




Express multi-element determination in lake sediments by laser ablation mass-spectrometry (LA-ICP-MS)

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Abstract

Analytical data on major and trace elements concentrations in lake sediments are frequently applied in a wide range of limnological, paleolimnological, and environmental studies. Conventionally applied methods are characterized by time-consuming, expensive, and (or) hazardous sample preparation. The proposed express method of simultaneous multi-element determination in lake sediments by laser ablation inductively coupled plasma mass-spectrometry (LA-ICP-MS) of pressed powdered pellets comprises a minimal sample preparation, special laser sampling, and calibration strategy aimed at overcoming the problems of the sample heterogeneity and application of non-matrix-matched external standards. The optimal sampling strategy, providing the best precision results for our simply pressed powdered pellets, was line scanning ablation with a rate of $10 \mu\text{m s}^{-1}$, a laser spot size of $110 \mu\text{m}$ and a fluence of $8\text{--}9 \text{ J cm}^{-2}$. Calibration strategy including external and internal standardization ensured the best precision ($<5\text{--}10\%$ RSD) and accuracy (within $1\text{--}20\%$ of reference values) even with non-matrix-matched external standards (GSD-1g, NIST SRM 612). In comparison with solution ICP-MS, the method recovered significantly higher range of analytes including 10 major and 49 trace elements and ensured a better accuracy of Zr, Hf, Ti, Nb, Ta, Sn, and Sb measurements. Application of the method to the Urals lake sediments ($n = 32$) showed that LA-ICP-MS results for most trace elements were within $1\text{--}30\%$ of the solution ICP-MS data.

Currently, major, minor, and trace elements concentrations in lake sediments are evaluated in a wide range of studies including reconstructions of paleoclimate and pollution history of watersheds, research of chemical elements behavior in lake ecosystems and in ecological monitoring. Inductively coupled plasma-source mass spectrometry (ICP-MS) is one of the best methods for characterization of different geological materials. Capability for multi-element analysis, high sensitivity, and low detection limits (LODs) are advantages of ICP-MS. Tedious sample preparations, the risk of contamination, and the potential loss of volatile elements (e.g., B, Se, As, Hg, and Sb) are disadvantages of solution ICP-MS techniques (Pupyshev and Surikov 2006; Becker 2007). Moreover, methods involving beaker hot plate HF-HNO₃-acid digestion often fail to completely digest bulk samples, that is, refractory minerals (Peters and Pettke 2016). Some of these deficiencies can be overcome with the help of direct analysis of non-destructive sediment. X-ray fluorescence (XRF) is often applied for this purpose. It is a well-accepted and actively used

analytical method to investigate the elemental composition of non-destructive materials including marine and terrestrial sediments (Rothwell and Rack 2006; Kalugin et al. 2007; Amosova et al. 2019). The XRF core scanning allows for the investigation of sediment records on subannual timescales, which is especially important for finely laminated or varved sediments (Croudace et al. 2006). However, XRF determination of trace elements often suffers from high LODs.

Laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) combining the advantages of ICP-MS and XRF has become one of the most widely applied techniques for direct solid analysis. The LA-ICP-MS analysis are capable for determination of trace, minor, and major elements simultaneously without requiring the use of multiple dilution sets as in digestion methods (Arroyo et al. 2009). LA-ICP-MS scanning of the embedded or dried blocks of lake sediments cores provides high resolution (up to $10 \mu\text{m}$) geochemical records of both major and trace elements concentrations (Rauch et al. 2006; Jilbert et al. 2008). However, such analysis could mostly provide only semi-quantitative results. In addition, tailing signals which often appeared at the layers transitions

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could significantly spoil a high resolution record (Hennekam et al. 2015). Moreover, sample preparation for laser scanning is very time-consuming and requires a great caution to a core disturbance during all steps of procedure. Meanwhile, many lake sediments studies need accurate quantitative elemental analysis and do not require such a high resolution. Bulk elemental analysis by LA-ICP-MS of different types of pellets could give accurate and reproducible data. The resolution of geochemical record in this case will depend on the sample technique and can be less than 1 mm when applying freeze coring which is enough for most paleolimnological studies (Dolor et al. 2009).

Sediments for direct bulk elemental analysis are often prepared as fused disks (Ødegård and Hamester 1997; Wu et al. 2018; Amosova et al. 2019), resin-embedded samples (Hennekam et al. 2015; Shaheen et al. 2017) or pressed pellets in the presence of a binder (Klemm and Bombach 2001; Peters and Pettke 2016). The application of fusion increases a sample preparation time and could provide contamination (Eggins 2003; Wu et al. 2018). It also may be problematic for analytes with low boiling points (below 1000°C), like Hg, As, Cd, Pb, and Zn, which could be volatilized during this step (Zhang et al. 2016). Binding agents create high blanks and might introduce contamination and dilution of the sample (Sylvester 2001). The resin embedding of powdered sediments is a very time-consuming procedure (Hennekam et al. 2015; Shaheen et al. 2017). Simple pressing of sediments into pellets without any binding agents, fusion, and resin embedding makes it possible to avoid these problems. This procedure is very attractive due to its simplicity and potential for quick analysis of a large number of samples. However, this simple technique has several limitations the main of which are a high sample heterogeneity and problems with pellet stability leading to a low analyses precision and accuracy (Limbeck et al. 2015).

These problems can be resolved, in part, by using of special milling techniques which makes it possible to obtain high precision ranged from 2% to 6% depending on the sample and accuracy within 8–15% (Arroyo et al. 2009). However, special milling protocol for all types of lake sediments is very hard to obtain due to their highly diverse mineral composition. It is the mix of hard and soft minerals, which could enhance grain cohesion with fineness, restricting further grinding as the material stuck to the grinding media (Mukherjee et al. 2013).

The previous evaluation of LA-ICP-MS analysis of pressed sediment pellets without fusion, binding agents, special milling, and homogenization procedures provided semiquantitative data (Durrant and Ward 1993) or acceptable quantitative data only for one (Tao et al. 2002) or a narrow list of trace elements (Baker et al. 1999; Lee et al. 2003). Difficulties with precise and accurate data of a wide list of major and trace elements concentrations in pressed pellets by LA-ICP-MS could be associated with a non-optimal sample and calibration strategy, problems with laser settings choice, application of

poorly absorbed longer laser wavelength, and Ar as the only in-cell carrier gas, uncertainties in external standards and matrix effect.

