



Laser-induced breakdown spectroscopy of archaeological findings with calibration-free inverse method: Comparison with classical laser-induced breakdown spectroscopy and conventional techniques



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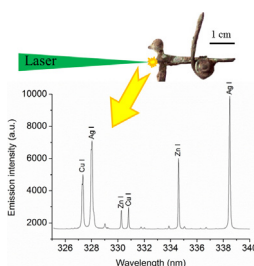
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HIGHLIGHTS

- A novel calibration-free LIBS method (inverse method) was developed and tested.
- The inverse method was applied to the analysis of a set of archaeological findings.
- The inverse method was validated by comparison with LA-ICP-MS and classical LIBS.

GRAPHICAL ABSTRACT



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ABSTRACT

A modified version of the calibration-free (CF) method was applied to the analysis of a set of archaeological brooches made of various copper-based alloys and coming from the archaeological site of Egnatia (Apulia, Southern Italy). The developed methodology consists in determining the plasma temperature by reversing the set of equations employed in the usual CF algorithm, and it is thus referred to as “inverse method”. The plasma temperature is determined for one certified standard, by using its known elemental composition as an input data, and then applied to the set of unknown samples to evaluate their composition in a CF mode. The feasibility of such an approach is demonstrated by comparing the results obtained with classical LIBS (drawing calibration lines with a series of matrix-matched certified standards) and with independent measurements performed with a conventional technique (LA-ICP-MS).

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1. Introduction

Laser-induced breakdown spectroscopy (LIBS) has been continuously attracting attention from many diverse fields of materials analysis, due to several well-known practical advantages, which

include: possibility of fast multi-elemental analysis of virtually any kind of sample, irrespective of its state of aggregation and chemical nature; no need of sampling or important sample preparation procedures; possibility of in situ and of remote analysis, even in extreme conditions of pressure and temperature, as well as under water [1–6]. One of the LIBS applications that benefits most from such features, as well as from its micro-destructivity, is that of the analysis of cultural heritage samples [4,7]. In the last decade LIBS has been successfully employed to the analysis of historical buildings [8,9], paintings and pigments [10–12], metals [13,14], even in

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Table 1
Composition and kind of the employed certified samples.

Standard sample	wt% Sn	wt% Pb	wt% Zn	wt% Cu	wt% Ni	Alloy	Manufacturer
B3	12.96	1.65	2.27	80.25	1.53	Bronze	TechLab, Metz, France
B4	11.05	2.50	1.21	84.00	0.57	Bronze	TechLab, Metz, France
B21	5.13	3.79	6.17	83.05	1.21	Bronze	TechLab, Metz, France
B22	3.85	6.12	4.40	82.75	2.56	Bronze	TechLab, Metz, France
HPb	5.30	5.60	5.90	82.40	–	Bronze	Homemade
LPb	9.80	0.77	0.47	88.20	–	Bronze	Homemade
CSM	7.90	1.80	–	90.10	–	Bronze	Homemade
LH11	0.44	1.26	26.20	66.80	2.91	Brass	TechLab, Metz, France
L3	1.50	1.02	32.70	62.35	0.90	Brass	TechLab, Metz, France
UZS	0.40	0.57	15.30	78.98	0.49	Brass	TechLab, Metz, France
SN1	11.75	5.17	0.804	79.93	2.17	Bronze	MBH, England
SN2	13.54	1.97	1.28	82.80	0.104	Bronze	MBH, England

