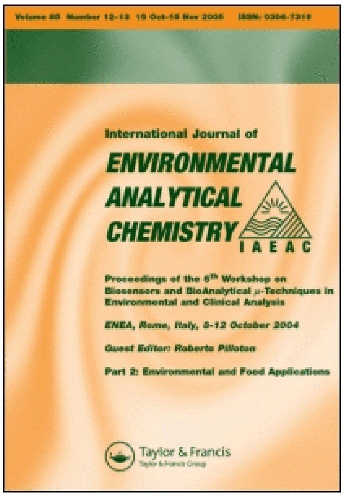

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Closed-vessel microwave digestion technique for lichens and leaves prior to determination of trace elements (Pb, Zn, Cu) and stable Pb isotope ratios

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CLOSED-VESSEL MICROWAVE DIGESTION TECHNIQUE FOR LICHENS AND LEAVES PRIOR TO DETERMINATION OF TRACE ELEMENTS (Pb, Zn, Cu) AND STABLE PB ISOTOPE RATIOS

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A reliable and robust procedure using closed-vessel microwave digestion of lichens and leaves for precise and accurate determination of trace elements (Pb, Zn and Cu) and stable Pb isotope ratios is presented. The method was developed using certified reference material CRM 482 *Pseudovernia furfurea* (Lichens), NIST 1515 (Apple Leaves) and NIST 1547 (Peach Leaves) and tested on lichens from a mining site in Russia. A mixture of 3 mL of HNO_3, 3 mL of H_2O_2, 2 mL of H_2O and 0.8 mL of HF ensured complete sample dissolution with $100 \pm 5\%$ recovery for Pb, Zn and Cu at a maximum temperature of 210°C and pressure of 350 psi. The amount of HF and microwave pressure significantly influenced Pb, Zn and Cu recovery. Comparison between EMMA-XRF and ICP-AES showed a good correlation between Pb, Zn and Cu concentrations. Using the newly developed digestion method, Pb isotopes in lichens from the mining site were determined with an internal precision better than 0.02%.

Keywords: Microwave digestion; Acid decomposition; Standard reference materials (SRM); Lichens; Solid particulates; Pb isotopes

INTRODUCTION

The accumulation of trace metals from atmospheric deposition by lichens, mosses and plant leaves is well documented [1–3]. Lichens in particular are regarded as suitable tools for monitoring levels of atmospheric pollution. Because their mineral nutrition depends on both wet and dry depositions from the atmosphere, they are able to accumulate and store many substances from the atmosphere [4]. In recent years, lichens were successfully used to assess natural vs. anthropogenic sources of airborne

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particulates using Pb isotopes and therefore to trace atmospheric pollution on local and regional scales [5–7].

Although HNO_3 and leaching are sufficient if only pollutant elements are assessed, a complete dissolution of lichens is needed if natural sources are also to be determined. This is of special importance if trace-element dispersal is studied in areas with low-level pollution where the main carrier of trace and potentially toxic elements might be incorporated in naturally derived sources, such as in silicate phases which are highly resistant to acid attack. These particles are trapped on the surface or within the lichens structure making acid decomposition of lichens different from that of leaves and other botanical samples. Both highly resistant inorganic phases (i.e. siliceous particles) and the organic matrix (lichens) must be completely destroyed to achieve complete dissolution of lichens.

In the last decade, closed-vessel microwave-assisted acid decomposition has been widely used for the digestion of lichens [8,9]. This technique has many advantages in comparison with traditional open vessel digestion such as speeding up the sample preparation process, safe operation of the digestion due to fully automated programming, preventing loss of volatile analytes during the digestion and eliminating sample contamination from other samples or the laboratory environment [10–13]. Furthermore, the ability to monitor and control reaction parameters such as temperature and pressure during the digestion process is advantageous in determining the efficiency of sample digestion; the higher temperatures attained under pressure in closed-vessel digestions result in a more complete sample matrix decomposition [10]. For safety reasons, 0.5 g of plant material is the maximum recommended amount to use in 15 mL vessels for closed-vessel microwave digestion [11]. Any larger quantity can significantly increase the internal pressure of the system, due to the large production of gaseous degradation products, and potentially lead to the rupture of the vessel.