Matrix effect (matrix-dependent fractionation) which appears during ablation is an outstanding problem of LA-ICP-MS. It depends on the internal structure of the substance (melting point, evaporation, thermal conductivity, absorption, and reflection coefficients, etc.). The difficulties with accurate quantitative analysis could appear due to various ablation degrees of the sample and reference material (RM). Involvement of the RM with a matrix composition similar to the analyzed sediments usually eliminates this effect. The most analytical research works based on a simple pressed sediments pellets approach used matrix-matched external standardization (Durrant and Ward 1993; Dolor et al. 2009; Duodu et al. 2015). Arroyo et al. (2009) emphasized the importance of using matrix-matched standards for soil analysis. However, a diversity of sediments compositions and a lack of suitably well characterized RMs for calibration complicate the selection of an appropriate matrix-matched external standard. Meanwhile, the review of a wide range of research works has shown that external calibration using ablation of a solid reference standard, in conjunction with internal standardization, could provide accurate results, even without matrix matching of sample and reference standard. It was suggested to be related to similar elemental fractionation behavior of internal standard and analyte (Jackson 2008 and references therein; Mukherjee et al. 2013). As shown in previous studies, femto-second (fs) laser is less prone to matrix-related problems when compared with ns laser (Poitrasson et al. 2003; Li et al. 2016) which was applied in this study. However, ns-LA-ICP-MS could provide the same quality of analytical results as fs-LA-ICP-MS, subject to the choice of the right laser settings (Li et al. 2016).

Our study was focused on evaluation of potential and limitations of LA-ICP-MS simultaneous multi-element determination in pressed powdered pellets of different types of lake sediments without application of any binders, special milling protocol, and matrix-matched external standardization. The final objective was the development and validation of the simple protocol for simultaneous precise and accurate quantitative multi-element determination in lake sediments based on experiments with laser parameters, sampling, and calibration strategies, different internal standards and comparison between matrix-matched pressed powdered pellets or non-matrix matched synthetic glasses calibrators.

Materials and procedures

Materials

Experiments with laser settings and sampling strategy were performed using several types of Urals lake sediments (32 samples) and reference materials (JLk-1 and BIL-1). Urals lake clay was enriched in lithophile elements (Si, Ti, Al, Na, and K) and

Table 1. Main composition of the studied Urals lake sediments.

% m m ⁻¹	Clay <i>n</i> = 9		Organic-rich gyttja <i>n</i> = 16		Carbonate-rich gyttja <i>n</i> = 7	
	Mean	Range	Mean	Range	Mean	Range
SiO ₂	45	44–46	41	35–50	5.7	1.7–8.5
TiO ₂	1.1	0.68–1.2	0.37	0.19–0.59	0.07	0.04–0.12
Al ₂ O ₃	11	10–13	6.2	3.8–9.0	1.2	0.5–2.3
Fe ₂ O ₃	6.8	5.4–9.3	5.0	2.1–7.6	1.4	0.6–2.5
MnO	0.12	0.08–0.19	0.08	0.02–0.19	0.09	0.06–0.14
MgO	2.6	2.1–3.2	2.14	0.37–3.7	0.85	0.68–1.14
CaO	8.1	4.9–11.2	1.2	0.30–2.1	32	23–38
Na ₂ O	1.2	0.88–2.2	0.63	0.14–1.08	0.18	0.13–0.26
K ₂ O	2.1	1.9–2.3	0.70	0.28–1.18	0.24	0.13–0.42
P ₂ O ₅	0.14	0.13–0.16	0.21	0.12–0.36	0.11	0.1–0.14
C _{org.}	1.5	0.76–2.8	15.07	13.6–18.0	4.7	1–11

depleted in organic matter (Table 1). Organic-rich gyttja was characterized by high concentration of organic matter and carbonate-rich gyttja was distinguished by high content of carbonates, Sr, Ca and depleted in organic matter and lithophile elements (Maslennikova and Udachin 2017).

LA-ICP-MS calibration was accomplished using lake sediments powdered pellets JLk-1, BIL-1, synthetic carbonate MACS-3, synthetic glasses GSD-1g and NIST SRM-612. In addition, JLk-1 and BIL-1 were analyzed as unknowns to evaluate the analytical performance of the proposed methodology. JLk-1 is the reference sample developed by the Geological Survey of Japan. It is freshwater lake sediment with a particle size of less than 18.6 μm collected from Lake Biwa (Terashima et al. 1990). BIL-1 is the RM developed by the Institute of Geochemistry, SB RAS, Russia. According to the certificate of analysis, the RM consists of Lake Baikal sediments with particles of less than 88 μm (Bulnayeve and Vakhromeyev 1993). NIST SRM-612 was developed by the National Institute of Standards and Technology, basalt glass GSD-1g (Jochum et al. 2005) and carbonate MACS-3 (Wilson et al. 2008) was developed by the United States Geological Survey. NIST SRM-612 and GSD-1g have concentrations of all trace elements which are similar and high enough for a precise primary calibration (about 50 mg g⁻¹). The major element composition of NIST SRM-612 is very different from that of any geological matrix. Major element composition of GSD-1g is similar to rocks.

The synthetic glasses are better characterized than lake sediments RMs (JLk-1 and BIL-1) and have homogeneous distribution of most elements (Jochum and Enzweiler 2014). Calcium carbonate powdered pellet MACS-3 contains more than 60 trace elements with high concentrations. The pellet is less homogeneous compared with reference glasses, which are homogeneous in the nanogram to microgram test portion mass range (Jochum et al. 2019). The recommended values of

major and trace elements for the reference materials were taken from the GeoReM (v.18) database (Jochum et al. 2005; <http://georem.mpch-mainz.gwdg.de>).

For ICP-MS solution method, chemically pure acids HNO₃, HF, and HCl were additionally purified with the BSB-939-IR distillation equipment (Berghoff, Germany). Deionized ultra-pure water was used for dilution. Lake sediment powder of JLk-1 and BIL-1 were used to evaluate the performance of solution ICP-MS. Standard multi-element solution of Agilent for all measuring concentrations was applied for calibration. Solution of In (concentration of 1000 $\mu\text{g L}^{-1}$) was used as an internal standard.

Pressed powdered pellets preparation

Since the purpose of our work was an obtaining of the simple protocol of simultaneous multi-element analysis, we did not use any expensive equipment or special milling technique (e.g., Arroyo et al. 2009; Garbe-Shönberg and Müller 2014). The lake sediment samples were dried and then ground to powder with a simple agate mortar. Lake sediments RMs (JLk-1 and BIL-1) were analyzed directly without grinding. Mixed and powdered lake sediments samples, as well as JLk-1 and BIL-1 were inserted into the stainless steel die and pressed by a PW-20 Brand Erbisdorf hydraulic press with a constant evacuation of air from the mold by a vacuum pump to form 1 mm thick pellets. The parameters of pressure and time of pressing depend on the pellet diameter. Stable pellets with a diameter of 13 mm were formed under a pressure of 15 t for 5 min. For tablets of smaller diameter, a pressure may be significantly decreased. Several pellets were fixed with a double-sided tape on a glass slide and placed into a laser ablation cell. The number of pellets depends on a size of laser ablation cell and a diameter of pellets.

