

Analysis of arsenic and calcium in soil samples by laser ablation mass spectrometry

Ana M. Beccaglia, Carlos A. Rinaldi*, Juan C. Ferrero

*INFIQC, Centro Laser de Ciencias Moleculares, Departamento de Físico Química, Facultad de Ciencias Químicas,
Universidad Nacional de Córdoba, Pabellón Argentina Ala I, 2do Piso, Ciudad Universitaria, 5000 Córdoba, Argentina*

Received 4 March 2006; received in revised form 6 July 2006; accepted 10 July 2006

Available online 14 July 2006

Abstract

We present an analytical procedure based on laser ablation mass spectrometry (LAMS) in order to detect and quantify arsenic and calcium in soil samples and we analyze the diverse factors that influence the precision of LAMS, such as laser fluence and matrix effect. The results indicate that a Zn matrix is a good choice for the analysis of those metals in soil samples. This work also provides a method for the direct determination of As in soil samples whose concentrations are lower than 100 ppm with a 70 ppm minimum detection limits (MDL).

© 2006 Elsevier B.V. All rights reserved.

Keywords: Laser ablation; Mass spectrometry; Elemental analysis; Soil sample; Calcium; Arsenic

1. Introduction

Arsenic is commonly found throughout the environment in a wide variety of chemical compounds, with different levels of toxicity and mobility. The main species of arsenic found in the environment are the As(III) and As(V) oxacids. In contaminated soils inorganic arsenates are the predominant species [1]. To determine the risk of As in the environment, it is obviously necessary to identify and quantify the amount present. The currently available laboratory assays used to measure As require sample pre-treatment with acid solution. The As in the sample is subsequently measured using one of several accepted analytical methods, such as atomic fluorescence spectroscopy (AFS) [2], graphite furnace atomic absorption (GFAA), hydride generation atomic absorption spectroscopy (HGAAS), inductively coupled plasma-atomic emission spectrometry (ICP-AES) and inductively coupled plasma-mass spectrometry (ICP-MS) [3]. Also X-ray fluorescence is a promising technique for field detection of arsenic and it is one of the few techniques that can directly measure arsenic in soil without requiring aqueous soil extractions [4]. Laser-induced breakdown spectroscopy has also become very useful for the detection of a wide variety of metals

in soil [5]. However, the minimum detection limit (MDL) of this method is strongly dependent on the emission coefficient of the element to be analyzed, which in the specific case of As precludes a successful use. In addition, the MDL is also a function of other variables such as plasma temperature, soil moisture and grain size. Reported detection limits for As, such as 705 ppm, are poor when compared with other methods [6]. Although improvements to this technique have reportedly brought this limit down to 400 ppm [7], LIBS still requires more studies to further improve its sensitivity for arsenic.

In addition to As, calcium was selected as analyte because it is one of the main components of soils and it plays a relevant role in determining its cohesibility and fertility. One important characteristic of soils is that several different salts of the same cation are usually present. Some of these are soluble either in water or in acids and they can easily be determined using standard techniques. Another kind of compounds, e.g., silicates, are not soluble and require more energetic treatments, such as melting at high temperatures or dissolution with hydrofluoric acid. The LIBS technique has proven to determine the total concentration of Ca, of both soluble and insoluble Ca compounds [8].

The main advantage of laser ablation methods is its simplicity, together with the rapid sample preparation and potential use as an in situ detection method. The main drawback is the dependence of the signal used to detect the species of interest on the properties of the matrix [9]. Changes in its composition affect

* Corresponding author. Tel.: +54 351 4334180; fax: +54 351 4334188.
E-mail address: crinaldi@fcq.unc.edu.ar (C.A. Rinaldi).

the absorption process and the amount of mass removed by the laser pulse [10]. This problem can be overcome using an internal standard method. Therefore, the selection of the matrix is of fundamental importance for soil analysis. In addition, the ablation process is associated with elemental fractionation, i.e. the analytical signal does not represent exactly the sample composition as a consequence of non-stoichiometric ablation [11,12]. However, good precision and accuracy have been reported when the fractionation of element to be determined is similar to the element added as an internal standard [13].

Recently, Brinckerhoff has been developing a laser ablation–time of flight–mass spectrometer (LA–TOF–MS) method [14,15] that has been optimized for elemental and isotopic analyses on airless bodies. These designs are of special interest for the geochemical analysis of neighbour planets, like Mars.

In this paper, we present a new procedure for the analysis of As and Ca in soil, based on laser ablation of a solid sample and quadrupole mass analysis, actually denominated laser ablation mass spectrometry (LAMS). Many of the problems due to the soil matrix were overcome by incorporating Zn to the sample and using this element as an internal standard.

