SPACE-TIME-RESOLVED OPTICAL EMISSION SPECTROSCOPY OF LASER ABLATION PLASMA FOR MICROANALYSIS OF UNIQUE SOLID SAMPLES

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Abstract. Space-, time- and spectrally resolved optical diagnostics of laser ablation plasma has provided the opportunity to realize absolute (calibration-free) analyses of solid or powder materials. This variant of optical emission spectroscopy of pulsed plasma allows the matrix effects to be overcome, yielding precise and accurate quantitative results on elemental composition of materials without use of calibration curves, certified reference materials, and internal standards. Such analysis is very close to the nondestructive mode with minimum possible ablated mass that is very important in many applications especially for unique museum exhibits and jeweler samples.

1. INTRODUCTION

Laser ablation (LA) of solid samples is a well-established analytical technique, which combines sampling and atomization in one step. Therefore, direct and express spectrochemical analysis without any sample preparation is possible. During the last decade, the necessity of applications of the LA optical emission spectroscopy technique to the "truly real life" problems (industrial, environmental, medical, archaeological, art, etc.) has extremely increased in number and in variety. Recently any variant of spectrochemical analysis of solid materials required obligatory calibration of a spectrometer with the help of the certificated reference materials (CRM). The nomenclature of solid CRM is limited mainly by the most widely used metals and alloys, some samples of ceramic materials, glasses etc. This circumstance is the main limitation of wide introduction of direct analysis of solid materials, for example laser-induced breakdown spectroscopy (LIBS) and LA-ICP, in routine practice. Moreover, even the small differences in matrixes and surface properties of analyzed materials as compared with the reference samples as well as

the possible variations in ablation laser energy must be thoroughly taken into account. Therefore, during the last decade different approaches have been undertaken to overcome or at least to discriminate the above mentioned problems in the most widely spread LA based analytical technique, namely LIBS. The realization of the main goal of the last time attempts to make LIBS really quantitative is based on the development of calibration-free algorithm of LIBS, which is in turn based on the perfection of optical diagnostics of pulsed plasma. In general, last achievements in instrumentation and data processing in optical emission spectroscopy of pulsed ablation plasma allows the matrix effects to be overcome, yielding precise and accurate quantitative results on elemental composition of materials without use of calibration curves, CRM, and internal standards [1-6]. LA is at present the only source of atomic spectra that allows realizing by detailed optical diagnostics of plasma the unique possibility of absolute (calibration-free) elemental analysis of solid materials. Starting from 1999 the really calibration-free technique is now developing in instrumentation and algorithms by research teams from Italy and Belarus and last time from Australia and USA, and is utilizing mainly for analyses of as much as possible variety of solid metallic and dielectric materials to optimize the analytical procedures and to examine once again the proposed technique.

In this work further development of calibration-free LIBS and its approbation for microanalyses of a material of unique solid samples on an example of determination of component concentrations of the bronze and gold alloys, flint glasses, fragments of jeweller ornaments of an archaeological origin, and pigments from easel paintings have been carried out.

2. THEORETICAL BACKGROUND

In general, with the LTE assumption, after determination of the plasma temperature (possible by different ways), the concentration of species of one of the element of interest in plasma can be obtained from the measurement of just one experimental emission line. When the concentration of atomic species of a given element is known, it is possible to determine the concentrations of the other ionization stages by making use the Saha-Boltzmann equation. Such procedure is commonly employed in plasma spectroscopy.

The basic assumptions concerning the state of the laser ablation plasma are as follows. (i) The plasma composition is representative of the actual target material composition prior to the ablation (stoichiometric ablation). This assumption is fulfilled in laser ablation conditions typical for the spectrochemical analysis, when the power density on the target exceeds 1 GW/cm^2. (ii) In the actual temporal and spatial observation window the plasma is locally in thermodynamic equilibrium. Theoretically, thermal plasmas at electron number densities higher than 10^{23} m^{-3} are considered to be in LTE. (iii) For the optical emission spectrometry the plasma is optically thin (no self-absorption). This assumption is usually well verified for non-resonant lines emitted in comparatively small plasma volume. Although the self-

absorption can be modeled and compensated, the safest approach in these cases is just to ignore the self-absorbed lines for the purpose of rapid quantitative analysis.

