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Original scientific paper

NEW OPTIMIZED LIQUID-LIQUID EXTRACTION METHOD FOR THE REMOVAL OF THALLIUM AS A MATRIX ELEMENT IN MINERALS

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Abstract: When screening the content of trace elements in minerals or other inorganic compounds, the detection limit is raised and determination by spectroscopic techniques is often questionable or even impossible due to their interference with the matrix elements of the minerals. Thus, some valuable trace elements may remain undetected, which lowers the estimation for potential economic exploration of the geological deposit or site. Therefore, the main objective of this research was to find a suitable, cost-effective, reliable and rapid method for the selective and consecutive elimination of thallium and arsenic in the analysis of As-Tl minerals and to lower the detection limit for the determination of the trace elements present. The method was based on the separate optimization of the molarity of HCl and the volume of organic solvents including diisopropyl ether, diethyl ether, *n*-amyl acetate and isoamyl acetate. The optimized HCl concentration enabled the extraction of thallium (as chloride complex) and its migration into the organic top layer. The optimization of the method was performed with thallium(I) nitrate and then realgar (As_4S_4) was added to simulate the composition matrix for lorandite ($TlAsS_2$), as the latter mineral is very rare and valuable to be used for screening. In addition, a multi-element standard solution (Ag, Al, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mo, Ni, Pb, Sr, Tl, V, Zn) was used to simulate the trace elements that may be present. Once all conditions were optimized, a two-step liquid-liquid extraction with n-amyl acetate (to eliminate Tl) and toluene with KI (to eliminate As) was performed for the dissolved lorandite. All elements were determined by inductively coupled plasma - atomic emission spectrometry and the results were correlated with those obtained by k_0-instrumental neutron activation analysis from the same, previously powdered, lorandite specimen.

Key words: matrix element; lorandite; thallium; trace elements; liquid-liquid extraction; ICP-AES; k_0-INAA

INTRODUCTION

The thallium, as a modesty abundant element in the Earth's crust (0.3–0.6 mg/kg) (Bannon, 2015), occurs naturally in 55 sulfides or sulfosalts of 77 minerals, which means that more than ¾ of all available minerals in which thallium is present as a matrix element are associated with sulfur. The production of thallium is rarely extracted from these minerals due to their scarcity and rare occurrence. The only known active mine for the exploration of arsenic, antimony and thallium was the Allchar deposit in Macedonia (Janković, 1988; Janković & Jelenković, 1994). The mineral lorandite ($TlAsS_2$) is even more fascinating and important for fundamental scientific research, as it can be used to determine the neutron flux from the Sun (Pavićević et al., 2018; Jovanovski et al., 2019; Necke et al., 2021).

Today, the most economical sources include copper-, lead-, zinc- and other heavy metal sulphide ores in which thallium is present in trace amounts

(Peter and Viraraghavan, 2005). Thallium is considered an extremely toxic element, exceeding the toxicity of As and Hg (Dmowski et al., 2015; Osorio-Rico et al., 2017; Campanella et al., 2016; Liu et al., 2019; Genchi et al., 2021). On the other hand, thallium is versatile and is used in optics (Rodney and Malitson, 1956; Kokorina, 1996; Kim et al., 2022), in electronics (Nayer and Hamilton, 1977), in high-temperature superconductors (Sheng and Hermann, 1988; Karbowska, 2016; Belzile and Chen, 2017) and as a radioactive isotope for nuclear cardiography (Lagunas-Solar et al., 1982).

Therefore, the removal of thallium from the contaminated waste materials is important (Xu et al., 2019; Hutapea et al., 2021; Ren et al., 2023). The importance of removing high concentrations of thallium in various samples is also valuable from an analytical point of view. The reason lies in the need to analyze trace elements where the high content of thallium hinders their accurate determination due to its elemental interference. Various methods for the elimination and/or concentration of thallium have been proposed in the literature. Irving (1951) and Horrocks and Voight (1957) investigated the extraction of thallium(III) from hydrochloric acid solutions in ether and isopropyl ether. The extraction behaviour of thallium(III) was later monitored with tributyl phosphate (TBP) and trinonylamine (TNA) from aqueous solutions, with TBP acting as an anion exchanger in the form of its chloride (Venkateswarlu and Charan Das, 1963). Liquid-liquid extraction methods for quantitative removal of microquantities of thallium(III) at pH 4.0 from 0.1 M malonic acid with 0.08 M amberlite LA-2 with benzene, toluene and xylene have also been postulated (Raghunadha Rao & Khopkar, 1984).

