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ORIGINAL PAPER

Thallium fractionation in polluted environmental samples using a modified BCR three-step sequential extraction procedure and its determination by electrothermal atomic absorption spectrometry[‡]

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Determination of thallium in polluted environmental samples and their extracts obtained by a modified BCR three-step sequential extraction procedure was used to study thallium distribution and mobility in the monitored polluted area affected by acidification (Šobov, Central Slovakia). The results of fractionation applied to 5 soil certified reference materials and 14 environmental samples show that the vast majority of thallium occurred in the residual fraction. This means that highly toxic thallium is strongly entrapped in the parent rock materials remains immobile and its environmental toxicity is therefore reduced. The limit of detection for thallium in the studied fractions was lower than 0.050 mg kg^{-1}, the precision (RSD) of the ultratrace determination of thallium in the studied fractions was better than 17 % and the accuracy of the used method was verified by analyzing certified reference materials.
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Introduction

Thallium is a heavy, very toxic metallic element occurring in earth's crust in an estimated abundance of 0.1–0.8 mg kg^{-1}. In environment, it is mainly combined with other elements (primarily oxygen, sulfur, halogens, K, and Rb) forming inorganic compounds. Thallium is quite stable in nature since it is neither easily transformed nor biodegraded. Thallium compounds are generally soluble in water and the element is found primarily as the monovalent ion Tl(I). Thallium tends to sorb onto soils and sediments (Frantz & Carlson, 1987) and to bioconcentrate in aquatic plants, vertebrates, and fish (Barrows et al., 1978). Terrestrial plants can also absorb thallium from soils (Emers, 1988). The main sources of pollution come from anthropogenic emissions from re-

fineries, coal-fired power stations, mining activities, metal smelters, and from cement industry (Kemper & Bertram, 1991). In natural waters, thallium can exist as either Tl(I) or Tl(III). Its oxidation state affects its complexation and the subsequent bioavailability and toxicity. Bowen (1979) reported a median soil thallium content of 0.20 mg kg^{-1} (in the range from 0.10 mg kg^{-1} to 0.80 mg kg^{-1}). Humans may be exposed to thallium by ingestion, inhalation, or dermal absorption. However, general population is most frequently exposed to thallium by ingestion of thallium-containing foods, especially homegrown fruits and green vegetables. Toxicity of thallium can be compared to that of cadmium and mercury considering the soil content, i.e. a potential risk for humans can arise at levels around 1 mg kg^{-1} (Kemper & Bertam, 1991). The lethal dose for humans is

Table 1. Instrumental parameters for the determination of thallium in soil extracts by ETAAS

Spectrometer	
Wavelength	276.8 nm
Bandwidth	0.7 nm
Lamp	Perkin-Elmer EDL system
Lamp power	7 W
Graphite tube	Pyrolytically coated with Ľvov platform
Sample volume	20 mm^3
Modifier volume I. (Pd(NO$_3$)$_2$ solution)	8 mm^3 (8 μg of Pd)
Modifier volume II. (ascorbic acid solution)	5 mm^3 (50 μg of ascorbic acid)

Temperature program					
Step	Temperature/°C	Ramp/s	Hold/s	Ar flow rate/(cm^3 min^{-1})	Read
Drying	90	10	20	250	
Drying	120	10	20	250	
Pyrolysis	800	20	10	250	
Atomization	2000	0	5	0	On
Cleaning	2400	1	3	250	

approximately 15–20 mg kg^{-1} (Boyarsky & Crisan, 2006).

