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Quantification of heavy metals in clays by dry plasma laser ablation-ICP-MS

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Abstract

Laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) is applied for the analysis of powdered clays used for water filtration. For the quantitative determination of trace element concentrations in clays, three matrix dilutions of red clay (RAIP) and brick clay-679 (NBS) reference materials are used to perform calibration curve. A mixture of ultrapure graphite and powders of the samples and reference materials are homogenized by using a shaker. It is found that the ablation efficiency is better in case of raster mode than single point mode in laser ablation. Calibration curves for trace elements were measured without and with ^{13}C as internal standard element. ^{13}C is used to compensate for signal fluctuations caused by the variation of the ablated sample mass. The regression coefficients of the calibration curves are better than 0.98 with internal standardization. This quantification method provided analytical results with deviations of 5–12% from the recommended and proposed values in clay-679 (NBS).

In order to compare two different approaches for the quantification of analytical results in LA-ICP-MS, relative sensitivity coefficients (RSCs) of trace elements is determined using ^{88}Sr as internal standard in red clay (RAIP). The experimentally obtained RSCs are in the range of 0.3–4.9 for all elements of interest. Therefore, the measured concentrations are corrected with RSCs. The relative standard deviation (R.S.D.) of the determination of the trace element concentration is about 3–9%. Heavy metal concentrations obtained by the two quantification methods in LA-ICP-MS are compared with the concentrations obtained by graphite furnace-atomic absorption spectrometry (GF-AAS).

Keywords: LA-ICP-MS; Ablation efficiency; RSC; Heavy metal; Clay

1. Introduction

Clay is used as filter for water purification [1]. Clay is mixed with water and molded in some shapes, then fired at high temperature (∼900 °C) to obtain containers for daily use. These containers were used in Egypt, and many other countries, for refrigeration of water. People who used pottery for refrigeration did not understand that this substance is a good decontaminating sorbent and their water is purified from the harmful metal ions. Recently, new models of filters are distributed in the market. The filter consists of a porous clay filter unit perched inside a lidded 5-gal spigoted receptacle of plastic. The unit has a flow rate of approximately 1–2 L water/h.

Several calibration techniques can be used to determine the concentration of analytes in a sample. External calibration is one of the easiest and most used techniques in ICP-MS. The external calibration methodology involves the preparation of standards, containing varying amounts of the analyte in a matrix, and the generation of a calibration curve. The response of the analyte is generally assumed to be linearly dependent on its concentration. Inaccuracies in the results can occur if the standards do not accurately represent the sample matrix. One of the most common calibration methodologies used on ICP-MS is external calibration with internal standardization. The selection of internal standards is not always easy. In selecting internal standards [2], several rules must be followed: (1) the internal standard must be present in low abundance (or not at all) in the sample; (2) the internal standard must not have any spectral interferences; (3) the internal standard must not cause any spectral interferences. Thompson and Houk [3] examined the response of over 50 elements to a sodium matrix under different operating conditions.

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They found that the amount of suppression and relative order of suppression of various analyte elements could differ for various matrix elements and various operating conditions. They stated that the criteria that they recommend for the selection of internal standards are to closely match the mass and the ionization potential of the internal standard to the analyte of interest. Doherty [4] found that mass-matching was the only criterion necessary for the selection of internal standards for the analysis of rare earth elements. Vanhaecke et al. [5] also found a mass dependence in the selection of internal standards for analyses in various matrices. Chen and Houk [6] found that the use of polyatomic ions as internal standards improved both accuracy and precision of the analysis. Vandecasteele et al. [7] found a mass dependence for elements in a NaCl matrix. Ridder et al. [8] described a model for multiple internal standard normalisation for drift in LA-ICP-MS measurements.

The aim of the present work is improving the precision and accuracy of heavy elements determination in clays used for water filtration by application of internal standardization methodology using two different quantification methods in laser ablation-ICP-MS.

2. Experimental

2.1. Instrumentation

LA-ICP-MS measurements were performed using a laser ablation system (LUV266) in combination with a ICP-MS (JMS-PLASMAX2). Measurements are performed with the UV laser wavelength of a frequency-quadrupled Nd:YAG laser. The mass spectrometric measurements are carried out at low mass resolution ($m/\Delta m = 300$). Additional heavy metals measurements are performed by graphite furnace-atomic absorption spectrometry (VARIO6, Analytik Jena GmbH, Germany). Matrix composition of clay samples and standard are measured by an energy-dispersive X-ray attachment EDS (Oxford Instruments) to a scanning electron microscope (SEM JSM-5600 LV, JEOL).

