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Elemental analysis of silicon based minerals by ultrasonic slurry sampling electrothermal vaporisation ICP-MS

Pablo Fernández Rodríguez [a], Juan Manuel Marchante-Gayón [b], Alfredo Sanz-Medel [b,*]

[a] *Departamento de Prevención Técnica, Instituto Nacional de Silicosis, c/Doctor Bellmunt s/n, 33006 Oviedo, Spain*
[b] *Departamento de Química Física y Analítica, Universidad de Oviedo, c/Julián Clavería 8, 33006 Oviedo, Spain*

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Abstract

Ultrasonic slurry sampling electrothermal vaporisation inductively coupled plasma mass spectrometry (USS-ETV-ICP-MS) was applied to the elemental analysis of silicate based minerals, such as talc or quartz, without any pre-treatment except the grinding of the sample. The electrothermal vaporisation device consists of a tungsten coil connected to a home-made power supply. The voltage program, carrier gas flow rate and sonication time were optimised in order to obtain the best sensitivity for elements determined. The relationship between the amount of sample in the slurry and the signal intensity was also evaluated. Unfortunately, in all cases, quantification had to be carried out by the standard additions method owing to the strong matrix interferences. The global precision of the proposed method was always better than 12%. The limits of detection, calculated as three times the standard deviation of the blank value divided by the slope of the calibration curve, were between 0.5 ng/g for As and 3.5 ng/g for Ba. The method was validated by comparing the concentrations found for Cu, Mn, Cr, V, Li, Pb, Sn, Mg, U, Ba, Sr, Zn, Sb, Rb and Ce using the proposed methodology with those obtained by conventional nebulisation ICP-MS after acid digestion of the samples in a microwave oven. The concentration range in the solid samples was between 0.2 μg/g for Cr and 60 μg/g for Ba. All results were statistically in agreement with those found by conventional nebulisation.

Keywords: Ultrasonic slurry sampling; Electrothermal vaporisation; ICP-MS; Silicate based minerals

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1. Introduction

The determination of trace and ultratrace elements in silicate based minerals is always a difficult task. Analytical methods usually involve digestions with hydrofluoric acid, in order to volatilise the silicon as tetrafluoride (SiF_4), and subsequent analysis of the resultant solution by electrothemal atomic absorption spectrometry [1], inductively coupled plasma optical emission spectrometry [2] or inductively coupled plasma mass spectrometry [3]. However, such procedures are time consuming, use a highly toxic acid and are prone to systematic errors owing to losses and/or contaminations. Consequently, alternative analytical methods avoiding the digestion of samples with high amounts of silicon are welcome.

In comparison with classical nebulisation, the coupling of electrothermal vaporisation (ETV) with inductively coupled plasma mass spectrometry (ICP-MS) has several advantages: higher sensitivity and lower limits of detection, lower sample volume requirements, higher sample transport efficiencies and the possibility of performing direct solid analysis [4–6]. Considering that the desolvation of the sample does not occur in the plasma greater energy is available there for atomisation and ionisation. Moreover, with an appropriated temperature program it is also possible to minimise efficiently matrix effects and spectroscopic interferences by the separation of the analyte from the sample matrix [5]. However, ETV devices do not produce steady-state signals and the ICP-MS instrument has to be capable of recording transient signals of several isotopes simultaneously. Thus, for this application the multi-elemental capability of scanning based analysers, such as quadrupole based instruments, is limited [7].

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* Corresponding author. Tel.: +34 985103474; fax: +34 985103125.
E-mail address: asm@uniovi.es (A. Sanz-Medel).

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Ultrasonic slurry sampling (USS) has been used in combination with ETV-ICP-MS for the analysis of soils, ceramic powders and geological materials [8–14]. Compared with traditional sample preparation methods, slurry sampling offers several advantages including reduced sample preparation time and contamination risks [5].

