compounds [17] and could serve as a reference method confirming the correctness of ICP MS measurements of Tl content in seawater samples. In comparison to ICP MS, electrochemical methods are less dependent on sample salinity, but are characterized by longer time of single analysis.

The necessity of high dilution of the saline seawater samples before ICP MS detection results in the detection limit low enough to determine total Tl and its dominating chemical form (Tl(I)), but too high for quantitative determination of other Tl species, which usually requires a preconcentration step. For preconcentration, liquid–liquid extraction can be useful, especially in the presence of complexing agents such as DDTC. Also radiochemical neutron activation analysis (RNAA) was successfully applied for determination of trace Tl content in natural samples after extraction with benzene [20]. Application of SPE allows to achieve even a 100-fold increase of Tl concentration. Several sorbents were used for that purpose. High-surface area zirconium oxide was used for preconcentration of a number of metals, including Tl(I), from river and seawater samples [21]. Octadecylsilicate modified with cationic surfactants and cellulose nitrate resin were used for sorption of Tl (III) (as $[TlCl_4]^-$) from river water [22,23]. Other sorbents used for preconcentration of Tl(III) were Chromosorb 105 resin, on which $[TlCl_4]^-$ and $[TlI_4]^-$ were retained [24], and nano-Al_2O_3 [25].

The aim of this study was to develop a reliable analytical procedure of separating Tl(III) from Tl(I), with simultaneous preconcentration of the oxidized form. Such proceeding would allow to determine directly both Tl(I) and Tl(III) and avoid calculating one form concentration as a difference between total thallium and concentration of the second form. The idea of the procedure is based on the differences in chemical properties of complexes formed by Tl(I) and Tl(III) with DDTC. The DDTC complex with Tl(I) is characterized by higher solubility in water than for a complex with Tl(III) [15] and the complex of DDTC with Tl (III) is highly soluble in organic solvents [14]. For separation, the ligand (DDTC) was deposited on a commercially available SGX C18 bed. As thallium concentrations in natural water samples are too low, the procedure was successfully applied to seawater enriched in Tl(I) and Tl (III). Our experiment by using Cellex-T as a sorbent did not give satisfying results, even for synthetic solutions.

2. Material and methods

2.1. Chemicals

68% HNO_3 ($d=1.42$ g mL^{-1}), CH_3COONa ($M=82.03$ g mol^{-1}), 96% CH_3COOH ($d=1.06$ g mL^{-1}) Suprapur (Merck, Darmstadt, Germany), diethylenetriaminepentaacetic acid—DTPA ($M=393.35$ g mol^{-1}) puriss. pro analysis (Sigma-Aldrich, St. Louis, MO, USA), sodium diethyldithiocarbamate—DDTC ($M=225.32$ g mol^{-1}) pure pro analysis (POCh, Gliwice, Poland), 30% NaOH ($d=1.33$ g mL^{-1}) Suprapur (Merck), 96% ethanol ($d=0.808$ g mL^{-1}) pure pro analysis (POCh), NaCl ($M=58.44$ g mol^{-1}) Suprapur (Merck), $Tl(NO_3)_3\cdot 3H_2O$ ($M=444.44$ g mol^{-1}) purum (Sigma-Aldrich). Standard solutions of Cd, Zn, Sn, Cu and Pb containing 1 g L^{-1} of the metal were prepared from Titrisol ampoules (Merck). Standard solution of $TlNO_3$ containing 1 mg L^{-1} Tl ($d=1.02$ g mL^{-1}) was obtained from Merck. All solutions were prepared using deionized water (DI) from Milli-Q-Water-System (Merck Millipore, Billerica, MA, USA). The solution containing 0.15 mol L^{-1} DTPA was prepared by dissolving 5.9 g DTPA with 0.7 mL 30% NaOH in water and diluting it to 100 mL. The 0.2 mol L^{-1} acetate solution was prepared by dissolving 1.3 g CH_3COONa and 300 μL 96% CH_3COOH in water, and diluting it to 100 mL. The standard solution of Tl(III) containing *ca.* 18 mg L^{-1} was prepared when needed by dissolving *ca.* 4 mg of Tl $(NO_3)_3\cdot 3H_2O$ (one crystal) in 100 mL of solution containing 0.025 mol L^{-1} DTPA and 0.1 mol L^{-1} acetic buffer.

2.2. Method of separation

Agilent SampliQ 12-Position Solid Phase Extraction chamber (Agilent, Santa Clara, *CA*, USA) connected with vacuum pump (KNF Neuberger, Freiburg-Munzingen, Germany) and Resprep C18 columns (3 mL) (Restek, Bellefonte, PA, USA) modified with DDTC were used for extraction. Solution flow rate was 1.3 mL min^{-1}. For separation and preconcentration of Tl(III) the following sequence of solutions was applied to the SPE column: (1) 2.0 mL of 0.1 mol L^{-1} HNO_3, (2) 1.0 mL H_2O, (3) 3.0 mL 0.01 mol L^{-1} Na-DDTC (recirculated twice), (4) 2.0 mL of sample, (5) 3.0 mL of 96% EtOH, (6) 1.0 mL of the obtained eluate was evaporated to dryness in a quartz crucible, then 1 mL of conc. HNO_3 was added, evaporated to dryness again and the residue was dissolved in 2 mL of H_2O. On the basis of the macro-scale experiment (see *Results and discussion*) some other eluents were checked for step 5. In this step one of the following solutions was applied: 0.1 mol L^{-1} acetate buffer (pH 4.0), NaOH solution (pH 8.0), 96% ethanol. Steps 1 and 2 are applied to clean the column. In the 3rd step the sorbent is modified with DDTC. After introducing the sample, Tl(III) forms a complex with DDTC. Tl(I) is supposed to leave the column in the 4th step, while Tl(III) should be retained and eluted in the 5th step.

