

## Tl<sup>I</sup> and Tl<sup>III</sup> presence in Suspended Particulate Matter: Speciation analysis of thallium in wastewater

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**Abstract.** Thallium (Tl) is a toxic element, whose toxicity is affected by its redox state. Compared with Tl<sup>III</sup>, Tl<sup>I</sup> is thermodynamically more stable and less reactive; therefore in aquatic environments, dissolved thallium is mostly present as Tl<sup>I</sup>. However, Tl<sup>III</sup> could be 1000 times more toxic than Tl<sup>I</sup>. A combination of a fractionation and a speciation study carried out in highly polluted wastewater samples from a mining area in southern Poland in order to characterise chemical speciation of Tl in physically defined fractions is presented here. Total, particulate and dissolved thallium was determined. A leaching experiment based on forming Tl<sup>III</sup> complexed with diethylene triamine penta-acetic acid – a Tl<sup>III</sup>–DTPA complex – was performed in filters containing suspended particulate matter after single (0.45- $\mu$ m) and sequential filtration (15 + 0.45- $\mu$ m) of wastewater samples. This is the first speciation study of Tl carried out in suspended particulate matter. The results obtained indicate that the dominant form of Tl in suspended particulate matter is Tl<sup>I</sup>, but Tl<sup>III</sup> could be found in suspended particulate matter fractions larger than 0.45  $\mu$ m.

### 1. Introduction

Toxicity, mobility, bioavailability, biogeochemical behaviour and environmental pathways of trace elements are highly related to their chemical species. Metal ions in the environment occur in different states of oxidation and form distinct species, which implies differences on their physicochemical properties,<sup>[1]</sup> e.g. Cr is toxic to plants, but Cr<sup>III</sup> is less toxic than Cr<sup>VI</sup>. Trivalent chromium remains bound to organic matter in soils and water, which decreases its mobility, but the toxicity of Cr<sup>VI</sup> is higher owing to its high solubility and oxidising potential.<sup>[2,3]</sup> Thus, quantification of total content or concentration of the elements is not always sufficient and speciation analysis becomes indispensable in order to understand their toxicity and biotransformation in the environment.

The term of speciation was introduced by Goldberg in 1954,<sup>[4]</sup> related to the biogeochemistry of trace metals in sea water. Chemical speciation may be defined as the determination of the specific forms in which an element can occur that together make up the total concentration of that element in a given matrix.<sup>[5,6]</sup> The speciation of trace elements requires two interconnected techniques: the first one for separation of the species (liquid extraction,<sup>[7,8]</sup> solid-phase extraction<sup>[9–11]</sup> based on ion-exchange,<sup>[12,13]</sup> Chelex-100 resin,<sup>[12,14]</sup> coprecipitation,<sup>[15,16]</sup> etc.), and the second one for its detection. Different detection techniques have been developed so far,<sup>[6,10]</sup> i.e. spectroscopic methods: UV-visible, atomic absorption (AAS), atomic emission (AES), inductively coupled plasma (ICP); electrochemical methods: polarography, voltammetry, capillary electrophoresis (CE), gel electrophoresis (GE); and chromatographic methods: gas

chromatography (GA), high-performance liquid chromatography (HPLC), ion chromatography (IC). The interest in speciation of trace elements has considerably increased during the last 20 years (the number of published papers increased ~80 % from 1994 to 2014), and currently, this topic is within the research agenda of different international programs such as GEOTRACES-International study of the global marine biogeochemical cycles of trace elements and their isotopes; IMBER-Integrated Marine Biogeochemistry and Ecosystem Research; SOLAS-Surface Ocean Lower Atmosphere Study; SCOR-Scientific Committee on Oceanic Research through its working groups 139 (Organic ligands – A key control on trace metal biogeochemistry in the ocean) and 145 (Chemical speciation modelling in seawater); and COST-European Cooperation in Science and Technology through its actions ES0801 (Ocean chemistry of bioactive trace elements and paleoclimate proxies) and ES1302 (European network on ecological functions of trace metals in anaerobic biotechnologies).