LA-ICP-MS analysis

Lake sediments were analyzed using an Agilent 7700x ICP-MS coupled to a New Wave Research UP-213 nm laser ablation system owned by the Southern Urals Science Center, Russia. Lake sediments contain both easily (organic matter, carbonates, sulfides) and hard (silicates) ablated material. Thus, intermediate values of repetition rate (10 Hz) were used for lake sediments pellets. Different laser parameters including ablation modes (single spot or line sampling), scanning rates (1–2 or 10 $\mu\text{m s}^{-1}$) and fluence (3.5–12.5 J cm^{-2}) were evaluated for lake sediments pellets and GSD-1g which is characterized by the same degree of ablation (Table 2).

NIST SRM-612 is relatively hard to ablate. So, high repetition rate of 20 Hz and fluence of 23–25 J cm^{-2} were applied for this glass. To reduce the sample heterogeneity effect on the LA-ICP-MS analysis accuracy and precision, we used large laser spot size (110 μm).

The detection limits were calculated with the Iolite software by the Normal method based on Longerich et al. (1996) and was used as a measure of sensitivity. The values reported (Table 3) is a mean value for 6 replicates of the LOD obtained after running the Jlk-1 and BIL-1. Production of molecular oxide species (i.e., $^{232}\text{Th}^{16}\text{O}/^{232}\text{Th}$) and doubly-charged ion species (i.e., $^{140}\text{Ce}^{++}/^{140}\text{Ce}^{+}$) was maintained at levels below 0.2%.

Calibration strategy

Laser sampling might result in a hugely variable amount of material being delivered to the ICP-MS, depending on how well the laser beam couples to the sample. Calibration strategies have been developed to correct for the variable “ablation yields” (Sylvester 2008). We use two variants of calibration

Table 2. LA-ICP-MS operating conditions for measurements on lake sediments pressed pellets.

ICP-MS type	Agilent 7700x
RF power	1550 W
Plasma gas	Ar (15 L min^{-1})
Auxiliary gas	Ar (1.0 L min^{-1})
Carrier gas	Ar (1.06 L min^{-1}) + He (0.65 L min^{-1})
Laser type	Nd-YAG (new wave research UP-213)
Wavelength	213 nm
Sampling strategy	Line sampling
Ablation line length	1500 μm
Scanning rate	10 $\mu\text{m s}^{-1}$
Repetition rate	10 Hz
Fluence	8–9 J cm^{-2}
Measurement delay	1 min
Ablation spot size	110 μm
Preablation time	10–15 s
Ablation time	180–205 s
Sample time	10–30 ms

strategy: external calibration by ablation of a solid reference standard only and external calibration by ablation of a solid reference standard plus internal standardization (Jackson 2008). We compared results obtained with application of both matrix-matched RMs (MACS-3—for carbonate-rich gytija, Jlk-1 and BIL-1 for other types of lake sediments) and non-matrix-matched RMs (NIST SRM-612 and GSD-1g).

The internal standard is employed to correct for ablation efficiency differences between the sample and external standards. Internal standardization also corrects for matrix suppression/enhancement effects and signal drift in the ICP-MS (Jackson 2008). We tested several internal standards (^{57}Fe , ^{43}Ca , ^{29}Si , ^{27}Al , and ^{55}Mn) to find the optimal for different types of lake sediments in applied analytical parameters. The calculation was carried out with the Iolite software (Paton et al. 2011) using naturally occurring internal standards.

Solution methods

For comparison with LA-ICP-MS, Jlk-1, BIL-1, and Urals lake sediments ($n = 32$) were also analyzed by ICP-MS. Samples (60 mg) digestion was carried out in the glassy carbon crucibles with a mixture of HF, HCl, and HNO_3 . For comparison of digestion methods lake sediments samples ($n = 7$), Jlk-1 and BIL-1 were also digested in a SpeedWave microwave decomposition system (Berghoff, Germany) in PTFE autoclaves with two-stage heating to a temperature of 180°C for 40 min in a mixture of HF, HCl, and HNO_3 . Further destruction of the fluoride complexes was carried out by a double evaporation of the dry sample residue with concentrated HNO_3 at a temperature of 110°C. Afterwards, obtained residues were dissolved in a hot solution of 0.5 N HNO_3 . Prepared solutions were analyzed by ICP-MS with an Agilent 7700x instrument using the MassHunter software package. ICP-MS data for lake sediments were obtained after digestion in glassy carbon crucibles using Agilent 7700x in the South Urals Research Center of Mineralogy and Geoecology, UB RAS ($n = 17$), Perkin Elmer ELAN 6000 in the Ural Electrochemical Integrated Plant ($n = 10$), Perkin Elmer ELAN 9000 in the Institute of geology and geochemistry, UB RAS ($n = 25$). Several samples ($n = 8$) was analyzed in all three labs and then compared for agreement evaluation.

The concentrations of internal standards in lake sediments were determined by complexometric and photometric methods (HCAM 138-X 2015) in the South Urals Research Center of Mineralogy and Geoecology, UB RAS. Quality assurance was provided by determination of elemental concentrations for duplicate samples and lake sediments reference samples (BIL-1 and BIL-2). Accuracy was within 1–4% for SiO_2 and Fe_2O_3 , 0.8–1.5% for Al_2O_3 , 1–8% for MnO and CaO. Relative standard deviation (% RSD) varied from 0.4% to 7%: SiO_2 (<2%), Al_2O_3 (<1%), F_2O_3 (<3%), MnO (<4%), CaO (<7%).

Table 3. Recovery, relative standard deviation (RSD) and limit of detection (LODs) of major, minor and trace elements in Jlk-1 and BIL-1 by LA-ICP-MS. GSD-1g—External standard, AI—Internal standard.

