



## Characterization of natural and treated diatomite by Laser-Induced Breakdown Spectroscopy (LIBS)



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### ABSTRACT

Differences and similarities between natural diatomite from Mascara, Algeria and its acid washed and microwave irradiated product have been assessed in this study using Laser Induced Breakdown Spectroscopy (LIBS). LIBS is demonstrated as a multi-elemental analysis technique of geological samples with a fast response. Diatomite is commonly used as filtration aid, mild abrasive in products such as metal polishes, adsorbent for liquids, and as porous support for chemical catalysts. LIBS analyses confirmed the reduction of calcium, magnesium, iron or sodium in treated diatomite with respect to natural one, which improves its characteristics as filters or as adsorbents. In the present study, the contents of Ca, Mg and K in the diatomite samples were analyzed with LIBS. Finally, Field Emission Scanning Electron Microscopy (FESEM) was employed for describing the morphology and microstructure of these materials.

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### 1. Introduction

Diatomaceous earth or diatomite is a fine-grained, siliceous natural sedimentary rock formed by fossilized microscopic skeletons of diatoms, which are unicellular algae found in aqueous systems (seawater or pure water). These skeletons are found in a variety of forms such as spheres, disks, wheels and needles. The main component of diatomite is amorphous silica ( $\text{SiO}_2 \cdot n\text{H}_2\text{O}$ ), with variable quantities of clays and mineral carbonates, quartz, feldspars and organic matter. Regarding physical properties, diatomite has a high permeability (0.1–10 mD) and porosity (35–65%) [1], high surface area [2–4] small particle size (typically from 10 to 200  $\mu\text{m}$ ), low thermal conductivity and low density (dry powdered natural rock may have 80 g/L to 250 g/L) [5,6]. The presence of water governs the properties of diatomite, such as hydrophobia, solubility, charge, acidity, ion exchange and adsorption capabilities [7–9].

Their low price, high abundance and exceptional physical and chemical properties such as permeability, porosity, chemical inertness, sorption capacity [10] make diatomite into an interesting material with plenty of possible uses. Diatomite is widely employed for industrial activities in filters [11], for the removal of chemicals from wastewaters [12] or as catalyst support [13,14]. Among the properties of diatomite,

the pore size distribution, the bulk density and the impurity content (clays, quartz, feldspars, etc.) are the dominant factors that determinate the quality of this material as catalyst carrier [15]. The reduction of those impurities can improve the properties of diatomite. Several approaches have been reported for this purpose [16–19]. In this work, a process comprising acidification with HCl 1 M and irradiation with microwave has been employed for reducing the impurities content of diatomite. It is known that HCl removes effectively alkali, alkaline earth and iron compounds whereas silica and alumina (or some compounds of aluminum) are slightly affected by the acid washing at room temperature [20].

Given the importance of an adequate characterization of the composition of diatomite for possible industrial uses, it is essential to investigate the optimal analytical techniques for the said purpose. Laser Induced Breakdown Spectroscopy (LIBS) is commonly used for analyzing complex solid samples [21–23]. It is an atomic emission spectroscopic technique, which uses a high-energetic pulse as excitation source. The laser beam is focused on the sample's surface, generating a plasma, whose light is collected and analyzed to obtain the elemental composition. LIBS is a simple, fast, robust and stable technique that offers some critical advantages over conventional techniques [24,25]. It offers micro-destructive analysis [26] and it can be performed under atmospheric conditions having variable spatial resolution [27,28] over the samples. Furthermore, LIBS generally does not require sample pretreatments, which often is the hardest and the most expensive tasks in chemical analyses.

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The composition of solid samples like diatomite could be determined by several techniques such as Fourier Transform Infrared Spectroscopy (FTIR), X-Ray Diffraction (XRD), Inductively Coupled Plasma-Mass Spectroscopy (ICP-MS) or Atomic Emission Spectroscopy (ICP-AES) (further information about these techniques can be found in [29]). FTIR is applicable for powder samples, provides analysis without interference and can be used for studies of the hydroxyl-stretching region of silicate minerals. The XRD can be used for the identification of the crystalline phases and ICP-MS or AES are powerful quantification techniques. Each of these techniques present advantages and disadvantages with respect to LIBS but, as stated before, LIBS does not require wet chemistry prior to analysis.

LIBS has been used for quantitative analysis of elements' concentrations or ratios in geomaterials [30]. LIBS greatest advantages for this purpose stem from the fact that every element in the periodic table emits light in measured LIBS range (200–1000 nm). Different LIBS approaches have been proposed to quantify a great variety of elements in different geological samples [31]. Some examples of studies based on LIBS are: the determination of Cr, Cu, Mn, Ni and Fe in mineral drill cores with normalization approach [32]; the analysis of Fe, Ca and Mg in ore samples with Ar internal standard [33] or the quantification of Fe, Mg, Si, Mn, Al, Ca and Ti in certified laboratory samples and rocks from meteorite impact sites [34].

In this work LIBS has been used to assess the differences in composition between natural and treated diatomite by means of the identification of its metallic components (calcium, aluminum, magnesium, silicon, iron, potassium and sodium) and the quantification of major elements (calcium, potassium and magnesium) using an external calibration standard. The capability of LIBS for the assessment of the effect of acidification and irradiation on diatomite rock has been evaluated. These two treatments affect the amount of previously mentioned impurities, which are crucial for its applications (filtration, absorbents, fillers or as ingredient in cements). Before that, the morphology and microstructure of the materials has also been studied using FESEM that provides topographical and elemental information at magnifications between 10 and 300,000 $\times$ .