Thallium is naturally dispersed in the environment – mainly in potassium minerals such as sylvite and pollucite, with an abundance in the Earth's crust ( $6 \times 10^{-5}$  wt %, <sup>[17]</sup> 0.1–1.7 mg kg<sup>-1</sup><sup>[18]</sup>) even higher than that of Cd and Pb. Natural mobilisation of Tl into the aquatic environment is related to soil erosion, brush fires and volcanic eruptions. Thallium is one of the 'Group 13 metals'<sup>[19]</sup>, an emerging contaminant<sup>[20]</sup> listed as priority pollutant metal by the US Environmental Protection Agency (EPA).<sup>[21]</sup> Major anthropogenic sources of Tl are extensive sulphide ore mining, flotation treatments and smelting works, because this element is a by-product of the refining process of Zn and Pb. Every year ~ 2000 to 5000 tonnes of Tl are mobilised by industrial processes,<sup>[18]</sup> and eventually into the water,<sup>[20]</sup> therefore, understanding the biogeochemistry and environmental behaviour of this pollutant is of great importance.

Thallium can be naturally found as Tl<sup>I</sup> and Tl<sup>III</sup>. Both forms are highly toxic, but – as in the case of Cr – its toxicity is affected by its redox state. A complete review by Couture et al.<sup>[17]</sup> highlights the differences – in terms of bioaccumulation and toxicity – of both Tl species in aquatic systems. Studies performed by Ralph and Twiss<sup>[22]</sup> in unicellular algae (*Chlorella* sp.) showed that Tl<sup>III</sup> is much more toxic than Tl<sup>I</sup>. Similar results have been also reported for freshwater cladoceran (*Daphnia magna*) by Lin and Lan.<sup>[23]</sup> Compared with trivalent Tl, monovalent Tl is thermodynamically more stable and less reactive; therefore in aquatic environments, dissolved thallium is mostly present as Tl<sup>I</sup>.<sup>[9,17]</sup> These differences draw attention to the importance of speciation studies of Tl, which may provide useful information about the behaviour of this metal for each one of its ionic forms.

During the last decade, high contents of thallium have been reported in Aznalcóllar, Spain,<sup>[24]</sup> Guizhou province, south-west China<sup>[20]</sup> and Upper Silesia, Poland,<sup>[25,26]</sup> mostly related to mining and smelting areas. In these regions, where dust particles can be an important source of contamination, it is necessary to separate the dust fraction before isolation of the suspended particulate matter (SPM). Dust fractions, defined as small solid particles usually in the size range from 1 to 100 µm,<sup>[27]</sup> contain a high content of tailings minerals. Nevertheless, dust fraction very often is not taken into account because is supposed to

settle out within a short time and without interaction with water and microorganisms. A potential content of trivalent thallium species in SPM has already been suggested,<sup>[12,28]</sup> but the problem is that it is necessary to have an amount of thallium large enough in the sample to carry out the analysis, because speciation analysis causes a large dissolution of sample.

Taking into account that most of the analytical methods for Tl speciation are monoselective, i.e. imply the reduction or oxidation of one of the oxidation states in order to determine the other state, different methods for the determination and separation of Tl<sup>I</sup> and Tl<sup>III</sup> have been applied.<sup>[9,11,12,29]</sup> HPLC techniques are one of the most used in speciation analysis owing to their high sensitivity, selectivity and versatility,<sup>[6,10,30]</sup> and recently were successful applied in Tl speciation.<sup>[31,32]</sup>

The present work is part of a study concerning the assessment of thallium contamination of an industrial area located in the vicinity of the mining and smelting works in Bukowno–Bolesław (southern Poland). The water reservoirs in that area are strongly polluted with dust released from the culm dumps, especially during a dry season. The dust contains tailings minerals with remarkable Tl content; therefore, in the current study, special attention was given to the dust fraction. A fractionation and speciation study was carried out in highly polluted wastewater samples, which ensured a sufficient metal content in order to characterise speciation of thallium in SPM. Total, particulate and dissolved thallium, as well as chemical speciation, were determined for each studied fraction (particles >15 µm, SPM >0.45 µm, and dissolved fraction).