Previously published methods of microwave-assisted digestion of botanical samples vary significantly and depend on the sample matrix and/or analysis targets. Routine decomposition methods involve procedures containing 5–10 mL of HNO_3, 0.5–1 mL of H_2O_2 and up to 0.2 mL of HF mixture [8,9,11,12,14–21]. The main findings were:

1. Quantitative recovery of Pb, Zn and Cu concentrations was achieved in lichen standard reference materials;
2. Decomposition of lichens included HF to decompose insoluble residues;
3. Insufficient amount of HF resulted in a lower recovery of Pb, Ni, Cr, Sn, V, Ti, Al and Fe, i.e. those elements that are correlated with the Si content;
4. During the analysis of real lichen samples characterized by different masses of dust particulate, the use of HF improved the accuracy.

However, most of the reported methods required filtering of the digests prior to elemental analysis [8,14,15,17]. This suggests incomplete dissolution of the sample matrices even in cases where 0.2 mL of HF was added [8,9]. None of the publications have addressed Pb isotope determination in lichens. Consequently, the aim of this study was to improve methods to achieve the complete dissolution of lichens using closed-vessel microwave-assisted digestion for the determination of Pb, Zn and Cu, and stable Pb isotope ratios. The existing closed-vessel microwave digestion methods [8,9] were modified by: (1) adjusting the amount of HF added to the sample matrices, (2) increasing the digestion time and (3) optimizing the microwave pressure. Although $HClO_4$ is conventionally used as an effective acid for the breakdown of the organic fractions, the use of this acid was avoided in our experimental development work for safety reasons [22]. To check the accuracy of the method, certified standard reference materials of lichens and leaves were included in the study. The modified digestion method was tested on lichens collected from the Orlovka-Spokoinoe mining district in Eastern Transbaikalia, Russia.

The inter-laboratory comparison study for Pb, Zn and Cu contents was performed using inductively coupled plasma atomic emission spectrometry (ICP-AES) and X-ray fluorescence spectrometry (EMMA-XRF). Following the microwave-assisted decomposition procedure, lichens from the mining site were analyzed for Pb isotopes.

EXPERIMENTAL DEVELOPMENT

Instrumentation

The acid digestions were accomplished using a CEM Microwave Accelerated Reaction System MARS-X with temperature and pressure control. Teflon vessels (100 mL, XP-1500) fitted with screw tops and with a pressure venting system were used as digestion vessels. Prior to their use, all vessels were thoroughly acid-cleaned in the microwave (for 15 min at 150°C) using 5 mL of concentrated HNO_3 and 5 mL of Milli-Q H_2O. After cooling, the contents of the vessels were discarded, and the vessels were rinsed with Milli-Q deionized H_2O (18 MΩ cm). One vessel out of 12 (i.e. control vessel) monitored pressure and temperature during the digestion, providing constant feedback control of reaction conditions. Pb, Zn and Cu were determined by Fison's Instruments ARL 3508B ICP-AES.

Selected samples were analyzed using energy-dispersive miniprobe multielement analysis (EMMA-XRF); analytical and instrumental details of the measurements are given elsewhere [23,24].

Pb isotopes in lichens were determined using a GVi IsoProbe multicollector inductively coupled plasma mass spectrometer (MC-ICP-MS). A CETAC Aridus nebulizer (Omaha, NE, USA) was used for sample uptake for the IsoProbe. Details of the measurements are given elsewhere [25].

Semi-quantative analysis of siliceous particles on the lichens surface was done using a Jeol 5900LV analytical scanning electron microscope (SEM), equipped with an Oxford Instruments Inca Pentafet energy-dispersive X-ray spectrometer (EDS).

Filtered and dried residues from digested lichens were analyzed by X-ray powder diffraction (XRD), which was performed using an Enraf-Nonius PDS120 diffractometer incorporating an Inel curved, position sensitive detector. Further details of the XRD measurements can be found elsewhere [26].

All instruments used for the study are at the Natural History Museum, London, apart from the EMMA-XRF facility, which is based at the University of Heidelberg.

Samples and Reagents

Three certified reference materials, NIST 1515 (Apple Leaves), NIST 1547 (Peach Leaves) and CRM 482 #10 *Pseudovernia furfura* (Lichens), were used. The certified concentrations values of Pb, Zn and Cu (μg/g) are listed in Table I.