Most ETV devices used in combination with ETV-ICP-MS are graphite furnaces. However, they have several limitations such as the occurrence of isobaric interferences owing to the carbon species [15,16] (e.g., $^{40}Ar^{12}C$ over ^{52}Cr), the formation of refractory carbides with the analyte and the restriction to vaporisation temperatures below 2600 °C. In order to overcome these problems, metal ETV devices, especially tungsten coils, have been also used [17–19]. Tungsten coils are easily obtained from halogen lamps. They have reproducible physical properties, enable high heating rates and temperatures up to 3000 °C even with a low cost power supply. Moreover, the coil can be placed in a small piece of quartz avoiding the dilution of the analyte in the gaseous phase.

In this work, a USS-ETV-ICP-MS methodology has been developed for the determination of trace and ultratrace elements in samples with high amounts of silicon such as talc or quartz samples using a home-made ETV device based on a tungsten coil. Several parameters (carrier gas flow, sonication time, voltage program, etc.) were optimised in order to obtain the best sensitivity and limits of detection. Also the maximum number of isotopes measured simultaneously using a quadrupole ICP-MS will be investigated. The proposed methodology was validated by comparing the results with those obtained by conventional nebulisation ICP-MS, after microwave acid digestion of the samples.

2. Experimental

2.1. Instrumentation

The ICP-MS instrument used was a quadrupole based instrument Hewlett-Packard (Yokogawa Analytical Systems Inc., Tokyo, Japan) model HP-4500.

The electrothermal vaporisation device (Fig. 1) consisted of a tungsten coil, type 64655 HLX, manufactured by Osram (Munich, Germany), connected to a home-made power supply (1–20 V and 250 W). Coils were connected to the power supply through a piece of ceramic with the electrical connections and allocated in a piece of quartz which dimensions are shown in Fig. 1. A mixture of argon and hydrogen, 90:10 (Air Liquid, Madrid, Spain), was used as carrier gas and introduced in the system through the piece of ceramic. Hydrogen was used in order to prevent the oxidation of the tungsten coil during the heating cycle. Samples were deposited on the coil through a small hole in the piece of quartz using a Hamilton microsyringe, closed after sampling using a quartz stopper. The vaporised sample was transported to the plasma via a glass tube. An additional flow of argon was introduced in the system using a glass T-piece.

The ICP-MS instrumental parameters were initially optimised monitoring the ^{93}Nb signal. This element is an impurity vaporised from the tungsten coil at 20 V. It was observed that the optimised voltages of the lens were similar to those obtained by conventional nebulisation. Consequently, these parameters were daily optimised by conventional nebulisation using a 10 μg/L multi-elemental solution of Li, Y and Tl. Typical instrumental operating conditions for the ETV device and the ICP-MS instrument are given in Table 1.

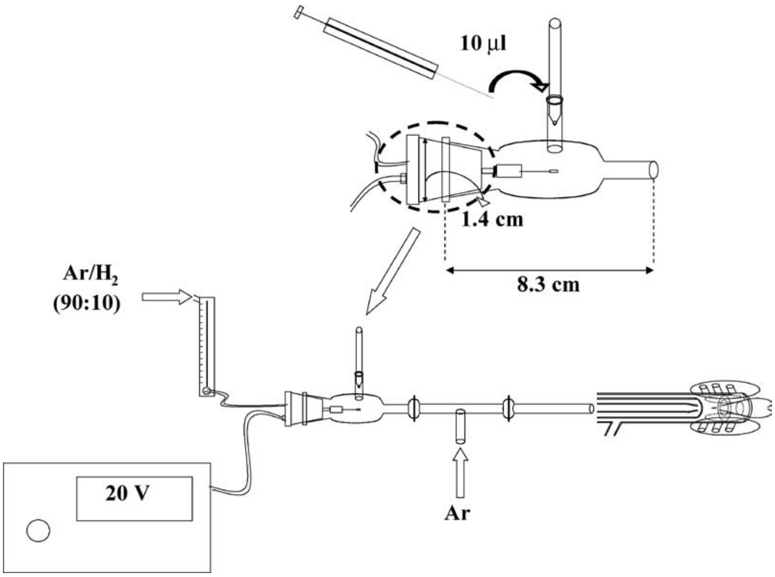

Fig. 1. Schematic diagram of the home-made electrothermal vaporisation device using a tungsten coil.