2.3. Methods of determination

For spectrometric determinations, an *ELAN* 6100 ICP mass spectrometer (PE-SCIEX, Concord, Ontario, Canada) with a cross-flow nebulizer fitted in a Rayton spray chamber and a Minipuls 3 peristaltic pump (Gilson, Villiers le Bel, France) were used. ICP MS determinations were performed with the following parameters: sweep: 5; replicates: 5; dwell time: 0.1 s; ICP RF power: 1220 W, lens voltage: 12 V, nebulizer gas flow: 0.80 L min^{-1}, plasma gas flow: 15.5 L min^{-1}. For spectrometric determinations calibration curves were applied. Standard solution was analyzed after every 5–10 samples to control the instrumental drift. To confirm the results of ICP MS measurements Tl was determined electrochemically in randomly chosen samples, according to the procedure described previously [17].

For separation of thallium species a model 1200 HPLC pump (Agilent), model 7725 injection valve with a 100 μL injection loop (Rheodyne, Cotati, *CA*, USA), and an anion exchange column Hamilton PRP-X100 (250 × 4.1 mm) (Hamilton, Reno, NV, USA) were used. The mobile phase consisted of 100 mmol L^{-1} ammonium acetate and 5 mmol L^{-1} DTPA (pH 6.2), flow rate: 1.5 mL min^{-1}. ^{203}Tl and ^{205}Tl were detected on-line by ICP MS.

2.4. Samples and sample pretreatment

The water sample from the Baltic Sea was collected in February 2011 in the Darłowo harbor (Polish West Coast). 100 μL conc. HCl was added to 1 L of seawater. The sample was stored at +4 °C. The original sample contained less than 1 μg L^{-1} of thallium and thus it was spiked with Tl(I) and/or Tl(III) standard solutions. Baltic seawater samples enriched in trace amounts of thallium were analyzed with the above proposed method.

3. Results and discussion

3.1. Macro-scale experiment

As the literature data are not precise, before optimizing the procedure of preconcentration on SPE column, some experiments in

macro scale were done in order to recognize the conditions in which Tl(I) and Tl(III) are precipitated by Na-DDTC. Metals react with a solution of Na-DDTC and form precipitates soluble in organic solvents. Most metals form highly stable complex compounds with carbamates. Metals that form stable sulphides, also form stable complexes with carbamates. Thallium (III) carbamate and sulphide are predicted to be less soluble and more stable than adequate compounds of Tl(I). Carbamates react with many metal ions, but the proper choice of the reaction conditions can make it even specific. According to the pH conditions, in which metal ions react with DDTC, they were divided into three groups. Thallium reacts with DDTC in water solution at pH > 11, together with Pd, Pb, Cd, Hg, Cu, Co(III), Ni, Ag and Au [26]. In the presence of NH_3 and tartaric acid ($C_4H_6O_6$, pH 9), DDTC precipitates the following ions, in order of decreasing solubility: Fe(III), Mn(II), Zn(II), Sb(III), Tl(III), Cd(II), Bi (III), Pb(II), Co(II), Ni(II), Cu(II), Ag(I) and Hg(II) [15]. In the presence of CH_3COOH (pH 5) precipitates are formed also by V, Cr(III), Nb, Mo (VI), Ga, U(VI), As(III), Sn(IV) and Se(IV) [14]. In the presence of EDTA (pH 9) only Sb(III), Tl(III), Bi(III), Pb(II) (partly), Cu(II), Ag(I) and Hg (II) are precipitated as complexes with DDTC [15].

The experiments were carried out in test-tubes. 1 mL of 1 g L^{-1} Tl(I) standard was mixed with 1 mL of solvent and then 1 mL of 0.01 mol L^{-1} DDTC was added. The solvents were water; NaOH solution (pH 9.5); 0.1 mol L^{-1} acetate buffer (pH 4.0, 4.5, 5.0); 3.5 mol L^{-1} acetic acid; acetic acid (conc., pH 2.5–3.0); HNO_3 (conc.). In neutral and basic pH no precipitates were observed after the addition of DDTC. In acidic pH white precipitate of Tl(I)–DDTC was observed for a few seconds, then dissolving completely. The higher the pH, the longer was the time of dissolution.

1 mL of 1 mg L^{-1} Tl(III) standard (in a form of Tl(III)–DTPA) was added to 1 mL of 0.01 mol L^{-1} Na-DDTC. Large amount of stable yellow Tl(III)–DDTC precipitate was observed immediately. Then, an aliquot of solvent was added to the test tube. The solvents were ammonia buffer (pH: 9.0, 12.5), 0.1 mol L^{-1} acetate buffer (pH: 4.0, 4.5, 5.0); 3.5 mol L^{-1} acetic acid; acetic acid (conc., pH 2.5–3.0); HNO_3 (conc.), 96% ethanol. The precipitate is insoluble in pH below 9.0, partly soluble in pH 12.5 and well-soluble in ethanol.