Several methods have been proposed for the determination of thallium in environmental and biological samples, e.g. anodic stripping voltammetry (Lukaszewski et al., 2003), spectrophotometry (Agnihotri et al., 1998), spectrofluorimetry (Ensafi & Rezaei, 1998), X-ray fluorescence spectrometry (Adriano, 2001), electrothermal, hydride generation and flame atomic absorption spectrometry (Cvetkovic et al., 2002; Zhu & Xu, 2000; Lin & Nriagu, 1999), inductively coupled plasma atomic emission spectrometry (Mossop & Davidson, 2003), and inductively coupled plasma mass spectrometry (Karlson et al., 2003). Knowledge of chemical forms of potentially toxic metals bound in environmental solid samples (e.g. soils, sediments) is a very important issue in the environmental pollution monitoring. Although the total metal concentration in such samples may provide relevant information about the degree of contamination, it has been recognized that knowledge of the metal fraction associated with significant phases is an essential requirement for assessing the mobility and bioavailability of the metal, which is directly related to its toxicological effects. In order to discover the distribution patterns of trace metals among specific solid phases, a sequential extraction procedure (SEP) with 3 to 6 steps is commonly used (Sager, 1992; Rauret et al., 2000; Villar et al., 2001). The original BCR three-step SEP (Vidal & Rauret, 1993) for the determination of extractable trace metal contents in soils was later modified (Rauret et al., 2000). In the modified BCR three-step SEP, 0.5 mol dm^{-3} hydroxylammonium hydrochloride of pH 1.5 instead of 0.1 mol dm^{-3} hydroxylammonium hydrochloride of pH 2 for the second step is recommended. Signifi-

cantly higher amounts of metal elements were isolated using the modified BCR three-step SEP compared to the original procedure (Mossop & Davidson, 2003).

The scope of this work was the use of an optimized electrothermal atomic absorption spectrometry (ETAAS) method for the determination of thallium in solid environmental samples and their extracts obtained by the modified BCR three-step SEP (Rauret et al., 2000) as well as the verification of reliability of the obtained analytical results by an analysis of the soil certified reference materials. The procedures were performed in order to evaluate the thallium distribution and mobility in the monitored polluted area (Šobov, Central Slovakia) affected by acidification.

Experimental

Instrumentation

Perkin-Elmer (Überlingen, Germany) Model Zeeman 3030 atomic absorption spectrometer equipped with HGA 600 graphite furnace and AS-60 autosampler was used. Background was corrected considering the Zeeman effect. Instrumental settings and heating programs employed for thalium determination using graphite tubes with pyrolytic graphite coating and graphite platform are shown in Table 1. Integrated absorbance was used for signal quantification. All measurements were carried out with at least four replicates.

Horizontal laboratory shaker LT 2 Kavalier (Sázava, Czech Republic) and centrifuge MPW-360 (Warsaw, Poland) were used for extraction and separation of the extracts from the residues resulting from the sequential extraction procedure.
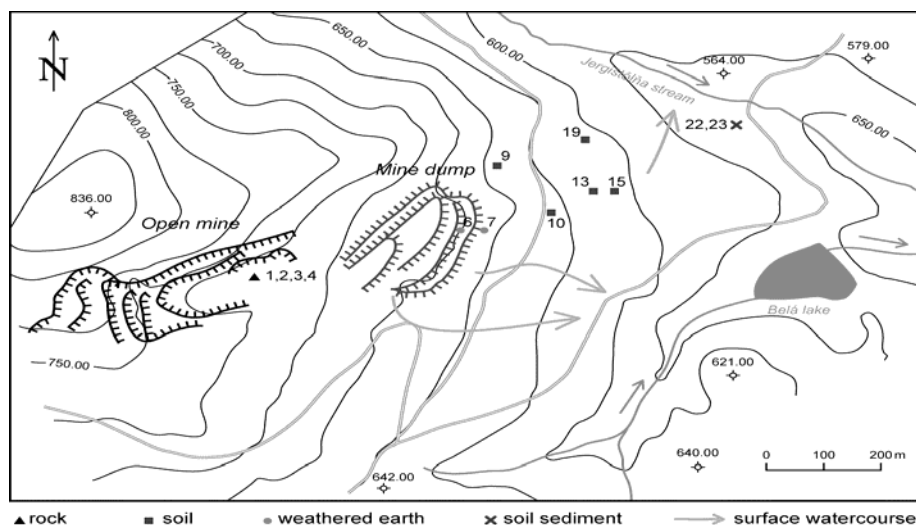
Fig. 1. Map of the open quartzite mine and mine dump surroundings with identification of the sampling area.

