

Application of laser-induced breakdown spectroscopy to the analysis of metals in soils

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Abstract. In this paper, the influence of plasma temperature on quantitative laser-induced breakdown spectroscopy (LIBS) measurements is discussed, and a simple theoretical approach is used to model the plasma generation. It is shown that an estimate of the temperature of the laser-induced plasma and its inclusion in a model for line emission allows for substantial reduction of the matrix effect. To illustrate the benefits of the proposed correction, some experimental results, obtained with the use of some reference sample soils, are finally presented.

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The LIBS technique has been developed as a useful method for determining the elemental composition of different materials either in solid, liquid, or gaseous phase [1, 2], by focusing a laser beam onto a sample to generate a spark-induced plasma. Emissions by atoms and ions of the plasma are collected by a suitable optical arrangement and analyzed by a spectrograph equipped with a gated detector. The spectral lines can be used for determining the elemental composition and concentration of different species on the sample surface. The main advantages of this technique are that it requires very little or even no sample preparation to produce almost on-line results and that, nowadays, it can be exploited by a compact setup which is readily transportable for in situ pollution monitoring.

On the other hand, the accuracy of quantitative analysis does depend on the overall sample composition, with a drawback usually known as the matrix effect [3, 4]. To account for deviations in retrieved concentrations due to the matrix effect, a sophisticated modeling of the entire LIBS process, properly including thermal effects, is required for correcting the intensities of detected spectra lines.

1 Theoretical background

Matrix effect reduction is possible with the theoretical understanding of some aspects of the plasma generation and heating, such as the laser–sample and the laser–plasma interactions, and by applying Boltzmann modeling to describe the actual state of the plasma triggered by the laser pulse and to reproduce the desired conditions of plasma generation. First let us consider the laser–sample interaction, which under normal working conditions has the effect of vaporizing and atomizing a small region of the sample surface, resulting in the production of a hot plume consisting of both the ejected material and the atmospheric plasma [5]. During this interaction, the laser beam energy is absorbed by the sample and by the atmospheric plasma, and several phenomena occur which are responsible for back reflection of the radiation, electron emission, sample heating, and phase changes which all affect the physical properties of the plume in a way peculiar to the sample composition [6].

Once formed, the plasma is usually assumed to reach, in a proper temporal and spatial observation window, a condition of local thermodynamical equilibrium (LTE). In this case, if reabsorption effects are negligible (i.e., the plasma is optically thin), the spectrally integrated line intensity, corresponding to the transition between levels E_k and E_i of the generic atomic species α with concentration C_α , can be expressed as

$$I_\alpha = F \cdot C_\alpha \frac{g_k A_{ki} e^{-E_{ki}/k_B T}}{U_\alpha(T)}, \quad (1)$$

where T is the plasma temperature, $U_\alpha(T)$ is the partition function, k_B is the Boltzmann constant, and F is a constant depending on experimental conditions. A first-order approximation of LIBS-measured concentrations can be obtained by the comparison of a given line intensity from an unknown sample to that from a certified sample [2]. Under the hypothesis of constant and easily reproducible

plasma temperature and plasma particle concentration, all factors in (1) are in common except for concentration and line intensity for each element. This allows one to establish a simple linear relationship between the specific line intensity and the relevant elemental concentration. In practical situations, the use of calibration curves built in this way has proven to be valid for retrieving the concentration of a single species and in a well-defined matrix [7], while the procedure appears inappropriate in complex cases, such as multi-elemental analysis or the lack of a priori knowledge of the sample (i.e., of the rough matrix composition).

The key conditions for unbiased quantitative LIBS measurements do strongly depend on correctly modeling the process of sample heating. For most material and soils, heating is essentially a thermal process, where the mean time between electron collisions is much shorter than the laser pulse duration. We therefore expect the heat rise in the sample to be spatially confined to the laser spot area, with a penetration roughly given by the inverse of the absorption coefficient at the laser wavelength. Therefore the plasma density (in terms of particles per unit volume), being tightly related to the volume of atomized sample, is strongly dependent upon sample composition. Even in highly conducting metallic samples, heat diffusion can play a role only for long interaction times (at least on the microsecond scale), which is not the case in LIBS experiments performed by means of pulsed Q-switched Nd:YAG lasers.