TABLE I Comparison of Pb, Zn and Cu recovery rates in CRM 482 (Lichens), NIST 1547 (Peach Leaves) and NIST 1515 (Apple Leaves) for 3 digestion experiments tested (see details of the Experiments in Table II)

Element/sample	*Certified values* (±2σ)	*Experiment I*	*Recovery (%)*	*Experiment II*	*Recovery (%)*	*Experiment III*	*Recovery (%)*
Pb							
Lichens CRM 482	40.9 ± 1.4	28.1 ± 5.1	68.8	34.6 ± 3.2	84.6	38.1 ± 1.6	93.2
Apple leaves NIST 1515	0.5 ± 0.024	0.5 ± 0.07	97.9	0.5 ± 0.07	95.8	0.5 ± 0.01	95.7
Peach leaves NIST 1547	0.9 ± 0.003	0.8 ± 0.03	86.7	0.9 ± 0.24	101	0.9 ± 0.01	98.9
Zn							
Lichens CRM 482	100.6 ± 2.2	62.2 ± 1.8	61.8	81.1 ± 1.2	80.6	92.6 ± 3.1	92
Apple leaves NIST 1515	12.5 ± 0.4	11.6 ± 0.1	92.6	11.4 ± 0.4	91.2	11.8 ± 0.1	94.4
Peach leaves NIST 1547	17.9 ± 0.4	15.9 ± 0.1	88.6	15.9 ± 5.6	88.8	17.9 ± 0.4	99.7
Cu							
Lichens CRM 482	7 ± 0.19	6.1 ± 0.2	86.3	6.8 ± 0.2	97.3	6.7 ± 0.7	95.3
Apple leaves NIST 1515	5.6 ± 0.3	5.2 ± 0.04	92.3	5.2 ± 0.2	91.8	5.7 ± 0.2	101
Peach leaves NIST 1547	3.7 ± 0.4	3.4 ± 0.2	90.5	3.6 ± 1.9	96.5	3.7 ± 0.4	98.9

Concentration values (μg/g) were determined by ICP-AES.

Two lichens species, i.e. *Xanthoparmelia* and *Parmelia ullophyllodes* ($n = 15$) collected from the Orlovka-Spokoinoe mining district in Eastern Transbaikalia (Russia) were used to test the developed digestion method. The study of lichens is a part of the environmental geochemical investigations on the Orlovka-Spokoinoe mining site [27].

Analytical-grade reagents (Aristar) 69% (v/v) HNO_3, 30% (v/v) H_2O_2 and 48% (v/v) HF were used throughout the study. All working solutions were prepared using high-purity water (18 MΩ cm, Millipore).

Sample Preparation

Approximately 50 g of lichen samples was removed from the birch trees bark using a stainless steel knife. The material was placed in cotton bags, allowed to air-dry and transported to the laboratory in sealed plastic bags. In the laboratory, rock/bark fragments adhering to the lichens were removed manually using plastic tweezers and wearing latex powder-free gloves and then oven-dried overnight at 40°C. The samples were then carefully ground in an agate mortar using liquid nitrogen, sieved through a 100-μm stainless steel sieve, placed in ceramic beakers and dried overnight at 40°C prior to analysis. All materials used were washed, rinsed with distilled water and dried between samples to avoid cross-contamination. After drying, all samples were transferred into acid-cleaned plastic bottles using a bony spoon and stored until further use.

Analytical Procedures

Microwave Digestion

Approximately 0.25 g of ground sample material was weighed directly into each digestion vessel on an analytical balance. Depending on the experimental design, 3–5 mL of HNO_3 was then added to each vessel (Table II). The mixture of HNO_3 and plant material was allowed to react in the vessel at atmospheric pressure in a vented hood for 20 min. Then, 3–5 mL of H_2O_2 (Table II) was added to the sample,

TABLE II Details of three experiments used in the study

	Experiment I	*Experiment II*	*Experiment III*
Acid used	5 mL HNO_3 + 5 mL H_2O_2 + 0.2 mL HF	5 mL HNO_3 + 5 mL H_2O_2 + 0.2–1 mL HF	3 mL HNO_3 + 3 mL H_2O_2 + 2 mL H_2O + 0.8 mL HF
Pressure (psi)	200	200	200–350
Temperature (°C)	210	210	210
Total time (min)	70	90	90

and samples were allowed to stand for approximately 20 min. Depending on the experimental design, 0.2–1 mL of HF and 2 mL of Milli-Q H_2O in Experiment III were added, and samples were subjected to a closed-vessel microwave digestion. The procedure utilized up to 100% of the 1200 W power setting for 70–90 min. After the power phase was completed, the vessels were cooled for about 20 min, transferred into acid-cleaned Teflon vessels and evaporated till dryness. In total, three digestion procedures were tested (Experiments I, II and III). Details of all experiments are given in Table II.