Table 1
Instrumental operating conditions selected for the ETV device and the ICP-MS instrument

ICP-MS operational conditions	
Forward power (kW)	1.30
Plasma gas flow rate (L/min)	15
Auxiliary gas flow rate (L/min)	1.0
Carrier gas flow rate (L/min)	0.8
Additional gas flow rate (L/min)	0.8
Sampling depth (mm)	6.0
Voltage of the lens (V)	
EM voltage	−2340
Extract 1	−82
Extract 2	−145
Einzel 1, 3	−169
Einzel 2	28
Omega bias	−65

Step	Voltage (V)	Time (s)	Ramp (V/s)
ETV operational conditions (injection volume 10 μL) (vaporisation program)			
Drying	0.55	25	0.011
Vaporisation	20	3	–

An ultrasonic probe Labsonic 1510 (B. Braun Melsungen AG, Melsungen, Germany) was used to prepare the slurries. A microwave oven (Socisole, Italy) was used for the digestion of the samples.

2.2. *Reagents and samples*

Argon of 99.998% purity from Air Liquid was used. As it was mentioned before, a 90% Ar–10% H_2 mixture was used as carrier gas in order to prevent oxidation of the tungsten coil during the heating cycle.

All 1 g/L standard solutions stabilised in 0.5 M HNO_3 were obtained from Merck (Darmstadt, Germany). Further multi-elemental solutions were prepared daily by diluting (weighting) an appropriate volume (weight) of those standard solutions with ultrapure water (Milli-Q System 185, Millipore, Molsheim, France). The nitric acid used in this work was subboiled from a 12 M HNO_3 solution (Merck).

The samples were: a “micronised talc” sample from “Sociedad Española del Talco” (León, Spain), a “quartz E-1” sample from “Sociedad de Minerales Silíceos de Cataluña” (Barcelona, Spain) and a “quartz reference material” CRM066 from “Community Bureau of Reference” (BCR). Only the granulometry of the latter sample is certified (2.5 μm), whereas the granulometry of the talc sample was below 10 μm.

2.3. *Procedure*

Slurries were prepared in 15 mL polystyrene vessels (Greiner, Fricckenhausen, Germany) by sonicating 10–1000 mg of sample in 10 mL of 0.5 M HNO_3. Slurries with sample concentrations below 1 g/L were prepared by diluting a more concentrated slurry and homogenised using an ultrasonic probe just before the deposition on the coil. A volume of 10 μL of slurry was analysed. Then, the heating cycle started and the signal of the sought elements was monitored using the instrumental conditions shown in Table 1. The calibration was performed by standard additions. To do that, slurries were spiked with different weights (volumes) of a multi-elemental standard solution of the monitored analytes. The total analysis time was about 2 min/sample (five elements). The number of firings which could be made using a filament was about 100.

3. Results and discussion

3.1. *Optimisation of the carrier gas flow*

As mentioned before, a mixture of argon–hydrogen (90:10) was used in order to create a reducing atmosphere and avoid the tungsten coil oxidation during the heating cycle. On the other hand, an additional flow of argon was also introduced after the ETV system in order to dilute the concentration of hydrogen in the plasma (see Fig. 1), which could eventually extinguish it.

These gas flows were optimised individually. First, the flow of the additional gas was fixed at 0.8 L/min and the flow of the mixture of argon and hydrogen varied between 0.6 and 0.9 L/min. Then, the flow of the mixture was fixed at the optimum value found previously and the flow of the additional gas varied between 0.6 and 0.9 L/min. A multi-elemental solution containing 50 ng/g of As, Ba, Cd, Cr, Cu, Ni, Pb, Sn, U and V was used for optimisation.

For the heavier elements slightly lower flows than those obtained for the lighter elements were observed. On the contrary, the optimum flow rates of the additional argon for the heavier elements were clearly higher than those obtained for the lighter elements. Consequently, argon–hydrogen mixture flow rate of 0.8 L/min and an additional argon flow rate of 0.8 L/min were selected as compromise values.

The total gas flow (1.6 L/min) was significantly higher than that used for conventional nebulisation. Several authors [20,21] have attributed this phenomenon to an earlier appearance of the maximum ion density in a dry plasma compared with a wet plasma. A higher gas flow counteracts this effect by moving the maximum ion density forward to the interface.