JLK-1		BIL-1										
Element	GeoReM value ($\mu\text{g g}^{-1}$)	Uncertainty ($\mu\text{g g}^{-1}$)	This work ($\mu\text{g g}^{-1}$)	RSD (%)	Recovery (%)	LOD ($\mu\text{g g}^{-1}$)	GeoReM value ($\mu\text{g g}^{-1}$)	Uncertainty ($\mu\text{g g}^{-1}$)	This work ($\mu\text{g g}^{-1}$)	RSD (%)	Recovery (%)	LOD ($\mu\text{g g}^{-1}$)
⁷ Li	54.7	2.79	54.4	0.8	99	0.038	37	4	45.3	2.5	122	0.04
⁹ Be	2.9	0.48	3.2	1.7	110	0.0315	2.7	0.4	2.8	0.5	103	0.028
¹⁰ B	45.7	3.2	46.2	2.7	101	0.34	34	6	27.5	26.6	81	0.26
²³ Na	7790	130	5751.3	2.5	74	1.2	14,540	520	12,506	5.4	86	4.6
²⁵ Mg	10,600	300	11,269	0.6	106	2.8	12,061	422	13,450	4.6	112	3.5
²⁷ Al	88,500	3600	88,016	1.3	99	14	71,819	690	74,056	1.8	103	18
²⁹ Si	266,850	1900	228,966	0.7	86	57	285,465	1215	260,166	3.1	91	82
³¹ P	900	300	726	0.9	81	2.5	1506	65	1216	8.2	81	3.6
³⁹ K	23,000	1500	23,653	1.2	103	4.5	18,346	665	18,913	1.5	103	4
JLK-1		BIL-1										
Element	GeoReM value ($\mu\text{g g}^{-1}$)	Uncertainty ($\mu\text{g g}^{-1}$)	This work ($\mu\text{g g}^{-1}$)	RSD (%)	Recovery (%)	LOD ($\mu\text{g g}^{-1}$)	GeoReM value ($\mu\text{g g}^{-1}$)	Uncertainty ($\mu\text{g g}^{-1}$)	This work ($\mu\text{g g}^{-1}$)	RSD (%)	Recovery (%)	LOD ($\mu\text{g g}^{-1}$)
⁴³ Ca	4970	150	4784	4.6	96	18	13,222	643	13,346	8.1	101	24
⁴⁵ Sc	16	0.44	17.6	0.9	110	0.022	13	2	16.3	6.7	126	0.031
⁴⁹ Ti	4060	90	4393	2.0	108	1.2	4137	180	4266	6.8	103	1.6
⁵¹ V	116	7.6	129	0.3	111	0.044	110	10	128	4.7	117	0.046
⁵² Cr	69	3.4	70.2	2.5	102	0.13	66	4	76.7	5.2	116	0.23
⁵⁵ Mn	2090	30	2170	1.0	104	0.29	3100	155	3706	8.1	120	0.69
⁵⁷ Fe	47,000	800	53,623	0.8	114	7.8	61,537	1750	58,596	2.2	95	12
⁵⁹ Co	18.1	0.72	19.6	1.2	108	0.014	18	2	19.4	3.1	108	0.017
⁶⁰ Ni	36.9	3.12	39.7	0.4	108	0.031	54	6	55.2	4.1	102	0.047
⁶⁵ Cu	59.8	4.9	70.3	1.6	118	0.059	52	7	59.7	1.1	115	0.063
JLK-1		BIL-1										
Element	GeoReM value ($\mu\text{g g}^{-1}$)	Uncertainty ($\mu\text{g g}^{-1}$)	This work ($\mu\text{g g}^{-1}$)	RSD (%)	Recovery (%)	LOD ($\mu\text{g g}^{-1}$)	GeoReM value ($\mu\text{g g}^{-1}$)	Uncertainty ($\mu\text{g g}^{-1}$)	This work ($\mu\text{g g}^{-1}$)	RSD (%)	Recovery (%)	LOD ($\mu\text{g g}^{-1}$)
⁶⁶ Zn	151	10	198.6	2.2	132	0.17	96	14	144	3.5	150	0.19
⁷¹ Ga	21.4	2.73	24.0	2.4	112	0.028	16	2	19.3	2.4	120	0.021
⁷² Ge	2.22		2.0	4.4	90	0.053	1.4	0.2	2.4	11.1	173	0.062
⁷⁵ As	24	7.9	25.7	2.0	107	0.078	18	3	15.5	3.2	86	0.091
⁷⁷ Se	0.641	0.199	0.5	6.8	73	0.057	—	—	0.6	14.3	—	0.095

(Continues)

Table 3. Continued

JLK-1	GeoReM						BIL-1					
	value ($\mu\text{g g}^{-1}$)	Uncertainty ($\mu\text{g g}^{-1}$)	This work ($\mu\text{g g}^{-1}$)	RSD (%)	Recovery (%)	LOD ($\mu\text{g g}^{-1}$)	value ($\mu\text{g g}^{-1}$)	Uncertainty ($\mu\text{g g}^{-1}$)	This work ($\mu\text{g g}^{-1}$)	RSD (%)	Recovery (%)	LOD ($\mu\text{g g}^{-1}$)
⁸⁵ Rb	144	10.8	151	1.5	105	0.053	93	5	103	1.7	111	0.044
⁸⁸ Sr	69	4.56	54.4	2.9	79	0.02	266	30	240	2.9	91	0.094
⁸⁹ Y	40.8	5.52	38.7	1.5	95	0.013	30	4	30.6	13.6	102	0.021
⁹⁰ Zr	146	8.72	117	5.0	80	0.03	156	13	115.1	14.5	74	0.088
⁹³ Nb	15.8	1.35	16.2	3.3	103	0.0085	12	2	12.5	18.1	104	0.0089
⁹⁵ Mo	2	0.41	1.8	4.2	91	0.01025	2.9	0.5	4.1	3.9	141	0.013
JLK-1	GeoReM	Uncertainty	This	RSD	Recovery	LOD	GeoReM	Uncertainty	This	RSD	Recovery	LOD
	value ($\mu\text{g g}^{-1}$)	($\mu\text{g g}^{-1}$)	work ($\mu\text{g g}^{-1}$)	(%)	(%)	($\mu\text{g g}^{-1}$)	value ($\mu\text{g g}^{-1}$)	($\mu\text{g g}^{-1}$)	work ($\mu\text{g g}^{-1}$)	(%)	(%)	($\mu\text{g g}^{-1}$)
¹⁰⁷ Ag	0.205	0.007	0.3	3.8	129	0.0035	—	—	0.2	7.8	—	0.0031
¹¹¹ Cd	0.54	0.015	0.5	1.7	85	0.0215	—	—	0.2	1.5	—	0.036
¹¹⁵ In	0.106	0.005	0.1	0.1	138	0.0029	—	—	0.1	10.5	—	0.0024
¹¹⁸ Sn	5.6	0.1	4.8	3.2	86	0.023	3.2	0.5	2.8	28.1	88	0.031
¹²¹ Sb	1.68	0.53	2.4	6.8	144	0.0125	—	—	1.0	7.6	—	0.012
¹³³ C	12.4	1.9	14.1	1.6	114	0.0094	6	1	7.2	1.6	119	0.0091
¹³⁷ Ba	574	43.8	558.	3.5	97	0.17	710	70	678.3	2.6	96	0.25
¹³⁹ La	41.3	1.33	37.7	3.2	91	0.012	45	6	45.9	10.1	102	0.014
¹⁴⁰ Ce	89.1	9.5	88.2	3.2	99	0.034	80	5	92.1	11.8	115	0.05
¹⁴¹ Pr	8.42	1.64	9.0	2.7	107	0.0042	—	—	10.7	14.0	—	0.0071
JLK-1	GeoReM	Uncertainty	This	RSD	Recovery	LOD	GeoReM	Uncertainty	This	RSD	Recovery	LOD
	value ($\mu\text{g g}^{-1}$)	($\mu\text{g g}^{-1}$)	work ($\mu\text{g g}^{-1}$)	(%)	(%)	($\mu\text{g g}^{-1}$)	value ($\mu\text{g g}^{-1}$)	($\mu\text{g g}^{-1}$)	work ($\mu\text{g g}^{-1}$)	(%)	(%)	($\mu\text{g g}^{-1}$)
¹⁴⁷ Sm	8.04	0.45	7.6	4.4	94	0.012	7	1	7.7	11.5	110	0.012
¹⁵¹ Eu	1.35	0.07	1.3	2.9	94	0.00225	1.4	0.2	1.4	9.2	103	0.0038
¹⁵⁷ Gd	5.6	0.82	7.2	2.5	129	0.007	—	—	6.7	10.2	—	0.014
¹⁵⁹ Tb	1.25	0.12	1.1	1.0	85	0.00093	—	—	0.9	10.5	—	0.0024
¹⁶³ Dy	6.54	0.79	6.6	0.1	102	0.009	—	—	5.4	12.8	—	0.0081
¹⁶⁵ Ho	1.4	0.42	1.3	1.8	95	0.0017	—	—	1.0	10.9	—	0.0015
¹⁶⁶ Er	3.53	0.42	3.9	1.4	110	0.00475	—	—	3.1	11.6	—	0.0067
¹⁶⁹ Tm	0.6	0.097	0.5	1.0	90	0.0009	—	—	0.4	13.7	—	0.0012
¹⁷² Yb	4.09	0.34	3.8	1.9	92	0.0055	2.9	0.4	2.9	14.3	101	0.0091
¹⁷⁵ Lu	0.6	0.079	0.5	2.1	91	0.000935	0.4	0.05	0.4	12.4	109	0.0012