## 2. Experimental section

### 2.1. Sampling and pretreatment

Wastewater samples were taken from a water outlet located in one of the most polluted areas in Poland, near the zinc–lead mining area of Bolesław and smelting works in Bukowno (50.29°N, 19.49°W). The region belongs to the Silesian-Cracowian ore deposits of the 'Mississippi Valley' type and is relatively rich in thallium and arsenic<sup>[33]</sup>. Extensive sulphide ore mining, flotation treatment and smelting processes characterise the area. Post-flotation wastes containing tailings minerals rich in thallium are deposited in large ponds located on the top of the heap (25–30 m high).<sup>[25]</sup>

Samples of wastewater for total determination of Tl were taken in a 1-L glass bottle, immediately acidified to pH 2 with HNO<sub>3</sub> and stored until analysis. Additionally, wastewater was taken in a 5-L HDPE gallon bottle, and after sampling, aliquots were separated into dissolved and particulate fractions by filtration (i) through a 15-µm soft filter (Filtrak GmbH, Bärenstein; (ii) through a 0.45-µm cellulose nitrate filter (Sartorius, Göttingen); (iii) in sequence through a 15-µm soft filter and then a 0.45-µm cellulose nitrate filter) (Fig. 1). Filtration was carried out at the Applied Analytical Chemistry Laboratory (Faculty of Chemistry, University of Warsaw). Filters were acid-washed with a prefiltration of 25 mL of 1 % HNO<sub>3</sub> and then rinsed with 150 mL of Milli-Q water. The dissolved fraction of the sample was kept in polypropylene plastic vials and acidified to pH 2 (HNO<sub>3</sub>) until analysis. Filters were dried at 40 °C, and SPM (milligrams per

litre) was calculated following standard methods.<sup>[34]</sup> Afterwards, filters were stored until digestion for particulate metal analysis.

## 2.2. Reagents

Nitric acid (68 %, density ( $\rho$ ) = 1.42 g mL<sup>-1</sup>), hydrochloric acid (30 %,  $\rho$  = 1.15 g mL<sup>-1</sup>), sodium acetate ( $M$  = 82.03 g mol<sup>-1</sup>) and acetic acid (96 %,  $\rho$  = 1.06 g mL<sup>-1</sup>) were Suprapur (Merck, Germany). Diethylene triamine penta-acetic acid (DTPA;  $M$  = 393.35 g mol<sup>-1</sup>) was pure pro-analysis (Merck, Germany). Standard solutions of TlNO<sub>3</sub> containing 1 mg mL<sup>-1</sup> ( $\rho$  = 1.02 g mL<sup>-1</sup>) were obtained also from Merck. All solutions were prepared using deionised water from a Milli-Q Water-System (Millipore, USA).

The base solution containing 0.15 mol L<sup>-1</sup> DTPA was prepared by dissolving 5.9 g DTPA with 0.7 mL 30 % NaOH in water and dilution up to 100 mL. Acetate buffer solution (0.2 mol L<sup>-1</sup>) was prepared by dissolving 1.3 g CH<sub>3</sub>COONa and 0.3 mL 96 % CH<sub>3</sub>COOH in water, and diluting up to 100 mL. Tl<sup>III</sup> standard solution (18.0 mg L<sup>-1</sup>) was prepared by dissolving 4.0 mg of Tl(NO<sub>3</sub>)<sub>3</sub>·3H<sub>2</sub>O in 100 mL of solution containing 0.025 mol L<sup>-1</sup> DTPA and 0.1 mol L<sup>-1</sup> acetate buffer (pH 5.5). Multi-element standard solutions were prepared by dilution of 1000-mg L<sup>-1</sup> commercial available stock solution (SPEX CentriPep), and nitric acid was used for pH adjustment.

## 2.3. Separation and determination of thallium species

Microwave digestion system Ethos 1 (Milestone, Italy) was used for digestion of filters and wastewater samples, applying a three-stage program (5 min, 80 °C, 1000 W; 10 min, 180 °C, 1000 W; 50 min, 200 °C, 1000 W). The 0.45- $\mu$ m membrane filters with SPM were digested in aqua regia using a closed microwave system. Digested samples were transferred into 5.00-mL volumetric flasks and diluted to the volume with Milli-Q water. Digestion of all samples was carried out in triplicate.