Finally, by observing that the integrated line intensity of (1) depends linearly, through the constant F , on the plasma density, we conclude that an increase of the accuracy in element concentration measurements can be obtained by using a reference sample with thermal properties as close as possible to those of the unknown sample. If this is the case, including the plasma temperature in the quantitative analysis allows us to improve the overall experimental accuracy. By rationing the line intensities originated by the sample and by a reference material (with known elemental concentration), at

temperatures T_α and T_r , respectively, we obtain from (1):

$$\frac{I_\alpha(T_\alpha)}{I_r(T_r)} = \frac{C_\alpha}{C_r} \frac{\exp(-E_{ki}/k(1/T_\alpha - 1/T_r))}{U_\alpha(T_\alpha)/U_r(T_r)}. \quad (2)$$

Equation (2) allows us to evaluate C_α from the measured LIBS line intensity, while the other parameters are derived from atomic databases at known plasma temperatures.

In order to estimate the plasma temperature, we obtain from the natural logarithm of (1)

$$\ln\left(\frac{I_\alpha}{g_k A_{ki}}\right) = -\frac{E_{ki}}{k_B T_\alpha} + \ln\left(\frac{C_\alpha F}{U_\alpha(T_\alpha)}\right). \quad (3)$$

In the two-dimensional Boltzmann plane identified by the left-hand term of (3) and by E_{ki} , different emission line intensities belonging to the same element in the same spectrum lie along a straight line with a slope of $1/k_B T_\alpha$. If experimental and theoretical data are available for each element in the sample, the combined use of (2) and (3) makes it possible to evaluate the element concentration.

2 Experimental setup and results

The experimental apparatus used for this work is an improved version of a measurement facility already operating at the ENEA Center in Frascati; it is fully described elsewhere [2, 7]. In this paper it will be shortly reviewed. The third harmonic Nd:YAG pulsed laser beam is driven to the sample surface by a custom-made seven-mirror optical arm, especially designed for easy outdoor field LIBS campaigns. The optical arm is terminated by a 250-mm focal length plano-convex lens which focuses the laser beam upon the sample surface. The light emitted by the plasma is collected by suitable receiver optics and carried by an optical-fiber bundle to the entrance slit of a 550-mm monochromator equipped with three gratings (1200, 2400, and 3600 g/mm) and having a flat focal exit plane of 30×15 mm (free of spherical

Table 1. LIBS system specifications

Transmitter		Detection unit	
Laser Nd:YAG 3rd harmonic @ 355 nm with unstable resonator	Quanta System	ICCD	ANDOR
Energy	20–40 mJ	Pixel size	25 μm
pulse width	8 ns	active pixels	690×256
prf	18 Hz	Dynamic range	18 bits
		Spectral range	180–550 nm
		Phosphor	P43
Receiver optic		Control unit	
Fiber optic coupling	ORIEL	PC	Pentium 166 MHz
F#	4	BUS control	IEEE 488
size	100 μm	SW	LabView
bundles	16		
Mobile arm	EL.EN.	Performances	
mirrors	7	Typical resolution	9000 $\Delta\lambda/\lambda$
focal length	25 cm	Acquisition time	3 min
Monochromator	ISA Jobin-Yvon	Elaboration time	5 min
fully computer controlled	TRIAx 550		
Length	550 mm		
Triple grate turret	1200–2400–3600 gr/mm		
F#	6.4		
Slit	10–100 μm		

and chromatic aberrations). At the exit plane, a multichannel analyzer based on gated ICCD records the LIBS spectra. All the equipment is controlled by custom-written software routines working in a Windows 95/98 environment. Great care has been devoted to operating the system in reproducible conditions at constant laser energy. The investigated sample, mechanically compacted by a press and inserted on a rotating holder, is constantly rotated in order to minimize crater effects and to partially compensate local inhomogeneities. The holder design ensures a constant distance of the surface sample from the lens. Sample movement, the number of laser shots, and other experimental parameters were adjusted to optimize the measurement reproducibility [8]. The current setup characteristics are summarized in Table 1.

For each sample and reference soil, a set of LIBS spectra is recorded covering the full visible range; for example, Fig. 1 shows a section of a typical spectrum for a reference sample of the Slovak Office of Standards, Metrology and Testing (Reference Material WT-H no. 12-3-14).