Element	JLk-1					BIL-1						
	GeoReM value ($\mu\text{g g}^{-1}$)	Uncertainty ($\mu\text{g g}^{-1}$)	This work ($\mu\text{g g}^{-1}$)	RSD (%)	Recovery (%)	LOD ($\mu\text{g g}^{-1}$)	GeoReM value ($\mu\text{g g}^{-1}$)	Uncertainty ($\mu\text{g g}^{-1}$)	This work ($\mu\text{g g}^{-1}$)	RSD (%)	Recovery (%)	LOD ($\mu\text{g g}^{-1}$)
^{179}Hf	3.93	0.28	3.2	3.9	82	0.0095	3.9	0.7	3.1	15.7	79	0.012
^{181}Ta	1.57	0.37	1.2	2.7	77	0.0015	0.84	0.15	0.8	25.9	99	0.0023
^{182}W	2.6	0.16	3.1	1.4	118	0.0095	—	—	4.6	6.9	—	0.012
^{197}Au	0.005	0.002	0.0073	13.2	146	0.0050	—	—	0.0056	20.7	—	0.0045
^{205}Tl	1.11	0.32	1.2	1.9	106	0.0057	—	—	0.6	0.7	—	0.0026
^{208}Pb	45	3.7	57.7	1.9	128	0.032	21	3	28.5	0.8	135	0.024
^{209}Bi	1.13	0.04	1.4	3.7	127	0.006	—	—	0.5	5.6	—	0.00335
^{232}Th	19.5	0.92	18.2	2.3	93	0.012	12.7	1.3	14.6	6.5	115	0.014
^{238}U	3.83	0.4	4.2	5.0	110	0.0028	12	1.1	14.6	3.3	122	0.012

Precision, accuracy and trueness

In order to report a precision, we analyzed three replicate laser tracks over the same sample (for LA-ICP-MS) and applied three replicate measurements of the sample solution (for ICP-MS). A precision (repeatability) of the LA-ICP-MS and ICP-MS measurements was reported as % RSD. Accuracy and trueness were assessed using JLk-1 and BIL-1 and were expressed as a percentage recovery: measured value/GeoReM value (for accuracy) and average measured value ($n = 3$)/GeoReM value (trueness).

Assessment

Optimization of analytical parameters

All obtained pellets had mechanical stability suitable for laser ablation micro-analysis. Organic matter or clay minerals could be performed as natural binders of the lake sediments. The best stability was obtained for organic-rich gyttja pellets. The lake clay, JLk-1, BIL-1 formed less stable pellets. The least stable but steel suitable pellets were prepared from carbonate-rich gyttja. Lake sediments have heterogeneous and variable mineral composition. So analytical parameters were optimized to overcome the heterogeneity of the pellets and to increase an analytical precision.

Quintupled (213 nm) energy is highly absorbed by a wide range of materials (Longerich 2008). The use of shorter laser wavelength improves the stability of plasma mass load during the analysis due to the concentration of laser energy in a smaller sample volume which is more completely vaporized. The particles produced by LA with a wavelength of 213 nm are smaller and more uniform than for 266 nm ablation, leading to more complete evaporation in the Ar plasma of the ICP (Günther and Koch 2008). Aerosol plume expands more rapidly into the lighter He gas than Ar gas and is thus more efficiently removed from the cell. The use of He as the in-cell carrier gas reduces the amount of material deposited around the crater rim and thus increases sensitivity (Eggins et al. 1998). So, it was expected that ablation in He and short wavelength will result in improved precision of laser ablation ICP-MS measurements in comparison with the earlier research focused on the LA-ICP-MS analysis of the simple pressed pellets (e.g., Durrant and Ward 1993; Baker et al. 1999).

A fluence and scanning rate were firstly determined empirically based on the experiments with geometry of laser crater. The best scanning ablation crater with the less debris was obtained in the conditions presented in Table 2. Then it was confirmed by assessment of precision for JLk-1, BIL-1, and Urals lake sediments samples at different analytical parameters (Supporting Information, Table S1). Line scanning in comparison with spot sampling improved precision in all analyzed samples. It was associated to a relatively constant supply and size distribution of particles to the ICP, provided by scanning ablation. Time-dependent variation in signal intensity reduced and constant plasma mass load produced which suppressed

the elemental and isotopic fractionation (Kořler 2008). In addition, line scanning could average out the local inhomogeneities, which result in more precise measurements (Baker et al. 1999). We did not observe any common regularities of changes in precision in dependence on fluence. However, the best scanning ablation crater with the less debris for most pellets was obtained under a fluence of 8–9 J cm⁻². An increase in ablation rate from 2 to 10 μm s⁻¹ significantly improved precision in all analyzed samples (RSD < 5–10% for most analytes) due to ablation from a larger sample surface area, eliminating sample heterogeneity.

Therefore, line scan ablation, a fluence of 8–9 J cm⁻², and scanning rate of 10 μm s⁻¹ were used in the lake sediment analysis. Increase in laser scanning rate improved the signals of the most analytes. Si and Na had a less signal intensity increase in comparison with other analytes, which implicated relatively incomplete ablation of quartz and feldspar in selected analytical parameters. This fractionation could lead to underestimation of Si and Na concentrations in the samples and overestimation of other analytes concentrations when using Si or Na as internal standards.