According to the classical equation for intensity of a spectral line, we have the following relation:

$$\bar{I}_j^{ki}/(A_{ki}g_k/U_j^a)=(FC_j)\exp(-E_k/T), \tag{1}$$

where $\bar{I}_j^{ki}$ is the line integral intensity corresponding to the transition between two levels k and i for the j element; A_{ki} is the transition probability; g_k and E_k are the k level degeneracy and energy; U_j^a is the partition function of the j atom; F is an experimental parameter that takes into account the optical efficiency of the collection system as well as some plasma parameters; C_j is the concentration of the emitting atomic species; T is the plasma temperature. With the help of the relation (1) first of all the value FC_j is determined for the atomic species of each element present in the sample taking into account LTE in the analytical volume of a plasma. Temperature is measured as a rule by conventional method from Boltzmann plots. On received values FC_j their sum is calculated with the account of ionic component in relation to which concentration of each of elements in an analyzed sample is determined:

$$\sum_j \{FC_j+b(U_j^i/U_j^a)\exp[-(V_j-\Delta V_j)/T](FC_j)\}=FM, \tag{2}$$

where $b=6.06\cdot10^{21}T^{3/2}/N_e$; T (eV), N_e (cm^{-3}) is the electron concentration; U_j^i is the partition function of the j ion; V_j and ΔV_j are the ionization potential and its decrease in plasma; M is the total concentration of atomic and ionic components in plasma. Electron concentration is usually measured with the help of Saha equation. For the j element ($j=1$) we can write:

$$\{FC_1+b(U_1^i/U_1^a)\exp[-(V_1-\Delta V_1)/T](FC_1)\}/FM=C_1^a+C_1^i. \tag{3}$$

The total concentration of atomic and ionic components is:

$$\sum_j (C_j^a+C_j^i)=1-\varepsilon, \tag{4}$$

where ε is the total concentration of all elements in the sample which are not detected experimentally by the spectrometer used (as a rule trace and microelements with concentrations below the detection limit).

3. EXPERIMENTAL

The LIBS instrumentation employed in our work is at present quite standard and maximum suitable for routine practice and relies on the use of multichannel detection for recording the space-, time-, and spectrally resolved emission, produced by focusing laser pulse on the surface of a sample under analysis (Fig. 1).
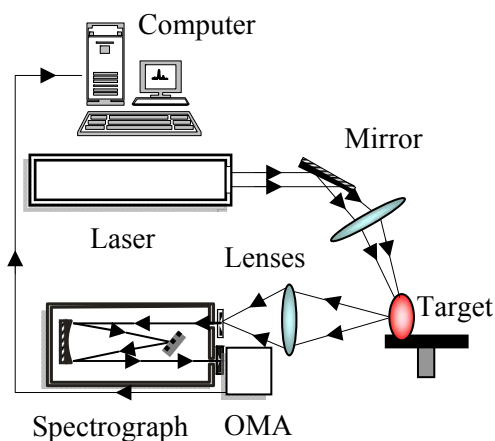
Fig. 1. Experimental set-up for LIBS.

The fundamental (1.06 μm) or the second harmonic (0.53 μm) of a nanosecond Q-switched Nd:YAG laser (LOTIS) with a pulse duration of 5-6 ns is employed in the LIBS measurements. The laser beam is focused on the sample surface by means of a 50 mm focal length plano-convex quartz lens, and a single- or multipulse measurements are performed. A sample-holding positioner can be used to maintain the ablation plume with controllable distance of the probing zone from the target surface and to preselect the irradiated surface zone. Laser pulse energy values range from 5 to 300 mJ with a spot diameter on the sample of approximately 30–100 μm. The light emitted from the plasma plume is collected with a plano-convex quartz lens with a 63 mm focal length into the compact spectrograph (SOLAR) equipped with appropriate diffraction gratings for high and medium spectral resolution measurements at a narrow or wide spectral range, respectively. The maximum spectral resolution, about 1 pm, can be obtained if necessary with the help of the echelle grating with double dispersion. The spectrum is recorded with the help of an optical multichannel analyzer (ORMINS) with a linear CCD detector (TOSHIBA).

4. RESULTS AND DISCUSSION

Detailed structural characterization and identification of key chemical constituents can uncover important information on historical and artistic significance of artworks. A major concern when an analysis is to be performed on valuable objects, such as museum exhibits is the preservation of its integrity and aesthetic value.

In general, the LA process can be divided schematically into two main stages: (i) evaporation of the solid target and formation of the laser plasma; (ii)

expansion of the ablated material into a background gas. Depending on the laser characteristics, LA of solids involves processes of heating, melting, vaporization, ejection of atoms, ions, molecules, clusters and larger solid and liquid particles, shock waves, plasma initiation and plasma expansion, ablation plume expansion in the afterglow.
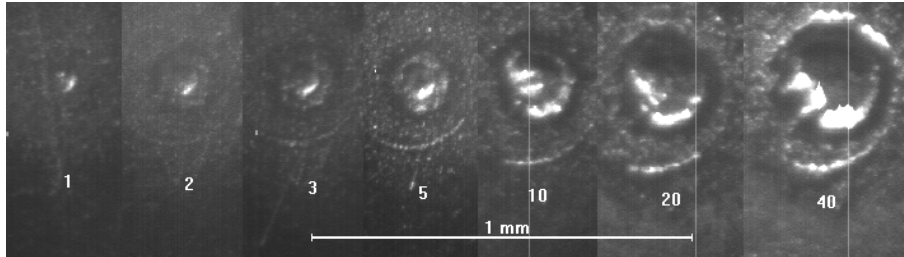

Fig. 2. Typical craters formed on a surface of a bronze sample at various number of laser shots.