Later, a crown-ethers were used to remove thallium. Vibhute and Khopkar (1989) propose to extract thallium(III) quantitatively from 4 M sulfuric acid containing 2 M potassium iodide with 0.05 M 18-crown-6-ether in dichloromethane and determine it spectrophotometrically at 400 nm, while thallium(I) was extracted quantitatively (pH 6.5) with 10^{-3} M kryptand 222 in chloroform with 10^{-3} M erythrosine (Gandhi and Khopkar, 1992), stripped from the organic phase with 0.1 M sulfuric acid and determined by atomic absorption spectrometry.

Liquid-liquid extraction was performed with isoamyl acetate to remove trace amounts of thallium in some sulfide minerals (Stafilov et al., 1993) after the iron had been re-extracted with sulfuric acid (Zendelovska and Stafilov, 2001). Trace amounts of thallium in high-purity indium are also separated from the matrix by extraction from 6 M hydrochloric acid with di-isopropyl ether (Marczenko et al., 1974). The most recent studies on liquid-liquid extraction of thallium(III) from succinate media were carried out using 2-octylaminopyridine in chloroform as an extractant (Mahamuni et al, 2008) and by bis-2,4,4-trimethylpentyl-n-octylphosphine oxide with careful adjustment of conditions for selective stripping of Tl(III) by pH and concentrated HCl in conjunction with Ga(III) and In(III) (Iyer and Dhadke, 2001) or by an aqueous two-phase system [polyethylene glycol(400) + ammonium sulfate] (Huang et al., 2020).

In addition to liquid-liquid extraction, an electrochemical quantitative separation of thallium at the anode from an ammoniacal solution containing silver ions as a cathodic depolarizer (under certain conditions, the deposition of silver at the cathode is an accurate measure of thallium) was developed earlier (Foley et al., 1956).

However, no analytical method has yet been proposed for the determination of traces in thallium minerals. For this purpose, lorandite ($TlAsS_2$) has been recommended as the most widespread natural Tl mineral (Jovanovski et al., 2018; Pavičević et al., 2018). The matrix elements of minerals can make the determination of trace elements in minerals difficult and sometimes impossible. Therefore, the main objective of this research was to develop a method for selective elimination of thallium and arsenic and furthermore to lower the detection limit for the remaining trace elements. Furthermore, thallium is an important toxic metal pollutant present in soils and the atmosphere and the development of methods for its elimination is at the forefront of analytical chemistry research.

MATERIALS AND METHODS

Reagents and samples

Pure crystals of the minerals lorandite and realgar collected at Allchar locality, North Macedonia, were picked up under an optical microscope and then used in the powder form.

The following reagents were used: $TlNO_3$ (p.a., Sigma-Aldrich), ICP multi-element standard solution IV (Merck), KI (p.a., Sigma-Aldrich), *n*-amyl acetate (for chromatography, Kemika, Zagreb), diisopropyl ether (p.a., Merck), isoamyl acetate (p.a., Merck), toluene (p.a., Alkaloid), HCl (35% *m/V*, p.a., Alkaloid).

Methods

Extraction of thallium. The optimization procedure was carried out with three organic solvents [diisopropyl ether (DIPE), *n*-amyl acetate (nAA) and isoamyl acetate (iAA)]. For each solvent, a total of 6 capped cylinder flasks were prepared by adding 2 ml of a 100 g/l multi-element standard solution (MES). For each solvent, a total of 6 capped cylinder flasks were prepared by adding 2 ml of a 100 g/l multi-element standard solution (MES). HCl was then added to adjust the concentration to the following values: 1, 2, 4, 6, 8, and 10 mol/l to a total flask volume of 10 ml. The next step involved liquid-liquid extraction by adding 5 ml of organic solvent in three consecutive replicates. The water phase was then quantitatively transferred to a 50 ml teflon beaker, slowly heated to 90 °C and evaporated to 3 ml to completely remove the organic solvent. The final step was to transfer the remaining solution and fill the 25 ml flask with deionized water. The optimization showed that nAA was the most suitable solvent for the selective extraction of thallium.

Extraction of arsenic. In a 50 ml capped graduated cylinder, 65 mg of thallium(I) nitrate, 1 ml of standard solution of As (1000 mg/kg) and 2 ml MES (100 mg/kg) were added. Then concentrated HCl was added to adjust the final concentration to 8 mol/l. Liquid-liquid extractions were made in triplicates by adding 5 ml (each) of nAA. After the extraction was complete and the thallium was quantitatively removed, 0.5 ml of 10% KI was added and another 6×5 ml toluene extraction was performed to remove As. The remaining aqueous solution was transferred to a 50 ml teflon beaker and heated to approximately 90 °C, where the solution evaporated to 3 ml and quantitatively transferred to a 25 ml volumetric flask by adding deionized water. The experiment was carried out 3 times to obtain better statistical data.