Similar experiments were done with $Tl(III)Cl_4^-$ instead of Tl (III)–DTPA standard. In all conditions no precipitate was observed.

On the basis of these experiments, a scheme of Tl(III) preconcentration and separation from Tl(I) was proposed (Table 1).

3.2. Application of Tl(I) standard

Firstly, only Tl(I) was applied to the SPE column (100 ng Tl in 2 mL of "sample"). The recovery was *ca.* 100%, regardless the eluent used in the 5th step. 90–93% of Tl was found in the eluate obtained in the 4th step, which shows that Tl(I) in not effectively retained on the column.

Table 1
The SPE procedure for separation and preconcentration of Tl(III).

Step	Reagent	Aim
1	2.0 mL 0.1 mol $^{-1}$ HNO_3	Conditioning
2	1.0 mL H_2O	Cleaning
3	3.0 mL 0.01 mol $^{-1}$ Na-DDTC (recirculate twice)	Chemical modification
4	2.0 mL of sample	Sample introduction
5	3.0 mL 0.1 mol $^{-1}$ acetate buffer (pH 4.0), NaOH solution (pH 8.0) or 96% EtOH	Elution of Tl(III)
6	1.0 mL of eluate obtained in the 5th step evaporate to dryness 1.0 mL conc. HNO_3 evaporate to dryness 2.0 mL H_2O	Decomposition of Tl(III)–DDTC

3.3. Application of $[Tl(III)Cl_4]^-$ standard

Tl(III) standard was applied to the SPE column in order to check whether Tl(III) is not being reduced during the separation procedure. 2 mL of the "sample" contained 22 ng of Tl(III) in a form of $[Tl(III)Cl_4]^-$. According to the literature data, Tl(III) should be stable in this form. After the 4th step (application of the sample) *ca.* 32% of thallium was found in the eluate. It is the part of Tl(III) that was reduced to Tl(I). To check the oxidation state of Tl ions LC ICP MS method was applied. For $[Tl(III)Cl_4]^-$ standard, the highest signal was recorded at $t_d = 190$ s, which corresponds to Tl(I). Then, during retention time 200–500 s, thallium ions have been continuously reaching the MS detector (Fig. 1). In the 5th step, various eluents were applied to check their efficiency in thallium elution: 0.1 mol L^{-1} acetate buffer (pH 4.0), NaOH solution (pH 8.0) and 96% ethanol. The recovery in the 5th step when using acetate buffer and NaOH solution was less than 5%. These solutions are not effective in elution of Tl(III) retained in the column. Application of ethanol resulted in 68–73% recovery in the 5th step, which means *ca*. 100% of total recovery. Me-DDTC complexes are usually well-soluble in organic solvents, which explains why ethanol occurred to be the most effective eluent. For ICP MS determinations it was necessary to reduce the content of organic compounds in the sample. Therefore, the ethanol eluates obtained in the 5th step were evaporated to dryness. As the residue [Tl(III)–DDTC complex] is not soluble in water, it was necessary to introduce the step of its chemical decomposition in order to obtain water-soluble form of Tl. For this purpose, 1.0 mL of conc. HNO_3 was added, evaporated to dryness again and finally the residue was dissolved in 2.0 mL H_2O. In further experiments the above described procedure was used.

3.4. Application of Tl(III)–DTPA standard

As Tl(III) applied to the SPE column in a form of $[Tl(III)Cl_4]^-$ is partially reduced to Tl(I), an experiment with a standard of Tl(III)–DTPA was done. According to the literature data, Tl(III)–DTPA standard is stable, only 1–3% of Tl(III) being reduced to Tl(I) [17,19]. After application on SPE column of 2.0 mL of a "sample" containing 46 ng of Tl(III) in a form of Tl(III)–DTPA, only about 2% of Tl was found in the eluate obtained in the 4th step. Separation

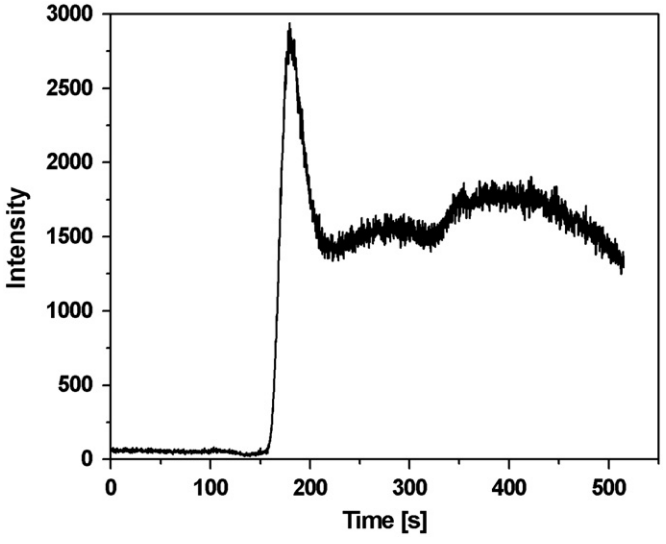

Fig. 1. LC ICP MS chromatogram of the solution containing 0.1 mol $^{-1}$ Cl^- and 100 μg L^{-1} Tl(III). Conditions: anion exchange column, mobile phase 100 mmol L^{-1} ammonium acetate and 5 mmol L^{-1} DTPA (pH 6.2), flow rate 1.5 mL min^{-1}, detected isotope ^{205}Tl.

procedure occurred to have no impact on the stability of Tl(III) when it is in a form of Tl(III)–DTPA.