3.2. *Maximum number of isotopes determined in one run*

Using a scanning based analyser (quadrupole mass filter) some difficulties in terms of precision, accuracy and/or sensitivity are expected when several isotopes have to be measured in a very fast transient signals (such as those produced by an ETV device).

The precision observed monitoring more than five isotopes was very poor. The peaks could not be properly followed (spectral skew apparent) even if low integration times were

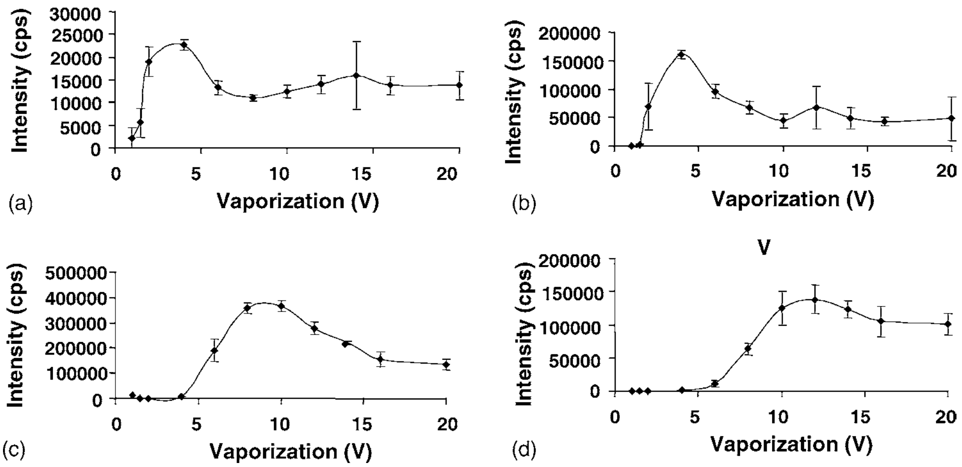

Fig. 2. Optimisation of the voltages used for the vaporisation of the samples: (a) cadmium; (b) lead; (c) uranium; (d) vanadium. A standard solution of 10 ng/g of each element in 0.5% of nitric acid was used in all cases.

assayed. Consequently, five isotopes were monitored simultaneously in one run using an integration time of 25 ms (simultaneous measurement of more isotopes led to a loss of sensitivity and unacceptable precision which could not be regained by further adjustments of the ICP-MS parameters).

3.3. Optimisation of the voltage program

Voltages, instead of temperatures, were measured and optimised in our home-made ETV device owing to the difficulties found to measure the actual temperature of the tungsten coil. In order to avoid sample contamination and to simplify the methodology, the use of chemical modifiers was not considered in this work. The final ETV program selected for multi-elemental analysis is shown in Table 1.

The voltage used to dry the samples was optimised using a volatile element (cadmium) in order to detect possible losses of the analytes and 0.55 V setting was finally selected. Higher voltages produced losses of the volatile analytes. Thus, a mineralisation step was discarded. On the other hand, volatile elements could be completely vaporised at 4 V, whereas non-volatile elements could be only vaporised at voltages higher than 10 V (see Fig. 2). A voltage of 15 V was finally selected in order to ensure the total vaporisation of all elements. Nevertheless, it must be borne in mind that this voltage was not the optimum for all elements (especially so in the case of volatile elements).

3.4. Optimisation of the sonication time

The sonication time was optimised using the quartz CRM. To do that, 5000 μg of sample was suspended in 1 g of water and several sonication times were assayed in order to produce the slurry. The homogeneity of the slurries was eventually ensured by sonicating 20 s before the deposition on the tungsten coil. One minute of sonication was found to be sufficient. Similar results were found using other samples. This fact can be attributed to the low granulometry of the samples assayed in this study.

3.5. Matrix interferences

An important signal suppression by the matrix was observed for all elements. Fig. 3 shows the mass response curve that is the signal intensity observed for increasing sample masses in the slurry. The response was non-linear in the range between 0 and 10 mg/g showing the influence of the matrix on the ICP-MS signals of the analytes. The observed slopes of the calibration curves obtained for aqueous standards were always higher than those obtained by standard additions to the slurry. Moreover, concentrations of sample in the slurry higher than 10 mg/g did not increase further the signal intensity (thus, concentrations of the sample in the slurry higher than 10 mg/g were not used).