Laser-induced plasma characterization will be very helpful for determining the optimal conditions of LIBS, and intensive experimental diagnostics must be in progress to get a more accurate knowledge of all the physical and chemical processes involved in the phenomenon. In this context some preliminary experiments have been carried out with the aim of optimization of laser ablation procedure. They mainly include bidimensial imaging with the help of the CCD matrix of the geometrical shape and size of: (i) the crater formed in the target material (Fig. 2) and (ii) the radiating ablation plume (Fig. 3).
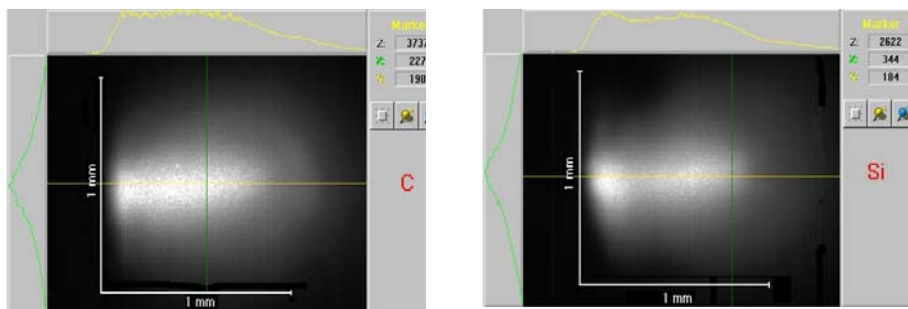

Fig. 3. Typical images of laser ablation plume near a carbon and silicon targets.

LIBS analysis is very close to the nondestructive mode with minimum possible ablated mass that is very important in many applications especially for unique museum exhibits and jeweler samples. Material consumption in a typical

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single pulse experiment is minimal (estimated around 10^{-8} -10^{-7} g for a typical crater formed). Thus, LIBS can be regarded as a nearly nondestructive technique. The spatial resolution achieved by LIBS across a surface is nearly microscopic. In addition, the technique has the capability of providing depth-profiling information.

One of the demonstrations of opportunities of the calibration-free variant of the LIBS technique has been experimentally realized for the analysis of a material of gold alloys to determine a caratage of tested samples (see the Table 1 below). Rather good conformity of the results of the calibration-free measurements of concentrations of gold in the analyzed materials to the certified data has been demonstrated. The maximum deviation is about 4% that is conventional for the analysis with the help of LA. The similar results have been also obtained for the bronze, brass and glass samples.

Table 1.

Sample	Caratage of Gold Alloys	
	Measured data	Reference data
1	359	375
2	581	583
3	588	585
4	797	831
5	903	899
6	916	900
7	990	998
8	1000	1000

Table 2.

Calibration-Free Analyses of Bracelets

Matrix:

$[PbO/SiO_2/CaO]+[Al_2O_3/Mn_2O_3/MgO/Na_2O/K_2O]$

Major components:

Sample I	Sample II
PbO – 43 %	PbO – 53 %
SiO$_2$ – 39 %	SiO$_2$ – 25 %
CaO – 11 %	CaO – 11 %

Minor components:

I	II
Cu$_2$O – 1.5 %	CuO – 2 %
Mn$_2$O$_3$ – 3.0 %	Mn$_2$O$_3$ – 1.5 %

As the typical archaeological objects for the calibration-free LIBS research, fragments of bracelets (presumably with a glass basis) from the National Museum of the History and Culture of Belarus have been chosen (see the Table 2 below). These samples were found in the compact places at excavations of: (i) the Minsk Fortress and (ii) the Polotsk Fortress. Polotsk is the oldest known town in territory of Belarus. The time period of the archeological layers, in which the given fragments of bracelets were found, is dated by the 11-13th centuries. Chemical composition of the glass matrixes and the components responsible for specific coloring of samples were determined taking into account recorded emission spectra and the data obtained by several researchers mainly with the help of conventional chemical analyses for the similar glass samples found in different regions of the world.

Besides, the calibration-free LIBS technique has been applied for the microanalysis of pigment materials from the different sections of the well-known easel paintings "Landscape of Pool with an Obelisk and Ruins of an Aqueduct" and "Garden of Borghese Villa in Rome" of the famous French artist Hubert Robert (1733-1808). These old paintings from the National Art Museum of Republic of Belarus require thorough investigations of the pigments for confirmation of their originality taking into account the rich biography of the paintings. Obtained quantitative data on elemental composition of the selected pigment microsamples from all paint layers including the ground layer alongside with art and historical examinations have formed the base for the exact identification of the originality of the tested paintings.

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