Total thallium was determined by means of an ICP mass spectrometer (ICP-MS) Nexlon 300D (PerkinElmer, USA) with Meihard-type nebuliser and Scott-type spray chamber. Measurements were performed applying the following experimental parameters: sweeps: 5; number of replicates: 5; dwell time: 50 ms; radio frequency ICP power: 1600 W; deflector voltage: -9 V; nebuliser gas flow: 1 L min<sup>-1</sup>; plasma gas flow: 18 L min<sup>-1</sup>; auxiliary gas flow: 1.2 mL min<sup>-1</sup>.

Tl<sup>I</sup> and Tl<sup>III</sup> species were simultaneously separated and determined by HPLC coupled with ICP-MS. Technical characteristics of the equipment used for separation of thallium species are the following: 1200 Series HPLC System (Agilent, USA), injection valve model 7725 with a 100-mL injection loop (Rheodyne, Cotati, CA), size-exclusion column Superdex Peptide 10/300 GL (310 x 10 mm, internal diameter 13  $\mu$ m), ICP-MS Elan 900 (PerkinElmer SCIEX, Canada) with a cross-flow nebuliser fitted in a Rayton spray chamber, and Minipuls 3 peristaltic pump (Gilson, France). Column efficiency ( $N$ ) calculated by half-peak-height method was 5381 plates, which validates the good performance of the column.

Chromatographic data acquisition was controlled by means of *Chromera* software (v. 1.2, PerkinElmer). To avoid the negative consequences of the tailing effect and overlapping of the signals, a size-exclusion

column was used for samples where a higher amount of Tl<sup>I</sup> than Tl<sup>III</sup> was expected. The mobile phase was 100-mmol L<sup>-1</sup> ammonium acetate with 5-mmol L<sup>-1</sup> DTPA (pH 6.2) at a flow rate of 0.75 mL min<sup>-1</sup> for size exclusion column. <sup>203</sup>Tl and <sup>205</sup>Tl were detected on line by ICP-MS.

### 3. Results and discussion

#### 3.1. Analytical figures of merit

A calibration curve method within a range of 1–100 ppb was applied to quantify element concentration, using indium as internal standard. Coefficients of variation for metal counts ( $n = 16$ ) ranged between 0.1 and 1 %. Procedural blanks were run for all the analyses and results were blank-corrected (Tl blank  $1.16 \pm 0.01$  ng L<sup>-1</sup>,  $n = 4$ , RSD 1.02 %). Limits of detection (LOD) of the analytical procedure (Table 1) were calculated as a mean value plus three times the standard deviation of the blank ( $\pm 3$  s.d.,  $n = 8$ ). The accuracy of the analytical procedure was checked by means of certified reference material (trace elements in water, SRM 1643d-NIST). Statistical comparison between certified ( $7.28 \pm 0.25$  µg Tl L<sup>-1</sup>) and measured ( $7.36 \pm 0.09$  µg Tl L<sup>-1</sup>) values did not show significant differences ( $t$ -test:  $t = 0.5319$ , d.f. = 2,  $P < 0.05$ ).

#### 3.2. Total content of Tl and other trace elements in wastewater

The studied wastewater samples contained thallium in amounts sufficient – at least 10 % of total Tl as Tl<sup>III</sup> – to perform the speciation analysis in the fractions defined physically by filtration. The total content of thallium and Co, Ni, Zn, Cd and Pb in wastewater is presented in Table 1. These values were compared with the Criteria Maximum Concentration (CMC) for aquatic life, defined as the highest concentration of a material in surface water to which an aquatic community can be exposed briefly without resulting in an unacceptable effect.<sup>[35]</sup> Co, Ni and Zn were under the reported CMC limit, but Cd and Pb exceed the CMC several times (Cd CMC = 4.3 µg L<sup>-1</sup>; Pb CMC = 65 µg L<sup>-1</sup>).

