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PROCEDURE FOR MATRIX EFFECT REDUCTION IN METAL ANALYSIS USING LASER-INDUCED BREAKDOWN SPECTROSCOPY[**]

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A procedure for matrix effect reduction is proposed to enhance the precision of quantitative analysis of metal alloys using laser-induced breakdown spectroscopy (LIBS). This procedure is based on a number of successive steps in order to correct the signal fluctuations caused by plasma interaction and the matrix effect. The first step is the selection of optimum parameter settings of the detection system, such as laser power, delay time, and focal distance. The second step is the estimation of the absolute or relative values of impurities on the basis of the internal standard calibration. The third step is the analysis of the metal basis of the alloy used as an internal standard, which requires spectrum averaging, whole integral spectrum normalization, and self-absorption correction. Three sets of metal-based alloys (aluminum, steel, and copper) are used in this investigation as reference standards for calibration and validation. Successive improvements of the quality of calibration curves are observed during the proposed procedure.

Keywords: *LIBS quantitative analysis, reduction of matrix effect, internal standard calibration, normalization, correction of self-absorption.*

УМЕНЬШЕНИЕ ЭФФЕКТА МАТРИЦЫ В АНАЛИЗЕ МЕТАЛЛОВ С ИСПОЛЬЗОВАНИЕМ ЛАЗЕРНО-ИНДУЦИРОВАННОЙ СПЕКТРОСКОПИИ

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Предлагаемая процедура уменьшения эффекта матрицы позволяет улучшить точность и снизить неопределенность количественного анализа металлических сплавов с помощью лазерной спектроскопии пробоя. Эта процедура основана на применении ряда последовательных действий по коррекции флуктуации сигнала, обусловленной взаимодействием плазмы и эффектом матрицы. Первый шаг — выбор оптимальных параметров системы детектирования: мощности лазера, времени задержки и фокусного расстояния. Второй этап — внутренняя стандартная калибровка для оценки абсолютных или относительных величин, характеризующих примеси. Третий — анализ металлической основы сплава, используемого в качестве внутреннего стандарта, который требует усреднения спектра, нормировки полного интегрального спектра и коррекции самопоглощения. Для калибровки и тестирования использованы три набора эталонных стандартных сплавов на основе алюминия, стали и меди. При выполнении предлагаемой процедуры наблюдались последовательные улучшения неопределенности и качества калибровочных кривых.

Ключевые слова: *количественный анализ методом лазерно-индуцированной спектроскопии пробоя, снижение эффекта матрицы, внутренняя стандартная калибровка, нормировка, коррекция самопоглощения.*

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Introduction. Laser-induced breakdown spectroscopy (LIBS) is used to detect plasma-emitted light generated by the interaction of a power laser beam with the surface of the analyzed material. The laser beam is focused by a lens on the surface of the target material, a small volume of which is highly heated, vaporized, and partially ionized, so the energy of radiation is released within a broad spectral range [1]. Analysis of atomic or ionic lines in the emitted spectra permits one to identify the elemental composition of the material [2]. LIBS has a number of advantages compared to other methods of atomic emission analysis: short time of measurement, simple process of sample preparation, versatility of the sample type, and possibility of qualitative and quantitative multi-elemental analysis [3–5].The above mentioned advantages of this analytical technique explain its wide application in environment, geological, and space studies [6–9], art work and jewelry [10, 11], industry, and many other fields [12–15].

However, LIBS is not devoid of serious disadvantages, among which are an elevated risk of errors and a relatively high limit of detection. These problems are mainly due to the fluctuations of such parameters as the laser-sample interaction process and physical and chemical matrix effects [16].The signal fluctuation can be caused by a small variation of the laser pulse energy and the interaction of the beam with the target surface and the surrounding atmosphere. The high uncertainty can be triggered by variations of the thermal properties of the samples, such as melting, boiling, or evaporation temperatures, and also by the chemical matrix effect, which is related to the different chemical reactions between the various components of the sample at plasma temperature [17, 18]. In practice, the above-mentioned phenomena – laser beam interaction and matrix effects – are expressed by a nonlinear relationship between the spectral line intensity and the analyte concentration. In the calibration curve, it manifests itself in a large dispersion of the measured points around the calibration straight line and, therefore, a less precise LIBS analysis, especially for solid samples like metal or geological materials. Many approaches have been developed to overcome this difficulty by using sophisticated methods of calculation, normalization, and matrix-matched standards, but they are costly and difficult to implement [19–24].