Reagents

All reagents used were of analytical grade and all solutions were prepared using redistilled water. Concentrated mineral acids (HNO_3, HF, $HClO_4$), hydrogen peroxide, acetic acid, hydroxylamine hydrochloride, ammonium acetate, and thallium stock solution (1000 mg dm^{-3}) were obtained from Merck (Darmstadt, Germany). Working thallium standard solutions were prepared by stepwise dilution of the stock solution in 3 vol. % HNO_3 and reagents used for extraction. Chemical modifier solutions, $Pd(NO_3)_2$ in 1 vol. % HNO_3 (1000 mg dm^{-3} of Pd), $Mg(NO_3)_2 \cdot 6H_2O$ in H_2O (1000 mg dm^{-3} of $Mg(NO_3)_2$), ascorbic acid in H_2O (10.0 g dm^{-3} of ascorbic acid) were obtained from Analytika (Prague, Czech Republic).

Certified reference materials (CRM) NIST SRM 2710 and NIST SRM 2711 (Montana Soils) were obtained from the National Institute of Standards and Technology (Gaithersburg, USA), CRM GBW 07103, and CRM GBW 07405 (Soils) were obtained from the National Research Center for Certified Reference Materials (Beijing, China), CRM SA-B (Sandy Soil) was obtained from High-Purity Standards (Charleston, USA).

Sampling area, samples, and sample treatment

The studied area of Šobov representing about 145 000 m^2 (Central Slovakia) is strongly affected by acidification. Sources of acidification in the region originate from a mine dump as well as from an open quartzite mine. Sulfuric acid originates from the pyrite oxidation by atmospheric oxygen. The acid attacks other minerals and causes high migration of different toxic elements. Thallium is one of the elements which can be mobilized from the decomposed pyrite and other sulfides.

Four argillaceous weathered rock – open quartzite mine (Nos. 1–4), two weathered earth – mine dump (Nos. 6, 7), six soil – region bellow the mine dump (Nos. 9, 10, 13, 15, 17, 19), and two soil sediment (Nos. 22, 23) samples were collected from the quartzite mine area of Šobov at the depth of 0–20 cm. The samples were air-dried, sieved through a 2 mm sieve and milled in an agate mortar. In this study, 100–250 μm particle size fractions were used for the analysis. The sampling location of the studied region is illustrated in Fig. 1 and some important properties of the studied samples are listed in Table 2.

The basic mineral sample composition was characterized by X-ray diffraction. The pH values of the samples were determined in a suspension after a 2 h mixing of the samples with redistilled water (volume of water to sample mass ratio of 1 : 2.5) (Van Reeuwijk, 1995). The electrical conductivity (EC) of the samples was determined in a suspension after a 2 h mixing of the samples with redistilled water (sample mass to volume of water ratio of 1 : 5) (Van Reeuwijk, 1995). The total sulfur concentration in the samples was determined gravimetrically as $BaSO_4$ after the decomposition of the samples.

The digestion method for the total and residual thallium determination in soils consisted of heating 500 mg of a sample in a PTFE vessel with a mixture of 48 % HF (15 cm^3), 65 % HNO_3 (1 cm^3), and 70 % $HClO_4$ (1 cm^3) in a water bath at 80 °C for 2 h. The mixture was allowed to settle down overnight. Next day, the sample was evaporated to wet salts, 5 cm^3 of HF was added and heated until fumes of $HClO_4$ were formed. Then, 1 cm^3 of HNO_3, 1 cm^3 of $HClO_4$, and 10 cm^3 of H_3BO_3 (saturated solution) were added and the sample was heated to dryness. The dried mass was heated again with an addition of 10 cm^3 of redistilled water on a water bath for 1–2 h. Subsequently, 3 cm^3 of HNO_3 and 3–5 drops of 30 % H_2O_2 were

