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Technical Note

Quantitative analysis of oxide materials by laser-induced breakdown spectroscopy with argon as an internal standard

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ABSTRACT

Laser-induced breakdown spectroscopy (LIBS) is demonstrated as a quantitative technique for geochemical analysis. This study demonstrates the applicability of LIBS to multielemental analysis of minerals using argon as an internal standard. Laser-induced breakdown spectroscopy has been applied to measure elements in oxide form. In the present study, the contents of several oxides, such as Fe_2O_3 , CaO and MgO , in geological samples from the Tierga Mine (Zaragoza, Spain) were analyzed by LIBS. An argon environment was used to eliminate interference from air at atmospheric pressure. Furthermore, argon was used as an internal standard. The result was enhanced signal and enhanced linearity of the calibration curves. The Fe_2O_3 , CaO and MgO concentrations determined by LIBS were compared with the results obtained using another analytical technique, inductively coupled plasma optical emission spectrometry (ICP-OES). The concentrations found using LIBS were in good agreement with the values obtained by ICP-OES.

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1. Introduction

Laser-induced breakdown spectroscopy (LIBS) enables geological researchers to obtain the atomic emission spectrum of a sample (solid, liquid or gas) [1], from which qualitative and quantitative information about the sample can be derived from adaptive spectral processing. LIBS's ability for multi-elemental quantitative analysis has been demonstrated in many fields, such as metallurgy, mining, environmental chemistry, art conservation, etc. [2–6]. The LIBS method has been employed to analyze different oxide materials, such as glasses [7], ores [8], pottery glaze [9] and iron oxide powders [10]. A very common application of LIBS consists of measuring a species' concentration in a sample from the species' calibration curve [11], i.e., from the intensity of a related spectral line. One of the major drawbacks of the technique is the need for calibration samples and standards in the same matrices as the samples under investigation. For quantitative analysis, other statistical methods have been used to process LIBS spectra, such as Partial Least-Squares (PLS) regression [12] and Artificial Neural Networks (ANN) [13]. To perform an accurate quantitative analysis, the three existing types of interferences, self-absorption, spectral overlap (spectral line interference, band interference), and matrix effects (chemical interferences), must be avoided in LIBS [14]. Due to self-absorption, the intensity of the line saturates, and depending on the spectroscopic features and the experiment, the calibration curve bends at concentrations higher than the critical value. Thus, the sensitivity of the curve decreases, and the measured line intensity is not proportional to the

concentration of the element in the sample. To self-absorption issues, resonance lines should only be used to measure trace elements. Care should be taken in the analysis to avoid spectral interference between lines. Emission lines are often superimposed on bands emitted by oxides and other molecular species in the air or sample. The matrix effect originates from the physical and chemical properties that change the laser-matter interaction from one sample matrix to another. As a consequence of these matrix effects, the final relationship between the LIBS signal and the analyte concentration depends on the matrix of the sample. This effect can be minimized by the use of internal standards and by calibration with proper reference samples characterized by similar matrix compositions [15]. In addition, the plasma formation dynamics, sample ablation and associated processes are highly nonlinear and are not fully understood, which may also be partially accountable for the matrix effect. Another common analytical procedure involves normalizing the analyte signal to a standard reference signal [1], although appropriate reference signals are not always readily available. These procedures overcome most matrix effects. Alternatively, the calibration-free LIBS approach [16] was successful in performing quantitative analyses of some materials, especially if all the major elements were detected and if the produced plasma preserved the sample stoichiometry.

The objective of this work is to demonstrate the capability of LIBS to simultaneously determine Fe_2O_3 , CaO and MgO in mineral samples while minimizing matrix effects. The solution to this problem was to use argon as an internal standard. Placing the samples in an argon atmosphere avoids interference from air and enhances the intensities of all the transition lines. The argon was used as an internal standard; the most important advantage is that argon can be used to analyze any type of sample without treatment because of argon's gaseous state.

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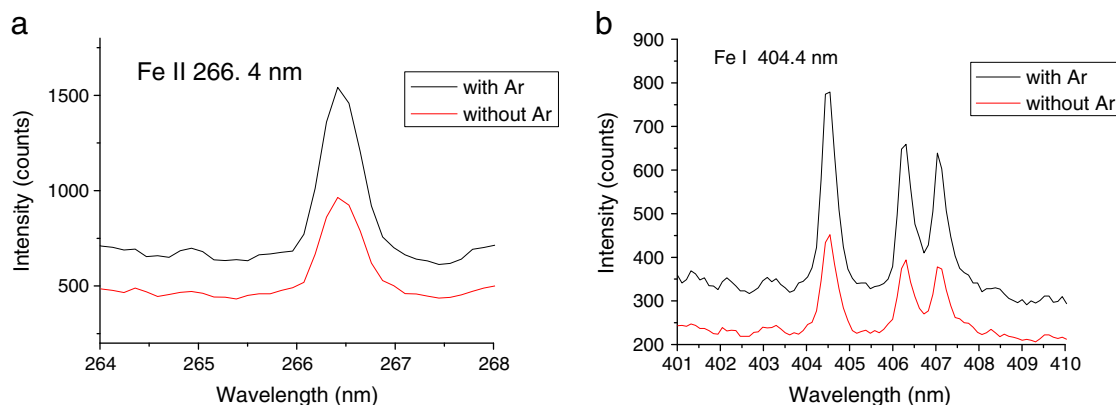


Fig. 1. Comparison of spectra obtained with and without the argon flow, a) Fe emission line at 266.4 nm, and b) Fe emission line at 404.4 nm.

