

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

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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.

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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 (SiF₄), and subsequent analysis of the resultant solution by electrothermal 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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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., $^{40}\text{Ar}^{12}\text{C}$ 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 $10\ \mu\text{g/L}$ 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.

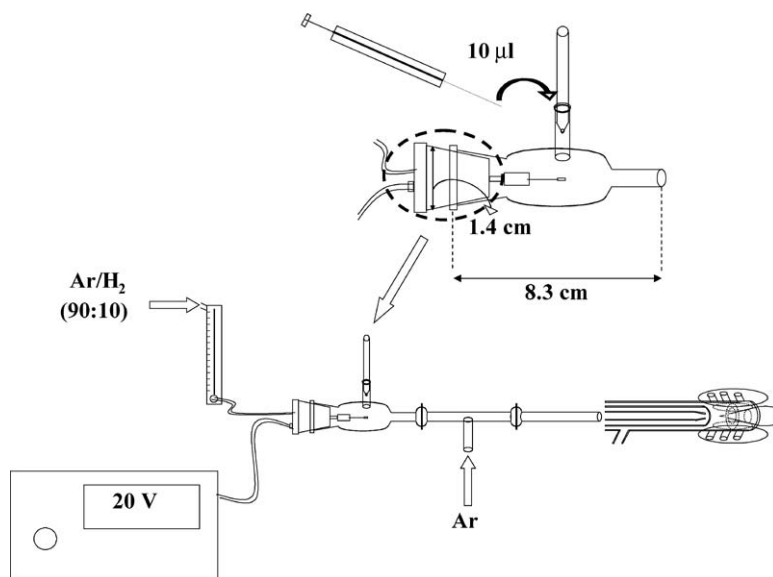


Fig. 1. Schematic diagram of the home-made electrothermal vaporisation device using a tungsten coil.

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