Contributed Paper

DEVELOPMENT OF CALIBRATION-FREE ALGORITHM IN LASER-INDUCED BREAKDOWN SPECTROSCOPY

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Abstract. Optical diagnostics of laser ablation plasma has provided the opportunity to realize quantitative calibration-free analyses of solid, liquid and gaseous materials. The results presented confirm the suitability of the approach for routine practical applications of our laser instrumentation and calibration free algorithm, while at the same time simplifying the overall analytical procedure.

1. INTRODUCTION

The realization of the main goal of attempts to make laser-induced breakdown spectroscopy (LIBS) really quantitative technique is based on the further detailed development and wide practical examination of the so-called calibration-free algorithm of LIBS. This approach is based on the application of a complete optical diagnostic procedure of pulsed plasma. Recent achievements in laser and spectrometric instrumentations and data processing of emission of pulsed ablation plasma have provided a fast analytical way to overcome the matrix effects, yielding precise and accurate quantitative results on elemental composition of materials without using calibration curves, certified reference materials and internal standards.

2. CALIBRATION-FREE ALGORITHM

For the case of optically thin plasma and LTE, the spectral line integral intensity recorded by spectrograph with CCD optical multichannel analyzer in the time window Δt is given by

$$I = F_1 \Delta t (Lld)\omega \frac{hc}{4\pi\lambda_0} A_{ij} g_i \frac{N_z}{U_z} \exp\left(-\frac{E_i}{kT}\right) \int_{-\infty}^{\infty} P(\lambda), \qquad (1)$$

where F_1 is the dimensionless coefficient that takes into account the efficiency of the collection and recording systems, Lld is the plasma volume projected on the registration system, where L is the plasma thickness, d is the width of the spectro-

graph entrance slit, l is the height of CCD pixel, ω is the collection solid angle, h is the Planck's constant, c is a velocity of light, λ_0 is a wavelength of line center, A_{ij} is the transition probability from the superior level i to the lower level j, g_i is the degeneracy or statistical weight of level i, N_z is the density of atoms of z constituent (chemical element) in plasma, U_z is the partition function of atoms of z constituent, E_i is the energy of state i, k is the Boltzmann's constant, T is a temperature of plasma and $\int_{-\infty}^{\infty} P(\lambda) = 1$ because $P(\lambda)$ is the normalized profile.

Let's multiply and divide the right part of the expression (1) on the total number of atoms and ions of all constituent s in plasma N:

$$I = F_1 \Delta t (Lld) \omega N \frac{hc}{4\pi\lambda_0} A_{ij} g_i \frac{N_z}{NU_z} \exp\left(-\frac{E_i}{kT}\right). \tag{2}$$

Let's designate $\dfrac{F_1 \Delta t (Lld) \omega N}{4\pi}$ as F, $\dfrac{N_z}{N}$ is the relative molar concentration of atoms of z constituent in plasma C_z. Thus, the expression (2) may be rewritten as

$$I = \frac{hc}{\lambda_0} A_{ij} g_i \frac{FC_z}{U_z} \exp\left(-\frac{E_i}{kT}\right). \tag{3}$$

In actual condition of LTE electronic temperature of plasma T may be obtained by the following way taking the natural logarithm of Eq. (3):

$$\ln\left(\frac{I\lambda_0}{hcA_{ij}g_i}\right) = -\frac{E_i}{kT} + \ln\left(\frac{FC_z}{U_z}\right). \tag{4}$$

As the value of $\ln\left(\dfrac{FC_z}{U_z}\right)$ is equal for all emission lines of z constituent in plasma, it is evident that $kT = \dfrac{1}{tg(\alpha)}$, where α is the slope of the Boltzmann plot, or experimentally of the linear best fit of the graphic relation of $Y = \ln\left(\dfrac{I\lambda_0}{hcA_{ij}g_i}\right)$ as a function of $X = E_i$.

