ISSN 0027-1314, Moscow University Chemistry Bulletin, 2008, Vol. 63, No. 4, pp. 219–223. © Allerton Press, Inc., 2008.
Original Russian Text © A.M. Popov, T.A. Labitin, N.B. Zorov, A.A. Gorbatenko, 2008, published in Vestnik Moskovskogo Universiteta. Khimiya, 2008, No. 4, pp. 265–270.

Nonlinear Normalization for Laser-Enhanced Ionization Spectrometry with Laser Sampling into a Flame

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Received November 22, 2007

Abstract—The conditions for the appearance of a significant linear correlation between laser-enhanced ionization and reference signals are found. The parameters of this correlation (polynomial coefficients) are suggested to be used as a normalized analytical signal. The use of nonlinear correlation makes it possible to extend the range of ablation laser energies.

DOI: 10.3103/S002713140804010X

Laser sampling is widely used in analytical practice for distant and rapid analysis of metals and alloys, glasses, and polymers, as well as different geological, archeological, and biological samples [1–4]. In analytical methods using laser sampling, a solid substance transforms into the gas phase, which allows one to avoid preliminary sample preparation. The minute amount of a material (up to 10^{-9} g) ablated per laser pulse makes it possible to carry out probe and layer-by-layer analyses of any materials with a resolution on the order of 10 μm and 10 nm, respectively. The combination of laser sampling with highly sensitive and selective laser-enhanced ionization (LEI) spectrometry makes it possible to carry out single-element microanalysis of different materials [5–11]. The major obstacle to wide analytical application of this approach is the significant effect of the solid matrix on the analytical signal. This necessitates the use of solid references of specified composition, which are difficult to prepare. Variations in the sample composition and ablation laser energy change the character of interaction of radiation with the sample, which leads to a considerable change in the sampled mass and the characteristics of the generated plasma [12]. In multielement methods, such as laser ablation inductively coupled plasma mass spectrometry or laser ablation optical emission spectrometry, this problem is solved by mainly using the signal of an internal standard [2, 3] or some reference signal [12]. The only attempt to apply an internal standard in the LEI method necessitated doubling of most units of the experimental setup [13] since this is a single-element method of analysis. It is of interest to develop methods of correction of the analytical signal in the LEI method in combination with laser sampling with the use of reference signals.

Previously [14–16], we showed that the use of parameters of a linear correlation between analytical and reference signals for correction of matrix effects on the analytical signal is promising. This method implies the use of the slope of the correlation line in the analytical signal–reference signal coordinates as a normalized analytical signal. This normalization makes it possible to reduce matrix effects on the analytical signal. This method requires choosing a range of laser beam energies in which there is a linear correlation between the signals. However, due to the threshold character of the correlation between these signals, the behavior of the correlation plot in a wider range of energies (from 10 to 80 mJ/pulse) is essentially nonlinear.

This work deals with study of the nonlinear correlation between the LEI signal of Li and the reference signal, as well as the possibility of using its parameters for correction of the LEI signal of lithium.

EXPERIMENTAL

The experiment was carried out in a setup that is a prototype of the laser LEI spectrometer described in detail in [14]. Let us consider the principle of its operation. The beam of an ablation Nd^{3+} laser with Q modulation was focused on the sample surface. A generated cloud of particles (laser torch) entered a flame. Lithium atoms were resonantly excited by dye lasers tuned at the wavelengths of electronic transitions of lithium atoms (λ = 670.8 and 610.4 nm). The excited atoms were ionized due to collisions in the flame. The ionization signal was detected by a cathode placed into the flame. In addition to the analytical LEI signal, a nonselective ionization (NSI) signal caused by nonselective ionization of atoms in the laser plasma was recorded. The NSI signal and the LEI signal of lithium are time resolved [17].