Table 2. Selected properties of the studied samples

| No. | Sample description | Basic mineral composition | pH | EC | S |
				μS cm^{-1}	%
1	Quartzite (open mine)	Quartz	NM	NM	NM
2	Argillaceous large rock (open mine)	Quartz, pyrophyllite, illite, pyrite	NM	NM	4.57
3	Argillaceous weathered rock (open mine)	Quartz, pyrophyllite, illite, pyrite, Ca plagioklas, gypsite, chalkantite	1.8	3350	3.30
4	Argillaceous weathered rock (open mine)	Quartz, pyrophyllite, illite, pyrite, Ca plagioklas, gypsite, chalkantite	2.0	2380	1.01
6	Weathered earth (mine dump)	Quartz, pyrophyllite, illite, chlorite, Na plagioklas, jarosite	2.5	1149	0.41
7	Weathered earth (mine dump)	Quartz, pyrophyllite, illite, chlorite, kaolinite, Na plagioklas, jarosite	2.4	1718	0.33
9	Soil from unacidified area (close to mine dump)	Quartz, pyrophyllite, illite, chlorite, kaolinite, Na plagioklas,	5.3	53.2	0.01
10	Soil from acidified area (bellow the mine dump)	Quartz, smektite, kaolinite, Ca-Na plagioklas, jarosite, ferrihydrite	3.0	571	0.21
13	Soil from acidified area (bellow the mine dump)	Quartz, illite, pyrophylite, smektite, kaolinite, Ca-Na plagioklas, jarosite, ferrihydrite	2.8	830	0.77
15	Soil from acidified area (bellow the mine dump)	Quartz, smektite, kaolinite, Ca-Na plagioklas, ferrihydrite	2.9	760	0.74
17	Soil from acidified area (bellow the mine dump)	Quartz, chlorite, kaolinite, Ca-Na plagioklas, ferrihydrite	3.0	548	0.19
19	Soil from unacidified area (bellow the mine dump)	Quartz, kaolinite, Ca-Na plagioklas, ferrihydrite	5.1	43.0	0.06
22	Soil sediment from the erosion trench (bellow the mine dump)	Quartz, smektite, chlorite, Ca plagioklas, ferrihydrite, sulfate, gypsite, chalcantite	3.1	671	0.69
23	Soil sediment from the erosion trench (bellow the mine dump)	Quartz, chlorite, kaolinite, Ca plagioklas, jarosite, boehmite	3.6	240	0.16

NM – not measured; EC – electrical conductivity; S – sulfur.

Table 3. Reagents and operating conditions applied in the modified BCR three-step SEP

Step	Fraction	Reagent	Treatment
1.	Acid soluble (e.g. carbonates)	20 cm^3 CH$_3$COOH (0.11 mol dm^{-3})	Shaking for 16 h at (22 ± 5) °C
2.	Reducible (e.g. Fe-Mn oxides)	20 cm^3 NH$_2$OH.HCl 0.5 mol dm^{-3} (in 0.05 mol dm^{-3} HNO$_3$)	Shaking for 16 h at (22 ± 5) °C
3.	Oxidizable (e.g. organic matter)	5 cm^3 H$_2$O$_2$ (8.8 mol dm^{-3}), 5 cm^3 H$_2$O$_2$ (8.8 mol dm^{-3}), 25 cm^3 CH$_3$COONH$_4$ (1.0 mol dm^{-3}) adjusted to pH 2.0 by HNO$_3$	Manual shaking for 1 h at 25 °C. Continued digestion for 1 h at (85 ± 2) °C. Shaking for 16 h at (22 ± 5) °C
	Residual	HF, HNO$_3$, HClO$_4$, H$_2$O$_2$	Medveď et al. (1998)

added (to purify the solution) and the solution was allowed to digest on the water bath until dissolving the residues. Then, the sample solution was transferred into a 25 cm^3 volumetric flask and filled-up to the mark with doubly redistilled water (Medveď et al., 1998).

Operating conditions used in the modified BCR tree-step sequential extraction procedure (SEP) were described in detail elsewhere (Rauret, 2000) and are briefly summarized in Table 3. In this study, 5 certified reference soil materials and 14 solid samples from the polluted area (see Table 2) were applied in the thallium fractionation.