As for the density of singly ionized atoms of z constituent in plasma N_z^{ion}, it's relative value may be determined by the above described procedure, recording available emission lines of ions or more simply by Saha equation:

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$$\frac{N_e N_z^{ion}}{N_z} = 2\frac{U_z^{ion}}{U_z}\left(\frac{m_e kT}{2\pi h^2}\right)^{\frac{3}{2}}\exp\left(-\frac{E_z^{ion} - \Delta E^{ion}}{kT}\right), \qquad (5)$$

where N_e is the electron density, U_z^{ion} is the partition function of singly ionized atoms of z constituent, m_e is the mass of electron, E_z^{ion} is the ionization energy and $\Delta E^{ion} = B\sqrt{\frac{N_e}{T}}$ is the correction of this quantity for interactions in the plasma, where B is the numerical coefficient.

Let's multiply numerator and denominator of the left part of the Eq. (5) on the $\frac{F}{N}$ to obtain the formula for calculation of FC_z^{ion} value, where C_z^{ion} is the relative molar concentration of ions of z constituent in plasma:

$$FC_z^{ion} = 2\frac{U_z^{ion} FC_z}{U_z N_e}\left(\frac{m_e kT}{2\pi h^2}\right)^{\frac{3}{2}}\exp\left(-\frac{E_z^{ion} - \Delta E^{ion}}{kT}\right). \qquad (6)$$

Electron density may be determined from Stark width and shift of suitable emission line (lines) or more simply from Eq. (6) for that chemical element in plasma for which atomic and ionic spectral lines are available (it is possible, if necessary, to add small amounts of such element with low ionization energy on a target surface).

The same steps may be undertaken for each ionization state of any chemical element present in the actual plasma.

Thus, the values of FC for all constituents ($1 \leq z \leq n$) and ionization states in the ablation plasma may be calculated taking into account that for relative concentrations we have $\sum_n (C_n + C_n^{ion} + C_n^{2ion} + C_n^{3ion} + ...) = 1 - \delta$, where δ 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). Usually in the time and space windows of experimental observation neutral and singly ionized species are only available. Therefore, we may write

$$\sum_n (FC_n + FC_n^{ion}) = F\sum_n (C_n + C_n^{ion}) = F, \qquad (7)$$

assuming the same value of F for all atomic and ionic species present in the plasma. Taking into account the LIPS accuracy this approximation (simplification of experimental procedure) is valid at least in all our experiments.

The value of relative molar concentration of each chemical element in the plasma including atomic and ionic species may be determined as follows:

$$C_z^{sum} = \frac{FC_z + FC_z^{ion}}{\sum\limits_{n}(FC_n + FC_n^{ion})}.$$ (8)

Therefore, in general it is not necessary to know the value of F_l that takes into account the efficiency of the collection and recording systems, or it may be determined if internal standard with known concentration is present or may be added in the target material.

As for the optimized experimental conditions the ablation is stoichiometric, the value C_z^{sum} is the same in the analyzed solid sample.

Finally, for the mass concentration we have

$$C_z^{mass} = \frac{M_z C_z^{sum}}{\sum\limits_{n} M_n C_n^{sum}},$$ (9)

where M_z is the atomic weight of selected chemical element.

LIBS often deals with self-absorbed or even self-reversed spectral lines. For the self-absorbed emission line we have with some approximations the following formula useful for calibration-free practice when recording and processing of emission line profile:

$$\frac{S^{thin}}{S^{thick}} = \left(-1 - \frac{K_0 L}{\lg\left(\frac{1 + \exp(-K_0 L)}{2}\right)} \right)^{-\frac{1}{2}} \frac{K_0 L}{1 - \exp(-K_0 L)},$$ (10)

where S is the surface of the processed line, K_0 is the absorption coefficient in the line center.

The above described algorithm of calibration-free spectrochemical analysis has been successfully tested for various solid samples with known chemical composition, including metals, glasses, composite materials, pigments, concretes, soils and others.