Calibration strategy choice

We compared trueness, accuracy and precision of JLk-1 and BIL-1 measurements with application of different calibration strategies and calibrators: (1) external calibration using ablation of a solid reference standard only; (2) external calibration using ablation of a solid reference standard plus internal standardization. As a reference material, we used lake sediments pressed powdered pellets RMs (BIL-1 for JLk-1 and JLk-1 for BIL-1) or synthetic glass standards (GSD-1g and NIST SRM-612) (Fig. 1).

Internal standardization improved a precision especially with non-matrix-matched standards, (Supporting Information, Table S2). The lowest but acceptable precision (RSD < 12% for most analytes) was obtained without internal standardization

with synthetic glass as calibrator. LA-ICP-MS without internal standardization even with matrix-matched external standards gave a significant excess of most elements concentrations for applied analytical parameters. Exceptions were a high ionization potential elements: As, P, B, Se, and Cd.

Internal and external standard choice

⁵⁷Fe, ⁴³Ca, ²⁹Si, ²⁷Al, and ⁵⁵Mn were tested as internal standards. The best precision for JLk-1, BIL-1, and organic-rich gyttja was observed with application of Al, Si, or Fe; for carbonate-rich gyttja, with Ca and Mn; and for lake clay, with Fe, Al, Si, or Mn as internal standards (Supporting Information, Table S3). These regularities could easily be explained by concentration and distribution of internal standards in different types of sediments. According to Jackson (2008), internal standard should be homogeneously distributed in the ablation volume and presented in the sample and standard at sufficient concentration. For instance, organic-rich gyttja depleted in Ca and carbonate-rich gyttja depleted in Fe were characterized by a low precision when using these elements as internal standards. The choice of internal standard is also dependent on external standard. For instance, application of Fe and Mn as internal standards with NIST SRM 612 as calibrator provides poor precision and inaccurate results due to relatively low concentrations of Fe and Mn in this synthetic glass.

An appropriate agreement with reference values for JLk-1 in selected analytical parameters was obtained with Al as internal standard (Table 3). The best agreement with ICP-MS data when using GSD-1g and JLk-1 as calibrators was provided with Ca for carbonate-rich gyttja and Fe for organic-rich gyttja. Fe and Al for lake clay were performed equally well (Supporting Information, Table S4).

Application of Si as internal standard lead to overestimation of all elements except for Na due to incomplete ablation of Si and Na minerals under selected laser sampling parameters. External calibration using ablation of a solid

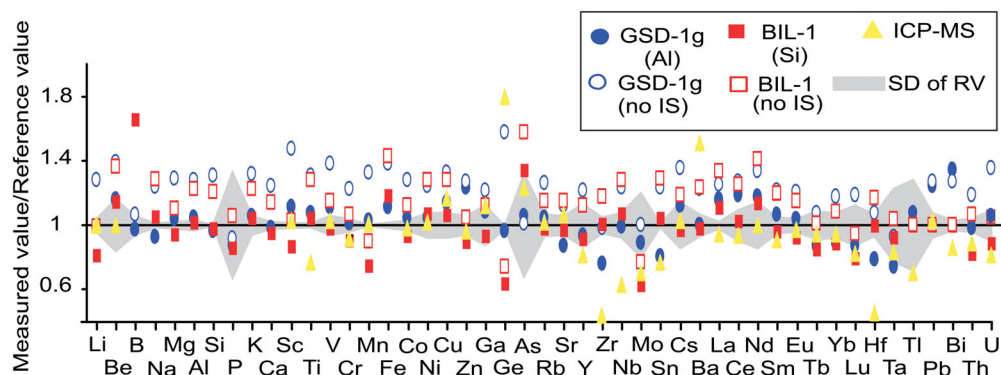


Fig. 1. Comparison of JLk-1 GeoREM values (Jochum et al. 2005) and LA-ICP-MS measurements of this study obtained with application of different calibration strategies and external standards. Data symbols are represented as circles when using GSD-1g as external standard and filled in color with application of internal standard (Al); represented as squares when using BIL-1 as external standard and filled with application of internal standard (Si); represented as triangles for solution ICP-MS. Gray line—SD of reference value (RV).

reference standard plus internal standardization did not provide any improvement in precision, accuracy and trueness when using matrix-matched standards (JLk-1, BIL-1, MACS-3) in comparison with synthetic glass standards (NIST SRM 612, GSD-1g). Thus, our results for lake sediments confirmed the opportunity of application of well characterized non-matrix-matched standards as calibrators when using an appropriate internal standard (Jackson 2008; Mukherjee et al. 2013).

Analytical results of LA-ICP-MS

A final precision value of LA-ICP-MS (with internal standardization and optimal analytical parameters) for JLk-1 could be compared with that of solution ICP-MS (RSD < 5% for most analytes) (Table 3, Supporting Information, Table S5). A good precision value for BIL-1 and lake sediments samples could be compared with that obtained for river sediments after special wet-milling procedure (RSD < 10% for most analytes) (Duodu et al. 2015) (Table 3, Supporting Information, Table S3). Better precision for JLk-1 could be related to a less particle size (<18.6 μm) in comparison with lake sediments samples and BIL-1 (<88 μm). This confirmed the conclusion that particle size of sediments influences the precision (Baker et al. 1999). Precision of Urals lake sediments analysis in the optimal analytical parameters was depended on particle size and mineral composition. The poorest precision (12–20% for most elements) was obtained for a sample of clastic-rich gyttja with a median particle size of 45–50 μm and abundance of resistant minerals (quartz, garnet, feldspar). A poor precision in all samples was obtained for Au (RSD = 13–42%) characterized by concentration levels near the respective LODs. Several lake sediment samples had poor precision (RSD = 13–20%) for Zr, Hf, REE, Ti, Cr, Nb, and Ta, which could be due to a presence of resistant mineral grains in the ablated sample volume (e.g., zircon, rutile, monazite, pyrochlore, chromite). It resulted in a distinct increase of corresponding analyte intensity in the spectrum. For example, variations in LA signal of Zr and Hf indicating a well-known zircon effect (e.g., Peters and Pettko 2016) are presented on Fig. 2.

Analyses of the lake sediments RMs (JLk-1 and BIL-1) were used to ascertain trueness, accuracy and sensitivity of the method. Compiled values of GeoReM database were used as representative of the reference values. With few exceptions, major and trace elements in the lake sediments reference materials could be analyzed by LA-ICP-MS within $\pm 20\%$ of the recommended values (Table 3, Fig. 3).

