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# Direct analysis of aluminum alloys by CSigma laser-induced breakdown spectroscopy

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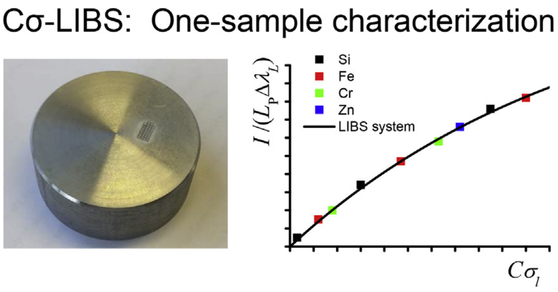
## HIGHLIGHTS

- Cσ-LIBS has been applied to direct analysis of aluminum alloys.
- After characterization with one sample, six certified alloys are analyzed.
- Average precision of 8.0% is obtained for concentrations higher than 0.1 wt %.

## GRAPHICAL ABSTRACT



Cσ-LIBS: One-sample characterization

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## ABSTRACT

We report the application of CSigma laser-induced breakdown spectroscopy (Cσ-LIBS) to quantitative analysis of aluminum alloys without sample preparation. Cσ-LIBS simplifies strongly the conventional calibration procedure of LIBS, replacing it with a characterization stage performed from the spectrum of a single standard sample. The aim of this work has been to provide a complete evaluation of the use of Cσ-LIBS for direct analysis by obtaining its figures of merit, including precision and limits of detection. Ten elements (Si, Fe, Cu, Mn, Mg, Cr, Ni, Zn, Ti and Ca) are determined in a set of six certified samples with a wide range of concentrations, from percent down to μg/g levels. The average precision is 8.0% for concentrations higher than 0.1 wt% and 13% for concentrations between 0.1 wt% and 0.01 wt%. The limits of detection are in the range 1.4–9.7 μg/g.

## 1. Introduction

Among the spectroscopic techniques allowing direct quantitative analysis of samples, laser-induced breakdown spectroscopy (LIBS) has attracted high interest due to its operational simplicity, versatility and relatively low cost [1]. Moreover, the use as spectroscopic source of a laser-induced plasma, which accomplishes local thermodynamic equilibrium (LTE) in many experimental situations, has prompted the formulation of so-called calibration-free laser-induced breakdown spectroscopy (CF-LIBS), proposed in 1999 by Ciucci et al. [2]. The features that make this concept so attractive are that it allows quantitative standardless analysis and its ability to overcome matrix effects. However, several experiments have shown that this method presents important limitations, specially a poor accuracy for minor components [3]. To improve the analytical performance, new approaches have relaxed

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the concept of calibration-free by considering the use of one or a few standard samples. Replacing the tedious conventional procedure of calibration for each element using a wide set of standards with a simpler measurement of the spectrum of one standard sample still entails a great simplification of the analytical process. Moreover, a frequent re-calibration of the analytical instrument using this simplified measurement is also an appealing possibility provided by these methods. Gaudiuso et al. [4] proposed so-called inverse CF-LIBS, an approach where the key plasma temperature is determined by minimization of the errors of concentrations determined for one standard sample. The Pisa group presented a variant of their original formulation of the method called one-point-calibration CF-LIBS [5], consisting in the empirical determination from a standard sample spectrum of essential experimental and spectroscopic parameters, whose knowledge is often imprecise or lacking. Our group has proposed recently CSigma laser-induced breakdown spectroscopy (Cσ-LIBS) [6,7], where Cσ graphs are obtained using at least one standard sample, after which the system becomes characterized and other samples may be analyzed. For a spectral line showing self-absorption, curves of growth are graphs of the line intensity vs. the optical depth, the latter being proportional to the elemental concentration in a sample. The curve of growth methodology was applied the first time to LIBS by Gornushkin et al. [8]. Cσ graphs may be considered as generalized curves of growth, as they allow to include several spectral lines of various elements in the same plot. The initial demonstration of Cσ-LIBS for slag analysis was presented in Ref. [6] and a second validation with a set of rock samples having a wider range of concentrations has been performed recently [9]. In both works, certified reference materials in powder form were prepared as fused-glass samples. Although fused-glass samples have been very convenient for the initial testing of Cσ-LIBS, they present some drawbacks, the main one being of course the time required for preparation, which nullifies the characteristic readiness of LIBS analysis. Also, the dilution of the sample increases the limits of detection, and the possibility of contamination by traces present in the solvent or accidentally during the preparation process is always present. Therefore, demonstration of the applicability of Cσ-LIBS to direct analysis, without sample preparation, is a relevant issue at the moment. Quantitative direct analysis by LIBS using the methods based on a plasma in LTE entails significant difficulties, such as the greater self-absorption of spectral lines expected for the higher concentrations in the samples, compared to those present in the diluted fused glass samples, and the higher chance of failure of the simple model used for the laser-induced plasma.

