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RAPID ANALYSIS OF EMISSION SPECTRA FOR GOLD ALLOYS

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We present the results of quantitative determination of the composition of gold alloys in laser spark emission spectrometry (also known as laser-induced breakdown spectrometry or LIBS), based on the contribution from each chemical element to the integrated intensity of the emission from the alloy. The method makes it possible to make real-time measurements using low-power lasers. We have measured the concentration of gold in alloys containing gold, copper, and silver using our method. We demonstrate the need for preliminary qualitative or semiquantitative measurements.

Key words: *emission spectrum, measurement of concentration, gold alloys, laser analysis.*

Introduction. Emission spectral analysis is a widely used method for rapid analysis of the composition of metal alloys. This is because data acquisition efficiency is of critical importance in an industrial process. Today some success has been achieved in the area of instrumental and procedural developments for laser spark emission spectrometry, also called laser-induced breakdown spectroscopy (LIBS) [1–4]. Nevertheless, contradictions remain between the high level of instrumental developments and the accuracy of measurement of the concentration for individual elements. These are associated with a wide variety of factors: instability of the plasma excitation source, the matrix effect, interference from third elements, chemical reactions in the plasma, etc. [4, 5]. This is especially apparent when real-time measurements are made and the analyte object does not undergo any special sample preparation.

Quantitative analysis of alloys of precious metals and articles made from them has always been and will always be an important problem. With demands made on the quality of alloys becoming more and more stringent, the need arises to analyze the composition of articles not only in specialized laboratories but also directly in production areas. In this case, the measurements should be made in the shortest time possible and preferably with very little sample preparation. The most widely used analysis methods for such alloys are densitometry, determination of gold content on a touchstone, cuppelation, and x-ray fluorescence analysis. In practice, other methods are not used due to their labor-intensiveness and high consumption of the analyte materials [6]. The efficiency of LIBS for analysis of alloys containing gold has been shown in [1, 2, 5]. However, the methods used in those papers for processing the spectral information do not make it possible to achieve the required accuracy of the measurements in a limited timeframe. Accordingly, the problem arose of developing new methods for processing emission spectra for rapid analysis of alloys, enabling measurement of the metal concentration in the alloy with specified uncertainty and in the shortest measurement time possible. In this paper, we present the results of measurement of the concentration of the base metal in alloys using analysis of the laser emission spectra by a method based on the contribution of each element to the total intensity of emission for the alloy. This allowed us to shorten the measurement time and made it possible to use low-power lasers for these purposes.

Measurement Procedure. General topics in construction of mathematical models for emission analysis have been developed rather well in [1, 2], but their adaptation to a specific subject area requires special studies. In processing the spectra of the plasma produced by laser-induced breakdown, we need to take into account the variety of chemical compositions of the analyte samples and the characteristic features of the spectral instrumentation [4].

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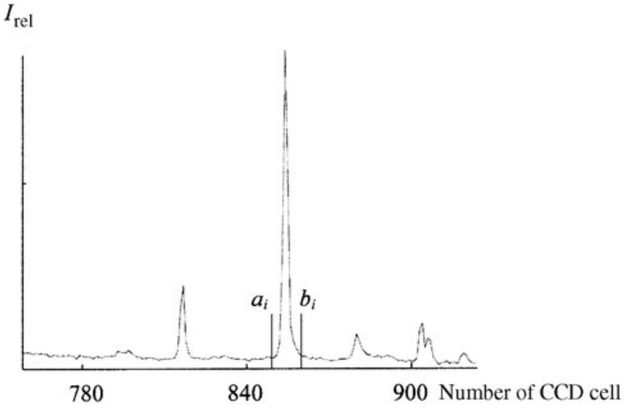

Fig. 1. Determination of a line in the spectrum.

From the general theory of spectral analysis, we know [7] that the intensity ratio of spectral lines for individual components of an alloy is proportional to the ratio of the concentrations for the corresponding elements. The intensity ratio is affected by a number of secondary phenomena in the light source (superposition of lines from individual elements, self-absorption) and the recording device (limited spectral range, background illumination). All these factors together can introduce significant systematic errors into the measurement results, and the effect of these errors on the measurement result increases as the concentration of the analyte element decreases. We can theoretically determine the magnitudes of some factors affecting the intensity ratio, and can make the required corrections to the measurement data when doing the analysis [4]. In practice, all the corrections usually cannot be made with the required degree of accuracy. Therefore from a formal standpoint, the major problem in developing a quantitative analysis method was reduced to choosing an informative parameter that would be less affected by the factors mentioned above. As the informative parameter, we chose the normalized intensity of the emission from the material.