The spectrometer design makes it possible to simultaneously record, along with the ionization signal, the optoacoustic (OA) signal, using a microphone, and the atomic emission (AE) signal from the laser torch, using

Table 1. Composition of the samples

Sample type	Description	Component and its content, wt %			
		Mg	Cu	Ag	Li
Al–Cu–Li alloys	No. 1	0.89 ± 0.05	4.1 ± 0.2	0.4	1.11 ± 0.02
	No. 2	0.63 ± 0.04	3.9 ± 0.4	0.4	0.92 ± 0.04
	No. 3	0.38 ± 0.03	4.2 ± 0.3	0.4	1.10 ± 0.04
	No. 4	–	2.9 ± 0.2	0.4	0.94 ± 0.02
	No. 5	0.59 ± 0.01	3.6 ± 0.1	0.4	1.06 ± 0.05
	No. 6	0.69 ± 0.02	2.8 ± 0.2	0.4	1.16 ± 0.04
	Description				Li
Lithium ferrites	$LiFeO_2$ annealed				7.2 ± 0.1
	$LiFe_5O_8$ annealed				1.67 ± 0.06
	$LiFe_5O_8$ unannealed, pyrolysis at $T = 750°C$				1.76 ± 0.05
	$LiFe_5O_8$ unannealed, pyrolysis at $T = 850°C$				0.85 ± 0.03
	$LiFe_5O_8$ unannealed, pyrolysis at $T = 950°C$				0.67 ± 0.02

a monochromator and a photoelectron multiplier. The ablation laser energy was changed with the use of a set of calibrated neutral light filters. All signals were recorded and processed on-line with the use of a high-speed analog-to-digital circuit board (the discretization frequency, 20 MHz) and software specifically developed for this board. Magnesium-, copper-, and silver-alloyed aluminum–lithium alloys Al–Cu–Li, manufactured at the All-Russia Institute of Aviation Materials, as well as lithium ferrites $LiFe_5O_8$ and $LiFeO_2$, synthesized in the Laboratory of Inorganic Materials Science at the Faculty of Chemistry of Moscow State University, were used as samples. The compositions of the samples, determined by flame photometry and flame atomic absorption spectrometry, are summarized in Table 1.

RESULTS AND DISCUSSION

Figure 1a shows the calibration plots for the determination of lithium in ferrites. As is seen, for none of the laser radiation energies do conditions exist under which the calibration plot can be approximated by a straight line. Such a behavior is due to the effect of the ferrite microstructure on the analytical signal. In particular, the strongest LEI signals are observed for annealed ferrites, whereas, for unannealed samples, the LEI signal is weak. At the same time, the presence of copper in Al–Cu–Li alloys with the same lithium content also exerts a significant effect on the analytical signal (Fig. 1b). It is worth noting that, in these cases, varying the ablation laser energy does not help to optimize the analysis. Therefore, it is necessary to develop other approaches that can minimize the matrix effects on the analysis results.

Appropriate reference signals were determined in accord with the recommendations expounded in [14]. The first maximum of the time dependence of the acoustic signal was chosen as the reference OA signal. As the reference AE signal, the AE signal of iron (λ = 382.4 nm) was selected for lithium ferrites and the aluminum signal (λ = 396.2 nm) was used for the alloys. Such a choice of the reference AE signal is dictated by the difference between the major components of the samples and the largest intensity of these lines in the emission spectra of the laser torch. Figures 2a and 2b show the plots of the intensities of the above signals versus the ablation pulse energy. For both ferrites and alloys, the analytical signal (curve *1*) increases with an increase in the laser radiation energy, which is due to the increase in the mass of the sampled material. Indeed, the OA signal, which appears when plasma breakdown from the sample surface takes place, also builds up with an increase in the laser radiation energy (curve *3*). It is worth noting that, during laser ablation of lithium ferrites, the NSI signal (curve *4*, Fig. 2a) is absent or very weak; therefore, it was not used as a reference signal. A similar situation was observed earlier for nonvolatile lithium polyvanadate pressed in pellets [10].