3.5. Application of a mixture of Tl(I) and Tl(III)–DTPA standards

During the following experiments, elution with eluents other than ethanol in the 5th step was discontinued, as it occurred to be ineffective. The "samples" applied to the SPE column contained Tl (III) (46 ng in 2.0 mL, as Tl(III)–DTPA) and 10-, 20-, 50-, 100- and 1000-fold excess of Tl(I). The recoveries of both Tl(I) and Tl(III) (4th and 5th step) were *ca.* 100% when the excess of Tl(I) was 10. When the excess was higher, total recovery decreased (up to 50%) and significant part of Tl(I) was eluted in the 5th step (up to 18% of total Tl applied to the column). The sorbent works properly when the excess of Tl(I) is not higher than 10.

3.6. Interferences from ions—Cd(II), Zn(II), Pb(II), Cu(II), Sn(II), chlorides

Sulfide ores of Zn, Cd, Cu and Pb may also contain small amounts of Tl [27]. It is probable that environmental samples containing Tl would also contain the above mentioned elements. Moreover, Cd(II), Zn(II), Pb(II), Sn(II) and Cu(II) react with carbamate ions similarly to Tl. The most stable is the complex with Pb, then Cd and Tl(III). In order to check the influence of these metals on the effectiveness of Tl extraction, the "samples" applied to the SPE column contained Tl(III) (46 ng in 2.0 mL, as Tl(III)–DTPA) and Cd(II), Zn(II), Pb(II), Cu(II) or Sn(II) (as nitrates) in a 10-, 100-, 200-, 500-, 700- or 1000-fold excess. No interferences with 1000-fold excess of Cu(II), 700-fold excess of Zn(II) and Sn(II), 500-fold excess of Pb(II) and 100-fold excess of Cd(II) were observed (Table 2). The complex of Cd-DDTC has the most similar properties (solubility in a variety of solutions) as Tl(III)–DDTC; therefore we expected the lowest tolerance to Cd(II) ions [15].

Chlorides are commonly present in many environmental samples. The salinity of Baltic seawater is relatively low and varies between 3‰ in the bays to 8‰ in west regions. As chlorides react with thallium, which can affect chemical equilibrium, the influence of chlorides on the extraction of Tl(III) was checked. The "samples" applied to the SPE column contained Tl (III) (46 ng in 2.0 mL, as Tl(III)–DTPA) in 1%, 2% or 3% NaCl. In all cases the recoveries were above 99%. No negative impact of chlorides on the extraction effectiveness was observed.

3.7. Some additional limitations

The sorption efficiency of SGX C18 modified with DDTC in dependence of the volume of the "sample" containing 46 ng Tl(III) (as Tl(III)–DTPA) allows the sorption with the maximum enrichment factor 10. The recovery is 100–102%.

The crucibles used for mineralization (after the 6th step of the extraction procedure) were conditioned by washing with boiling nitric acid (diluted 1:5 with water). The blank was checked by evaporating to dryness 1 mL 96% ethanol, then 1 mL conc. HNO_3 and adding to the crucible 2.0 mL H_2O. Thallium concentration was measured by ICP MS and it was below the LOD of the method.

4. Application

The procedure was applied to the seawater samples enriched in Tl(I) and Tl(III) (in various proportions).

First sample was enriched in Tl(III) only. A 4.3 mg crystal of Tl $(NO_3)_3 \cdot 3H_2O$ was added to 120 mL of seawater, together with 10.0 mL 0.05 mol L^{-1} DTPA to minimize the reduction of Tl(III). Such obtained solution was diluted 167 times with 5 mmol L^{-1}

Table 2
Recoveries for Tl in the presence of various interfering ions. The SPE procedure was applied to 2.0 mL of solution containing 46 ng of Tl(III) (as Tl(III)–DTPA) and Cd(II), Zn(II), Pb(II), Cu(II) or Sn(II) (as nitrates) in a 10-, 100-, 200-, 500-, 700- or 1000-fold excess. Thallium was determined by ICP MS in the eluates obtained after 4th and 6th step of the SPE procedure, $n=3$–6.