Instrumental techniques applied

k_0-Instrumental neutron activation analysis (*k_0-INAA*). For k_0-INAA purposes, the samples were irradiated in powder form in the 250 kW TRIGA Mark II reactor at the Jožef Stefan Institute (JSI) in Ljubljana, Slovenia. About 100 mg of the sample was sealed into a pure polyethylene ampoule (SPRONK system, Lexmond, Netherlands). A sample and a standard Al-0.1%Au disc IRMM-530R (IRMM, 2007) with a diameter of 6 mm and a thickness of 0.1 mm were stacked and fixed in the polyethylene ampoule in sandwich form and irradiated. Depending on the purpose of the analysis, two irradiations were typically performed: a short irradiation (up to a few minutes) to determine the elements via their corresponding short half-life radionuclides and a second irradiation (up to 12 hours) at a thermal neutron flux of 1.1×10^{12} cm^{-2} s^{-1} in the carousel facility (CF) of the TRIGA reactor to determine the elements via their corresponding medium/long half-life radionuclides.

After short irradiation (15 s), the polyethylene ampoules were measured twice after 2 min and after 2 h cooling time on the absolutely calibrated HPGe detectors (Smodiš et al., 1988; De Corte et al., 2001). This allowed the determination of elements via radionuclides with relatively short/medium half-lives (a few minutes to a few hours). Subsequently, after an appropriate cooling time (8–10 days), the same ampoules were irradiated again for 12 hours (long irradiation) in the CF of the TRIGA reactor. After this long irradiation, the ampoules were opened and measured on the absolutely calibrated HPGe detectors after 2–3, 8–10 and 30 days of cooling time.

The HyperLab (2002) was used to evaluate the peak areas in a gamma spectrum. A software Kayzero for Windows (KayWin®) (2005), which is based on the k_0-standardization method of the NAA, was used to calculate the element concentrations and the effective solid angle between a sample and an HPGe detector. The KayWin® software is frequently updated and uses the recommended core data library (k_0-database) (Jaćimović et al., 2014).

Inductively coupled plasma – atomic emission spectrometry. The analyses for 21 elements (Ag, Al, As, B, Ba, Ca, Cd, Co, Cr, Cu, Fe, Li, Mg, Mn, Na, Ni, Pb, Sr, Tl, V, and Zn) in the digestion samples were carried out using inductively coupled plasma – atomic emission spectrometry (ICP-AES, Varian 715-ES). The QA/QC of the applied technique were performed using the standard addition method and it was found that the recovery rate for the analyzed elements was between 98.5% and 101.2%. The same method were applied for the determination of the analyzed elements in the reference materials JSAC 0401 (soil) and SARM 3 (rock) and yielded values ranged from 94.9% to 105.4% in the certified ones. The sensitivity with respect to the lower detection limit was performed.

Matrix interferences from thallium

The interference of thallium with the trace elements was investigated by adding 1 mg/kg MES solution to volumetric flasks in comparison with another 1 mg/kg MES solution to which 50 mg $TlNO_3$ had previously been added to simulate the lorandite matrix.

Mineral extraction. After optimizing the procedure, two parallel samples of lorandite were prepared and used. In a 50 ml teflon beaker, 50 mg of lorandite was added and dissolved with 3 ml of concentrated HNO_3 and heated over a hot plate to complete the digestion. The solution was evaporated to 0.5 ml , transferred to sealed cylinders and Tl and As extraction was performed as described above.

RESULTS AND DISCUSSION

The elemental content values of the studied mineral sample of lorandite ($TlAsS_2$) obtained by k_0-INAA are given in Table 1 and compared with the results for the same mineral collected and analyzed earlier (Frantz et al., 1994; Jaćimović et al., 2002; Pavićević et al., 2018). As can be seen from these results, the lorandite sample used in this study has a very similar content of the majority of the analyzed major and trace elements compared to the previous results. This study again indicates that the lorandite samples are exceptionally pure, as evidenced by the fact that the concentration of a large number of trace elements is below the corresponding detection limit of the solid-state technique used. The inability to determine two of the major elements (Tl and S), as well as the large uncertainty of the content of most trace elements analyzed in lorandite by the k_0-INAA method, obviously make it necessary to eliminate arsenic and thallium to allow their determination in the mineral matrix. Therefore, in order to eliminate the interferences caused by the main matrix elements (Tl, As, S), the liquid-liquid extraction was developed after a complete acid digestion of the solid sample.