For each material included in the analyte alloys, we selected all the emission lines whose intensity exceeds the noise threshold of the spectrometer in the recorded wavelength range. In particular, for gold the list includes 19 lines; for silver, 10 lines; and for copper, 7 lines. For the selected lines, we determined their position in the spectrum by indicating the points a_i^M and b_i^M between which the line is found (Fig. 1), where M = {Au, Ag, Cu} means to which element the line belongs. The value of a_i^M (b_i^M) is determined as the closest point on the left (right) of the maximum for the i-th line of the element M in the alloy with illumination equal to the level of the constant spectral background with coefficient 1.1. Furthermore, for the spectra we calculated the normalization coefficient N satisfying the condition

$$\sum_{M=\text{Au,Ag,Cu}} \sum_i \sum_{k=a_i^M}^{b_i^M} \frac{A_k}{N} = C, \tag{1}$$

where C = 3648 is the number of elements in the photosensitive detector array; A_k is the intensity at λ_k measured by the k-th element in the photodetector.

The normalized intensity of the emission from components of the alloy is determined using the formulas:

$$I^{\text{Au}} = \sum_i \sum_{k=a_i^{\text{Au}}}^{b_i^{\text{Au}}} \frac{A_k}{N}, \quad I^{\text{Ag}} = \sum_i \sum_{k=a_i^{\text{Ag}}}^{b_i^{\text{Ag}}} \frac{A_k}{N}, \quad I^{\text{Cu}} = \sum_i \sum_{k=a_i^{\text{Cu}}}^{b_i^{\text{Cu}}} \frac{A_k}{N}. \tag{2}$$

Let us hypothesize that the laser pulse energy is absorbed by components of the alloy in proportion to their concentration, i.e., let us neglect absorption selectivity effects. Then according to [7], the brightness of the lines from

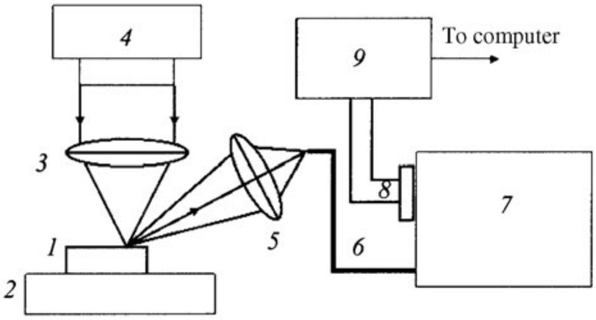

Fig. 2. Block diagram of spectrometer.

individual components is proportional to the amount of absorbed energy and the concentration of the components in the alloy K^M, which makes it possible to use the normalized intensity of the emission as the parameter in plotting the calibration curve $K^M = f(I^M)$.

Experimental Section. In order to study the laser emission spectra of the alloys, we designed and built a spectrometer (working range 390–830 nm, spectral resolution 1.2 Å/pix), the block diagram for which is shown in Fig. 2. As the radiation source, we used an ytterbium fiber laser 4 (λ_{las} = 1.06 μm). Periodic pulse operation of the laser provides the following parameters: pulse energy, 0.5 mJ; pulse duration, 80 nsec; repetition frequency, 10 kHz. Using objective 3, having focal length 80 mm, the laser radiation is focused on specimen 1, which is placed on stage 2. As the radiation interacts with the specimen surface, a cloud of low-temperature ablation plasma is formed above it. The emission of the plasma is focused on the end of quartz optical fiber 6 using objective 5 and then is transmitted to the optical module 7, where it is decomposed into a spectrum using a 100 lines/mm diffraction grating. The spectrum is recorded using photodetector 8, as which we use a TCD 1304DG linear CCD array (Toshiba), consisting of 3648 photocells (8 × 200 μm). The electrical signals from the output of the CCD array are converted to digital form, after which they are fed to the computer through a USB interface. The operation of the spectral analyzer (selection of the parameters of the CCD array, recording time, and delay time between recording the spectrum and the appearance of emission) is controlled by control module 9 according to commands coming from the computer.

As the specimens, in the experiments we used alloys of gold with copper and silver in the form of test needles (116 specimens of different fineness, from 333 to 999 inclusive) and standard specimens of gold alloys (8 specimens in the fineness range 201–989.96).[*] The gold concentration here and below is indicated in fineness units (one fineness unit corresponds to 0.1%).