This effect can be also observed in the profiles of the peaks obtained. Fig. 4 shows the signal time profiles obtained for 25 pg of copper in a 0.5% HNO_3 solution, in the slurry (about 50 pg of copper) and in the slurry spiked with 50 pg of copper. As it can be seen, the signal intensity obtained for the aqueous solution is higher than those obtained for the slurry or the slurry spiked with the element in spite of the higher concentration of copper in these latter cases. Similar behaviour was observed for the rest of elements under study. Moreover, the peak profiles obtained for the slurries showed a tailing in the signals. This effect has been also observed by other authors [22]. Nevertheless, integrated signals were monitored in order to avoid the influence of the signal shape. Fortunately, the behaviour of the analyte spiked to the sample and the analyte contained in the sample matrix seems to be similar. Thus, if the concentration in the sample is doubled the signal intensity too. Consequently, standard additions could be used as calibration methodology for the analysis of the samples.

The suppression of analyte signals in the presence of large amounts of matrix in the plasma is a very well-known phe-

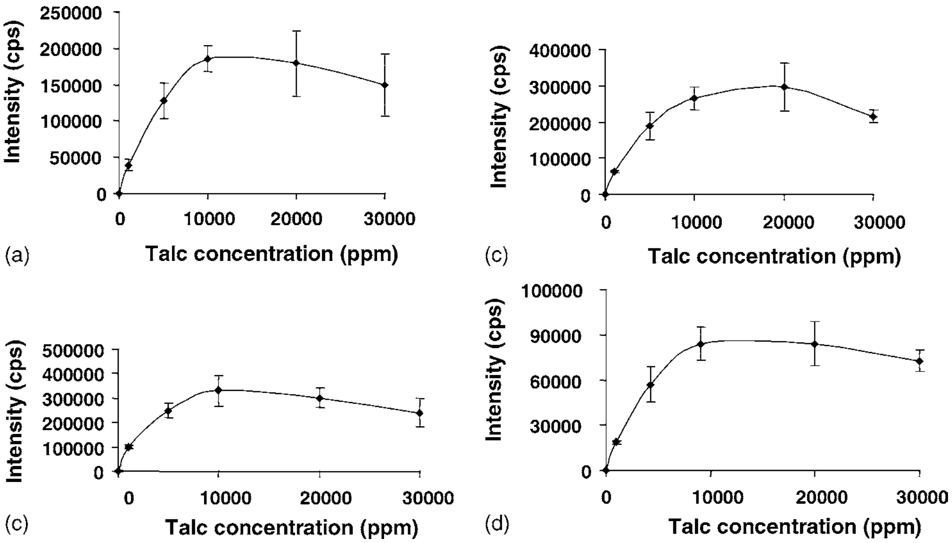

Fig. 3. Signal intensity according to the slurry concentration: (a) lithium; (b) manganese; (c) copper; (d) vanadium. Talc sample was used in all cases.

nomenon in the analysis of slurries by ETV-ICP-MS [23]. It can be caused by changes in the plasma conditions during the vaporisation and decomposition of the matrix aerosol (e.g., cooling of the plasma). Other factors such as the ionisation efficiency as well as the site of the maximum ion density could be also important. However, the atomisation power of a tungsten coil is considerably lower than that of a graphite furnace and most likely this could explain the main problems found to vaporise concentrations higher than 10 mg/g of sample in the slurry.

3.6. Limits of detection

The limits of detection shown in Table 2 were calculated as three times the standard deviation of the blank value divided by the slope of the calibration curve. An aqueous solution containing 0.5% of nitric acid was used as blank solution. The limits of detection found measuring the elements in the slurry were compared with those found by measuring them in an aqueous solution and also by conventional nebulisation (see Table 2).

The relative limits of detection (ng/g) found by ETV-ICP-MS are about 2–10 times worse (higher) than those found by conventional nebulisation. This fact can be attributed to the low volume of sample deposited on the tungsten coil (10 μL). Consequently, the absolute limits of detection found atomising the elements from an aqueous standard solution are extremely low (less than 1 pg for most elements).