To our knowledge, the only work where Cσ-LIBS has been applied to direct analysis is a recent article by Grifoni et al. [10]. In this work, three methods including one-point-calibration CF-LIBS, inverse CF-LIBS and Cσ-LIBS are tested and compared on spectra acquired on modern bronze samples. The average percent error obtained for Cσ-LIBS for the four elements analyzed is 19%, a relatively high value taking into account that the elemental concentrations in the six samples used exceeded 0.8% in all cases. A study of the limits of detection is not included in this work. Our goal in the present work has been to test Cσ-LIBS for direct analysis, performing a complete check of the analytical figures of merit. To this aim, we have used a wide set of aluminum alloys, including elements with concentrations from percent down to μg/g levels, which has allowed us to determine the precision for different contents and to estimate the limits of detection.

## 2. Experimental

The LIBS experimental setup was the same used previously [9], so it is only described briefly, highlighting changes performed. Laser-induced plasmas are generated in air at atmospheric pressure by a Nd:YAG laser (wavelength 1064 nm, pulse energy 60 mJ, pulse width 4.5 ns, repetition rate 20 Hz) focused by a lens of 126-mm focal length with a lens-to-sample distance of 116 mm. For collecting the plasma emission, we modified the previous configuration based on image formation with a system of mirrors, replacing it with a 0.22 numerical aperture optical fiber of 600-μm core diameter, placed at 10 mm from the plasma. The use of the optical fiber has allowed to improve the long-term stability of the intensity of the spectra. The fiber transmits the radiation from the plasma to a Czerny-Turner spectrometer (focal length 0.5-m, grating of 3600 lines mm$^{-1}$), equipped with an intensified charge-coupled device detector. The spectral efficiency of the system has been measured using radiance-calibrated deuterium and tungsten standard lamps. Each spectrum results from the accumulation of 100 laser shots while the sample rotates at 100 rpm. All the spectra were acquired with a time delay of 1.6 μs from the laser pulse and a time integration gate of 0.9 us. We checked that, at this time window, the spectra showed a good line-to-continuum ratio for both neutral atom and ion emission lines.

The samples used in this experiment are seven aluminum alloy certified reference materials (HYDRO Aluminum Rolled Products GmbH, Germany). The manufacturer produces the reference aluminum alloys by means of DC-casting, which is especially suitable for producing homogeneous samples, and checks the homogeneity of the samples by S-OES and XRF. Anyway, as problems associated with sample inhomogeneity have been reported in laser ablation methods [11], all experimental data have been obtained averaging five measurements at different positions of the sample, so that the effect of a possible remaining inhomogeneity is reduced. The certified samples are cylindrical, of 38 mm diameter and 30 mm height and have been used as supplied by the manufacturer, i.e., the plasmas have been generated on the flat surface without performing any finishing or cleaning action. We have included in the study all the main elements of the samples, i.e. those having concentrations higher than 1 wt% (with the exception of the matrix aluminum element), as well as several minor elements with low concentrations down to the μg/g range. Sample 1004, with trace-level content for all elements, has also been included in order to obtain the limits of detection for some elements whose concentrations are too high in the rest of samples. Sample 3003 has been used in the characterization stage of Cσ-LIBS, and then the rest of the samples have been analyzed for validation.

## 3. Results and discussion

### 3.1. Selection of spectral lines

The details of the Cσ-LIBS procedure are described in a previous work [6]. Firstly, the method requires a careful selection of the spectral lines used for characterization and analysis. The lines chosen need to have known accurate oscillator strengths and at least an estimation of their Stark widths. A bibliographic search has been performed to get accurate values of the atomic data which have not yet been included in available atomic databases. Table 1 lists the lines used in the present work to construct the Cσ graphs for aluminum alloy samples, showing their atomic data.

The Cσ-LIBS method is based on a set of parameter definitions. The $k_t$ parameter depends on the plasma temperature $T$ and is given by