Using standard samples, several calibration curves were prepared for each element. The LIBS results were compared with results obtained using ICP-OES.

2. Experimental

2.1. Instrumental setup

The experimental setup was a Q-switched Nd:YAG laser (Quantel, model Ultra CFR) at 1064 nm (pulse width of 7.7 ns and maximum pulse energy of 50 mJ) focused on each sample with a 150 mm focal length lens. The target surface was positioned approximately 70 mm above the focal plane to avoid breakdown in air, and the resulting laser spot diameter was $d \approx 1$ mm. Radiation from the laser spark was collected with a bifurcated optical fiber (QBIF600-UV-VIS, 600 μm , Premium Bifurcated Fiber, UV/VIS, 2 m, ATO) that had been connected to a dual-channel Ocean-Optics spectrometer (LIBS2500plus, Ocean Optics Inc., Dunedin, FL, USA). The plasma was collected in a noncollinear mode. The pulse energy used was approximately 7.5 mJ because some emission line signals were saturated at higher energies. The position of the collimating lens (74-UV Ocean Optics, f/2 fused silica lens for 200–2000 nm, 5 mm diameter, 10 mm focal length) was adjusted for a maximum light collection at 45° relative to the sample surface. The spectrometer has the following characteristics: channel one, a HR2000 + grating H5, selected from 205 to 220 nm, best from 200 to 400 nm, and a DET2B-UV ILX-511B detector, with a UV2 window and an optical bench entrance aperture 10 μm in width; and channel two, a HR2000 + grating H3, selected from 410 to 440 nm, best from 350 to 850 nm, and a DET2B-VIS ILX-511B detector with a VIS window, an

optical bench entrance aperture 10 μm in width, and an F1-GG395 longpass filter (transmits > 395 nm). The optimal experimental conditions were a delay time of 2.5 μs , with respect to the laser pulse, and a gate time of 10 μs . The delay time was sufficient to suppress background signals from continuum plasma radiation. The spectrometer is triggered to acquire and read out data simultaneously. A LIBS Sample Chamber (LIBS-SC, Ocean Optics) was used to purge air. The chamber was flushed with argon at a rate of 0.9 L/min to purge air during each measurement at atmospheric pressure. For all measurements, the target was moved horizontally between shots, so each laser pulse sampled a fresh location to improve the reproducibility of the mass ablation. Each sample measurement consisted of 5 replicas; one replica is the average of 50 laser shots using an average delay between scans of 100 ms. 250 LIBS spectra were recorded for each sample. The optimized experimental parameters for the laser pulse energy, gate delay time, gate width and number of shots averaged per spectrum were fixed for all experimental data acquisition procedures.

2.2. Preparation of samples and standards

A series of ore samples of known compositions were supplied by the Tierga Mine (Zaragoza, Spain) to assess the viability of using the LIBS system to quantify the concentrations of Fe_2O_3 , CaO and MgO. The samples were collected from different areas of the mine. A total of seven samples (2G3C, 3G4C, 4GFND, LS31, MP2, MP5 and MP7) were analyzed. The mineral samples were ball milled to a fine powder, and pellets were produced for the LIBS measurement. In addition, to prepare the standards, five different reagents (Fe_2O_3 , CaCO_3 , MgO, SiO_2 and Al_2O_3) in powder form were mixed together in different mass ratios.

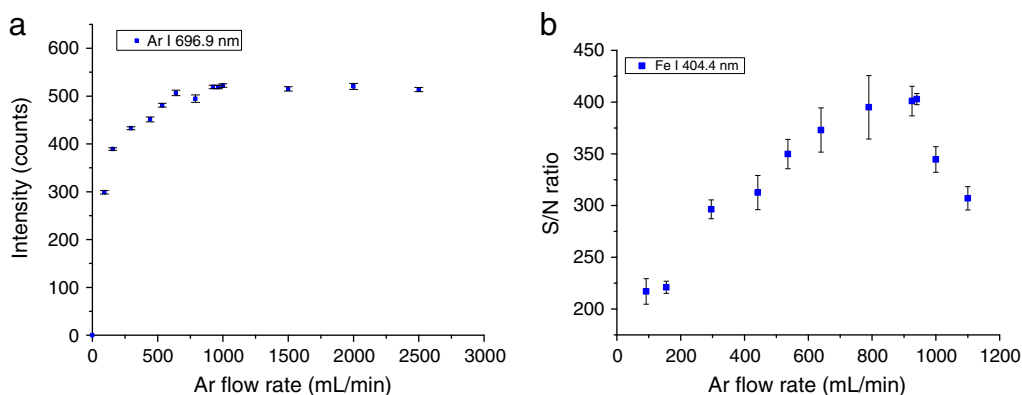


Fig. 2. Optimization of the argon flow rate. In these plots, the error bars of the experimental LIBS data points show the standard deviation.

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