The results of the first optimization, which was performed separately with three organic solvents (DIPE, nAA and iAA), showed that Tl was quantitatively eliminated as soon as the molarity of HCl was adjusted to 8 mol/l (Figure 1). At this HCl concentration, the ICP-AES method used determined that practically all of the Tl was removed by using either nAA or DIPE as the solvent (Figure 1). Although it is claimed in the literature that traces of Tl are removed from some other sulfide minerals (realgar, orpiment, sphalerite, galena) by iAA (Zendelovska and Stafilov, 2001), it was found here that at this molarity almost a quarter of the Tl remained in solution, whereas the higher concentration HCl solution (10 mol/l) allowed about 89% of the thallium to be removed. However, although a high percentage of Tl was eliminated, the results obtained with iAA were significantly worse compared to those of DIPE and nAA extraction at this HCl concentration of 8 mol/l. The other elements from the multi-element standard solution remained almost quantitatively in the water phase when the HCl molarity was continuously increased, in contrast to iron, which also showed a similar behavior to Tl and was completely eliminated by iAA and nAA extraction (25% of iron remained in the water solution when DIPE was used as extraction solvent at 8 mol/l HCl). The color maps (Figure 1) have shown that further optimization of the method with nAA in 8 mol/l HCl medium (Figure 2) should be performed, as the best recovery for all other elements studied was observed in the range of 89–100%.

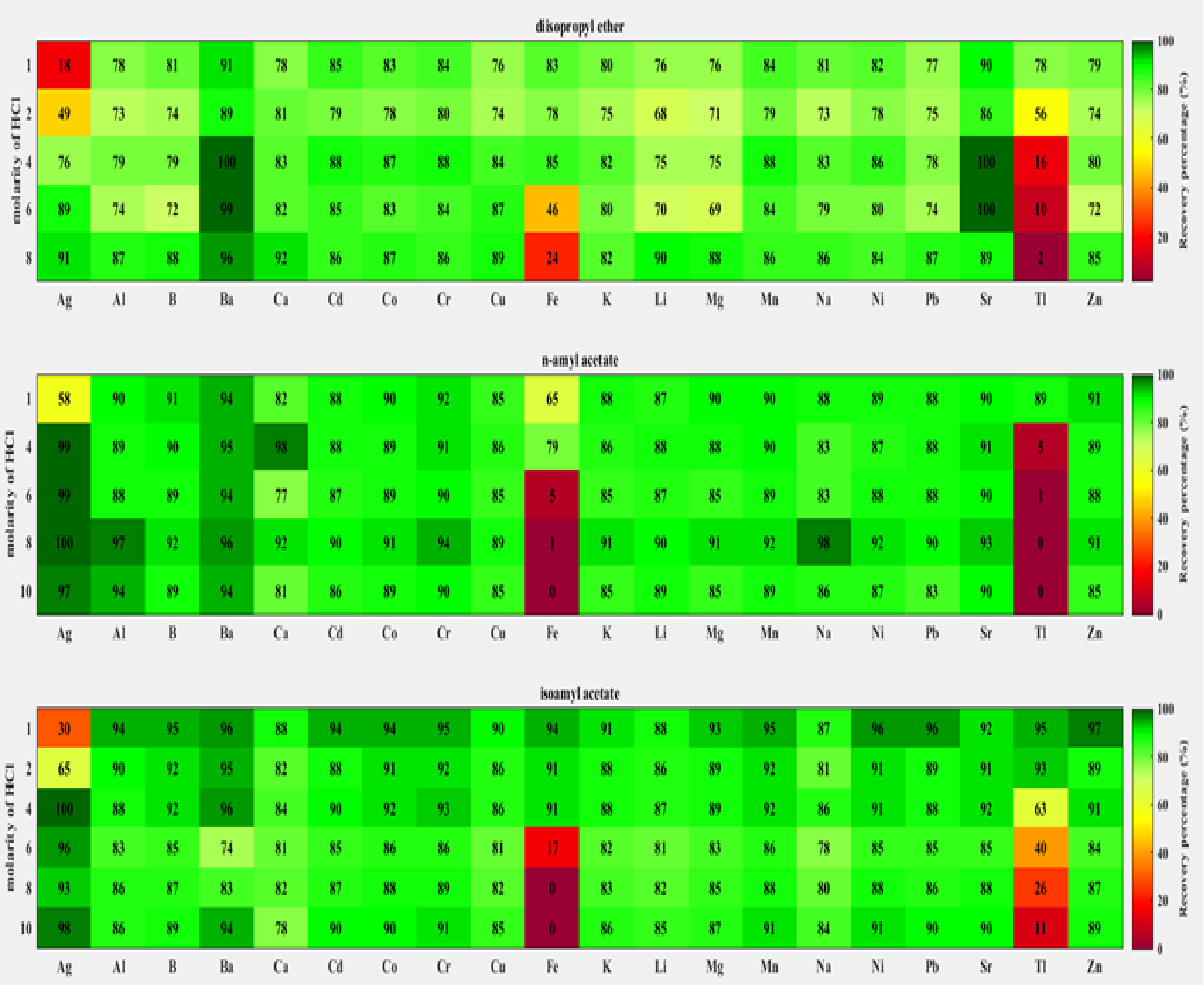
The next optimization step involved increasing the Tl concentration to 2000 mg/kg to simulate the thallium as a matrix element of the system by adding $TlNO_3$. In addition to $TlNO_3$, the concentration of the other elements of the stock solution was fixed at 4 mg/kg and the optimized extraction method by nAA in 8 mol/l HCl medium was applied. The results showed that Tl and Fe were quantitatively extracted by the organic solvent (recoveries of 0.40% and 0.33%, respectively), while all other analyzed elements remained in the water phase (Table 2). The recovery of the microelements ranges between 85.7% and 104.4%, confirming the non-specificity of the method used in the extraction of all these elements, in contrast to the different behavior of Tl, Fe and, to some extent, As (Table 2).