Analysis by ICP-MS of total concentration of trace elements in water usually does not require previous digestion of the samples; however, an experimental test was carried out in order to identify interference during the analysis due to the presence of organic matter in the samples. Table 1 shows the total concentration of trace elements in samples treated with and without microwave digestion. It is important to point out that when wastewater samples were analysed directly without prior digestion, nearly 28 % of the total metal content was underestimated. Therefore, procedures to eliminate organic matter interference during analysis of wastewater samples should be always considered.<sup>[36]</sup>

#### 3.3. Speciation analysis of thallium

The speciation analysis of thallium presented consisted in fractionation and determination of chemical speciation for each fraction. A preliminary characterisation of SPM present in wastewater samples is presented in Table 2. Determination of dissolved, particulate and total thallium was performed following a fractionation scheme (Fig. 1) and showed clearly that the dominant fraction is the dissolved fraction. The thallium content in SPM fractions from 0.45 to 15 µm and fractions higher than 15 µm was similar.

### 3.4. $Tl^{III}$ extraction from SPM

Developing of a procedure to extract the unstable oxidised form of thallium –  $Tl^{III}$  – from SPM deposited on the filters was necessary. Tl is more stable in its monovalent state than in the trivalent state; therefore, standard reduction potential ( $E_{red}$ ) of  $Tl^{III}$  to  $Tl^I$  ( $E_{red}(Tl^{3+}/Tl^+) = +1.26$  V) and also hydrolysis of  $Tl^{III}$  at  $pH < 7$  can be observed in water samples.<sup>[37]</sup>

Thallium(III) in the chloride complex is reduced up to 40 %, in the complex with acetates up to 80 % and in the DTPA complex just up to 1–3 %.<sup>[36]</sup> Furthermore, precipitation of thallium hydroxide is observed in aqueous solutions at  $pH \approx 5$ . DTPA is usually added to the examined samples, in order to prevent reduction and hydrolysis processes.<sup>[38]</sup> The  $Tl^{III}$ –DTPA complex is very stable ( $\log K[Tl^{III}\text{-DTPA}] = 46$ ) and the stability of this complex is practically independent of pH and the presence of other ions. Thus, leaching based on forming the  $Tl^{III}$ –DTPA complex was introduced.

To validate the methodology proposed, an artificial experiment was also performed. Because  $Tl^{III}$  could be precipitated as  $Tl(OH)_3$  at high pH values,<sup>[39]</sup> dissolved  $Tl(NO_3)_3$  was precipitated as  $Tl(OH)_3$  on a filter membrane in a pH-controlled medium ( $pH \approx 7$ ). The filter was stored in a plastic vial with DTPA/ $NH_4Ac$  (~8 mL). Thallium speciation analysis was carried out after 1 week of storage, showing a partial reduction (20–25 %) of  $Tl^{III}$  to  $Tl^I$  (Fig. 2a). Therefore, further results must be considered semiquantitatively.

The extraction was also performed with filters containing SPM after single filtration through 0.45  $\mu m$  (Fig. 2b) as well as with sequential filtration (15  $\mu m$ , then 0.45  $\mu m$ , Fig. 2c), stored 1 week prior to analysis by HPLC–ICP-MS. The chromatograms obtained show that when particles larger than 0.45  $\mu m$  are considered, 9 % (uncertainty  $\pm 1$  %) of the total content of Tl in SPM is present as  $Tl^{III}$  and 91 % as  $Tl^I$  (Fig. 2b). However, when only the fraction between 0.45 and 15  $\mu m$  is considered (filtration in sequence; Fig. 2c), the extract of SPM did not contain a noticeable amount of  $Tl^{III}$ –DTPA, thallium being present mainly as  $Tl^I$ . The HPLC separation was also carried out for the dissolved fraction after 0.45- $\mu m$  filtration, where the  $Tl^{III}$ –DTPA complex was at an unnoticeable level (Fig. 2d). Therefore it was concluded that the dominant form of thallium in SPM is monovalent thallium although trivalent thallium is present in fractions larger than 0.45  $\mu m$ .

Sequential filtration (Fig. 1a) showed that the total content of Tl in the fraction larger than 15  $\mu m$  was higher than in the fraction between 0.45 and 15  $\mu m$ . The above results highlight the importance of the dust fraction in the cycle and contribution of thallium to the environment, and the possibility of Tl being recovered as a by-product of the smelting process in this industrial area.