This paper focuses on a simple procedure to reduce the matrix effect in the LIBS analysis of metal alloys. This procedure is based on a number of successive steps and starts from the selection of the optimum controlled parameters of the detection system: laser power, delay time, and focal distance. After that, internal standard calibration was used to determine the absolute or relative impurities present in the metal samples. The last step consists of the determination (if needed) of the metal concentration. This step requires spectra averaging, whole spectrum normalization, and self-absorption correction, if necessary.

Experimental investigation. *Instruments and material.* The LIBS system used in this investigation is a Spectrolaser-7000 from Laser Analysis Technologies, Australia, described in detail in [25]. Briefly, this integrated system is fully software-controlled and consists of an excitation laser, optical spectrographs, gated CCD detectors, and a personal computer. The laser source employed is a high-power (0.5–350 mJ) Q-switched Nd:YAG-laser (New Wave Research, US) operating at the fundamental wavelength ($\lambda = 1064$ nm); it yields a 7 ns pulse at a repetition rate of up to 15 Hz. The laser source is focused on the sample through a 50 mm focal lens. The sample is placed on a fast translation stage X-Y-Z that moves it between laser pulses for exposing new areas of the sample to each successive laser pulse. The total wavelength range covered by the seven channels is 190–940 nm.

The sample materials chosen for this investigation are three sets of reference standards of metal alloys (aluminum, steel, and copper) provided by MBH Analytical, Ltd., and Brammer Standard. The aluminum alloys set contains about one percent of impurities shared between four main elements: Mg, Mn, Fe, and Pb. The steel alloys set contains iron (from 49 to 98 %) and five other elements: C, Al, Si, Cr, and Ni. The copper alloys set can be divided into two sub-sets: in the first, called brass material (Cu-Zn), the major matrix elements are copper and zinc; in the second, called bronze material (Cu-Sn, Pb, Ni), the major elements are copper and tin. The copper basis of these alloys varies from about 55 to 99%, and the rest is shared between the other elements. For these sets, a significant matrix effect occurs due to large differences in the physical properties of the metal constituents [26, 27]. Hence, the selection of these three metal sets, which cover the majority of industrial needs, is intended for the investigation of matrix effect reduction.

Methodology. The first step of this investigation is the determination of optimum parameters of the LIBS control system based on a compromise between the maximum area without saturation of the line, the lowest relative standard deviation (RSD), and the highest signal-to-background ratio (S/Bg) [25].

The second step of this investigation is adjusting the LIBS system with the selected optimum parameters for each element. After that, all standard metal alloy sets are experimentally studied. Spectra are obtained for five different surface areas of each reference standard. The experiment for each area is carried out three times. For construction of the calibration curves, we use the internal standard calibration method [28, 29]. The absolute or relative impurities concentrations of the analyzed samples can be determined depending on the variation of the internal standard concentrations.

The third step is necessary if the concentration of the major matrix element, which is used as an internal standard (IS), is dispersed. Therefore, the construction of the calibration curve for determining the IS concentration is necessary for deducing the absolute values of the concentrations of impurities. The construction of this curve requires spectra averaging, whole spectrum normalization, and self-absorption corrections. The self-absorption method used in this investigation is based on the ratio of the intensities of the selected (distorted) analyzed line and a reference line such as the α-line of hydrogen (656.27 nm), which appears in all spectra due to the very low concentration of this element in the air [30].

Results and discussion. Three sets of metal alloys are selected to investigate the reduction of the matrix effect. However, the first one (aluminum) has a nearly constant concentration of aluminum (IS). Therefore, the calibration curves of the intensities ratio of *X* and aluminum impurities *I*(*X*/Al) versus the impurity concentration *C* ct.(*X*) give the absolute impurities concentration. The coefficient of determinations R^2 of these curves is close to unit (Fig. 1).

The second set is steel alloys, which have a large variation of the Fe (IS) concentration. However, the analysis in this case is focused on the relative concentration *C* ct.(*X*/Fe). Therefore, the calibration of the intensities ratio of *X* and Fe impurities I(X/Fe) versus the relative concentrations C ct.(*X*/Fe) gives the relative impurities concentration (Fig. 2).