During all three experiments, sample size (0.25 g), acids used (HNO_3, H_2O_2 and HF), maximum temperature (210°C) and pre-digestion procedure prior to microwave acid attack were kept the same. The parameters that varied were: (1) proportions of acids (5 mL HNO_3 and 5 mL H_2O_2 in Experiment I and II, 3 mL HNO_3 and 3 mL H_2O_2 in Experiment III); (2) amount of HF (0.2 mL in Experiment I, 0.2–1 mL in Experiment II and 0.8 mL in Experiment III); (3) pressure (200 psi in Experiment I and II and 350 psi in Experiment III); and (4) digestion time (70 min in Experiment I and 90 min in Experiments II and III). In all experiments, four sample duplicates were used.

Determination of Pb, Zn and Cu Concentrations and Pb Isotope Ratios

After samples were digested and evaporated, they were subsequently redissolved in 5 mL of 1 M HCl prior to total element concentration analysis. This ensured a constant chemically stable acid matrix for the ICP-AES analysis. The detection limits for Pb, Zn and Cu were 0.03, 0.001 and 0.001 μg/g, respectively. The precision and accuracy were within 10%. Analytical results for the total Pb, Zn and Cu concentrations (μg/g) for three experiments are listed in Table I.

Prior to Pb isotope analysis, all samples were passed through an ion-exchange column with chromatographic Sr resin (EiChrom) to isolate the Pb fraction from the rest of the sample matrix. For this purpose, after the microwave digestion, samples were dried and redissolved in 2 mL of 2.4 M HCl. Pb separation was achieved using different strengths of HCl during the procedure. Samples were then evaporated to dryness and redissolved in 2% v/v HNO_3 for Pb isotope analysis on MC-ICP-MS. Raw MC-ICP-MS data were corrected for isobaric interferences on ^{204}Pb using ^{200}Hg. A mass discrimination correction was made using NBS 997 Tl as an internal standard. The Pb/Tl ratio was kept to 2 : 1 during the measurements. The NBS 997 ^{205}Tl/^{203}Tl ratio was optimized based on repeated measurements of spiked NBS 981 Pb. Further details of ion exchange procedure and Pb isotope measurements are given elsewhere [28].

RESULTS AND DISCUSSION

Amount of HF and Digestion Time as Critical Parameters of Microwave Digestion

In Experiment I, 0.2 mL of HF was added, similar to previous procedures [8,9] for the same size of lichen samples. As shown in Table I, the recovery of Pb, Zn and Cu varied between elements and among the samples. Lead recovery was high for the NIST 1515 (Apple Leaves), 97.9%, moderate for the NIST 1547 (Peach Leaves), 86.7%, and low for the CRM 482 (Lichens), 68.8%.

Similar recovery rates were observed for Zn and Cu (Table II). The poor recovery in lichens and the presence of visible residues in the final digests can be attributed to an insufficient amount of HF used in the experiment to dissolve the inorganic fraction. Consequently, the increase in the amount of HF from 0.2 to 1 mL in Experiment II significantly influenced Pb, Zn and Cu recovery, i.e. by 12% for Cu, 22% for Pb and 30% for Zn. (Fig. 1). However, the full recovery of all elements was not achieved at this stage. It should be noted that recovery rates for all three elements did not improve significantly when more than 0.8 mL of HF was added because of the formation of fluoride precipitates, which will be discussed further below.

Fluoride Precipitates

When more than 0.8 mL of HF was added to 10 mL of acid mixture and 0.25 g of samples, the formation of whitish residues was observed. Digests were filtered, dried and analysed by semi-quantative scanning electron microscopy (SEM). The SEM analysis showed perfectly shaped needle-like crystals of mostly Ca, Al and F composition, and further X-ray powder diffraction (XRD) analysis identified the precipitates as artificial fluorides ($CaAlF_5$). Both high Ca concentrations of up to 4–5% in leaves and lichens and an excess of HF led to the formation of artificial fluorides during microwave acid decomposition. The coprecipitation of many incompatible trace elements (e.g. Rb, Sr, Y, Cs, Ba, REE, Pb, Th and U) in the structure of insoluble fluorides formed during HF digestion of silicate rocks, hindering the accurate determination of these elements, was previously reported [29]. A lower degree of elemental recovery with excess of HF was also reported for peat samples [30]. Similar to lichens, peat contains a significant amount of inorganic fraction derived from soil dust that requires HF to achieve its complete dissolution.