Unfortunately, the matrix signal suppression worsened the limits of detection 10–50 times (see USS-ETV-ICP-MS column in Table 2) compared to those obtained by atomising an aqueous standard solution. Nevertheless, the limits of detection obtained are low enough to allow the determination of these elements in the samples under study. It must be mentioned that the limits of detection found for vanadium were always comparatively high in our ETV device because this element is present as impurity in the tungsten coils.

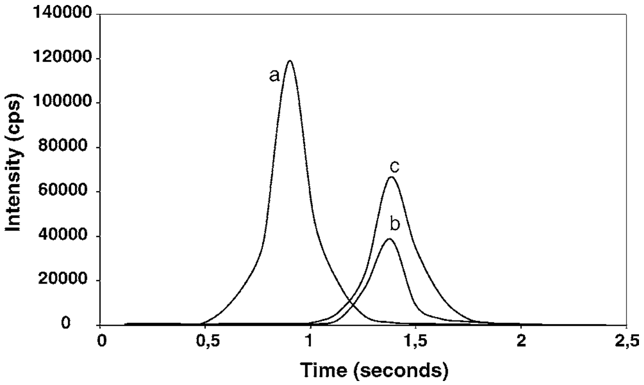

Fig. 4. Signals profiles obtained for copper using the ETV device: (a) 25 pg of Cu in 0.5% of nitric acid; (b) a talc slurry containing about 50 pg of Cu; (c) a talc slurry (about 50 pg of Cu) spiked with 50 pg of Cu.

Table 2
Relative limits of detection (ng/g) obtained for USS-ETV-ICP-MS, ETV-ICP-MS (atomising an aqueous standard solution) and ICP-MS (conventional nebulisation)

	USS-ETV-ICP-MS	ETV-ICP-MS	ICP-MS
As	0.5 (5)	0.064 (0.64)	0.021
Ce	0.8 (8)	0.091 (0.91)	0.008
Cd	0.9 (9)	0.020 (0.20)	0.004
U	0.3 (3)	0.002 (0.02)	0.001
V	0.5 (5)	0.488 (4.9)	0.005
Pb	1.3 (13)	0.063 (0.63)	0.020
Li	0.9 (9)	0.022 (0.22)	0.004
Rb	0.5 (5)	0.041 (0.41)	0.006
Sb	0.6 (6)	0.034 (0.34)	0.006
Ba	3.3 (33)	0.237 (2.4)	0.029

Absolute limits of detection (pg) are shown in parentheses.

Table 3
Microwave program used for the digestion of the samples

Step	Time (min)	Power (W)
1	2.0	200
2	3.5	400
3	7.0	700
4	15	0

3.7. Analysis of samples

Three samples, a micronised talc sample, a quartz E-1 sample and a quartz reference material CRM066 were analysed using the ETV device by aqueous calibration and by standard additions (see Section 2.3). On the other hand, the same samples were also analysed by aqueous calibration using conventional nebulisation after microwave digestion of the samples in order to validate the results found with the ETV device. To do that, 0.2 g of solid sample was weighted in a PTFE vessel. Then, 3 mL of 65% nitric acid (subboiled) and 2 mL of concentrated hydrofluoric acid were added to the samples. The vessels were closed, allocated into the microwave oven and the microwave program shown in Table 3 started. The digested samples were finally diluted up to 50 mL with ultrapure water.

In all cases, ^{115}In was selected as internal standard in order to correct medium to long-term instrumental sensitivity drifts. This isotope was selected as internal standard because its mass is in the middle of the mass spectrum, it has a high abundance (95.6%) and it was not detected in the samples under study. Unfortunately, this internal standard could not be used for the correction of matrix interferences as sought elements show different behaviour during the vaporisation process (especially when volatile and non-volatile elements are vaporised simultaneously). Moreover, the matrix signal suppression depends on the analyte and consequently, it is not possible to find a single element to correct matrix interferences for all elements.