2.2. Measurement procedures

Quantitative analyses in LA-ICP-MS should be performed with a continuous and representative sample transfer to the ICP. This can be obtained by rastering the laser beam over the sample surface or by continuously ablating at a single point. Using the raster mode avoids difficulties due to inhomogeneities of the samples. In this investigation – where homogeneous targets were prepared – the rastering mode was used to avoid local sample heating that causes elemental fractionation [9]. The time to produce one raster (raster width: 3 mm × 3 mm) was about 50 s, this means that the laser beam was rastered three times over the sample surface during the total acquisition time of 115 s. At the start of each analysis, the laser was focused on the sample surface. All samples were run twice at the beginning of the analysis, then all the standards are measured. Samples are re-run three times at the end of the analysis to ensure operating conditions had been maintained throughout the analysis. In this study, 100 sweeps are performed for each measurement to observe signal intensity with time. So we are able to estimate whether significant fractionation effects occur. Ion intensities were averaged over 100 sweeps in order to minimize the influence of plasma instabilities and variations of the amount of ablated material. All operating conditions of laser ablation system and ICP-MS are listed in detail in Table 1.

2.3. Samples and chemicals

Reference materials brick clay-679 from the National Bureau of Standard (NBS) and red clay from Research Institute of applied Physics (RIAP) are employed to quantify the analytical results. Ultrapure graphite is added to clay standard with ratios 1:3, 1:2 and 1:1 to perform calibration curves of elements of interest.

2.4. Limits of detection

In solid-state analytical methods, determination of the limits of detection (LOD) is hampered by the difficulty in sourcing suitable ultrahigh purity materials in solid form. Therefore, the use of gas blanks in LA-ICP-MS is very common. In the present work, sample preparation was performed only with ultrapure graphite in order to prepare a blank target and to determine the blank values. Thus, contamination occurring during sample preparation can be checked by LA-ICP-MS measurements on a blank target. It is also possible to take into account interferences arising from polyatomic of matrix elements with argon, oxygen or nitrogen. For comparison, gas blank values are also used for

Table 1
Operating parameters of LA-ICP-MS

Mass spectrometer (JMS-Plasmax2)		Laser ablation	
RF power	1250 W	Laser type	Nd:YAG laser
Coolant gas flow rate	14 L/min	Wavelength	266 (4th harmonic)
Auxiliary gas flow rate	0.8 L/min	Pulse duration	6 ns
Carrier gas flow rate	0.99 L/min	Repetition frequency	10 Hz
Mass resolution	300	Pulse energy	10 mJ
Acquisition mode	Peak area	Laser power density	6×10^9 W/cm^2
Dwell time	20 ms	Spot diameter	160 μm
No. of sweeps	100	Raster width	3 mm × 3 mm
No. of replicates	5	Tubes	Tygon 2075
Total acquisition time	115 s		

Table 2
Matrix composition (%) of clays measured by SEM-EDX

Main composition	Clay-679		Red clays		Clay-I	Clay-II	Clay-III	Clay-IV
	Certified	Measured	Certified	Measured				
SiO_2	52.12	51.18	48.8	44.36	54.75	41.00	47.09	47.18
Al_2O_3	20.8	21.01	15.97	16.30	21.06	38.37	29.08	32.86
Fe_2O_3	12.95	12.91	9.01	8.42	0.81	0.24	0.93	1.85
MgO	1.25	1.38	3.17	3.34	2.03	0.04	0.41	0.20
CaO	0.23	0.24	3.03	2.78	–	0.08	0.16	0.05
Na_2O	0.18	0.25	3.50	3.85	1.45	0.02	0.18	0.02
K_2O	2.93	2.55	2.79	3.10	4.30	0.03	0.89	0.52
TiO_2	0.96	0.85	0.98	0.82	0.78	1.70	1.24	0.80
P_2O_5	–	0.09	0.72	0.81	0.11	0.17	0.15	0.08

the determination of the limits of detection. Limits of detection were determined using the 3σ-criterion ($LOD = m_b + 3\sigma_b$, where m_b is the mean value of the blank measurements and σ the standard deviation).