Application of BIL-1 as calibrator provided an overestimation in B (185%), As (139%) and underestimation in Mo (66%) and Ge (62%) (Supporting Information, Table S2). NIST SRM-612 as calibrator ensured unacceptable results for P (17%), Fe (39%), Se (225%), overestimation in Ge (134%) and underestimation in Tl (68%) and Bi (74%). The concentrations of Sb, Na, In, Ta, Pb, and Zn measured using GSD-1g as calibrator are within 30% of the recommended values (Fig. 3, Table 3, Supporting Information, Table S2). Application of

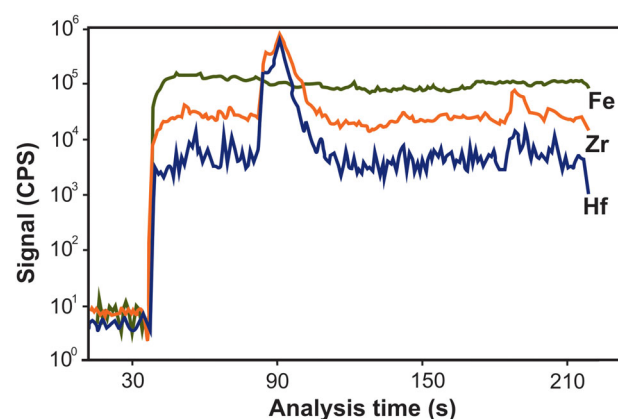


Fig. 2. Time-resolved LA-ICP-MS signals for Fe, Zr and Hf from the analysis of organic-rich gyttja. Increase in Hf and Zr signal intensities shows a “zircon effect”.

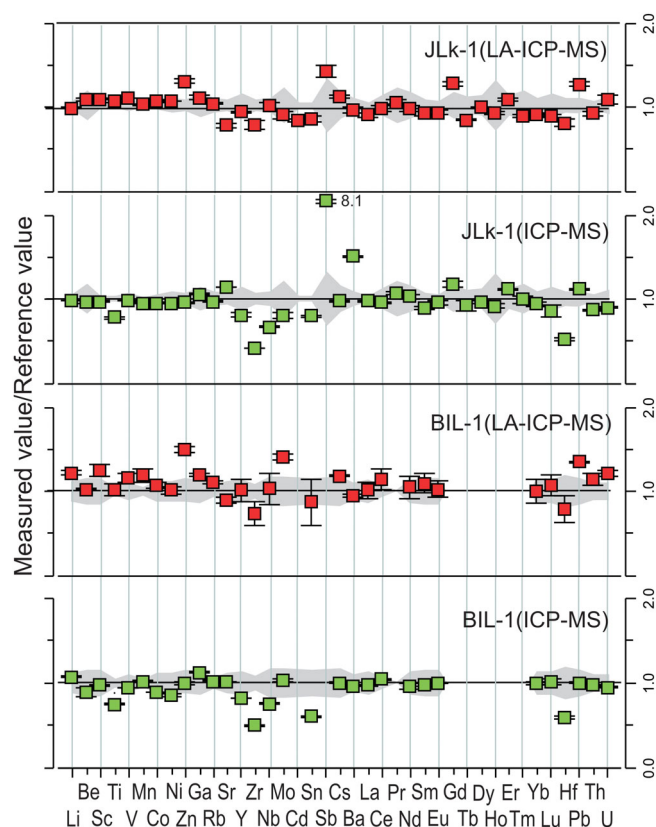


Fig. 3. Plots illustrating LA-ICP-MS and solution ICP-MS measurement trueness and repeatability (precision) for lake sediments reference materials BIL-1 and JLk-1. LA-ICP-MS data listed in Table 3, ICP-MS data listed in Supporting Information, Table S5.

several different RMs as calibrators could minimize the error propagated from reference values (Wu et al. 2018). In addition, inconsistency with recommended values could be associated with uncertainties of GeoReM values of RMs applied as

the sample (BIL-1 and Jlk-1). Significant overestimation in Mo and Ge for BIL-1 as a sample independently on applied calibrator could be caused by the given reference values, which are compiled from a limited number of published values.

Analytical results of solution ICP-MS

Minor and trace elements in Jlk-1 and BIL-1 were analyzed to evaluate performance of ICP solution method. Precision of solution ICP-MS was generally better than LA-ICP-MS. Relative standard deviation was less than 5% for most elements not only for Jlk-1 but for BIL-1 and lake sediments as the samples (Fig. 3, Supporting Information, Table S5).

Almost all trace elements were analyzed within 20% of recommended values. Tl was measured within 30% of recommended values. ICP-MS data for Jlk-1 and BIL-1 were overestimated in Ge (180–259%) and substantially underestimated in Hf, Zr, Nb, Ta, and Ti. The last could be caused by incomplete dissolution of accessory minerals (Yu et al. 2007; Eggins 2003). Ge overestimation could be related to spectral interferences ($^{72}\text{Ge}^{40}\text{Ar} + ^{32}\text{S}$ and $^{40}\text{Ar} + ^{16}\text{O}_2$), which are especially noticeable at low concentration of the analyte. In addition, solution ICP-MS concentrations of Sb in Jlk-1 was significantly different from the recommended values. Concentrations of As, Se (for all samples), Sb, Sn, and W which were obtained in different laboratories for the Urals lake sediments deviated significantly. Two different digestion methods applied to the Urals lake sediments ($n = 7$) in the same laboratory provided significant discrepancies in determination of As, Se, Sb, Sn, Cr, and Hf. Higher concentrations of Sn, Cr, and Hf measured after microwave digestion related to a more complete digestion of refractory minerals (e.g., cassiterite, chrome spinelide, zircon). Questionable data on As, Se, and Sb could be associated with limitations of acid digestion method to determination of volatile elements concentrations.

LA-ICP-MS and solution ICP-MS of Urals lake sediments

Sediment samples ($n = 32$) obtained from six Urals lakes were analyzed to assess how the two methods compare with each other. Recovery of LA-ICP-MS and ICP-MS data for different types of lake sediments for most trace elements varied from 70% to 130% (Supporting Information, Table S6). Siderophile and lithophile elements are distinguished by a good agreement between methods except for Zr, Hf, Ge, and in several cases for Ta, Nb, Ti, and Cr. Chalcophile elements Cu, Zn, Tl, Bi, and Pb give feasible agreement in most cases (Fig. 4). Discrepancies suggested to be related to incomplete dissolution of refractory minerals in the ICP-MS or questionable solution ICP-MS data (As, Se, Sb, Sn, and W). Thus, with few exceptions, the LA-ICP-MS results for studied lake sediments are matched with solution mode and reported values.