Table 1

Comparison of the content of the analyzed major and trace elements in lorandite determined by the k_0-INAA method in this work (mass fraction with combined standard uncertainty) and in the previously published works. The results are given in mg/kg

El.	This work (k_0–INAA)	Frantz et al., 1994 (INAA)	Jaćimović et al., 2002 (k_0–INAA)	Pavićević et al., 2018 (ICP–MS) (average of 10 samples)
Ag	<0.37	–	<0.5	–
Al	–	–	49.1 ± 4.9	<1
As	207800 ± 7400	195600; 197200; 205300	213000 ± 9000	214820*
Au	<0.040	–	<0.05	–
Ba	<52	–	<50	0.6
Br	<6.25	–	<10	–
Ca	<9487	–	<5000	–
Cd	<44.4	<100	<100	<0.05
Ce	<1.31	–	<1	–
Cl	–	–	<60	–
Co	0.327 ± 0.024	<0.4; <0.8; <1.5	0.69 ± 0.03	<0.05
Cr	<2.2	15; 20; 23	0.80 ± 0.09	2.98
Cs	<0.11	–	0.095 ± 0.017	–
Cu	<51760	<300; <1000	–	0.12
Eu	<0.038	<0.03; <0.07; <0.14;	<1	–
Fe	2121 ± 75	590; 1260; 1960	2490 ± 100	844
Ga	<1680	<7; <15; <30	–	<0.05
Hf	<0.15	–	–	–
Hg	1.082 ± 0.081	<0.85; 1.4	0.390 ± 0.075	1.6
Ho	–	–	–	–
I	<40	–	<40	–
In	<3.2	<0.20; <2.5	–	–
K	<240000	<310; <500; <650	–	–
La	<0.84	<0.43; <1.00	<2	–
Mg	–	–	<900	–
Mn	29.9 ± 1.1	9; 49; 58	36.5 ± 1.5	681
Mo	<24	8.6; <15	<20	0.1
Na	<145	<30; 37; 40	–	–
Nd	<6.3	–	–	–
Ni	–	<35; <40; <500		1
Pb	–	–	–	0.31
Rb	<5.3	–	<3	–
S	N.D.**	–	–	202310*
Sb	604 ± 21	258; 278; 379	269 ± 11	–
Sc	0.0159 ± 0.0012	<0.01; <0.03; 0.046	0.0184 ± 0.0018	–
Se	0.65 ± 0.23		0.93 ± 0.21	1.4
Sm	<0.32	<016; <0.13; <0.2	–	–
Sr	<61	–	–	0.17
Ta	0.312 ± 0.019	<0.15; <0.3	–	–
Tb	<0.062	–	<0.1	
Te	–	–	<2	
Th	<0.16	<0.16; <0.4	<0.1	<0.1
Ti	<1000	–	<1000	8
Tl	N/A***	–	–	572430*
U	<2.1	<1.0	<1	0.14
V	–	–	<0.6	1.3
W	<55	<10	–	–
Yb	<0.25	<0.45; <0.5	<0.5	–
Zn	4.93 ± 0.53	<6; <10	7.7 ± 1.0	–
Zr	<57	–	<50	–