2.5. Quantification methods

The quantitative determination of trace element concentrations in clays with laser ablation-ICP-MS was carried out using brick clay-679 (NBS) and red clay (RIAP) as reference materials. Matrix compositions in the clay samples are similar to the composition of reference materials, as shown in Table 2.

A better quantification of analytical results is possible using a set of solid calibration standards in order to measure calibration curves. Therefore, calibration curves for different elements are generated using matrix dilutions of brick clay-679 and red clay (RIAP) reference materials. ^{13}C is employed as internal standard element [10], because it has low degree of ionization (ionization potential = 11.25 eV) and consequently, not cause serve spectral interferences compared to oxygen [11].

The relative sensitivity coefficients (RSCs) of elements, defined as the ratio of experimentally measured concentration to certified (true) concentration of an element in a given matrix, are determined using the reference material red clay (RAIP). Strontium is used as internal standard element. Correction of measured values with RSCs is quantification method using only one reference material.

Results of the two different quantification methods (calibration curves, correction of measured values by relative sensitivity coefficients) are compared in order to estimate quantification methods in LA-ICP-MS. Furthermore, the results obtained by LA-ICP-MS are compared with additional measurements by GF-AAS.

3. Results and discussion

For "dry" plasma, the elemental material that is contributed to the plasma from air entrainment becomes significant. Gray [12] has reported the use of a flared torch bonnet, which fits over the ICP torch in a manner similar to traditional bonnets. This bonnet was flared to match the angle of the sampler and had an outer diameter equal to that of the sampler cone. Ince et al. [13] showed that a significant reduction in ICP-MS signal noise was obtained when using this bonnet. The noise reduction was related to a decrease in the interaction of the plasma with atmospheric gases, i.e., the reduction of air entrainment into the plasma. Use of the flared bonnet reduces air entrainment and results in lower polyatomic backgrounds and enhanced sensitivity for the lighter elements.

Rege et al. [10] used a similar flared bonnet in an ongoing effort to reduce the effect of the air entrainment. They introduced externally Kr gas into the torch box at an approximate rate of 1.2 L/min. Kr was chosen as it is easy to detect, is not a major component of air, and the background levels are low. Kr levels were measured using both a conventional bonnet and a flared bonnet. It was found the Kr gas entrainment was reduced with the flared (4.4×10^6 signal cps for ^{83}Kr using the normal bonnet, 0.64×10^6 signal cps for ^{83}Kr using the flared bonnet). In the present study, we used normal bonnet because the analyte ions concentrated in the central channel of plasma [14,15] (~3 mm wide when plasma depth about 5 mm), meanwhile, on the torch axis, the cooler central gas stream shows a relatively low Ar^+ population, but at each side of the centre, the higher degree of ionization of Ar in the hotter induction region (14 mm).

In order to study different sampling methods, the laser beam was rastered over the sample surface during laser ablation and additionally, an ablation at a single point was investigated. It is found that single point measurements lead to high relative standard deviations of ion intensities (>50%) because of a loss of ion intensities with time. As the laser beam is defocused during a single point measurement, laser power density changes with time and for that reason a loss of ion intensities was observed. Therefore, ion intensities are a factor of 50 lower during a single point measurement compared to the sampling method where the laser beam was rastered over the sample surface. For these reasons, the analytical signals are greatly affected by the sample mass ablated by the laser beam. The efficiency of the ablation (E) defined as [16] the ratio of the ablated mass to the incident energy (μg/mJ) depends on the coupling condition between the laser beam and the sample surface. Measurements are performed with a focused laser beam rastered over the sample surface because better precision and higher sensitivity were observed in this case. Fig. 1 shows the time dependent ablation efficiency (E) for Co and Ba in clay-679 (NBS) in case of single point mode and raster mode of laser ablation. Ablation efficiency decrease to