TABLE III Heating program of the Experiment III for the digestion of SRM (NIST 1515 Apple Leaves, NIST 1547 Peach Leaves and CRM 482 Lichens)

Stage	*Pressure (psi)*	*Temperature (°C)*	*Time (min)*
1	20	90	10
2	40	120	10
3	80	160	10
4	200	180	30
5	350	210	30

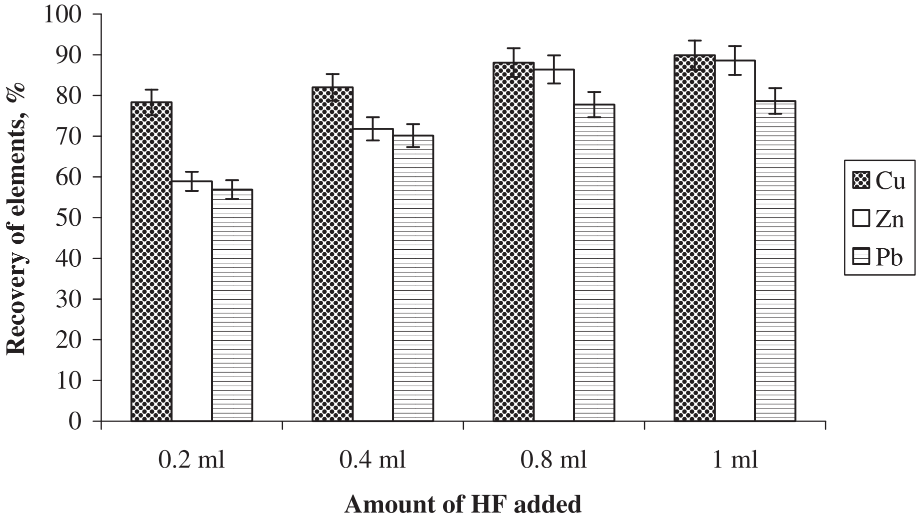

FIGURE 1 Recoveries of Pb, Zn and Cu in CRM 482 *Pseudovernia furfura* lichens as a function of HF amount added to the samples. Lichens were digested under a pressure of 200 psi and a temperature of 210°C using a mixture of 5 mL of HNO_3, 5 mL of H_2O_2, and 0.2–1 mL of HF. The error bars show the 95% confidence interval, $n = 4$ (where n denotes the number of replicates).

Influence of Digestion Time and Pressure on Pb, Zn and Cu Recovery

Digestion time is known to influence elemental recovery from botanical samples. For example, Pb recovery improved and stabilized only after about 1.5 h of microwave digestion [16]. The holding digestion time at the final stage of the procedure in Experiment II was increased by 20 min after the pressure and temperature reached 200 psi and 210°C, respectively. As a result, Pb, Zn and Cu concentrations increased on average by ~3% and led to the recovery of 85–100% for Pb, 81–91% for Zn and 92–97% for Cu. Also, previous research compared elemental recovery from peach and orchard leaves using 175 psi and 530 psi of microwave pressure [31] using 0.3 g of material, 5 mL of HNO_3 and a final temperature of 175°C. The results of their study showed that the higher pressure led to 7–9% increase in Pb, Zn and Cu concentrations. In Experiment III, the pressure was consequently changed from 200 to 350 psi. At the end of the digestion, resultant solutions were clear and colorless, indicating the total decomposition of lichens and leaves matrices. As shown on Fig. 2, quantitative recovery of 100 ± 5% for Pb, Zn and Cu was achieved.

Lichens from the Orlovka-Spokoinoe Mining District

Lichens collected from different localities (settlement, quarry, tailing pond, etc.) of the Orlovka-Spokoinoe mining district (Eastern Transbaikalia, Russia) were digested using the procedure of Experiment III (see Tables II and III for full details of the method). Despite the different density of particles trapped by the lichens (Fig. 3A, B) and an ash content of up to 24%, the microwave acid decomposition of all samples yielded clear solutions. No filtering or additional treatment of digests was required.