According to [5], the optimal recording time for the spectrum is the interval from when the laser action stops to when the luminescence of the plasma ends. The experiments showed that using low-power lasers leads to the need for periodic pulse operation of the source. Accordingly, all the spectra were recorded for the laser turned on, with a 15 msec delay from the time the laser radiation appeared. The recording delay was selected considering the maximum repeatability of the spectrum, and its lower bound was the time required for the laser to reach its nominal output power.

As the basic criterion for choosing the recording time for the spectrum, we assumed maximum utilization of the dynamic range of the spectrometer. Since the CCD detector array operates with accumulation of the signal over time, the recording time has a strong effect on the intensity of the spectral lines (Fig. 3). With an increase in recording time for the spectrum, the background component of the spectrum sharply increases, which for a recording time >30 msec leads to saturation of the CCD and loss of useful signal. But in order to reduce the signal quantization error and the effect of the intrinsic noise of the CCD array, the intensity of the lines used should be as high as possible (for a recording time of 10 msec, the intensity of most of the lines is comparable with the intrinsic noise of the CCD

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[*] The difference between the test needles and standard specimens is the fact that the needles may have grainy inclusions of the components with sizes up to 50 μm, while the standard specimens designed for calibration of spectral instruments are homogeneous.

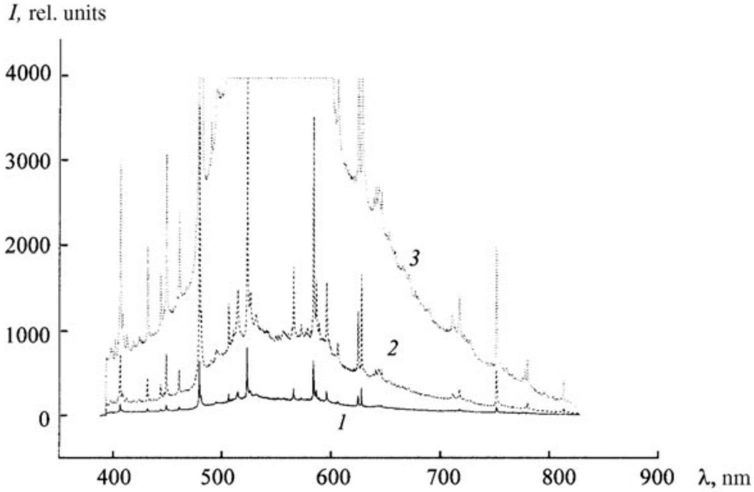

Fig. 3. Emission spectra of specimen Au 999 with recording time 10 msec (1), 20 msec (2), and 35 msec (3).

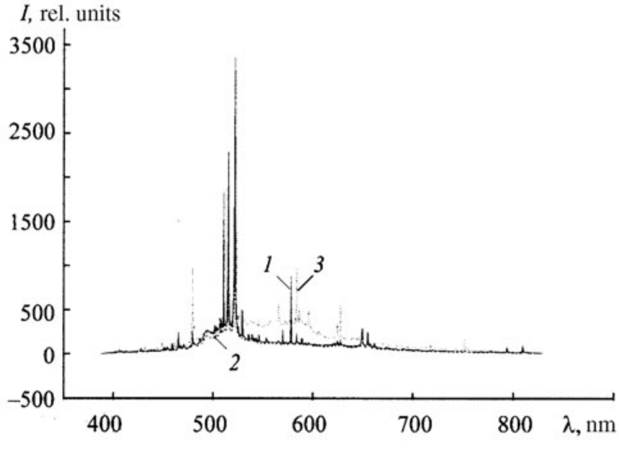

Fig. 4. Emission spectrum of different gold alloys for recording time 20 msec: fineness 375 (1), 585 (2), and 999 (3).

array). Consequently, spectra obtained in a time ≤15 msec are not suitable for quantitative analysis with satisfactory accuracy.

Thus the recording time should be as long as possible, but should avoid saturation of the CCD array. Taking into account the characteristic composition of the specimens (non-saturation of the brightest lines: copper triplet 521.1, 515.3, 510.5 nm and silver doublet 546.5, 520.9 nm), all the measurements were made with recording time 20 msec (Fig. 4). With a constant laser pulse energy, we recorded the emission spectrum in a specified range for alloys with different concentrations of the material, and then we plotted the calibration curve showing the concentration of this material in the alloy vs. the normalized intensity of its emission (2) (Fig. 5).