Interferent	Cd						Zn				
Excess	10	100	200	500	700	1000	10	100	500	700	1000
4th step recovery	2.2–4.3%	2.2%	8.4–10.2%	8.6–11.0%	8.9–12.3%	6.5–10.9%	4.3%	4.3%	4.3–6.5%	6.1–8.3%	4.3–10.9%
6th step recovery	91.3–100%	102–104%	89.1–121%	91.9–104%	90.5–99.1%	111–130%	89.1–100%	78.3–93.5%	97.8%	100–104%	54.3–84.8%
Total recovery	95.7–102%	104–106%	98.5–131%	100–113%	103–108%	117–132%	93.5–104%	82.6–97.8%	102–104%	106–113%	58.7–95.7%
Interferent	Pb						Cu		Sn		
Excess	10	100	500	700	1000		500	1000	500	700	1000
4th step recovery	< 1.7%	< 0.4%	1.5–2.0%	1.5–4.1%	< 0.4%		4.3–10.7%	2.2–6.1%	2.2–6.5%	8.3–10.2%	65.2–69.6%
6th step recovery	97.8–107%	97.8–100%	91.3–100%	113–120%	93.5–111%		84.8–93.5%	100–102%	89.1–102%	82.6–97.8%	69.6–76.1%
Total recovery	97.8–107%	97.8–100%	93.5–102%	117–122%	93.5–111%		95.7–97.8%	102–104%	95.7–104%	104–106%	92.8–106%	135–146%

DTPA and applied as a sample (182 ng Tl in 2 mL) to the SPE column. The recovery for Tl was 6.4% in the 4th step, 96% in the 6th step and the total recovery (both steps together) was 103%. Part of Tl(III) added to the sample was reduced to Tl(I), which was confirmed by LC ICP MS measurements. A well defined signal was recorded at the retention time of about 190s, which corresponds to Tl(I) (Fig. 2a). Next, seawater was enriched in both Tl species—Tl(I) and Tl(III) (as Tl(III)–DTPA), in various proportions. The concentration of Tl(I) was always higher than Tl(III), because such a situation is more likely to occur in environmental samples. Also, some samples were diluted 5 times. In all cases, an addition of DTPA was made to ensure the stability of Tl(III). Such obtained solutions were applied to the SPE column, according to the optimized procedure. The recoveries are presented in Table 3.

Elevated and unrepeatable recovery of Tl(III) might be explained by co-precipitation of Tl(I) with Tl(III) in the 4th step and elution of both forms in the 5th step. Even small amounts of Tl (I) eluted in the 5th step have a noticeable impact on the recovery of Tl(III) (Table 3, sample A). In turn, lowered recovery of Tl(III) (Table 3, samples B and C) is probably due to reduction of Tl(III) to Tl(I). 1–3% reduction is observed even during preparation of Tl(III)–DTPA standard solution [8,16,19]. In seawater, which is a sample of high content of the inorganic ions, the equilibria are changed and the reduction proceeds faster. Lowered recovery of Tl(I) and elevated recovery of Tl(III) in diluted samples (Table 3, samples D and E) confirm that Tl(I) partly precipitates with DDTC in the 4th step and is eluted in the 5th step. The total recovery being *ca.* 95% might be a result of precipitation of TlCl due to the presence of chlorides in seawater. The precipitate is retained in the column, which lowers both the recovery of Tl(I) and the total recovery. Additionally, the reduction of Tl(III) standard might also have an impact on the obtained recoveries.

In order to identify the main cause of the dissatisfying results, a sample of seawater enriched in Tl(III) only (28 ng Tl(III) as Tl(III)–DTPA in 2 mL) was applied to the SPE column (Table 4). About 10% of Tl(III) was reduced and eluted in the 4th step of the procedure, which shows that the reduction is more significant in seawater. In turn, concerning possible Tl(I) precipitation, application of the additional step (4A) was proposed to elute the part of Tl(I) retained in the column after the 4th step. A solution of CH_3COOH (pH 3.5) was used as an eluate [28]. Firstly, the same sample as before (containing only Tl(III)) was applied to the SPE column (Table 4). No Tl was detected in the eluate after the 4A step, which proves that the presence of acetic acid does not increase the solubility of Tl(III)–DDTC precipitate. Therefore, a sample of seawater enriched both in Tl(I) and Tl(III) (200 ng Tl(I) and 50 ng Tl(III) in 2 mL) was applied to the SPE column. The elution of Tl(I) was complete (Table 4), acetic acid is a proper eluate to be used in the additional

Table 3
Recoveries for Tl from seawater enriched in Tl(I) and Tl(III) in various ratios, and from seawater diluted 5-fold enriched in Tl(I) and Tl(III) in various ratios, sample volume: 2.0 mL. Thallium was determined by ICP MS in the eluates obtained after 4th (Tl(I)) and 6th step (Tl(III)) of the SPE procedure. The results are presented as a mean value ± SD, $n=5$–9.

Sample matrix	Seawater			5-fold diluted seawater	
Sample	A	B	C	D	E
Tl (I) added	834 ng	417 ng	200 ng	83.4 ng	40.0 ng
Tl (III) added	50.0 ng	50.0 ng	50.0 ng	10.0 ng	10.0 ng
Tl(I): Tl(III) ratio	17:1	8:1	4:1	8:1	4:1
Tl(I) recovery	100 ± 4%	102 ± 2%	104 ± 2%	81 ± 3%	80 ± 2%
Tl(III) recovery	130 ± 21%	98 ± 4%	81 ± 6%	208 ± 16%	160 ± 16%
Total recovery	102 ± 4%	101 ± 2%	99 ± 2%	94 ± 3%	96 ± 4%

Table 4
Recoveries for Tl from seawater enriched in Tl(III), after the SPE procedure with and without the 4A step. The results are presented as a mean value ± SD, $n=3$–4.