*SEM-EDS (average of 46 samples); **N.D. – not detected via S-37 ($T_{1/2}$ = 5.05 min) due to short irradiation (15 s) and high content of As; ***N/A – not applicable by k_0 – INAA (no suitable radionuclides of Tl for NAA)



diisopropyl ether

molarity of HCl	Ag	Al	B	Ba	Ca	Cd	Co	Cr	Cu	Fe	K	Li	Mg	Mn	Na	Ni	Pb	Sr	Tl	Zn
1	18	78	81	91	78	85	83	84	76	83	80	76	76	84	81	82	77	90	78	79
2	49	73	74	89	81	79	78	80	74	78	75	68	71	79	73	78	75	86	56	74
4	76	79	79	100	83	88	87	88	84	85	82	75	75	88	83	86	78	100	16	80
6	89	74	72	99	82	85	83	84	87	46	80	70	69	84	79	80	74	100	10	72
8	91	87	88	96	92	86	87	86	89	24	82	90	88	86	86	84	87	89	2	85

n-amyl acetate

molarity of HCl	Ag	Al	B	Ba	Ca	Cd	Co	Cr	Cu	Fe	K	Li	Mg	Mn	Na	Ni	Pb	Sr	Tl	Zn
1	58	90	91	94	82	88	90	92	85	65	88	87	90	90	88	89	88	90	89	91
4	99	89	90	95	98	88	89	91	86	79	86	88	88	90	83	87	88	91	5	89
6	99	88	89	94	77	87	89	90	85	5	85	87	85	89	83	88	88	90	1	88
8	100	97	92	96	92	90	91	94	89	1	91	90	91	92	98	92	90	93	0	91
10	97	94	89	94	81	86	89	90	85	0	85	89	85	89	86	87	83	90	0	85

isoamyl acetate

molarity of HCl	Ag	Al	B	Ba	Ca	Cd	Co	Cr	Cu	Fe	K	Li	Mg	Mn	Na	Ni	Pb	Sr	Tl	Zn
1	30	94	95	96	88	94	94	95	90	94	91	88	93	95	87	96	96	92	95	97
2	65	90	92	95	82	88	91	92	86	91	88	86	89	92	81	91	89	91	93	89
4	100	88	92	96	84	90	92	93	86	91	88	87	89	92	86	91	88	92	63	91
6	96	83	85	74	81	85	86	86	81	17	82	81	83	86	78	85	85	85	40	84
8	93	86	87	83	82	87	88	89	82	0	83	82	85	88	80	88	86	88	26	87
10	98	86	89	94	78	90	90	91	85	0	86	85	87	91	84	91	90	90	11	89

Fig. 1. Colormaps of the results for the recoveries (in %) of all analyzed elements obtained from the optimization procedure by using three organic solvents at different HCl concentrations

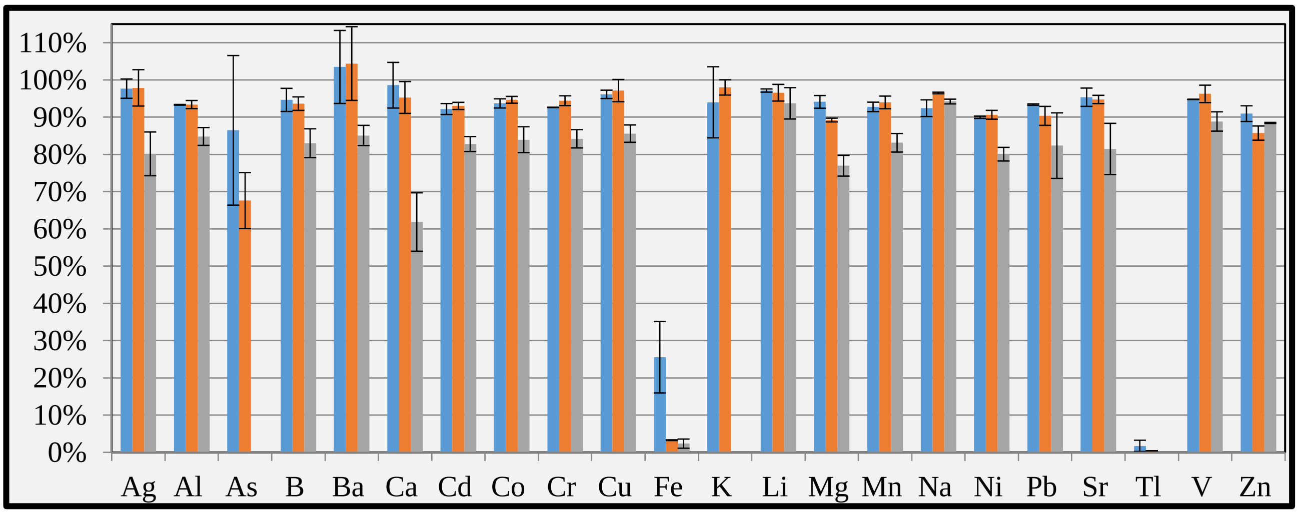


Fig. 2. Extraction recovery (in %) of elements from standard solution with 8 mol/l HCl using diisopropyl ether (blue columns), *n*-amyl acetate (red color) and consecutively *n*-amyl acetate and toluene (gray color). KI is added with toluene while using *n*-amyl acetate for extraction of As and therefore the third column for this element is not shown

