Quantification of fluorite mass-content in powdered ores using a Laser-Induced Breakdown Spectroscopy method based on the detection of minor elements and CaF molecular bands ☆

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ABSTRACT

Laser Induced Breakdown Spectroscopy (LIBS) is investigated as a fast and robust method to determine the fluorite (CaF_2) mass-content of powdered ore samples. Calibrating samples covering a wide CaF_2 concentration range (from 2.3 to 97.6%) are employed. LIBS operating conditions are optimized for the analysis of elemental emission lines and molecular bands, respectively. In particular, LIBS emission intensities from different CaF molecular bands are evaluated to calibrate the fluorite concentration as an alternative to the use of atomic fluorine F I emission lines. Furthermore, the determination of LIBS emission signals from minor elements (e.g. Si I and Mg I) is studied to further improve the accuracy and precision of pure fluorite sample analyses (e.g. [CaF_2] > 75%). The proposed LIBS method avoids the tedious dissolution processes that are required by other analytical methods employed in mining industry for the quantitative analysis of fluorite.

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1. Introduction

Fluorite (or fluorspar) is a mineral composed of calcium fluoride (CaF_2) that is mainly used for the production of hydrofluoric acid, which is the principal feedstock for the vast majority of fluorine related chemicals. Other uses of this mineral include the production of aluminum fluoride, iron and steel casting, manufacture of abrasive compounds, welding items and high quality optical element manufacturing [1]. The measurement of the mineral purity in the processing of the fluorite ore is a key point in mining industry as certain quality standards need to be satisfied. Therefore, the development of robust, accurate and fast analytical methods to evaluate the composition of the fluorite ores is highly demanded.

The main analytical methods employed in the mining industry to evaluate the fluorite ores are based on the recommendations given by ISO normative. Some of these methodologies include the use of fluoride-ion sensitive electrode (ISO 5439:1978) or the spectrometric measurement of the absorbance (ISO 5438:1993). In particular, the grade or content of fluorite in the sample might define the most appropriate method [2]. It has to be noted that this sort of analyses takes several hours and implies the use of reactants to dissolve the fluorite.

Other analytical approaches for fluorine chemical determination include ICP–OES and ICP–MS. These techniques, that also require sample solution, are typically based on the use of an Ar-plasma where the ionization and excitation of fluorine is quite inefficient due to the high first ionization potential of this element (17.42 eV) as compared to Argon (15.76 eV) [3]. To overcome this drawback, fluorine-containing polyatomic ions formed in the ICP, such as BaF^+, have been also used to improve sensitivity and limits of detection in the determination of fluorine mass content [4].

Another interesting approach in the determination of fluorite concentration would be the use of direct solid analysis techniques that allow faster calibration methods. In this sense, neutron activation techniques have demonstrated its capability for quantifying CaF_2 content in fluorite ores [5]. However, these methods involve radioactive installations (e.g. samples are bombarded by neutrons and gamma photons are measured from the radioactive products) that complicate its use as a routine and in-situ technique. As an alternative, it is considered the use of Laser-Induced Breakdown Spectroscopy (LIBS), which is a powerful and versatile technique that provides analytical and physical information from the spectral emission of laser-induced plasmas [6]. LIBS is based on the use of a short-duration pulsed laser that is focused onto a sample surface producing a breakdown, and thus creating a high temperature plasma and converting the analyzed sample into vapor and particles [7,8]. The main advantages of LIBS include, fast analysis time, multi-element detection in any kind of material (solid, liquid, or gas) with high spatial resolution (at the μm range), and the potential to carry out in-situ or stand-off analysis [9,10]. Moreover, LIBS is sensitive to light elements (e.g. He, Li, Be), which are difficult to be determined by

other analytical techniques. Additionally LIBS requires minimum sample preparation, avoiding complex and time consuming procedures.

Among the different applications of LIBS, geochemical and environmental analyses have shown a growing interest [11]. For instance, recent studies have been published on the use of geochemical fingerprints from LIBS spectra for the rapid analysis and discrimination of minerals [12–14]. In relation to the determination of fluorine, the strongest emission lines of this element are found in the VUV spectral range (100–190 nm) [15]. However, the detection of the LIBS emission spectra in this region would require the operation of the experimental set-up at vacuum conditions or the use of a nitrogen-purged spectrometer to remove the presence of oxygen, which has a strong absorption in this spectral region. Alternatively, it is possible to measure fluorine from the F I emission lines in the range 680–705 nm, although the intensity of these LIBS emission lines is significantly lower. Several studies have been carried out in order to investigate the LIBS analytical potential for the detection of fluorine in this region, concluding that the use of a He atmosphere significantly improves the limits of detection. For instance, D. A. Cremers and Radziemski [16], demonstrated that the fluorine detection limit could be improved from 2000 ng to 3 ng for fluoride analyses in gas phase. Further studies by Tran et al. [17,18], also showed an improvement in the detection of gaseous and particulate fluorides and in the detection of fluorine in solid organic compounds. Additionally, Asimellis et al. [19], demonstrated that together with the use of a He atmosphere, the control of the pressure in the ablation chamber is a key parameter. In particular, it was shown that the determination of fluorine in pharmaceutical products was improved using a He atmosphere at 60 mbar.