Step	Seawater+Tl(III)	Seawater+Tl(III)	Seawater+Tl(I) and Tl(III)
4	10.5 ± 0.9%	16.8 ± 0.4%	91 ± 3%
4A	Not applied	< 0.4%	9 ± 1%
6 [Tl(III)]	95 ± 6%	99 ± 8%	95 ± 18%
4+4A [Tl(I)]	10.5 ± 0.9%	16.8 ± 0.4%	100 ± 3%
Total recovery	105 ± 6%	113 ± 8%	99 ± 5%

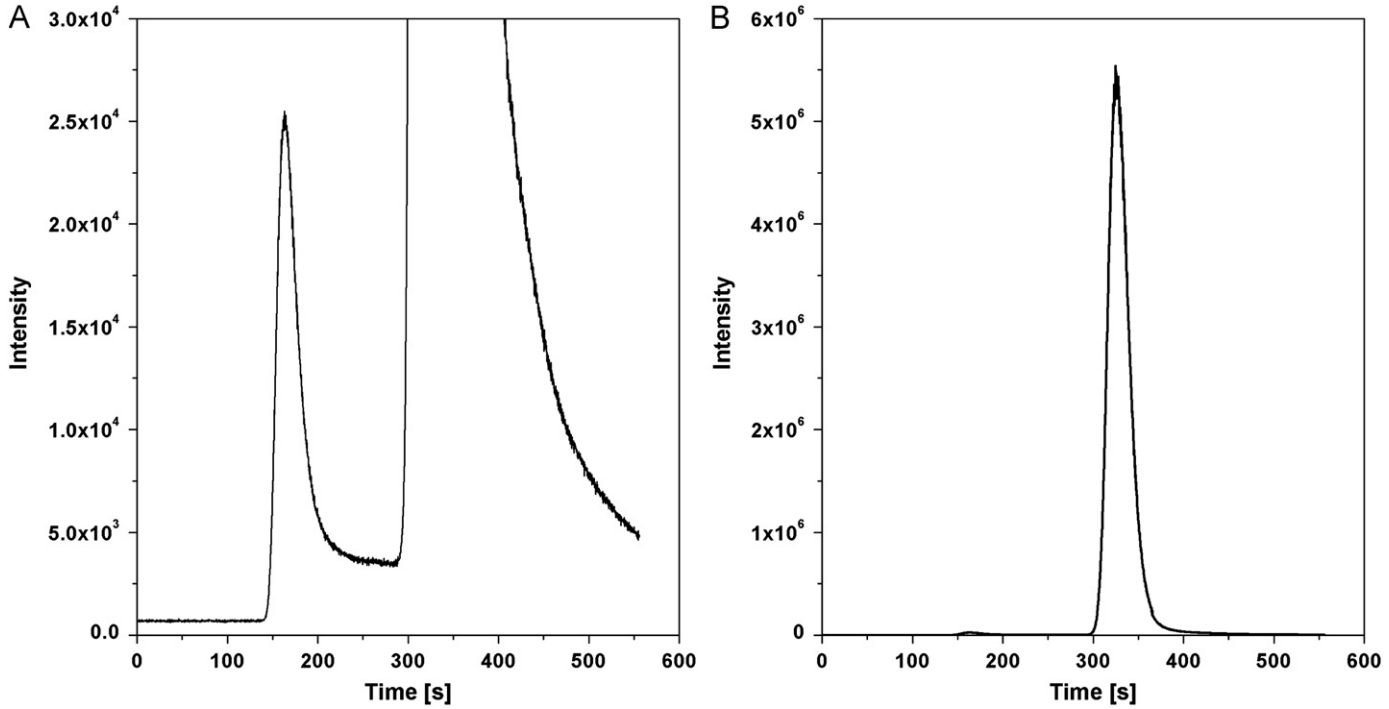

Fig. 2. LC ICP MS chromatogram of seawater enriched in Tl(III), diluted 10 times (16.2 μg mL^{-1} Tl). A - signal corresponding to Tl(I), B - signal corresponding to Tl(III)–DTPA.

4A step of the separation procedure, before eluting of Tl(III) with EtOH in the 5th step.

Unfortunately, ICP MS, which is very accurate for Tl determinations, is also sensitive to organic compounds. For this reason, an attempt was made to find an inorganic eluent, which would be equally effective as acetic acid. On the basis of the earlier macroscale experiment, four eluents were proposed for application in the 4A step: HNO_3 (pH 1.5), HNO_3 (pH 2.5), H_2O (DI), NaOH (pH 8.4). Seawater enriched in Tl(I) (210 ng in 2 mL) was applied as a sample to check the elution efficiency. In all cases the additional elution occurred to be effective, resulting in total recovery of about 101–102%. About 2% of thallium was eluted in the 6th step. No significant differences were observed between samples treated with various eluents. The same experiment was conducted with seawater enriched in both Tl(I) and Tl(III) (4:1) as a sample (210 ng Tl(I) and 50 ng Tl(III) in 2 mL) (Table 5). Again, all eluents used in the 4A step of the procedure were similarly effective. Considering that Tl(III) forms stable complexes with OH^- ions ($\log \beta_4 = 30.75$ [12]), usage of NaOH solution creates a risk of increasing the solubility of Tl(III)–DTPA precipitate and therefore it would be safer to use nitric acid or water.