## 2. Materials and methods

### 2.1. LIBS instrumentation

The LIBS set-up is based on a Q-switched Nd:YAG laser (Brilliant Quantel, model Ultra CFR) at 1064 nm which creates a 7.7 ns pulse width and 2.6 mm diameter laser beam with a maximum pulse energy of 50 mJ. Radiation from the laser spark is collected with a bifurcated optical fiber (QBIF600-UV-VIS, 600  $\mu$ m, Premium Bifurcated Fiber, UV/VIS, 2 m, ATO) that had been connected to a dual-channel Ocean-Optics spectrometer (LIBS 2500plus, Ocean Optics Inc., Dunedin, FL, USA) The laser beam is directly focused on samples through a 150 mm focal length lens.

LIBS set-up presents two parameters to be modified: laser energy and lens-sample distance. The resulting spectrum should have good signal-noise relation and spectral lines need to be intense and well-separated for quantifying the different major components. Thus, energy of 35 mJ was chosen to maximize peak intensities without saturating the CCD. Using higher energies resulting on saturation of the most intense signals and using lower energies may present reproducibility problems. The lens-sample distance is strongly influenced by the laser energy. For the selected energy, about 9.5 mm offered the best resulted spectrum.

During the analysis, the laser beam is absorbed by the sample, which is melted, ablationated and then, a high-temperature plasma is formed, generally exceeds 10,000 K. The light is then collected by an optic fiber and diffracted by the Ocean-Optics spectrometer. The position of the collimating lens (74-UV Ocean Optics, f/2 fused silica lens for 200–2000 nm, 5 mm diameter, and 10 mm focal length) was adjusted at

45° respect to the sample surfaces. The main characteristic of the spectrometer is its dual channel: 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  $\mu$ m 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  $\mu$ m in width, and an F1-GC395 longpass filter (transmits >395 nm).

The sample was shot at a hundred different positions to obtain a single average spectrum and sampling positions covered at least  $3 \times 1 \text{ cm}^2$  of the surface of the rock. In addition, 0.16 g of irradiated diatomite powder was grinded with an aghata mortar and compressed by a manual hydraulic press (Perkin Elmer IR Accessory Hydraulic Press) with  $5 \times 10^4 \text{ N}$  for 2 min. The resulting pellet was also shot 100 times in different spots to obtain a single average spectrum.

### 2.2. Acid-washing and microwave processes

The treatment applied to the diatomite sample consisted in washing it several times with demineralized water (conductivity  $\leq 1 \mu\text{S/cm}$ ) and drying it in an oven at 105 °C for 10 h. Then, the material was allowed to cool in a desiccator. After that, hydrochloric acid 1 M was used to remove impurities. For this purpose, 100 g of crude diatomite were suspended in 1 L of acid solution. The mixture was subject to mechanical agitation for 30 min and was followed by microwave heating under reflux. This operation was repeated three times. After cooling, filtrated diatomite was washed several times with distilled water to a pH of 8–9. Finally, the powder thus prepared was dried by microwave for 2 h and pressed into pellets for carrying out the analysis with LIBS.

### 2.3. Preparation of samples and standards

For preparing the calibration standards, six different reagents were mixed in different mass ratios: Al<sub>2</sub>O<sub>3</sub> (Scharlau, synthesis grade), CaCO<sub>3</sub> (Scharlau, precipitate, purissimum), Fe<sub>2</sub>O<sub>3</sub> (Scharlau, synthesis grade), KAc (Panreac, pure, pharma grade), MgO (Scharlau, extra pure), NaAc (Labkem, extra pure) and SiO<sub>2</sub> (Acros Organics, extra pure). Element concentrations of each standard are shown in Table 1. The mixtures were homogenized using a ball mill (BeadBug Microtube Homogenizer, Model D1030(E), Benchmark) for 3 min at 4000 rpm. After that, pellets of standards were made with a manual hydraulic press under a pressure of 5000 kPa for 2 min.

The natural diatomite was directly analyzed without preliminary steps, whereas, as mentioned above, the treated diatomite powder was pressed into a pellet.

### 2.4. FESEM instrumentation

The Merlin Field emission scanning electron microscopy (FESEM) was used for the initial morphological study of our material and was performed by General Services Research Support of University of Zaragoza. Compared with conventional SEM, FESEM produces clearer, less

**Table 1**  
Percentages values of each element in calibration standards (CS). SiO<sub>2</sub> were used as matrix.

	CS1	CS2	CS3	CS4	CS5	CS6	CS7
Al	0.72	0.70	0.52	0.62	0.79	0.55	0.64
Ca	0.45	0.97	3.08	5.04	7.00	10.03	12.11
Fe	0.45	0.51	0.62	0.54	0.49	0.60	0.55
Mg	0.30	0.52	0.66	1.00	3.09	5.00	7.78
K	0.61	1.00	2.57	3.89	4.94	6.97	9.99
Na	1.70	1.84	2.27	1.58	1.66	1.90	2.15

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