Discussion of Results. The experiments show that the calibration curves have different shapes, depending on the copper and silver content in the alloy. The differences can be explained by the presence in the function $K^M = f(I^M)$ of a coefficient characterizing the efficiency of conversion of the energy absorbed by the material to the energy of the characteristic emission. This coefficient depends on the composition of the alloy, so the preliminary step in

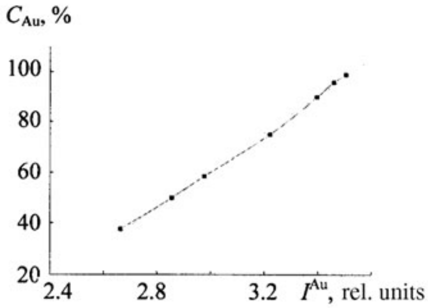

Fig. 5. Calibration curve (logarithmic) for gold content in alloy vs. normalized intensity of gold emission.

TABLE 1. Gold Concentration in Alloys, Measured From Normalized Spectrum (I) and From Intensity Ratio for Individual Lines (II)

Type of alloy	I			II		
	Mean value 0.1%	MSD	Measurement time, sec	Mean value 0.1%	MSD	Measurement time, sec
ZlM-375	344.10	8.91	1.8	368.50	14.34	23.1
ZlSrNM-375-350-8.0	390.23	9.58	2.3	370.93	10.20	18.7
ZlSrM-585-80	643.00	7.62	2.4	590.20	12.02	14.2
ZlNTsM-585-12.5-4	532.75	6.70	2.1	540.43	8.31	19.3
ZlSr-750	753.75	5.38	1.7	749.75	7.63	20.2
ZlM-750	724.75	5.62	1.6	761.50	4.04	18.5
ZlIPdM-958-10-10	937.04	12.47	2.1	968.17	14.40	16.1

Note. MSD = mean-square deviation. [Russian alloy designations: Zl = gold, M = copper, Sr = silver, N = nickel, Ts = zinc, I = iridium, Pd = palladium.]

measurement of the concentration was qualitative determination of the composition of the alloy, in particular, determination of the presence in it of (besides gold) silver and copper, based on the presence of the characteristic lines for these metals in the spectrum.

The error in the basic measurements in this case varied in the range from 0.8% (for specimens with gold content >75%) to 2.5% (for specimens with gold content 40%–60%). The measurements were made by averaging ten runs of the spectrum at different points on the specimen (time required for a single measurement ≤2.5 sec).

The results of the gold concentration measurement for a number of specimens are shown in Table 1; for comparison, we also show the results obtained when using the method based on measurement of the intensity ratio of individual lines. We see that measurement of the concentration using the normalized intensity of the emission gives greater error than the method based on the intensity ratio of individual lines, although it also makes it possible to reduce the mean square deviation of the measured value. However, we would like to note a few points connected with practical application of these methods. First of all, quantitative analysis of the composition by the method based on measurement of the intensity ratio of individual lines requires a time interval for analysis almost an order of magnitude longer than for the method we are considering here, which may be unacceptable in real-time monitoring systems. Secondly, in order to obtain accurate results by the method using the intensity ratio of individual lines, we need preliminary semiquantitative estimation of the composition. Depending on the preliminary estimate, specific lines are selected in the spectrum for exact determination of the concentration of the components. Thirdly, a distinguishing feature of the analysis method we used for the alloys is the possibility of using low-power lasers with pulse energy ≈0.5 mJ. For quantitative analysis using the intensity ratio of individual lines, we need more powerful lasers (10–200 mJ) [4, 8].

The listed features allow us to conclude that the method based on using the normalized intensity of the emission is more suited to industrial purposes for real-time rapid analysis, while the method based on measurement of the intensity ratios of the spectral lines, although it gives better results, requires separate equipment and additional training of personnel.

Conclusion. Our studies have shown that it is efficient to use a method based on the contribution of each element to the integrated intensity of the emission for quantitative analysis of alloys. Despite the fact that this method gives somewhat greater error in measurements of the concentration of the base metal than the method based on the intensity ratio of the spectral lines, it allows us to considerably shorten the analysis time. Furthermore, the method described allows us to use low-power periodic pulse lasers as the atomizer.

We have built a rapid analyzer for emission analysis of gold alloys based on low-power (0.5 mJ) lasers. The analysis time was no longer than 2.5 sec, which makes it possible to combine analysis of the composition with the process of applying markings. Using the rapid analyzer makes it possible to monitor the composition of all machinable articles, resorting to the laboratory analysis method only when doubts arise concerning the grade of the article.

Our method can be integrated into already existing laser machining systems for materials (laser marking, cutting, high volume sampling, etc.), which considerably reduces the cost of the equipment for the analysis.

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