The concurrent buildup of the signals with the laser radiation energy implies the existence of a correlation between these signals. To study this correlation, we constructed correlation diagrams for each sample. Figure 3 shows an example of such a diagram. Each point of the diagram corresponds to the simultaneous measurement of the analytical and reference signals for one pulse at a definite ablation laser energy. Three regions can be conventionally distinguished in this diagram. In the first region, the LEI signal is almost zero, whereas

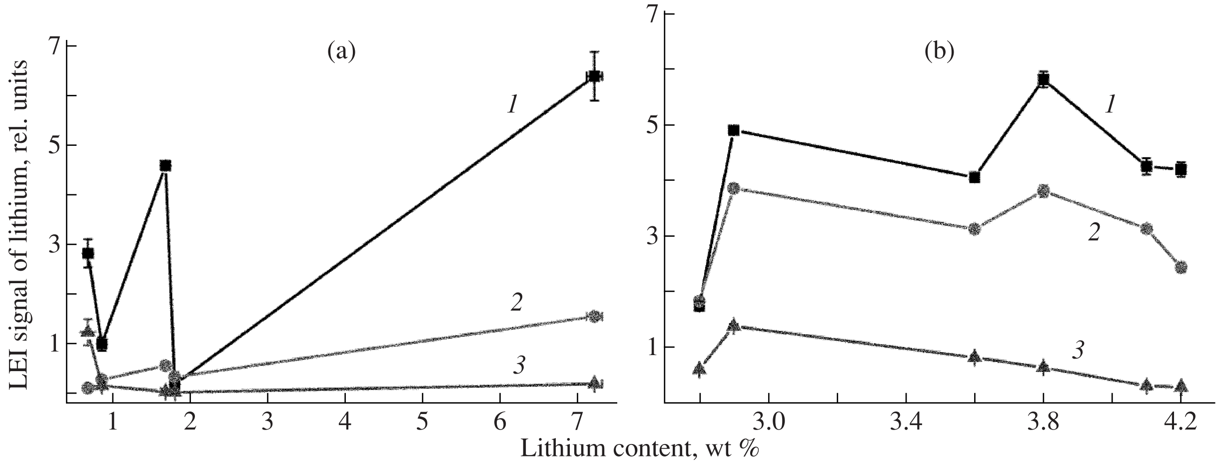

Fig. 1. Dependence of the analytical LEI signal of lithium on (a) the lithium content in ferrites and the copper content in Al–Cu–Li (b) for different laser pulse energies (mJ): (*1*) 80, (*2*) 50, and (*3*) 20.

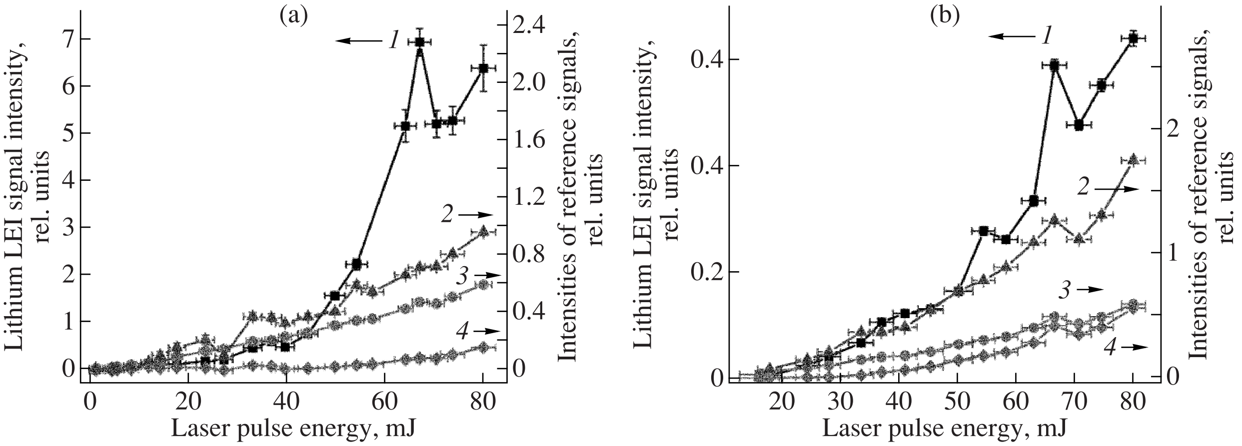

Fig. 2. Dependence of the (*1*) LEI, (*2*) AE, (*3*) OA, and (*4*) NSI on the laser pulse energy for (a) lithium ferrites and (b) Al–Cu–Li alloys.

the reference signal is nonzero. In the second region, the LEI signal increases nonlinearly with the buildup of the reference signal. This region corresponds to the near-threshold regime of analytical signal formation. In the third region, the LEI signal increases linearly with the reference signal. Each region of the diagram corresponds to a definite range of laser radiation energies. In particular, the linear correlation between the signals in observed in the pulse energy range of 40–80 mJ for metals and 45–75 mJ for nonmetal samples. The correlation between the analytical and reference signals for the entire range of pulse energies is evidently cannot be described by a linear equation.