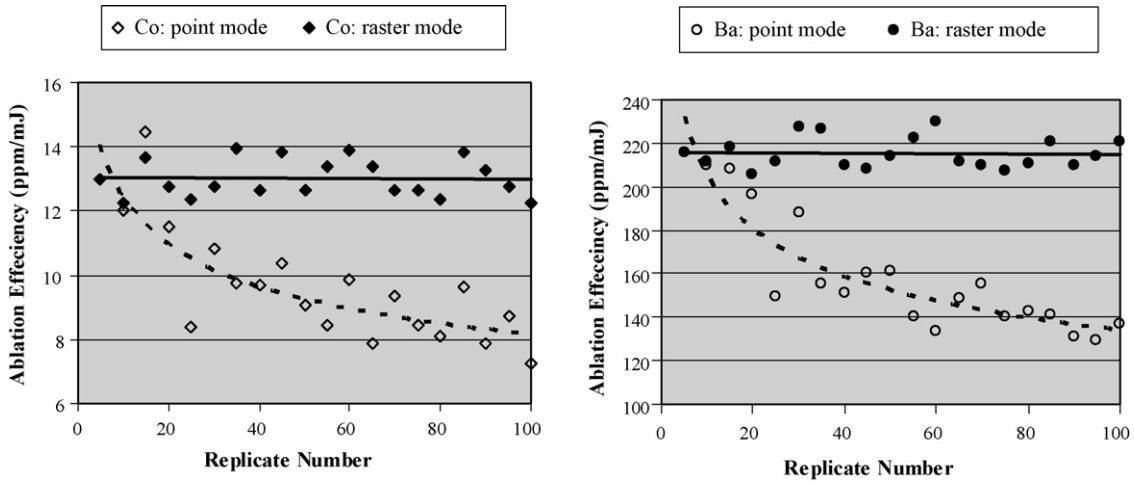

Fig. 1. Variation in ablation efficiency (ppm/mJ) with replicate number for Co and Ba.

Table 3
The detection limits (3σ) of heavy metals using clay-679 and red clay (RIAP) standard reference materials in graphite target by LA-ICP-MS

Elements	Limit of detection (ppm)	Elements	Limit of detection (ppm)
^{107}Ag	0.039	^{64}Zn	7.1
^{75}As	2.12	^{45}Sc	0.16
^{138}Ba	7.9	^{59}Co	1.2
^{111}Cd	0.09	^{133}Cs	0.28
^{52}Cr	5.58	^{140}Ce	0.17
^{63}Cu	0.83	^{149}Sm	0.11
^{55}Mn	18.2	^{178}Hf	0.18
^{98}Mo	0.18	^{88}Sr	3.4
^{60}Ni	0.62	^{51}V	0.82
^{208}Pb	0.22	^{232}Th	0.03
^{82}Se	0.14	^{238}U	0.04
^{120}Sn	0.25		

about 50% in case of single point mode, while it is stable in raster mode within the experimental errors.

The limits of detection for all elements determined in the clays are listed in Table 3. A comparison of LODs determined using the pressed pellet graphite target and the gas blank demonstrates that contamination of the ultrapure graphite used and molecular ions formed with matrix elements are the reason for higher LODs; except for Mn, where a memory effect causes a higher limit of detection.

3.1. Calibration curves in LA-ICP-MS

In LA-ICP-MS analysis, normalization of the response for an analyte to an internal standard is necessary to obtain quantitative analyses. This internal standard commonly is a minor isotope of a major element. Internal standardization is very effective in correcting for ablation related effects and may be effective for correcting plasma-related effects [9,16–20]. It is obviously important that the matrix effect influence both the internal standard to the same extent as the analyte. Under the chosen experimental conditions, using a laser power density of 6×10^9 W/cm^2, a time-dependent elemental fractionation relative to the internal standard element ^{13}C was not observed.

The quantification of analytical results on clays using calibration curves is investigated. ^{13}C is used to compensate for signal fluctuations caused by the variation of the ablated sample mass. The regression coefficients for calibration curves obtained without the use of an internal standard element are better than 0.90 for all investigated elements. Correlation is improved in the same

Table 4
Comparison of relative standard deviations (precision) in LA-ICP-MS using calibration curves obtained without and with internal standard on clay-679 (NBS)