In order to test the above described correction procedure, we performed an LIBS analysis of several soil samples. The computation utilizes several experimental data taken in different spectral regions. Peak intensities were estimated by fitting each experimental line with an analytical expression containing both a Voigt line shape and the instrumental trans-

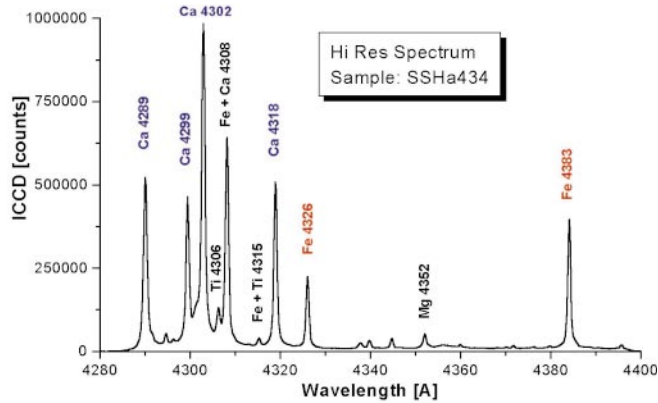


Fig. 1. Section of a High-Resolution Spectrum containing Iron and Calcium lines significant for qualitative and quantitative analysis

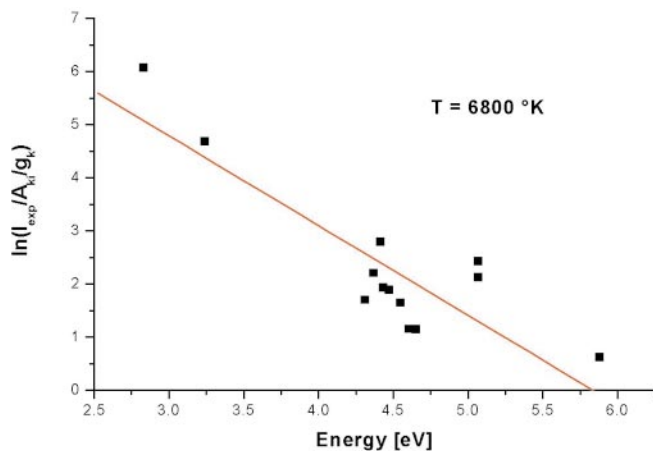


Fig. 2. Saha Boltzman plot for Fe lines

Table 2. Temperature correction of LIBS integrated line intensities

Sample	Raw LIBS	Temp LIBS K	Corr ppm	ICP ppm
BCR 17	22541	7150	18178	14604
BCR 235	23400	6950	22286	22345
BCR 475	24610	7200	19078	16224
BCR 1037	20400	6900	20400	21898
ES 3	35530	7200	27543	23700
ES 4	32900	7600	18693	18542
REF 1	39240	7500	24525	24362
REF 2	40950	7400	27669	24492
ANTA	24500	7400	16554	17080
Correlation	0.64		0.87	

fer function; a special deconvolution routine was also written to discriminate and fit multiple peaks.

The complete analysis carried on Fe with well-known spectroscopic parameters [9, 10] is presented in detail as an example. After the identification and assignment of all relevant line emissions, a table is built containing frequency transitions and line width parameters. A raw estimation of element content is made by means of linear comparison of the average LIBS line intensity in the unknown sample with the corresponding one taken from the certified reference. Then, assuming the validity of the LTE condition, the plasma temperature is estimated from the Saha Boltzman plot (see Fig. 2). Once the experimental parameters and spectroscopic data are available, the line intensity correction procedure, which takes into account the proper plasma temperature as described in the preceding section, is finally performed. In Table 2, both uncorrected (second column) and corrected (fifth column) LIBS results are compared to conventional inductively coupled plasma (ICP) analytical determinations upon the same samples.

The improvement obtained is substantial and the correlation between LIBS versus ICP analytical determination is increased from 0.64 to 0.87 for uncorrected and corrected data, respectively (see also Table 2). The departure of uncorrected LIBS measurements from ICP determinations (circles in Fig. 3) shows the matrix effect, in spite of the fact that an optimum matrix matching was attempted so that there would be identical thermal properties between samples and references.