Table 5
Recoveries for Tl from seawater enriched in Tl(I) and Tl(III), after the SPE procedure including the 4A step—additional elution using various solutions. The results are presented as a mean value ± SD, $n=3$.

Step	Eluent used in the 4A step			
	HNO_3 pH 1.5	HNO_3 pH 2.5	NaOH pH 8.4	H_2O (DI)
4	94 ± 2%	96 ± 1%	96 ± 1%	96 ± 1%
4A	5.8 ± 0.5%	5.3 ± 0.6%	5.4 ± 0.2%	5.5 ± 0.1%
6 [Tl(III)]	96 ± 9%	101 ± 6%	100 ± 11%	106 ± 14%
4+4A [Tl(I)]	100 ± 2%	101 ± 1%	102 ± 1%	101 ± 1%
Total recovery	99 ± 2%	101 ± 1%	101 ± 2%	102 ± 3%

Table 6
Recoveries for Tl from 5-fold diluted seawater enriched in Tl(I) and Tl(III), after the SPE procedure including the 4A step—additional elution using various solutions. The results are presented as a mean value ± SD, $n=3$.

Step	Tl(I):Tl(III)			
	4:1		9:1	
	HNO_3 pH 2.5	H_2O (DI)	HNO_3 pH 2.5	H_2O
4	96 ± 2%	95 ± 1%	94 ± 1%	92 ± 1%
4A	5.5 ± 0.2%	5.2 ± 0.3%	5.6 ± 0.2%	5.7 ± 0.1%
6 [Tl(III)]	107 ± 6%	103 ± 2%	117 ± 5%	116 ± 2%
4+4A [Tl(I)]	102 ± 2%	100 ± 1%	99 ± 1%	98 ± 1%
Total recovery	103 ± 2%	101 ± 1%	101 ± 1%	100 ± 1%

Water and nitric acid solution (pH 2.5) were chosen for further experiments. The sample was 5-fold diluted seawater enriched in Tl(I) and Tl(III) in the ratio 4:1 or 9:1 (44 or 88 ng Tl(I) and 10 ng Tl (III) in 2 mL) (Table 6). When the excess of Tl(I) was 4, the additional elution was effective and the recoveries for both Tl(I) (steps 4+4A) and Tl(III) (step 6) were *ca.* 100%. Elevated recoveries were obtained for Tl(III) from the second sample (9:1), which shows that even trace amounts of Tl(I) retained in the column as Tl (I)–DDTC and eluted in the 5th step have significant impact on the results. Also, such a complex procedure, including mineralization in an open system, leads to dispersed results (RSD up to 4% for Tl (I) and up to 20% for Tl(III)).

When the sample contains significant amounts of Tl(I), the 4A step should be included in the procedure of separation and preconcentration of Tl(III) from seawater samples. Eventually, the following procedure was proposed (Table 7). Apply a sequence of solutions to the SPE column: (1) 2.0 mL of 0.1 mol L^{-1} HNO_3, (2) 1.0 mL H_2O (DI), (3) 3.0 mL 0.01 mol L^{-1} Na-DDTC (recirculate twice), (4) 2.0 mL of sample, (4A) 3.0 mL of H_2O or HNO_3 solution (pH 2.5), (5) 3.0 mL 96% ethanol. In a quartz crucible evaporate to dryness 1.0 mL of the eluate obtained in the 5th step, then add 1.0 mL of conc. HNO_3, evaporate to dryness again and dissolve the residue in 2.0 mL of H_2O (6th step).

The limit of detection (LOD) was calculated as a mean value increased by 3-times the standard deviation of thallium concentration in the blank sample ($\bar{x}$ ± 3 SD, $n=7$), and it amounted to 0.05 ng mL^{-1} for Tl(I) and 0.21 ng mL^{-1} for Tl(III). The limit of quantification (LOQ) was calculated as a mean value increased by 10-times the standard deviation of thallium concentration in the blank sample ($\bar{x}$ ± 10 SD, $n=7$), and it amounted to 0.12 ng mL^{-1} for Tl(I) and 0.42 ng mL^{-1} for Tl(III). The LOD and the LOQ were evaluated in the presence of seawater as a matrix.

In comparison to other methods of Tl(III) separation from Tl(I), the method proposed in this study has as high tolerance for chloride ions as method of retention on silica C18 modified with cationic surfactants [22] and much higher than on Chromosorb 105 [24] and nano-Al_2O_3 [25]. The efficiency of retention is less affected by the presence of interfering ions, such as Cu [24,25], Zn, Cd and Pb [25]. The LOD is comparable [24] or better [22,25] but the breakthrough volume is lower [22,24] than in the above mentioned methods. The great advantage of the proposed procedure is the possibility of direct determination of both Tl(I) and Tl (III), without the necessity of mathematical calculation of the concentration of one of Tl forms [24,25].

5. Conclusion

The proposed method of speciation analysis of Tl, based on the differences in chemical properties of complexes formed by Tl

Table 7
The SPE procedure for separation and preconcentration of Tl(III) from seawater samples.