Elements	Certified conc. (ppm)	Without internal standard		Internal standard = ^{13}C	
		Conc. (ppm)	Precision (%) ($n=6$)	Conc. (ppm)	Precision (%) ($n=6$)
Ba	432.2 ± 9.8	389 ± 38.6	9.9	428 ± 16.6	4.1
Ce	105[a]	114 ± 10.3	8.99	111 ± 6.7	6.0
Co	26[a]	23.97 ± 1.87	7.8	26.1 ± 1.8	7.2
Cr	109.7 ± 4.9	123 ± 14.9	12.1	112 ± 2.5	2.2
Cs	9.6[a]	8.42 ± 1.04	12.3	9.43 ± 0.79	8.6
Hf	4.6[a]	4.21 ± 0.35	8.4	4.77 ± 0.2	3.8
Sc	22.5[a]	18.27 ± 3.43	18.8	23.94 ± 1.51	6.4
Sr	73.4 ± 2.6	79.13 ± 6.17	7.8	72 ± 2.01	2.8
Th	14[a]	14.7 ± 0.81	5.5	14.8 ± 0.82	5.7
Zn	150[a]	160 ± 10.4	6.5	145 ± 4.51	3.1

n, Number of determinations.
[a] Information value.

Table 5
Relative sensitivity coefficients in LA-ICP-MS determined using the pressed pellet of the reference material red clay (RIAP)

Elements	RSC	Elements	RSC
As	2.17	Ni	3.35
Ba	3.28	Pb	4.85
Cd	1.19	Sc	0.61
Ce	3.67	Sm	3.54
Co	0.32	Sn	2.89
Cr	0.92	Sr	Internal standard
Cs	2.89	Th	4.22
Cu	0.66	U	6.32
Hf	4.02	V	0.86
La	2.91	Zn	0.28
Mo	1.57		

way using ^{13}C as internal standard element ($R^2 = 0.957–0.989$) in comparison to the approach without the use of an internal standard element.

The relative standard deviation (R.S.D.) for 5 measurements without sample changing (internal reproducibility) is about 2–8% using ^{13}C as internal standard element and range from 4 to 19% if no internal standard element is used. Thus, precision could be improved by using an internal standard element, as shown in Table 4, whereas the accuracy of the analytical results will be the same. This result indicates that quantitative LA-ICP-MS analyses can be carried out without pre-information on the concentration of one element (internal standard element) in the unknown sample if the LA-ICP-MS system is stable during the measurement of standards and samples. Platzner et al. [21] reported that stability of an LA-ICP-MS system is limited by the stability of the laser energy. So, if samples and standards are measured at the same laser power density, quantitative measurements by LA-ICP-MS can be performed without the use of an internal standard element to correct for the amount of ablated material, whereby precision deteriorates to 4–11%. But this is only possible where matrix-matched standards are used.

3.2. Relative sensitivity coefficients in LA-ICP-MS

In order to determine trace element concentrations in pressed pellet targets of clays RSCs were measured on a pressed pellet target of the red clay reference material (RIAP). RSCs range from 0.3 to 4.9 (Table 5) for heavy elements of interest. Relative sensitivity coefficients have to be measured in the same run as the samples, because their value changes from one day to the next [22,23]. This means that trace analysis of solid samples by LA-ICP-MS should be performed under the same experimental conditions as the reference material. In fused lithium borate targets [24], the dependence for RSCs is found as a function of mass for different elements.

3.3. Trace analysis of clays

A comparison of the determined element concentration in clay samples obtained using calibration curves (with ^{13}C as internal standard element) and relative sensitivity coefficients is given in Tables 6 and 7. Most values agree within the analytical precision.