Discussion and applications

Thus, the proposed rapid method enables simultaneous analysis of trace and major elements with a precision better

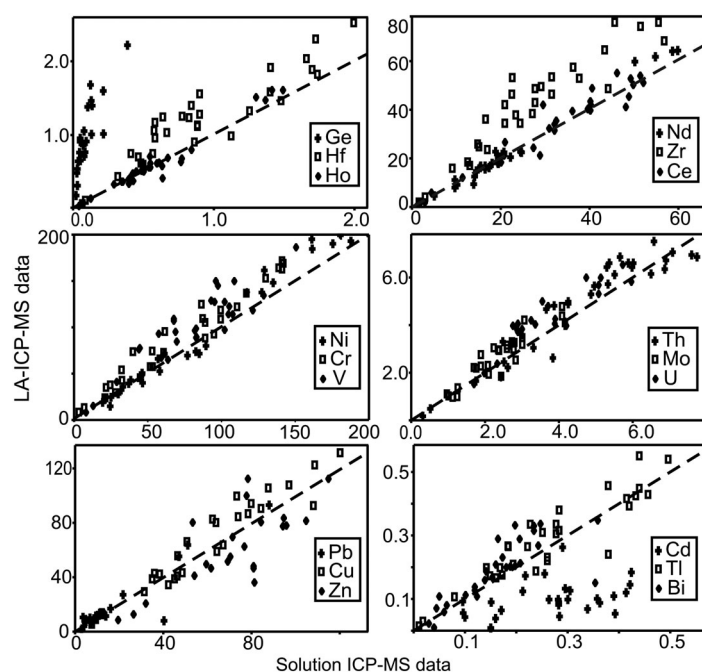


Fig. 4. Comparison between LA-ICP-MS and solution ICP-MS measurements of several trace elements in the Urals lake sediments ($n = 32$). The concentrations are presented in units of $\mu\text{g g}^{-1}$. Recovery data listed in Supporting Information, Table S6.

than 5–10%, reliable accuracy (within $\pm 20\%$ of RMs reference values) and good agreement with solution ICP-MS measurements obtained for most analytes. The main advantage of the method in comparison with XRF is the low limits of detection of trace elements. Compared to solution ICP-MS the method ensured wider range of analytes and provided more reliable data on Zr, Hf, Nb, Ta, Sn, and Sb without time-consuming and hazardous sample preparation. A more straightforward sample preparation in comparison with other LA-ICP-MS approaches of bulk sediments analysis (Peters and Pettke 2016; Shaheen et al. 2017; Wu et al. 2018) not only saves the time but eliminates contamination risk.

Special ablation protocol together with the quantification strategy partly overcome the matrix effects and heterogeneity problems which prevented the obtaining of precise and accurate data. Our results confirmed the possibility of application of well characterized non-matrix-matched external standards (e.g., GSD-1g, NIST-SRM-612) with appropriate internal standard for obtaining of reliable quantitative data for most analytes measured in the lake sediments (Jackson 2008). For higher accuracy several external standards should be applied. It will minimize uncertainty of calibrators' reference values which is the important reason of inaccurate LA-ICP-MS data (Wu et al. 2018).

Opportunity of quick obtaining of the quantitative results for toxic and potentially hazardous elements will lead to the wide use of this method for aquatic studies dealing with

human-induced impact assessment and reconstructions of mining history. In addition to the possibility of using this express quantitative method for limnological research of water-sediment systems and ecological monitoring programs, it could be applied in variety of paleolimnological studies. The data resolution will be dependent on coring technique and could be less than 1 mm in freeze-coring (Dolor et al. 2009). So, the data obtained by our method are inferior in resolution to the results of LA-ICP-MS scanning of resin embedding core (μm -scale) (Jilbert and Slomp 2013; Hennekam et al. 2015). However, most paleolimnological studies do not need μm -scale resolution, especially for non-laminated sediments. Additionally, our method does not suffer from tailing signals and ensured the reliable quantitative results which is problematic in most cases in the whole core LA-ICP-MS scanning analysis (Rauch et al. 2006; Hennekam et al. 2015).

Analysis of completely unknown samples (without internal standardization) enables precision of less than 10–12% for most elements. Significant excess of almost all elements concentrations (with exception of As, Se, Cd, P, and B) could be compensated by application of elemental ratios which are frequently used in paleolimnology and environmental studies (e.g., Dolor et al. 2009; Jilbert and Slomp 2013). However, reliable quantitative results could be provided only with external and internal standardization especially with non-matrix-matched calibrators. If we have a long sediment core consisting of several hundreds of samples, determination of internal standard concentration in each sample becomes tedious and almost nullifies the idea of quick simultaneous major and minor elements determination. For overcoming of this problem quantitative analysis of several samples in the core using internal and external standardization should be carried out. The next step is regression of LA-ICP-MS data obtained with internal standardization and LA-ICP-MS data of unknown samples. Then regression equation could be applied to ablation yield correction. This approach is similar to that applied for correction of Mo/Al value of resin embedded core samples (Jilbert and Slomp 2013) except for avoiding of ICP-OES solution procedures for analysis of discrete samples. So if the concentration of one element is known only in several samples of lake sediment core we can estimate the value of excess and obtain the reliable quantitative results.

Conclusions

Hence, we presented the simple method for simultaneous determination of major and trace elements concentrations in lake sediments by LA-ICP-MS of pressed powdered pellets. This technique is characterized by a minimal sample preparation, special laser sampling, and calibration strategy aimed at overcoming the sample heterogeneity problem and reducing the matrix effects for obtaining of precise and accurate data even with non-matrix matched external standards.

The analytical parameters were investigated and optimized to overcome the heterogeneity problem. The best precision results

(RSD < 5–10% for most analytes) were obtained using line scan ablation, fluence of 8–9 J cm⁻², and scanning rate of 10 $\mu\text{m s}^{-1}$.

Our results further proved opportunity of using synthetic glass standards (NIST SRM-612 and GSD-1g) for LA-ICP-MS analysis of lake sediments. Calibration strategy including application of the appropriate internal standard makes it possible to obtain the reliable quantitative results even with non-matrix-matched calibrators. Internal standard choice was dependent on the sample and calibrator. The best results for lake clay was obtained with Al and Fe; for organic-rich gyttja with Fe (except for NIST SRM 612 as calibrator); for carbonate-rich gyttja with Ca.

The applicability of this method was evaluated using two lake sediments reference materials (BIL-1 and Jlk-1) and 32 samples of Urals lake sediments. The list of analytes included 10 major elements and 49 trace elements. The reliability of the method was demonstrated by satisfactory accuracy, trueness and precision of the LA-ICP-MS measurements. The analytical data of lake sediments RMs were generally agreed with the recommended values, with discrepancies of 1–20% for most elements. A precision of LA-ICP-MS measurements for BIL-1, Jlk-1, and Urals lake sediments with few exceptions (e.g., Zr, Hf, Cd, and Au) did not exceed 10%.

A precision of ICP-MS (RSD < 5%) was generally better than that of LA-ICP-MS. However, compared with solution ICP-MS, our method recovers significantly higher range of analytes including major and trace elements and ensures better accuracy of Hf, Zr, Ti, Nb, Sn, and Sb measurements. The obtained LA-ICP-MS results in most cases were within 30% of solution data.

Analysis of completely unknown samples (without internal standardization) provides only semiquantitative data. Significant excess of elemental concentrations should be compensated by normalization or application of elemental ratios. Quantitative data for all samples of long sediment core could be obtained by regression and calibration procedure based on several samples with known internal standard concentration.

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Conflict of Interest

None declared.

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