submerged environment [15–18], ceramics [19–21], also coupled with Raman spectroscopy [22], and to monitor the laser cleaning procedure of a variety of different samples from dirt and protective coatings [23–25]. Another inherent advantage of LIBS is the possibility of performing semi-quantitative and quantitative analyses in calibration-free (CF) mode. This methodology, first proposed in [26] and extensively studied since ([27] and references therein), does not require the use of calibration standards and thus appears particularly well suited for the analysis of samples with complicated and highly inhomogeneous matrices, such as meteorites [28,29], minerals [30–32] and archaeological objects [33], for which suitable matrix-matched standards may be not available. In particular, CF-LIBS appears as a suitable candidate for routine museum analyses, e.g. for samples pre-screening to establish their matrix and as a fast micro-destructive method for quantitative determination of major and minor elements. CF-LIBS relies on the assumption of local thermodynamic equilibrium (LTE) and on the plasma parameters (i.e. excitation temperature and electron density), that are determined experimentally. Several variants of the classical CF method have appeared in the literature (see [27] and references therein). The aim of this work was to test an alternative approach to CF-LIBS (in the following referred to as “inverse method”), that was first presented in [30] and discussed and validated in [34]. The inverse method is based on the usual set of assumptions of analytical LIBS, as well as on the LTE assumption, but it introduces a further practical assumption, i.e., that if different samples with similar matrices are ablated in the same conditions, the excitation temperature of the produced plasmas is the same. In the present paper this method is applied to the determination of the composition of a set of ancient brooches. The obtained results are compared with those of classical LIBS (i.e. obtained by drawing calibration lines for the investigated elements with a series of matrix-matched standards) and of a conventional technique (laser ablation-inductively coupled plasma-mass spectrometry, LA-ICP-MS) that were used for analysing these brooches in a series of independent experiments [35].

2. Experimental

2.1. LIBS setup and acquisition conditions

The employed apparatus is a standard LIBS setup which comprises: a 7 ns Nd:YAG laser (Giant, Quanta System) operated at its second harmonic (532 nm) with repetition frequency of 10 Hz and energy of 13 mJ; a spectrograph (TRIAx 550, JobinYvon, 1800 gr mm⁻¹ grating, 0.011 nm nominal spectral resolution at 312.57 nm) and an ICCD (i3000 JobinYvon) for the detection of the radiation emitted by the plasma; a pulse generator (Stanford Inc. DG 535) to synchronize the plasma emission and the spectra acquisition. The laser beam was focused on the sample surface with a 10 cm focusing lens, which provided an ablation spot of ~200 μm. The radiation emitted by the plasma was coupled directly with the

entrance slit of the spectrograph by means of a mirror placed at 45° with respect to the plasma propagation axis and a 7.5 cm collection lens. The time parameters were 1 μs delay time (t_d) and 5 μs gate width (t_g). Calibration lines were drawn for the main elements with certified samples of copper-based alloys, whose composition is reported in Table 1. The standard samples were rotated constantly during the ablation, so to offer a fresh surface to the incoming laser beam. The archaeological samples were kept fixed to limit their damage, but two or more spots were analyzed for each object, so as to detect and account for possible composition inhomogeneity. Moreover, in order to ablate a sample layer as representative as possible of the actual bulk, about 100 laser shots were focused on the surface prior to each acquisition, so to locally remove the external layers of the corrosion patina. The estimated thickness of the layer removed by each laser shot was around 5 μm in the employed experimental conditions. LIBS spectra of sample 4207 in the spectral windows used for the analysis are shown as examples in Fig. S1(a)–(d), Supplementary material.

2.2. LA-ICP-MS setup and acquisition conditions

The LA-ICP-MS experiments were performed with a New Wave Research UP-213AI Nd:YAG 4-ns laser, operated at the fifth harmonic (213 nm) and with a 55 μm spot diameter for the sampling and a Thermo Electron X series I ICP-MS. LA-ICP-MS measurements were carried out on sections (of few mm³) sampled from the specimens so as to be representative of the bulk of the objects, not on the whole object. A large number of spectra was acquired (lined at least 55 μm wide and 400 μm long) and averaged so to account for the inhomogeneity of the sample and of the dimensions of the laser spot. Further details about the employed experimental procedures and setup may be found in [35].

2.3. Samples

A set of brooches (*fibulae*), dating from VI century BC to VI–VII century AD and coming from Egnatia (BR, Italy), were analyzed. Egnatia, one of the most important archaeological sites in Southern Italy, was inhabited from the XVI Century BC up to the Middle Ages and had a central role in Mediterranean commercial trades by land, because of the via Traiana, and by sea, because of its harbour. Moreover, during Late Roman and Mediaeval Age, being Episcopal see, it became a place of transit towards the Holy Land [36–38]. Detailed archaeological information about analyzed fibulae, previously studied with typical archaeometric analyses, are reported in [35]. Images of the samples and of the spots where the laser was focused for the LIBS analysis are reported in Section 4 and sub-sections, along with the relative discussion of the obtained results. The measurements here presented are focused on the main elements, i.e., Cu, Sn, Pb, and, when present, Zn and Ag, while trace

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