Table 6
Concentration (ppm) of Heavy metals in clay samples I and II

Elements	Clay-I			Clay-II		
	LA-ICP-MS		GF-AAS	LA-ICP-MS		GF-AAS
	Calibration curve	RSC		Calibration curve	RSC	
Ag	–	0.109 ± 0.01	0.101 ± 0.01	–	0.2 ± 0.014	0.177 ± 0.01
As	3.29 ± 0.09	2.47 ± 0.15	3.01 ± 0.04	3.75 ± 0.15	5.47 ± 0.93	5.09 ± 0.09
Ba	384 ± 10	410 ± 21	389 ± 6	556 ± 23	578 ± 42	569 ± 12
Cd	1.88 ± 0.04	1.79 ± 0.11	2.08 ± 0.03	1.26 ± 0.05	1.10 ± 0.08	1.11 ± 0.02
Cr	50.7 ± 1.5	–	47.22 ± 0.88	36.7 ± 1.66	33 ± 2.5	35 ± 0.4
Cu	19.7 ± 0.51	21.6 ± 1.13	17.3 ± 0.38	12.3 ± 0.65	14 ± 1.2	13.6 ± 0.25
Mn	531 ± 14	556 ± 30	539 ± 9	358 ± 19	402 ± 26	411 ± 14
Mo	1.34 ± 0.03	1.15 ± 0.04	1.25 ± 0.02	0.78 ± 0.05	0.87 ± 0.06	0.89 ± 0.02
Ni	27 ± 0.71	26 ± 1.5	29 ± 0.53	22.7 ± 0.92	19.8 ± 1.42	20.4 ± 0.44
Pb	8.91 ± 0.24	7.52 ± 0.4	7.51 ± 0.12	14.4 ± 0.69	13.3 ± 0.99	12.4 ± 0.11
Se	–	0.60 ± 0.03	0.63 ± 0.01	–	0.32 ± 0.01	0.20 ± 0.01
Sn	1.17 ± 0.02	1.19 ± 0.06	2.11 ± 0.01	0.67 ± 0.03	0.58 ± 0.04	0.58 ± 0.02
Zn	62 ± 1.27	59.8 ± 4.35	65 ± 1.1	50.45 ± 2.3	48 ± 3.8	54 ± 1.04
Sc	9.75 ± 0.25	7.42 ± 0.55	10.39 ± 0.12	5.75 ± 0.25	4.87 ± 0.35	4.74 ± 0.21
Co	14.38 ± 0.83	15.4 ± 0.79	17.16 ± 0.25	8.47 ± 0.32	9.48 ± 0.6	8.52 ± 0.35
Cs	0.70 ± 0.02	0.71 ± 0.04	0.82 ± 0.01	1.17 ± 0.05	1.05 ± 0.1	1.15 ± 0.02
Ce	49.63 ± 1.35	53.8 ± 5.3	–	72.6 ± 3.5	70.9 ± 6	–
Sm	2.74 ± 0.07	2.69 ± 0.14	–	7.08 ± 0.38	7.54 ± 0.55	–
Hf	5.22 ± 0.15	5.15 ± 0.27	–	5.76 ± 0.26	5.28 ± 0.43	–
Sr	217 ± 8	220 ± 14	228 ± 5	628 ± 30	622 ± 46	642 ± 9
V	114 ± 4.1	121 ± 6.5	109 ± 2	71.91 ± 3.2	70.67 ± 5.3	73.15 ± 1.8
Th	2.33 ± 0.06	1.16 ± 0.07	–	10.8 ± 0.41	12.5 ± 0.72	–
U	0.72 ± 0.02	0.62 ± 0.03	–	1.04 ± 0.05	0.98 ± 0.07	–