Results and discussion

Optimization of temperature program for determination of thallium in extracts

Optimization of furnace conditions for the determination of thallium in each fraction of the original BCR three-step SEP focused mainly on the study of pyrolysis, atomization temperatures and the amount of chemical modifiers used was made by Villar et al. (2001). Since in this study, modified BCR tree-step SEP was used, the main attention was focused on the pyrolysis and atomization temperatures op-

Table 4. Recovery of thallium in spiked fractions of the soil CRM GBW 07405 and the soil sample No. 17 ($n = 4$)

Soil sample	Fraction	Thallium content/(ng cm^{-3})		Recovery
		Before spiking	After spiking*	%
CRM GBW 07405	Total	30 ± 1.0	54 ± 6.0	90.0
	Step I	< LOQ	28 ± 3.0	93.3
	Step II	7.0 ± 0.8	36 ± 5.0	97.3
	Step III	< LOQ	29 ± 3.0	96.7
	Residue IV	24 ± 3.0	52 ± 8.0	96.3
No. 17	Total	62 ± 4.0	90 ± 11	97.8
	Step I	< LOQ	28 ± 3.0	93.3
	Step II	4.0 ± 0.6	31 ± 4.0	91.2
	Step III	3.7 ± 0.4	32 ± 5.0	95.0
	Residue IV	54 ± 8.0	81 ± 9.0	96.4

*Each fraction was spiked with 30 ng cm^{-3} of Tl. LOQ values (in ng cm^{-3}) for each step of the used BCR three-step SEP are shown in Table 5. Total recovery was evaluated by comparing the overall thallium content in the sample with the certified one. The recovery of individual extraction steps was calculated by comparing the Tl content in a spiked sample with the sum of Tl content determined in unspiked sample and the amount added.

timization in the second step of the SEP used. In the modified BCR tree-step SEP, it is recommended to use 0.5 mol dm^{-3} hydroxylamine hydrochloride of pH 1.5 instead of 0.1 mol dm^{-3} hydroxylamine hydrochloride of pH 2. The main reason of this study is that higher chloride concentrations cause significant interferences in the thallium determination by ETAAS. Two different mixed modifiers were tested; Pd-ascorbic acid modifier (8 μg of Pd + 50 μg of ascorbic acid) and Pd-Mg(NO$_3$)$_2$ modifier (8 μg of Pd + 3 μg of Mg(NO$_3$)$_2$) (Welz et al., 1988; Tsalev & Slaveykova, 1990; Volynsky, 2000; Ni & Shan, 1987). Thallium standard solution (100 ng cm^{-3}) prepared in 0.5 mol dm^{-3} hydroxylamine hydrochloride was used for the pyrolysis and atomization curves measurement. The pyrolysis and atomization curves obtained in the presence of the studied mixed modifiers and in the absence of any modifier are shown in Fig. 2. With no modifier, thallium was evaporated and was lost already at relatively low pyrolysis temperature (500 °C). Mixed modifiers containing palladium stabilized the thallium efficiently; loss of thallium was observed at about 900 °C. The optimum atomization temperature of 2000 °C can be used in all mentioned cases. Comparing sensitivity and accuracy of ETAAS in the presence and in the absence of mixed modifiers, higher sensitivity and satisfactory accuracy were observed in the presence of both mixed modifiers. Thus, both studied modifiers could be used for the determination of thallium in the hydroxylamine hydrochloride reagent. Finally, the mixed modifier palladium-ascorbic acid was selected and used in all measurements. The optimum temperature program for the determination of thallium in this study (in the presence of the mixed modifier Pd-ascorbic acid) is shown in Table 1.
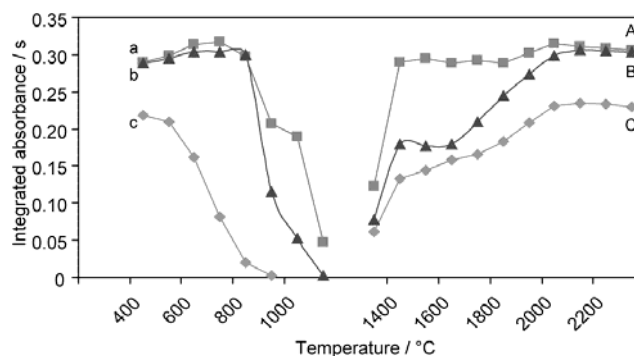

Fig. 2. Pyrolysis (a, b, c) and atomization (A, B, C) curves for 100 ng cm^{-3} of Tl prepared in 0.5 mol dm^{-3} hydroxylamine hydrochloride. Tl sample with Pd + ascorbic acid (a, A), with Pd + Mg(NO$_3$)$_2$ (b, B), and without any modifier (c, C).