2. Experimental

2.1. Instrumentation

A schematic diagram of the experimental set-up is shown in Fig. 1. It consists of a laser, a vacuum chamber with a motorized stage, a quadrupole mass spectrometer, control electronics and a computer for data acquisition. The Nd–YAG laser delivered a 10-ns pulse of 55 mJ at 1064 nm at repetition rate of 5 Hz. The laser beam was focused to a 0.48-mm diameter spot on the target surface by using a 7.5-cm focal length lens. Under these experimental conditions the laser fluence could be adjusted in the range 0.1–40.0 J cm⁻². The samples were pressed pellets, mounted on an ablation disc whose position was changed using a motorized stage. All the system was located in a vacuum chamber at 10⁻⁶ Torr of total pressure. The axis of a mass quadrupole (Baltzer QMS 200) spectrometer was set normal to the ablation surface in order to detect the ablated material. The QMS was set at 30 cm from the ablation point after a skimmer with a 2 mm

Table 1

Instrumental operating conditions

Laser	Nd:YAG
Wavelength (nm)	1064
Laser mode	Q-switched
Energy/pulse (mJ)	55
Frequency (Hz)	5
Spot diameter (mm)	0.48
Fluence (J cm ⁻²)	30
Mass spectrometer	QMS 200
Measurement mode	Peak hopping
Dwell time (ms)	10
Data acquisition time (s)	15
Background offset time (s)	5
Points per peak	1
Resolution mode (0–300)	$R = \Delta M(\text{peak width})/M(\text{mass}) = 30$
Integration parameters	
Processing mode	Peak area integration
Integration time (s)	10
Replicates	6

diameter orifice. This distance from the ablation point and the use of the skimmer was set in order to reduce the huge amount of particles produced in the ablation entering in the QMS and also to maintain it clean. The atoms produced in the plume were ionized by electronic impact, with 70 eV of energy. No ions were detected directly from the ablation plume when the ionizer of the QMS was turned off. Each result reported is the mean value of six measurements obtained from ablation on different spots on the sample. Technical details of the LAMS experimental set-up are given in Table 1.

Data were acquired in the peak hopping mode with a dwell time of 10 ms. Background levels for each element were established by acquiring data for approximately 20 s prior to the beginning of laser ablation. Laser sampling for quantitative analysis was performed at 5 Hz and the laser was fired for 10 s to obtain steady-state signals. Count rates were collected using the QMS software as an experimental data file which was then converted in a spreadsheet file. The intensity signal during the ablation time was integrate for each element and corrected by the background. Once the integration was made the different signal intensity ratio was calculated.

2.2. Preparation of the samples

The pellets were prepared using Zn metal powder (Mallinckrodt, 99.99%), CaCO₃ (Aldrich powder 99.99%), stock solution of As 1041 ppm and the soil. In order to determine the purity of the Zn metal a pellet was prepared with Zn as a sole component and analyzed using the LAMS set-up. It was found that the purity was in agreement with the claim of the manufacturer. The composition of the pellets (50% Zn; 50% soil) used in the internal standard method is shown in Table 2. The pellets were prepared by mixing all the components in a mortar, which were subsequently powdered using a mill and then pressed in two stages. In the first stage, a pressure of 36 kpsi was applied for 10 min and in a second stage the pellets were additionally pressed with 54 kpsi during 5 min. The grain size of the powder of the pellets was

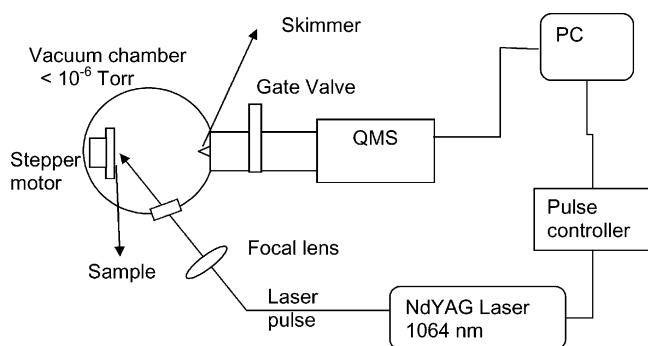


Fig. 1. Schematic diagram of the experimental set-up. QMS: quadrupole mass spectrometer and PC: personal computer.

Download English Version:

<https://daneshyari.com/en/article/1171990>

Download Persian Version:

<https://daneshyari.com/article/1171990>

[Daneshyari.com](https://daneshyari.com)