Step	Reagent	Aim
1	2.0 mL 0.1 mol L^{-1} HNO_3	Conditioning
2	1.0 mL H_2O	Cleaning
3	3.0 mL 0.01 mol L^{-1} Na-DDTC (recirculate twice)	Chemical modification
4	2.0 mL of sample	Sample introduction
4A	3.0 mL H_2O or HNO_3 solution (pH 2.5)	Additional elution of Tl(I) retained in the column after step 4
5	3.0 mL 96% EtOH	Elution of Tl(III)
6	1.0 mL of eluate obtained in step 5 evaporate to dryness 1.0 mL conc. HNO_3 evaporate to dryness 2.0 mL H_2O	Decomposition of Tl(III)–DDTC

(I) and Tl(III) with DDTC, is characterized by low sensitivity to interfering ions. No impact of 1000-fold excess of Cu(II), 700-fold excess of Zn(II) and Sn(II), 500-fold excess of Pb(II) and 100-fold excess of Cd(II) was observed. Also the chlorides (up to 3% NaCl) do not affect the results. The limit of detection (LOD), evaluated for 2 mL of sample solution, was 0.10 ng for Tl(I) and 0.43 ng for Tl(III). Obtained results were confirmed by intermethod comparison with ion chromatography hyphenated with ICP MS. The method can be applied for direct speciation analysis of thallium in seawater.

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References

[1] B. Krasnodębska-Ostręga, K. Dmowski, E. Stryjewska, J. Golimowski, J. Soils Sediments 5 (2005) 71–73.
[2] M.J. Marques, E. Martinez-Conde, J.V. Rovira, S. Ordonez, Environ. Geol. 40 (2001) 1125–1137.
[3] A. Sasmaz, O. Sen, G. Kaya, M. Yaman, A. Sagiroglu, At. Spectrosc. 28 (2007) 157–163.
[4] G.P. Zhang, C.Q. Liu, Y.G. Yang, P. Wu, Water, Air, Soil Pollut. 155 (2004) 51–62.
[5] S. Galván-Arzate, A. Santamaria, Toxicol. Lett. 99 (1998) 1–13.
[6] O.F. Schedlbauer, K.G. Heumann, Anal. Chem. 71 (1999) 5459–5464.
[7] T.S. Lin, J.O. Nriagu, Anal. Chim. Acta 395 (1999) 301–307.
[8] B. Krasnodębska-Ostręga, M. Asztemborska, J. Golimowski, K. Strusińska, J. Anal. At. Spectrom. 23 (2008) 1632–1635.
[9] B. Krasnodębska-Ostręga, M. Sadowska, S. Ostrowska, Talanta 93 (2012) 326–329.
[10] C.H. Lan, T.S. Lin, Ecotoxicol. Environ. Saf. 61 (2005) 432–435.
[11] L. Ralf, M.R. Twiss, Bull. Environ. Contam. Toxicol. 68 (2002) 261–268.
[12] J.O. Nriagu, Thallium in the Environment, John Wiley & Sons, Inc., New York, 1998.
[13] A.K. Das, M. Dutta, M.L. Cervera, M. de la Guardia, Microchem. J. 86 (2007) 2–8.
[14] A. Hulanicki, Talanta 14 (1967) 1371–1392.
[15] G.D. Thorn, R.A. Ludwig, The Dithiocarbamates and Related Compounds, ElsevierAmsterdam-New York, 1962.
[16] U. Karlsson, A. Düker, S. Karlsson, J. Environ. Sci. Health, Part A: Toxic/Hazard. Subst. Environ. Eng. 41 (2006) 1157–1169.
[17] B. Krasnodębska-Ostręga, J. Pałdyna, M. Wawrzyńska, E. Stryjewska, Electroanalysis 23 (2011) 605–610.
[18] Y.L. Chu, R.Y. Wang, S.J. Jiang, J. Chin. Chem. Soc. 59 (2012) 219–225.
[19] A. Nolan, D. Schaumlöffel, E. Lombi, L. Ouerdane, R. Łobiński, M. McLaughlin, J. Anal. At. Spectrom. 19 (2004) 757–761.
[20] J. Kučera, M. Vobecky, L. Soukal, D. Zákoucky, D. Vénos, J. Radioanal. Nucl. Chem. 217 (1997) 131–137.
[21] E. Vassileva, N. Furuta, Fresenius J. Anal. Chem. 370 (2001) 52–59.
[22] K. Urbánková, L. Sommer, Microchim. Acta 162 (2008) 127–132.
[23] R. Horiguchi, I. Nukatsuka, Y. Shimizu, S. Sekikawa, Bunseki Kagaku 51 (2002) 675–679.
[24] A. Karatepe, M. Soylak, L. Elçi, Talanta 85 (2011) 1974–1979.
[25] L. Zhang, T. Huang, X. Liu, M. Zhang, K. Li, J. Anal. Chem. 66 (2011) 368–372.
[26] H. Bode, Fresenius Z. Anal. Chem. 142 (1954) 414–423.
[27] B. Alloway, Heavy Metals in Soils, Blackie Acad. & Professionals, London-Glasgow, 1990.
[28] V. Camel, Spectrochim. Acta, Part B 58 (2003) 1177–1233.