Recovery studies of spiked extracts

The influence of macro-components present in the soil extracts on the determination of thallium was evaluated by examination of the thallium recovery from spiked extracts of the CRM soil GBW 07405 and the soil sample No. 17. Each extract and each residual fraction were spiked with 30 ng cm^{-3} of thallium The results are summarized in Table 4. The recovery of thallium added to the samples ranged between 90 % and 97 %. Precision (expressed as a relative standard deviation (RSD)) determined from the within-run and between-run measurements ranged from 3 % to 15 %. From these results, no statistically significant influence of the macro-components present in the studied samples on the determination of thallium can be observed.

Table 5. Limit of detection (LOD) and limit of determination (LOQ) for thallium in the sequential extraction and residual decomposition reagents

Fraction	LOD		LOQ	
	ng cm^{-3}	mg kg^{-1}	ng cm^{-3}	mg kg^{-1}
Step I	0.83	0.04	2.22	0.11
Step II	0.64	0.03	1.83	0.09
Step III	0.66	0.03	2.01	0.10
Residue IV	1.02	0.05	3.04	0.15

Analytical figures of merit

The calibration curve used for the thallium concentration determination was linear at least up to 100 ng cm^{-3}. The limit of detection (LOD) and the limit of determination (LOQ) expressed in ng cm^{-3} were calculated as follows

$$\mathrm{LOD} = x_{\mathrm{bl}} + 3s_{\mathrm{bl}} \tag{1}$$

$$\mathrm{LOQ} = x_{\mathrm{bl}} + 10s_{\mathrm{bl}} \tag{2}$$

where x_{bl} is the mean of the blank measurements and s_{bl} is the standard deviation of the blank measurements. The LOD and LOQ values for thallium in the sequential extraction and the residual decomposition reagents are shown in Table 5. Then, LOD and LOQ were expressed also in mg of Tl per kg of sample. The worst LOQ value (3.04 ng cm^{-3}) corresponding to 0.15 mg kg^{-1} was achieved for blanks obtained by the decomposition procedure (used for the total thallium determination and Tl determination in the residual fraction).

Since no CRM was available for the determination of extractable amounts of thallium in the extracts of the BCR three-step SEP, the accuracy of analytical results for thallium in the soils was verified by an analysis of the total Tl concentrations in the soils CRMs NIST 2710, NIST 2711, GBW 07103, GBW 07405, and

HPS SA-B (see Table 6). The *t*-test ($\alpha = 0.05$) showed no statistically significant differences either between the obtained total Tl contents and the certified values or between the sum of the extractable amounts of thallium in steps I–III plus the thallium content in residue and the certified values. These results confirm a satisfactory accuracy of the proposed ETAAS method and of the used BCR three-step SEP. Precision expressed as RSD and determined from the within-run and between-run measurements varied in the range from 2.5 % to 17 %. These results were achieved using the standard addition technique. This means that the standard addition technique is necessary for a reliable determination of thallium in the studied extracts.

Application of modified BCR three-step SEP to polluted environmental samples

Fractionation of polluted environmental samples by the modified BCR three-step SEP was performed in order to evaluate the thallium distribution and mobility in the monitored area. The results of this fractionation applied to 14 samples (see Table 2) are pre-
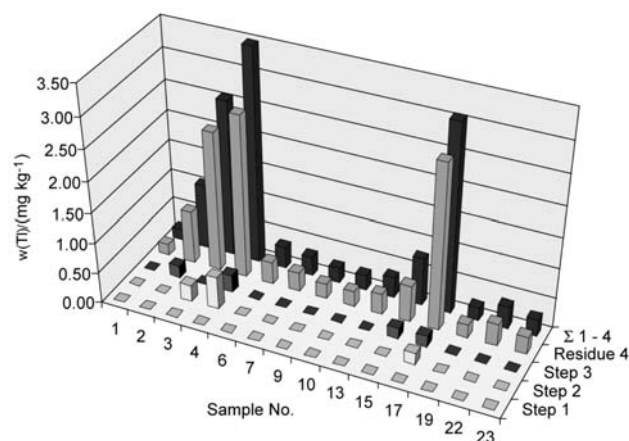
Fig. 3. Thallium distribution in polluted environmental samples determined using the modified BCR three-step SEP.