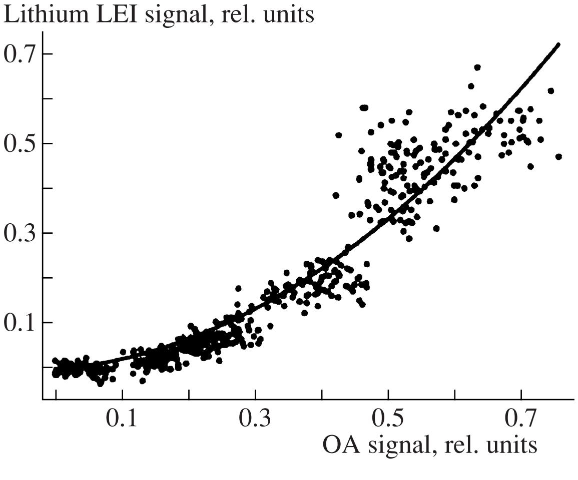

Fig. 3. Nonlinear correlation diagram between the lithium LEI signal and the OA signal for the Al–Cu–Li alloy. The quadratic regression parameters: $\text{LEI} = b\text{OA} + c\text{OA}^2$, where $b = 0.12 \pm 0.03$, $c = 1.12 \pm 0.05$, $r^2 = 0.889$, and $N = 480$.

To describe the nonlinear correlation between the intensities of the analytical I_a and reference I_r signals, we used a second-order polynomial

$$I_a = a + bI_r + cI_r^2, \quad (1)$$

Table 2. Nonlinear correlation coefficients r^2 between the LEI signal of lithium and the reference signals for the Al–Cu–Li alloys and lithium ferrites

Sample		*N*	Correlation coefficient r^2		
			LEI and OA	LEI and AE	LEI and NSI
Al–Cu–Li	No. 1	480	0.910	0.889	0.924
	No. 2	480	0.913	0.896	0.910
	No. 3	480	0.840	0.795	0.680
	No. 4	480	0.917	0.890	0.856
	No. 5	480	0.889	0.927	0.928
	No. 6	480	0.862	0.891	0.828
Lithium ferrites	$LiFeO_2$ annealed	480	0.806	0.804	0.574
	$LiFe_5O_8$ annealed	480	0.881	0.922	0.912
	$LiFe_5O_8$ unannealed, pyrolysis at $T = 750°C$	240	0.823	0.863	0.224
	$LiFe_5O_8$ unannealed, pyrolysis at $T = 850°C$	240	0.808	0.809	0.198
	$LiFe_5O_8$ unannealed, pyrolysis at $T = 950°C$	240	0.741	0.828	0.532

where *a*, *b*, and *c* are the nonlinear correlation coefficients. The coefficient *a* can be taken as zero since, at $I_r = 0$, the analytical signal should be equal to zero assuming that the deviation from linearity is adequately described by this quadratic trinomial. The geometric meaning of the coefficient *c* is that it is the curvature of the parabola described by Eq. (1), since it is its second derivative. Inasmuch as the analytical signal depends on the content of the analyte *C* and the reference signal does not depend on this content, the coefficients *b* and *c* in Eq. (1) should depend on *C*.

Table 2 presents the squared coefficients of a nonlinear correlation of type (1) between the LEI signal and the reference signals. Most correlation coefficients are close to unity, which is evidence that the nonlinear correlation is significant. Relatively small r^2 values for the nonselective reference signal are presumably associated with the lack of the NSI signal in the course of vaporization of unannealed lithium ferrites. The number of measurements used for constructing a nonlinear correlation is much larger than for the linear one ($N = 180$), which is associated with wider ranges of signals and laser radiation energies. For example, the nonlinear correlation diagram was constructed and the coefficient values *c* were determined in the laser energy range of 15–80 mJ for Al–Cu–Li alloy and 5–75 mJ for lithium ferrites.