In this work, the use of F I emission lines is evaluated; as well as an alternative approach for the determination of the fluorite concentration in ore powdered samples using LIBS in an air atmosphere. This new method is based on the measurement of the emission from CaF molecular bands. This strategy was originally proposed nearby the 1930s to be used in arc spectroscopy [20,21]. In particular, it was shown that CaF molecular bands have a stronger optical emission than F elemental lines, probably due to the lower ionization potential of the CaF molecule (5.83 eV) [22]. It is known that using LIBS it is possible to measure small molecules, which are produced by recombination processes during plasma cooling, selecting larger acquisition delay times [23–26]. Also the correlation between the presence of minor elements was investigated, such as Si and Mg in samples with high fluorite mass-content and its suitability to be used to quantify fluorite concentrations

2. Experimental

2.1. Instrumentation

A Nd:YAG laser (EKSPLA, NL301HT) operating at 1064 nm, with pulse duration of 4.5 ns, was used as excitation source. The laser pulse energy was set to 100 mJ/pulse using an attenuator (LOTIS-TII), and the laser repetition rate was fixed at 1 Hz. The laser beam was focused in the sample surface using an objective with 35 mm of focal length (Thorlabs; LMH-5X-1064). In particular, the sample was placed in a vertical positioner (Newport, Big Lab Jack, 9204-M) and the lens-to-sample distance was measured by a laser sensor with a maximum resolution of 0.6 μm. Moreover, it was possible to move the sample using a motorized X-Y translation stage (Newport; TRA25CC), with a 0.2 μm step and a maximum velocity of 0.4 mm/s.

Plasma optical emission was focused into an optical fiber, placed with an angle of 45° with respect to the laser beam, using a combination of fused silica plano-convex lenses (Newport, SPX022AR.10 and Thorlabs, LA4148). The light was then introduced through the optical fiber into a Czerny–Turner spectrometer (Andor Shamrock SR-500i-D1) that has a focal length of 500 mm and a grating of 1200 lines/mm. Emission signals were finally recorded using an iCCD (Andor iStar) with 1024 × 1024 pixels that have an effective size per pixel of

19.5×19.5 μm. This experimental set-up allowed the acquisition of spectral windows with a spectral width of about 30 nm.

2.2. Samples

A set of 8 fluorite ore powdered samples, with a grain size below 110 μm, were used to optimize the LIBS operating conditions and to evaluate the analytical potential of this technique. These samples were collected from different extraction regions of an Asturian (Spain) mine. Table 1a lists the CaF_2 and Si concentrations of these samples. In particular, these concentration values were obtained from fluorite standardized chemical analysis (ASTM E1506–08) and from neutron activation analysis [5]. As it is observed, these samples cover the concentration range of CaF_2 between 2.28 and 97.60%. In order to obtain more calibration points, further samples were prepared mixing these samples on different proportions using a high precise (± 0.1 mg) analytical balance (Shimadzu, AUW320). Table 1b lists the fluorite concentrations of these additional samples as well as the original samples employed to produce them. From the sample set, two samples: 'No4' [CaF_2] = 42.05% and 'L' [CaF_2] = 92.95%, were considered as validation samples. Therefore, these samples were not used to obtain the calibration curves.

The powdered samples were deposited on a double-side tape that was fixed in a glass microscope slide to make the sample handling easier. This sample preparation method was fast, simple and implied minimum sample consumption (~0.01 g).

Four raster lines, with a length of 14 mm and separated 1 mm, were analyzed in the deposited powdered samples. At each line, 35 single shot emission spectra were accumulated. Precision of the measurements was calculated as the standard deviation of the 4 raster line analysis carried out on each sample. Additionally, it was checked that LIBS emission spectra from the double-side tape did not show any spectral interference and/or any significant emission signal from the elements of interest. All data treatment was performed using the total area of the emission lines and emission bands. Integration of the signal was carried out using the LA/LIBS data analysis software by Applied Spectra, Inc. Fremont, CA, USA.

3. Results and discussion

3.1. LIBS fluorite calibration using F I atomic emission signal

In the first step the calibration of the fluorite ores through the LIBS analysis of fluorine emission signal at 685.60 nm was investigated [15]. The delay time between the laser pulse and the beginning of the signal acquisition was optimized to get the maximum sensitivity for this atomic emission line, and a value of 0.4 μs was selected. Moreover, the gate width, time during which the acquisition is open, was set to 4 μs.

At these operating conditions, the atomic fluorine emission line was investigated to quantify the fluorite concentrations of the powdered ore samples. Fig. 1 shows the LIBS background normalized LIBS signals from F I emission line at 685.60 nm versus the fluorite concentrations. A non-linear trend is observed when the whole range of fluorite concentrations under study is considered. In this vein, previous studies have also

Table 1a
Concentration of fluorite and silicon in the original samples collected from the mine.

Sample	[CaF_2] (%)	[Si] (%)
No1	2.28	75.42
No2	11.39	34.23
No3	27.05	55.17
No4	42.05	36.88
No5	59.92	25.26
No6	76.50	14.06
No7	90.98	5.04
No8	97.60	0.92