To summarise, the presence of  $Tl^{III}$  in SPM (>15  $\mu m$ ) of wastewater was noticed. The chemical properties of  $Tl^{III}$  – i.e. its instability in water solution – predispose SPM to deposit  $Tl^{III}$  compounds in the sample. The source of this species of thallium remains unknown and requires further studies.

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**Table 1. Total concentration of trace elements in wastewater from Bolesław–Bukowno mining area with and without microwave digestion treatment before inductively coupled plasma mass spectrometry (ICP-MS) analysis**

Data are presented as mean  $\pm$  standard deviation ( $n = 3$ ). % loss, loss percentage of total concentration due to underestimation when the sample is not digested; LOD, limit of detection ( $\bar{x} \pm 3$  s.d.,  $n = 8$ )

Element	Isotope	Unit	Digested samples	Undigested samples	% loss	LOD
Co	59	$\mu\text{g L}^{-1}$	$51 \pm 3$	$33 \pm 1$	35	0.22
Ni	61	$\mu\text{g L}^{-1}$	$285 \pm 12$	$203 \pm 7$	29	0.03
Zn	66	$\text{mg L}^{-1}$	$67 \pm 34$	$45 \pm 14$	32	0.03
Cd	111	$\mu\text{g L}^{-1}$	$530 \pm 28$	$374 \pm 13$	29	0.08
Tl	203	$\mu\text{g L}^{-1}$	$50 \pm 2$	$34 \pm 1$	32	0.07
Tl	205	$\mu\text{g L}^{-1}$	$50 \pm 2$	$35 \pm 1$	30	0.06
Pb	208	$\mu\text{g L}^{-1}$	$720 \pm 48$	$632 \pm 18$	12	0.49

**Table 2. Characteristics of the separated suspended particulate matter fractions**

Data are presented as mean  $\pm$  standard deviation ( $n = 3$ ).  
Total SPM ( $\text{mg L}^{-1}$ ) =  $349 \pm 81$

Size fraction ( $\mu\text{m}$ )	Mean mass (mg)	Filtered volume (L)	Percentage of total SPM	RSD %
>0.45	$105 \pm 24$	0.3	100	23
0.45–15	$84 \pm 24$	0.3	80	29
>15	$20 \pm 1$	0.3	20	10