Table 6. Extractable amounts of Tl determined by the modified BCR three-step SEP, and the total Tl concentration in five CRM soils ($n = 4$)

CRM soil	Thallium content/(mg kg^{-1})							Recovery
	Certified value	Found value	Step I	Step II	Step III	Residue IV	$\sum$	%
NIST 2710	0.63	0.60 ± 0.06	< LOQ	< LOQ	< LOQ	0.59 ± 0.05	0.59	93.7
NIST 2711	2.47 ± 0.15	2.40 ± 0.06	< LOQ	0.19 ± 0.02	0.20 ± 0.03	2.02 ± 0.35	2.41	97.7
GBW 07103	1.93 ± 0.26	1.89 ± 0.05	0.16 ± 0.02	< LOQ	< LOQ	1.69 ± 0.20	1.85	95.8
GBW 07405	1.60 ± 0.40	1.50 ± 0.12	< LOQ	0.33 ± 0.03	< LOQ	1.20 ± 0.07	1.53	95.5
HPS SA-B	58.0 ± 2.00	58.16 ± 2.19	32.5 ± 1.8	22.8 ± 3.2	1.96 ± 0.26	0.42 ± 0.05	57.7	99.5

LOQ values (in mg kg^{-1}) for every step of the used BCR three-step SEP are shown in Table 5. Recovery was calculated by comparing the total thallium content in the sample with the certified one.

sented in Fig. 3. The figure shows the distribution of thallium among fractions: exchangeable and associated with carbonates (step I); associated with easily and moderately reducible iron and manganese oxyhydroxides (step II); associated with organic matter and sulfides (step III); and the metal residual fraction (residue IV) – i.e. Tl bound in mineral lattice. It is evident that the vast majority of thallium occurs in the residual fraction, bound in mineral lattice and it represents the immobile fraction. On the contrary, no thallium was found in the first fraction which represents the exchangeable, simply available and the most mobile fraction of thallium. Small amounts of thallium bound in the second fraction were determined in samples Nos. 3, 4, and 17 (samples Nos. 3 and 4 are freshly weathered rocks). This fraction represents reducible forms of thallium. Oxidizable forms of thallium (the third fraction) were determined in samples Nos. 2, 4, 15, and 17. The amount of thallium in the second and the third fraction can be considered as negligible and it represents no increased risk of environmental contamination caused by Tl mobility. In these samples, the highest amounts of total Tl among all studied samples were determined and higher amounts of sulfur were observed. Other properties of the studied samples (e.g. pH, EC, and basic mineral composition) showed no influence on the fractionation of thallium.

Conclusions

An optimized ETAAS method for the determination of thallium in solid environmental samples and their extracts obtained by modified BCR three-step SEP was used for the study of thallium distribution and mobility in the monitored polluted area affected by acidification (Šobov, Central Slovakia).

The results of fractionation applied to 5 CRM soils and 14 environmental samples show that the vast majority of thallium is present in the residue obtained after carrying out SEP. This means that highly toxic Tl is strongly entrapped in the parent rock materials remains immobile and its environmental toxicity is reduced. The same conclusion was also drawn by other authors in very recent papers concerning Tl in fractions of flood-plain soil (Jakubowska et al., 2007) as well as in the fractions of soil CRM GBW 07401 (Jakubowska et al., 2006), and in pyrite cinder derived ground (Yang et al., 2005).

Since no CRM for the determination of extractable amounts of thallium in the extracts of the BCR three-step SEP is available, an internal verification of the sequential extraction was performed by comparing the total amount of thallium removed from the soil sample during the procedure with the total certified amounts of thallium in several CRM soils. No statistically significant differences between the obtained and the certified data confirmed the acceptable accuracy of the proposed method and the sequential extraction proce-

dure. The limit of detection for thallium in the studied fractions was better than 0.050 mg kg^{-1}. Precision in the ultra-trace determination of thallium in the studied fractions was better than 17 %.

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