Table 2

The extraction recovery of Tl added as major constituent from the standard solution versus other microelements after nAA extraction from 8 M HCl medium

Element	Ag	Al	**As**	B	Ba	Ca	Cd	Co	Cr	Cu	**Fe**	Li	Mg	Mn	Na	Ni	Pb	Sr	**Tl**	V	Zn
Before extraction, mg/kg	4.00	4.00	**4.00**	4.00	4.00	4.00	4.00	4.00	4.00	4.00	**4.00**	4.00	4.00	4.00	4.00	4.00	4.00	4.00	**2000**	4.00	4.00
After extraction, mg/kg	3.92	3.74	**2.70**	3.75	4.18	3.81	3.72	3.79	3.78	3.89	**0.01**	3.86	3.57	3.76	3.86	3.63	3.61	3.79	**7.96**	3.85	3.43
Recovery, %	97.9	93.4	**67.6**	93.6	104.4	95.3	93.0	94.7	94.4	97.1	**0.33**	96.6	89.2	94.0	96.5	90.6	90.4	94.8	**0.40**	96.3	85.7

To validate the method used to mimic the lorandite matrix ($TlAsS_2$), a solution of dissolved $TlNO_3$ and digested realgar mineral (As_4S_4) was prepared. Then a two-step extraction was performed with nAA in 8 HCl medium (to remove the Tl), followed by extraction with toluene to remove the arsenic. The results showed that Tl and As were successfully extracted in the organic solvents (recovery for both elements was 99.4%, Table 3). However, the two-step extraction procedure used showed that some other elements were also removed by the NAA (iron) and toluene (Ca and Na) extractions. The recovery of the other elements is between 86.2% (Mg) and 100.1% (V), showing their insensitivity to the two extraction solvents used.

Table 4 compares the results of major (Tl and As) and trace elements in a solid sample of lorandite (k_0-INAA) with those obtained for the dissolved as well as extracted lorandite mineral by ICP-AES. It is important to note that the arsenic content was very similar using the k_0-INAA and ICP-AES methods, indicating that the mineral sample was fully digested prior to ICP-AES analysis. Further supporting the assertion that the mineral was fully digested is the evidence that the ICP-AES method and the previous SEM-EDS data independently returned similar values for thallium content (Tables 1 and 4). Furthermore, the ICP-AES results prior to the start of the extraction process indicate that the sample analyzed is indeed very pure lorandite, as very low grades were found for all trace elements (with the exception of Fe, which is present at 1749 mg/kg). Analysis of the aqueous solution using the optimized extraction method with nAA and toluene showed that all elements (including the matrix elements Tl and As) were quantitatively transferred to the organic phase. The only elements that remained in the water phase were Mg and Mn.

Table 3

Extraction recovery for Tl and As (by adding $TlNO_3$ and As_4S_4) versus the remaining stock solution elements, measured after two-step consecutive extraction by nAA and toluene from 8 M HCl solution

Element	Ag	Al	**As**	B	Ba	Ca	Cd	Co	Cr	Cu	**Fe**	Li	Mg	Mn	Na	Ni	Pb	Sr	**Tl**	V	Zn
Before extraction, mg/kg.	4.00	4.00	**40.0**	4.00	4.00	4.00	4.00	4.00	4.00	4.00	**4.00**	4.00	4.00	4.00	4.00	4.00	4.00	4.00	**2013**	4.00	4.00
After extraction, mg/kg	3.88	3.82	**0.02**	3.69	3.83	2.59	3.74	3.75	3.79	3.86	**0.38**	3.87	3.45	3.74	0.01	3.62	3.50	3.52	**1.21**	4.00	3.53
Recovery, %	96.9	95.6	**0.06**	92.3	95.6	64.7	93.6	93.7	94.8	96.5	**9.60**	96.7	86.2	93.6	0.25	90.6	87.6	88.1	**0.06**	100.1	88.3

Table 4

Elemental analysis (in mg/kg) of trace elements of the lorandite sample determined with k_0-INAA (solid sample), ICP-AES of the dissolved mineral in nitric acid, and extraction of the dissolved mineral