Table 4
Concentrations (in microgram of analyte per gram of solid sample) found by USS-ETV-ICP-MS using aqueous calibration and standard additions and by conventional nebulisation after microwave digestion of the samples using aqueous calibration with internal standards

Element	USS-ETV-ICP-MS		Conventional nebulisation
	Aqueous calibration	Standard additions	Aqueous calibration
Talc sample			
Cu	2.1 ± 0.4	3.9 ± 0.4	3.5 ± 0.1
Mn	0.7 ± 0.1	3.6 ± 0.5	3.3 ± 0.2
Cr	0.12 ± 0.04	0.36 ± 0.04	0.25 ± 0.03
V	0.64 ± 0.08	0.72 ± 0.06	0.62 ± 0.04
Li	0.7 ± 0.2	2.5 ± 0.4	2.6 ± 0.2
Quartz reference material CRM066			
Cu	0.65 ± 0.13	1.02 ± 0.10	0.95 ± 0.04
Pb	1.6 ± 0.3	2.9 ± 0.4	2.8 ± 0.1
Mn	4.8 ± 0.5	5.6 ± 0.7	5.2 ± 0.3
Cr	1.2 ± 0.3	3.3 ± 0.4	3.0 ± 0.1
Sn	0.30 ± 0.08	0.65 ± 0.07	0.70 ± 0.02
Mg	18 ± 2	25 ± 4	33 ± 1
U	2.09 ± 0.42	2.25 ± 0.20	2.23 ± 0.04
Ba	52 ± 8	61 ± 7	62 ± 2
Sr	3.8 ± 0.1	4.8 ± 0.4	4.9 ± 0.1
Zn	4.2 ± 0.1	9.0 ± 0.9	9.2 ± 0.1
Sb	0.48 ± 0.06	0.60 ± 0.07	0.55 ± 0.07
Rb	1.03 ± 0.11	1.31 ± 0.16	1.22 ± 0.04
Ce	3.2 ± 0.3	3.5 ± 0.4	3.7 ± 0.1
Quartz E-1			
Cu	0.4 ± 0.1	0.9 ± 0.1	0.9 ± 0.1
Pb	3.5 ± 0.4	6.1 ± 0.6	5.9 ± 0.2
Mn	0.9 ± 0.2	1.3 ± 0.2	1.2 ± 0.1
Sn	0.55 ± 0.12	0.83 ± 0.10	0.75 ± 0.03
Mg	8 ± 2	11 ± 2	20 ± 1
U	1.8 ± 0.4	2.1 ± 0.3	2.0 ± 0.1
Ba	12 ± 2	16 ± 2	15 ± 1
Sr	3.0 ± 0.2	3.6 ± 0.4	3.5 ± 0.1
Zn	1.1 ± 0.2	2.7 ± 0.3	2.7 ± 0.1
Sb	0.7 ± 0.1	1.0 ± 0.1	1.0 ± 0.1
Rb	1.8 ± 0.1	1.9 ± 0.2	1.9 ± 0.1
Ce	2.1 ± 0.3	2.3 ± 0.2	2.2 ± 0.1

Results are shown in Table 4. As it can be seen, the concentrations found by standard additions to the slurry samples (USS-ETV-ICP-MS) are in good agreement with those found by ICP-MS with aqueous calibration using conventional nebulisation (microwave digestion of the samples). As expected, the concentrations found using the ETV device and aqueous calibration were always lower than those found by standard additions (owing to matrix effects).

Some elements could not be determined because their signal saturated the detector. This was the case for aluminium, iron (owing to their relatively high content in the tungsten coil), titanium and calcium (contained in high concentrations in the quartz and talc samples). Also, magnesium in the talc samples could not be determined due to its high concentration in such samples.

4. Conclusions

The analytical methodology proposed here allows the determination of ultratrace elements in high silicon content samples without acid digestion or melting of the samples. The analysis of the slurries with the home-made ETV device (tungsten coil) coupled to an ICP-MS detector reduces the risk of contamination, is less time consuming and avoids the digestion of the samples and the use of hydrofluoric acid.

Unfortunately, strong matrix interferences were found as the main limitation of this method. Consequently, calibration by standard additions was mandatory. Additionally, the relative limits of detection are at less one to two orders of magnitude poorer (higher) than those found by conventional nebulisation. Nevertheless, the absolute limits of detection are in the level of picograms and they are low enough to allow the quantification of ultratrace elements in this kind of samples.

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