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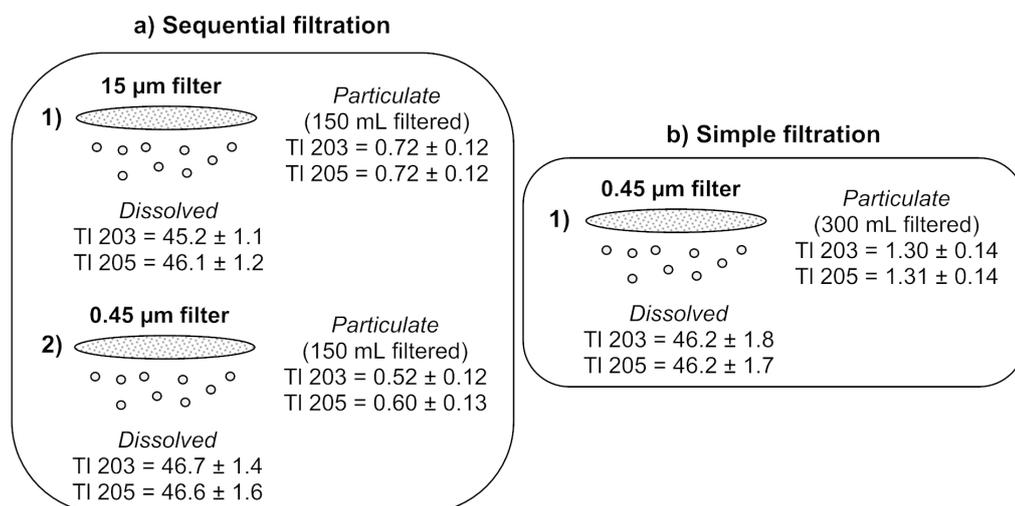
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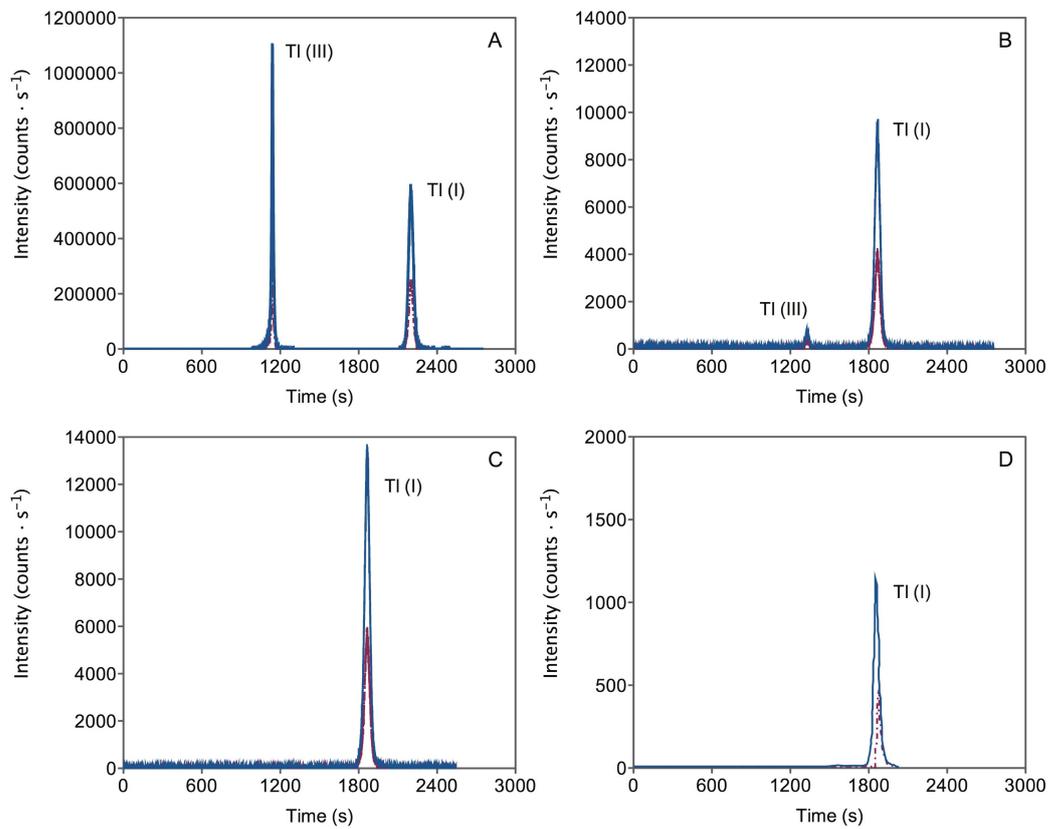
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**Fig. 1.** Fractionation scheme for wastewater from Bolesław–Bukowno (southern Poland). Dissolved and particulate fractions were separated by: (a) sequential filtration (through 0.45- $\mu\text{m}$  filter membrane after prefiltration through 15  $\mu\text{m}$ ); and (b) simple filtration (only through 0.45- $\mu\text{m}$  filter membrane). Values are presented in parts per billion ( $\mu\text{g L}^{-3}$ ) as mean  $\pm$  standard deviation. All filtrations and analytical determinations were performed in triplicate.



**Fig. 2.** LC-ICP-MS chromatographic profiles of Tl<sup>I</sup> and Tl<sup>III</sup> in different solutions: (a) artificial experiment of Tl(NO<sub>3</sub>)<sub>3</sub> precipitation; (b) suspended particulate matter (SPM) >0.45 μm (filter + diethylene triamine pentaacetic acid (DTPA)), after single filtration; (c) SPM from 0.45 to 15 μm (filter + DTPA), after filtration in sequence; (d) dissolved fraction (wastewater + DTPA), after filtration through 0.45 μm. Red dotted line corresponds to <sup>203</sup>Tl and blue solid line to <sup>205</sup>Tl.