As was shown above, a nonlinear correlation between the analytical and reference signals is observed for Al–Cu–Li alloys and lithium ferrite samples. Therefore, an attempt was made to apply nonlinear correlation normalization to these samples. As the analytical signal, the coefficient *c* in a polynomial of type (1) was used. Note that the curvature coefficient for the nonlinear correlation diagrams of the LEI signal of lithium and the NSI signal should be negative. This is due to the fact that the threshold value of the laser pulse energy for formation of the NSI signal, ~40 mJ, is larger than that for the LEI signal of lithium (10–20 mJ for the alloys and ferrites); hence, the zero coefficient of the linear correlation between the signals should be positive. For comparison of the results obtained for different reference signals, the magnitude of the curvature coefficient *c* was used.

As is seen from Fig. 4a, the effect of the microstructure and composition of lithium ferrite samples on the analytical signal was not decreased. At the same time, for the Al–Cu–Li alloys (Fig. 4b), the effect of copper on the analytical signal was reduced using the procedure of normalization to one reference signal. It is likely that the basic reason for such a behavior of the normalized signal is that the changes in the series of lithium ferrites cannot be attributed to small changes in the sample composition. At the same time, the use of nonlinear normalization is limited to a series of samples close in composition and microstructure. An analogous situation was observed when a linear correlation between the reference and LEI signal was used. However, for a linear correlation to exist, some conditions should be met. One of such conditions is the existence of a linear dependence of signals on the laser radiation energy in the range of higher E_{pulse} values. At the same time, the possibility of taking into account the processes that occur during laser sampling and the processes of interaction of the laser torch with the surface of a material can significantly improve the metrological characteristics of lithium determination.

Thus, the use of the nonlinear correlation between the analytical and reference signals can be recommended only in those cases when, for some reasons,

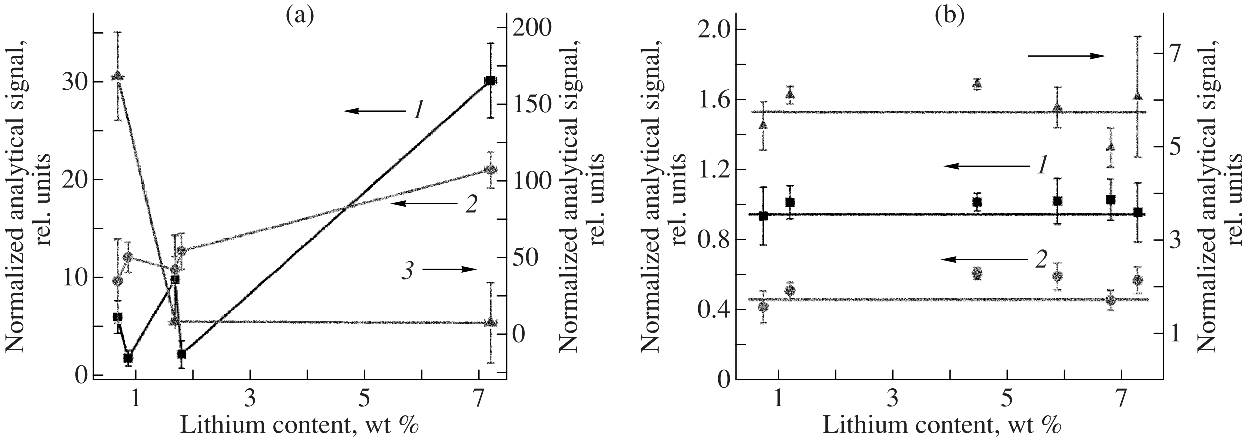

Fig. 4. Dependences of the lithium LEI signal normalized to the (*1*) OA, (*2*) AE, and (*3*) NSI signals on the basis of nonlinear correlation on (a) the lithium content in ferrites and (b) and the copper content in Al–Cu–Li alloys.

analytical measurements should be taken in the near-threshold region of the correlation diagram. Otherwise, it is preferable to normalize the analytical signal to the reference one with the use of the linear correlation.

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