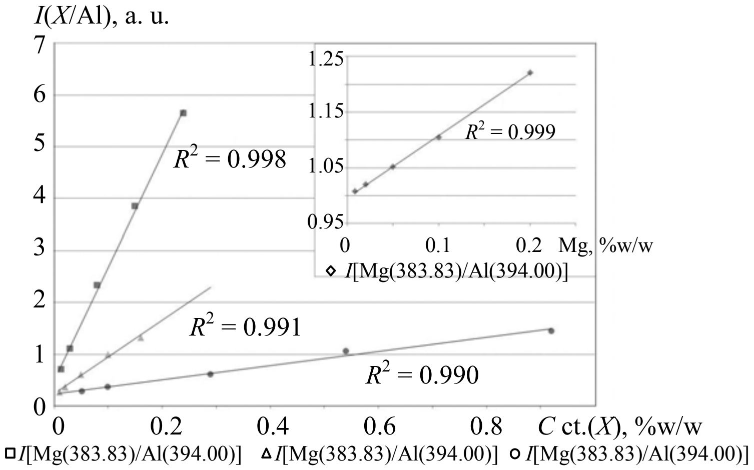

Fig. 1. Calibration dependence of the intensity ratio *I*(*X*/Al) on the absolute concentration of the impurities *C*ct(*X*) for Al-Alloys. R^2 is the determination coefficient.

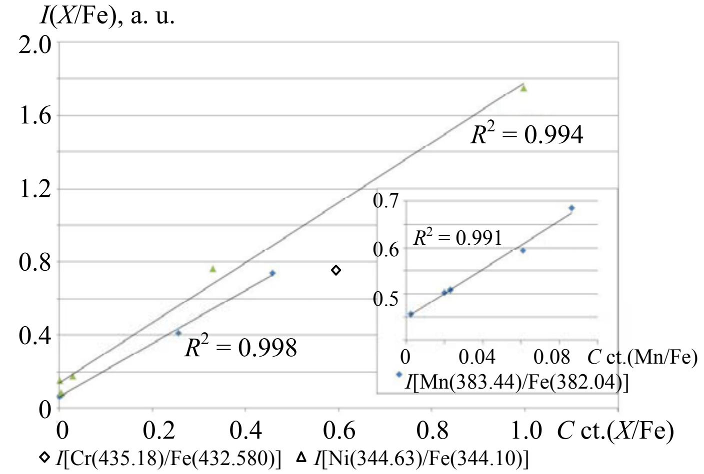

Fig. 2. Calibration dependence of the intensity ratio *I*(*X*/Fe) on the absolute concentration of the impurities *C*ct(*X*) for Fe-Alloys. R^2 is the determination coefficient.

The third set is copper alloys, which have a large variation of the Cu concentration. The relative impurities concentration can be determined as for the steel set described above (Fig. 3). The bronze analysis gives the absolute concentrations of most elements of the sample. The calibration curve for copper is constructed for this analysis, which requires averaging the spectra, whole integral spectrum normalization, and self-absorption corrections. Table 1 shows the variation of the determination coefficient. Using the values of the relative impurities concentration of the copper alloys from the calibration curves (Fig. 3) and the absolute concentration of copper in these alloys (Fig. 4), one can determine the absolute concentration of the impurities.

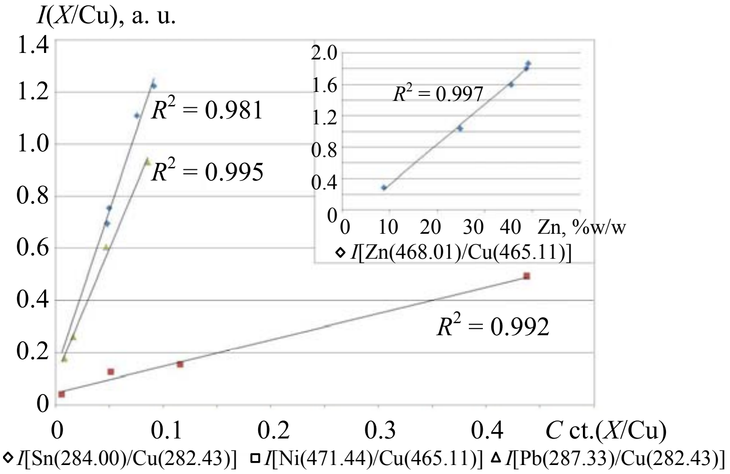

Fig. 3. Calibration dependence of the intensity ratio $I(X/\text{Cu})$ on the relative concentration of the impurities $C\text{ct}(X/\text{Cu})$, and the calibration curve of Brass.