Element	k_0-INAA	ICP-AES		Recovery/%
	Powder sample	Dissolved sample	Water solution after the extraction	Extracted/dissolved
Ag	<0.37	<1	<1	
Al		<10	<10	
As	207800	217192	<10	<0.005
Au	<0.040			
Ba	<52	<10	<10	
Br	<6.25			
Ca	<9487	<10	<10	
Cd	<44.4	<1	<1	
Ce	<1.31			
Co	0.327	<1	<1	
Cr	<2.2	<1	<1	
Cs	<0.11			
Cu	<51760	<1	<1	
Eu	<0.038			
Fe	2121	1749	<10	<0.57
Ga	<1680			
Hf	<0.15			
Hg	1.08			
In	<3.2			
K	<240000	<10	added	
La	<0.84			
Li		<1	<1	
Mg		17.4	14.1	81.03
Mn	29.9	10.2	9.3	91.17
Mo	<24	<10	<10	
Na	<145	<10	<10	
Nd	<6.3			
Ni		<10	<10	
Pb		<10	<10	
Rb	<5.3			
Sb	604			
Sc	0.0159			
Se	0.647			
Sm	<0.32			
Sr	<61	<1	<1	
Ta	0.312			
Tb	<0.062			
Th	<0.16			
Tl	N/A*	591814	<1	<0.0002
U	<2.1			
V		<1	<1	
W	<55			
Yb	<0.25			
Zn	4.93	<1	<1	
Zr	<57			

*N/A – not applicable by k_0-INAA (no suitable radionuclides of Tl for NAA)

CONCLUSIONS

A novel liquid-liquid extraction method was optimized for the elimination of the macro-elements (arsenic and thallium) to minimize matrix interferences and to determine the trace elements in the mineral lorandite ($TlAsS_2$). For this purpose, the concentration of HCl after dissolution of the mineral as well as the volume of the organic solvents: DIPE, nAA and iAA were optimized. It was found that at HCl concentration of 8 mol/l, the highest recoveries of thallium and arsenic were achieved by separately using any of the three organic solvents. However, it was found that the best results were obtained when nAA was used as an organic solvent. Once all conditions were optimized, a two-step liquid-liquid extraction with nAA (to eliminate Tl) and toluene with KI (to eliminate As) was performed for the dissolved lorandite mineral. All elements were determined by inductively coupled plasma – atomic emission spectrometry (ICP-AES) and the results were correlated with those of untreated, pure lorandite. This method can be also applied for other important geological and mineralogical studies on other thallium and/or arsenic ores or minerals where the elimination of those reported matrix elements is needed.

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Резиме

НОВ ОПТИМИЗИРАН МЕТОД НА ТЕЧНО-ТЕЧНА ЕКСТРАКЦИЈА ЗА ОТСТРАНУВАЊЕ НА ТАЛИУМ КАКО МАТРИЧЕН ЕЛЕМЕНТ ВО МИНЕРАЛИ

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Клучни зборови: матричен елемент; лорандит; талиум; елементи во траги; течно-течна екстракција; ICP-AES; k_0-INAA

При следење на содржината на елементите во траги во минерали и други неоргански соединенија, доаѓа до зголемување на границата на детекција и нивното определување е отежнато, па дури и невозможно, како резултат на интерференцијата на матричните елементи на минералот. Така може да се случи некои од важните елементи во траги да не бидат определени во анализираниот минерал, што го намалува потенцијалот на економската значајност на геолошкиот локалитет или рудник. Главниот фокус на оваа студија е изнаоѓање соодветен, релативно евтин и брз метод за селективно и последователно отстранување на талиум и на арсен од As-Tl-минерали во насока на намалување на границата на детекција за определување на присутните елементи во траги. Методот е заснован на засебна оптимизација на моларноста на HCl и на волуменот на употребениот органски растворувач. Како органски растворувачи, засебно, се користени диизопропилетер, диетилетер, *n*-амил ацетат и изоамил ацетат. Оптимизацијата на концентрацијата на HCl овозможи екстракција на талиумот (како хлориден комплекс) и негово одведување во органскиот горен слој. Оптимизацијата на методот е направена со користење на талиум(I)нитрат, со последователно додавање на минералот реалгар (As_4S_4), при што е симулирана матрица со сличен елементен состав како оној на минералот лорандит ($TlAsS_2$). Самиот лорандит не е користен за оптимизација поради тоа што овој минерал е редок и многу скапоцен за прелиминарни тестови. Дополнително, преку симулација, е направен тест за екстракцијата и на ретките елементи (Ag, Al, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mo, Ni, Pb, Sr, Tl, V, Zn) кои се внесени преку стандарден мултиелементен раствор. Откако се оптимизирани сите услови, користена е течно-течна екстракција, во два чекора, врз растворен примерок од лорандит. Првата екстракција е направена со *n*-амил ацетат (за отстранување на Tl), а последователно е направена и втората екстракција со толуен во кој е растворен KI (за елиминација на As). Сите анализирани елементи се определени со индуктивно спрегната плазма со атомска емисиона спектрометрија, а резултатите се споредени со оние добиени со k_0-инструментална неутронско-активациона анализа на истиот, претходно спрашен, примерок од лорандит.