Table 7
Concentration (ppm) of heavy metals in clay samples III and IV

Elements	Clay-III			Clay-IV		
	LA-ICP-MS		GF-AAS	LA-ICP-MS		GF-AAS
	Calibration curve	RSC		Calibration curve	RSC	
Ag	–	0.04 ± 0.002	0.02 ± 0.001	–	0.18 ± 0.02	0.22 ± 0.004
As	12.78 ± 0.36	9.6 ± 0.52	–	1.51 ± 0.07	2.25 ± 0.18	3.81 ± 0.11
Ba	20 ± 0.045	21 ± 1.14	24 ± 0.5	412 ± 18	401 ± 27	389 ± 7.7
Cd	2.29 ± 0.05	2.16 ± 0.12	4.02 ± 0.06	–	–	–
Cr	9.89 ± 0.28	11.9 ± 0.64	9.2 ± 0.12	32 ± 1.5	27 ± 2	24.3 ± 0.43
Cu	3.04 ± 0.09	2.9 ± 0.15	3.63 ± 0.08	11.28 ± 0.5	12.9 ± 0.92	13.9 ± 0.3
Mn	214 ± 6	198 ± 10	232 ± 4	747 ± 33	795 ± 56	771 ± 13
Mo	0.92 ± 0.03	0.8 ± 0.04	0.85 ± 0.03	0.51 ± 0.02	1.93 ± 0.14	0.51 ± 0.01
Ni	3.79 ± 0.17	3.49 ± 0.19	2.54 ± 0.05	26.16 ± 1.16	22.46 ± 1.6	30.6 ± 0.52
Pb	1.40 ± 0.04	2.24 ± 0.12	1.17 ± 0.02	10.04 ± 0.45	7.9 ± 0.58	6.10 ± 0.11
Se	–	0.20 ± 0.01	0.18 ± 0.01	–	0.45 ± 0.03	0.33 ± 0.01
Sn	0.40 ± 0.01	0.61 ± 0.03	0.63 ± 0.01	1.36 ± 0.06	1.30 ± 0.08	1.24 ± 0.02
Zn	10.7 ± 0.23	9.7 ± 0.55	12.2 ± 0.19	74 ± 3.3	71 ± 5.1	80 ± 1.4
Sc	0.46 ± 0.01	0.49 ± 0.04	–	10.96 ± 0.41	9.73 ± 0.69	10.5 ± 0.18
Co	1.43 ± 0.06	1.6 ± 0.1	1.85 ± 0.03	14.64 ± 0.56	10.5 ± 0.75	17.4 ± 0.31
Cs	0.38 ± 0.02	0.3 ± 0.02	0.47 ± 0.01	0.85 ± 0.05	1.82 ± 0.13	1.01 ± 0.02
Ce	–	0.2 ± 0.01	–	51 ± 2.2	55 ± 4	–
Sm	0.28 ± 0.01	0.43 ± 0.03	–	5.69 ± 0.22	7.07 ± 0.6	–
Hf	0.25 ± 0.01	1.13 ± 0.05	–	5.09 ± 0.25	4.07 ± 0.29	–
Sr	3596 ± 91	4946 ± 264	4759 ± 82	537 ± 22	559 ± 38	570 ± 8
V	17.9 ± 0.48	22.5 ± 1.2	12.8 ± 0.22	106 ± 4.7	101 ± 7.4	121 ± 3
Th	–	58 ± 3.1	–	3.47 ± 0.15	4.06 ± 0.3	–
U	5.12 ± 0.14	4.54 ± 0.24	–	1.02 ± 0.04	1.13 ± 0.07	–

Both quantification methods lead to different results in the case of Ba, Sc, Ce and V. The Mn concentration determined in clay-I using calibration curves is different from the concentration of 556 ppm for Mn obtained with RSCs. However, the latter value is in good agreement with the atomic absorption spectrometry (GF-AAS) result of 539 ppm. The Mn concentration in clay samples are out of the calibration range (3424–13699 ppm) of the measured calibration curve, for that reason, a low Mn concentration was determined. So, for quantification via calibration curves the element concentration must be in the calibration range and at least three reference materials are needed. Alternatively, dilute one matrix-matched reference material and the samples by ultrapure graphite and measure at the same conditions. Fig. 2 shows comparison between the analytical results obtained by calibration curves in LA-ICP-MS and GF-AAS.

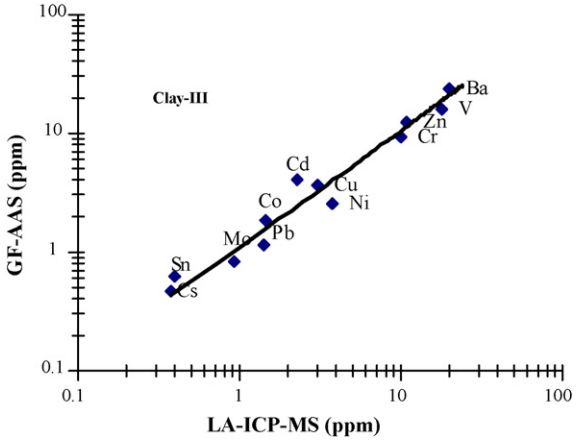

Fig. 2. LA-ICP-MS values obtained by calibrations curves plotted against values obtained by GF-AAS.

4. Conclusion

With LA-ICP-MS, it is possible to analyze clays with less sample preparation in comparison to ICP-MS. Normalization of the ion intensities of analytes to an internal standard is necessary to obtain quantitative analyses in LA-ICP-MS analyses. Internal standardization is very effective in correcting for ablation process, transportation and plasma related effects. Using one matrix-matched standard reference material, it is possible to obtain accurate and precise analyses using the relative sensitivity coefficient (RSC) method or dilute the standard reference material by ultrapure graphite to perform calibration curves.

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