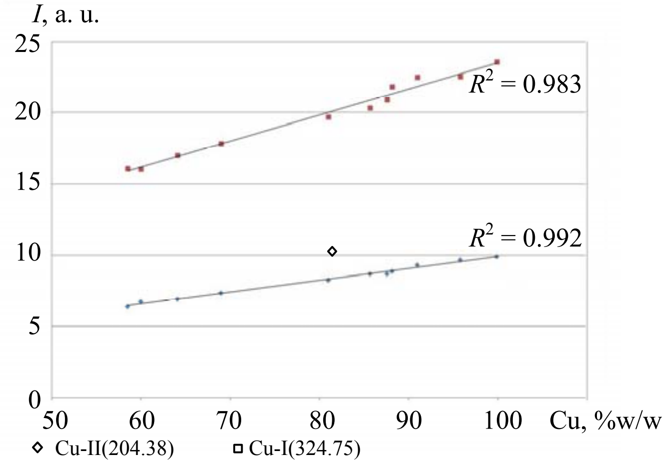

Fig. 4. Calibration curves of two Copper lines; Cu II and Cu I lines, versus the copper concentration $C\text{ct}(\text{Cu})$ after normalization and self-absorption correction.

Note that the calibration curve in Fig. 3 is used to determine the concentration of zinc in the brass alloy without prior knowledge of the copper concentration because in this case the basis copper concentration is close to the constant.

In general, metal alloys are subjected to an unfavorable matrix effect, especially the copper alloy due to its large differences in the physical properties of the metal constituents [26]. For this reason, the calibration curve of the intensity or the area of the copper line versus the concentration is useless. For some lines, the intensity decreases even when the concentration increases. However, with appropriate data processing, including various normalization methods, the linearity of the calibration curve can be improved. The best method for this purpose is based on averaging, whole integral spectrum normalization, and self-absorption correction (Table 1 and Fig. 4).

TABLE 1. Variation of the Determination Coefficient R^2 of Copper Calibration Curve

Curves	Cu-II (204.8)	Cu-I (324.75)
Intensity vs Cu (%w/w)	0.361	0.137
Normalized intensity[*] vs Cu (%w/w)	0.954	0.906
Final Data processing[**] vs Cu (%w/w)	0.990	0.982

[*] Normalized Intensity: Normalization with whole integral spectrum.
[**] Final data processing: Normalized signal multiplied by the correction of self-absorption.

The validation of the proposed procedure is realized by measuring three new standards, not used in the calibration: made from steel, brass, and bronze, which are known as complicated cases. The relative error between the standard value and that determined by the proposed procedure is less than 5% (Table 2).

TABLE 2. Validation of the Proposed Procedure for the Metal-Alloys Analysis

Element concentration	Standard, %	Predicted, %	Error, %
Conct.(Cr/Fe)* in Steel	4.15	3.96	4.58
Conct.(Zn)** in Brass	38.73	40.13	3.62
Conct.(Pb/Cu)in Bronze	7.07	6.72	4.95
Conct.(Cu) in Cu-Alloys	81.42	82.58	2.65
Conct.(Pb) in Bronze	5.76	5.54	3.82

[*] Conct.(Cr/Fe): Relative concentration of chromium in the steel.
[**] Conct.(Zn): Absolute concentration of Zn in the brass.

The internal standard calibration method is used to overcome signal fluctuations and compensate the matrix effect. This method is based on the addition of equal amounts of similar substances to samples and standards before analysis, which is ideal for liquids and powder samples. Unfortunately, this is not possible for solid samples, such as metal alloys, but to get the benefit of this method, an emission line of the major matrix element is selected as the internal standard line [31]. However, in LIBS, the choice of the IS line is crucial to obtain good results, so it must meet the following criteria: 1) the IS line must be homologous with the analyte line; 2) the detection efficiencies of the IS and analyte lines must be the same, which means that their wavelengths must be as close as possible; 3) the energy of the upper level of the IS line should be close to that of the analyte.

It is not always easy to find a suitable internal standard, but with some effort and in agreement with the above conditions the IS lines selected in this investigation for metal alloys analysis are able to give satisfactory results.

Conclusion. The reduction of the matrix effect is crucial to improve the precision of LIBS analysis of metal alloys. These materials are subjected to a significant matrix effect due to a large variation of their physical and chemical constituents. In this investigation, a simple procedure composed of three steps is proposed to reduce this effect. The first step is the selection of optimum parameters of the detection system. The second step is the estimation of the absolute or relative values of impurities based on the internal standard calibration. The third one, if needed, is the analysis of the metal basis of the alloy used as an internal standard. The three sets of metal alloys (Al, Fe, and Cu) used in this investigation cover the majority of industrial needs. This procedure is validated by measuring steel and copper alloys standards. The relative error obtained between the standard values and the measured ones is less than 5% even for the complex copper alloys. These results can be generalized for quantitative analysis of other materials, such as geological and soil samples, by LIBS.

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