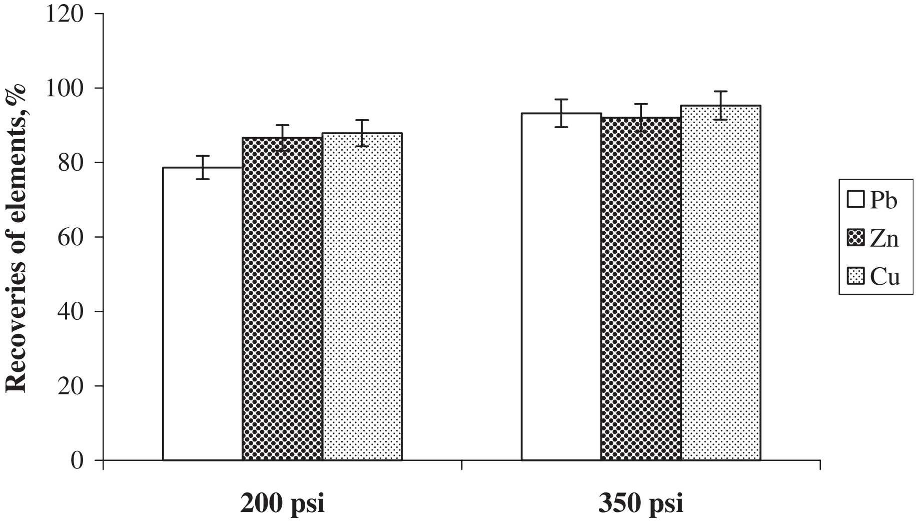

FIGURE 2 Recoveries of Pb, Zn and Cu in CRM 482 *Pseudovernia furfura* lichens as a function of pressure (psi). Lichens were digested under a pressure of 350 psi and a temperature of 210°C using a mixture of 3 mL of HNO_3, 3 mL of H_2O_2, 2 mL of H_2O and 0.8 mL of HF. The error bars show the 95% confidence interval, $n = 4$ (where n denotes the number of replicates).

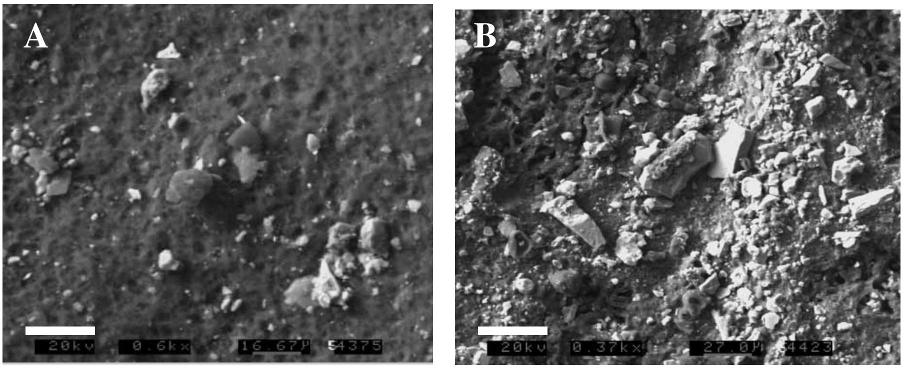

FIGURE 3 Semi-quantative SEM images of lichens collected from the Orlovka-Spokoinoe mining district (Eastern Transbaikalia, Russia) with siliceous particles on the surface. The white bar corresponds to 16.7 µm in (A) and 27 µm in (B).

Table IV lists the Pb, Zn and Cu concentrations in lichens collected from the Orlovka mining district. Pb concentrations ranged between 4 and 29 µg/g for Pb, 35–98 µg/g for Zn and 6–9 µg/g for Cu. To further assess the accuracy, Pb, Zn and Cu concentrations were determined in subsamples by EMMA-XRF at the University of Heidelberg. The two data sets showed a good correlation for Pb, Zn and Cu concentrations with $R^2 = 0.938$–0.999, a slope of 0.993–0.999 and an intercept of 0.2–0.4. The slope and intercept fell within the 95% confidence interval, indicating that regressions showed no statistically significant difference between ICP-AES and XRF data.