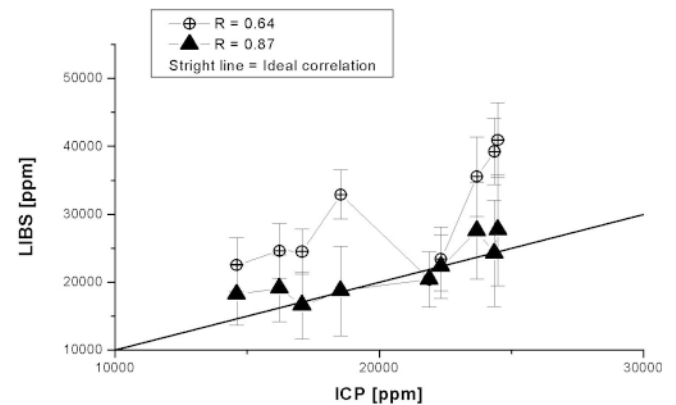


Fig. 3. Uncorrected (circles) and temperature-corrected (triangles) LIBS concentrations vs. ICP concentrations

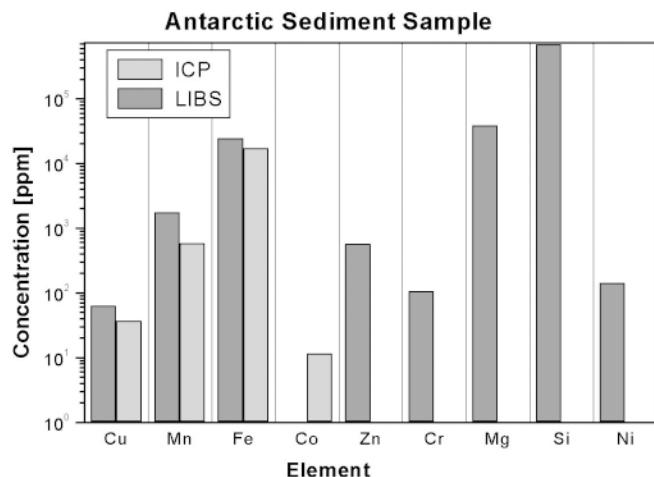


Fig. 4. Composition of an Antarctic sediment determined by LIBS and ICP techniques

The technique has been finally used to analyze Antarctic sea-bottom sediments. A quantitative determination of several metals has been achieved on a wide range of concentrations, spanning more than five orders of magnitude (see Fig. 4). The current LIBS uncertainties (error bar between 10 to 20%) are comparable with the ICP ones, which are estimated to be about 5% after the pretreatment for sands and marine sediments.

Work is in progress to fully automate the measurement procedure and to design a neural network-based software algorithm to improve the analysis of LIBS experimental spectra.

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References

1. L.J. Radziemsky, T.R. Loree, D.A. Cremers, N.M. Hoffman: *Anal. Chem.* **55**, 1246 (1983)
2. G. Arca, A. Rastelli, V. Palleschi, R. Barbini, F. Colao, R. Fantoni, A. Palucci, A. Ribezzo, H.J.L. van der Steen: *Appl. Phys. B* **63**, 185 (1996)
3. A. Ciucci, M. Corsi, V. Palleschi, A. Rastelli, A. Salvetti, E. Tognoni: *Appl. Spectrosc.* (accepted)
4. B.C. Castle, K. Talabardon, B.W. Smith, J.D. Winefordner: *Appl. Spectrosc.* **52**, 649 (1998)
5. E.H. Piepmeier: *Laser Ablation for Atomic Spectroscopy*, in *Analytical Application of Laser*, ed. by E.H. Piepmaier (Wiley, New York 1986)
6. J.L. Todoli, J.M. Mermet: *Spectrochim. Acta B* **53**, 1645 (1998)
7. R. Barbini, R. Fantoni, A. Palucci, A. Ribezzo, H.J.L. van der Steen, M. Angelone: *Appl. Phys. B* **65**, 101 (1997)
8. B.C. Castle, K. Talabardon, B.W. Smith, J.D. Winefordner: *Appl. Spectrosc.* **52**, 649 (1998)
9. A.N. Zaidel', V.K. Prokof'ev, S.M. Raiskii, V.A. Slavnyi, E.YA. Shreider: *Tables of Spectral Lines* (Plenum, New York 1970)
10. NIST electronic database, available at <http://physlab.nist.gov/PhysRefData/contents-atomic.html>