Table IV shows Pb isotopes ratios for selected lichen samples from the mining site with the internal precision expressed in $\pm 2\sigma$ (%). The error of the internal isotope

TABLE IV Pb, Zn and Cu concentration values (μg/g) determined by ICP-AES and Pb isotope ratios measured by MC-ICP-MS in lichens from the Orlovka-Spokoinoe mining district, Eastern Transbaikalia, Russia

Sample ID	*Sample description*	*Pb*	*Zn*	*Cu*	$^{206}Pb/^{204}Pb$	*±2SE(%)*	$^{207}Pb/^{204}Pb$	*±2SE(%)*	$^{208}Pb/^{204}Pb$	*±2SE(%)*
SEL5	Lichens, Orlovka	28.6	97.8	8.9	18.077	0.0009	15.572	0.0005	38.093	0.0011
SEL6	Lichens, Orlovka	9.5	96.1	7.4	18.114	0.0010	15.566	0.0006	38.120	0.0016
L1 C	Lichens, Orlovka	12.6	42.2	6.2	18.113	0.0007	15.560	0.0004	38.159	0.0010
L1 ED	Lichens, Orlovka	8.12	46.2	5.6	18.053	0.0008	15.544	0.0006	38.077	0.0016
L2	Lichens, Orlovka	16.3	35	8.2	18.100	0.0007	15.555	0.0004	38.113	0.0011
TPL1 ED	Lichens, Orlovka	10.3	86.9	6.7	18.299	0.0006	15.567	0.0004	38.180	0.0009
TPL2	Lichens, Orlovka	10.3	82.9	6.7	18.255	0.0007	15.563	0.0004	38.185	0.0010
TPL3	Lichens, Orlovka	9.8	79.3	7.2	18.457	0.0010	15.591	0.0006	38.330	0.0015
TPL4	Lichens, Orlovka	12.6	85.3	8.3	18.806	0.0011	15.611	0.0006	38.430	0.0015
OQL2	Lichens, Orlovka	10.1	38.4	6.2	18.127	0.0005	15.564	0.0003	38.170	0.0008
OQL3	Lichens, Orlovka	9.6	37.8	5.7	18.089	0.0005	15.562	0.0004	38.139	0.0009
OQL4C	Lichens, Orlovka	9.8	37.6	5.5	18.114	0.0007	15.555	0.0004	38.148	0.0010
OQL5B	Lichens, Orlovka	13.3	76.3	7.1	18.128	0.0009	15.548	0.0006	38.134	0.0016
SML7	Lichens, Orlovka	19.7	87.9	8.9	18.140	0.0010	15.574	0.0007	38.139	0.0018
LBL1	Lichens, Lake Baikal	4.2	63.8	8.5	18.152	0.0007	15.561	0.0004	38.321	0.0009

measurements is below 0.02% for all ratios. The data set will be discussed in detail in a follow-up publication on environmental application of Pb isotopes in lichens from the Orlovka-Spokoinoe mining site.

CONCLUSIONS

This study has demonstrated the following:

1. Microwave-assisted acid decomposition of NIST 1515 (Apple Leaves), NIST 1547 (Peach Leaves) and CRM 482 #10 *Pseudovernia furfura* (Lichens) standards using 6 mL of $HNO_3 + 2$ mL of $H_2O_2 + 2$ mL of $H_2O + 0.8$ mL of HF resulted in quantitative recovery of Pb, Zn and Cu.
2. 0.8 mL of HF in 10 mL of acid mixture was found to be sufficient and effective for the complete dissolution of lichen matrix independently from the degree of the lichen 'contamination' with siliceous airborne particulates.
3. The addition of more than 0.8 mL of HF in 10 mL of acid mixture used for the lichen digestion resulted in the formation of fluoride.
4. The increase in pressure from 200 to 350 psi proved to be effective in achieving quantitative recovery of Pb, Zn and Cu;
5. A good agreement was achieved between ICP-AES and EMMA-XRF techniques for lichen samples digested using the developed method.

The developed closed-vessel microwave digestion method offers an easy and reliable method for the complete dissolution of lichens and leaves matrices prior to the determination of trace elements and stable Pb isotope ratios. The method was successfully used in the development study of a peat reference material for the determination of elemental concentrations [32] and for the digestion of lichens from the polluted smelter town of Karabash, Russia [33].

Accurate and precise Pb isotope analyses of lichens from the mining site allow assessment of sources of lead pollution.

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