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Short communication

Reduction of the matrix influence on analytical signal in laser-enhanced ionization spectrometry with laser sampling

Alexander A. Gorbatenko, Timur A. Labutin*, Andrey M. Popov, Nikita B. Zorov

Department of Chemistry, M.V. Lomonosov Moscow State University, Leninskie Gory, 1 Build. 3, GSP-2, 119992 Moscow, Russia

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Abstract

The novel approach using a slope of correlation line (laser-enhanced ionization of lithium versus laser-induced plasma emission of aluminum) as analytical signal was proposed for reduction of matrix interferences in laser-enhanced ionization spectrometric determination of Li with laser sampling.

Keywords: Laser-enhanced ionisation (LEI); Normalization; Reference signal; Lithium–aluminum alloys; Laser sampling

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1. Introduction

Laser sampling is widely used in analytical practice [1,2]. The advantages of this technique include the absence of any sample preparation, small amounts (up to 10 ng) of the sampled material [3], the opportunity of local and depth profile analysis [4,5]. However, variations of the sample matrix composition and the evaporation conditions lead to the uncontrolled changes of both the amount of ablated material and characteristics of a generated particle cloud. Using an internal standard [6,7] or reference signal [3,7–12] sometimes allows for the correction of the influence of both the matrix and the laser irradiance on the analytical signal. Usually optoacoustic and atomic emission (AE) signals are used as the reference ones. The optoacoustic signal depends on the amount of ablated material, the laser irradiance, and on the matrix composition [3,7,9]. The emission signal also depends on these parameters [3,7]. Besides, interaction of the laser plume with the outside ambient [2], the plasma electronic excitation temperature and the electron density [8] influence the emission signal. Therefore, the emission signal was chosen as a reference signal for the normalization procedure to correct the above-mentioned effects on the analytical signal.

The proposed approach is based on the correlation between laser-enhanced ionization (LEI) and AE signals because these signals depend on both ablated mass and laser irradiance. To determine this correlation, LEI and AE signals were simultaneously measured at the different laser energies, so that every pair of signal values corresponded to definite energy. The energy range was chosen where the LEI signal noticeably depended on the energy and increased monotonically. Since a correlation curve is plotted in this range, neither laser energy nor laser irradiance influence the coefficients of the correlation equation. If these coefficients (e.g. the slope and intercept of the correlation line) depend on the analyte content, they can be used for calibration. Unlike the conventional direct normalization of the analytical signal by the reference one, the proposed approach allows the reduction of the effect of the evaporation conditions on the analytical results. In other words, this method allows the plotting of the calibration curve, which is independent from changes of matrix composition and laser irradiance [13]. Huang and Lin [14] used a similar calibration approach to reduce the effect of the evaporation conditions on the LIBS signal. Unfortunately, this implementation covers a small energy range and does not exclude the influence of irradiance even for a homogeneous liquid, whereas the normalization suggested here for wide laser energy range allows the consideration of pulse-to-pulse changes of the sample surface.

2. Experimental

The experimental set-up consisted of a home-made LEI spectrometer with laser evaporation of the sample into a flame. The

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* Corresponding author. Tel.: +7 495 9393635.
E-mail address: timurla@laser.chem.msu.ru (T.A. Labutin).

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Table 1
Aluminium alloys composition (wt.%)

	Sample no.			
	I	II	III	IV
Al	Main component			
Li	0.6	0.9	2.1	2.6
Sc	0.41	0.62	0.62	0.45
Cu	–	0.5	–	–

radiation of Nd^{3+}:YAG laser with $\lambda = 1064$ nm was focused by a microscope onto the surface of a solid sample. The laser irradiance was 3 ± 1 GW cm^{-2}. The laser energy E_{las} was decreased by a set of neutral filters. The samples were placed into a specially designed burner head. Interaction of laser radiation with a sample resulted in the formation of a laser plume, which expanded into a methane-air flame. Tunable dye lasers (with $\lambda = 610.4$ and 670.8 nm) were pumped by Nd^{3+}:YALO laser with $\lambda = 540$ nm and used for the excitation of lithium atoms. An iridium wire cathode in the flame detected the lithium ions generated. A grounded burner head served as the anode. The aluminum AE signal at $\lambda = 396.1$ nm was used as the reference one [15] and recorded by a monochromator and PMT. Al–Sc–Li alloys were used as samples. Their compositions are given in Table 1.

3. Results and discussion

To plot the relationship between LEI and AE signals, the correlation diagram was used. Each of seven points in the diagram (LEI versus AE) corresponds to a measurement at the definite E_{las}. Every point is the average of 50 signal measurements. The correlation was approximated by a straight line. The linear correlation coefficients R, calculated for each of the samples, are listed in Table 2. The correlation coefficients are greater than the critical value of $R = 0.875$ ($f = 5$ and $P = 0.99$), thus demonstrating the statistical validity of the linear correlation between LEI and AE signals. As described in our earlier paper [15], the slope of correlation line depends on the lithium content in the studied samples and does not depend on laser irradiance. Therefore, the slope may be used as a novel type of normalized analytical signal. This normalization method will be referred to as the correlative normalization.

The LEI signal dependencies on the lithium content in the samples are shown in Fig. 1 for three different E_{las}. Their nonlinearity does not allow them to be used for calibration purposes. The analytical signal decreases for E_{las} equal to 70 and 60 mJ (Fig. 1, curves C and B, respectively), when the lithium content is changed from 0.6 to 0.9 wt.%. However, the LEI signal grows in the same content range for $E_{las} = 47$ mJ (curve A in Fig. 1). Hence, the copper has an unpredictable influence on the LEI signal for the sample no. II (see Table 1), when E_{las} is changed. Then we have normalized the analytical signal by the aluminum AE signal. The normalized analytical signal dependencies on the lithium content in the samples are shown in Fig. 2. When

Table 2
The coefficients of linear correlation (LEI vs. AE)

Sample no.	R
I	0.989
II	0.955
III	0.989
IV	0.963

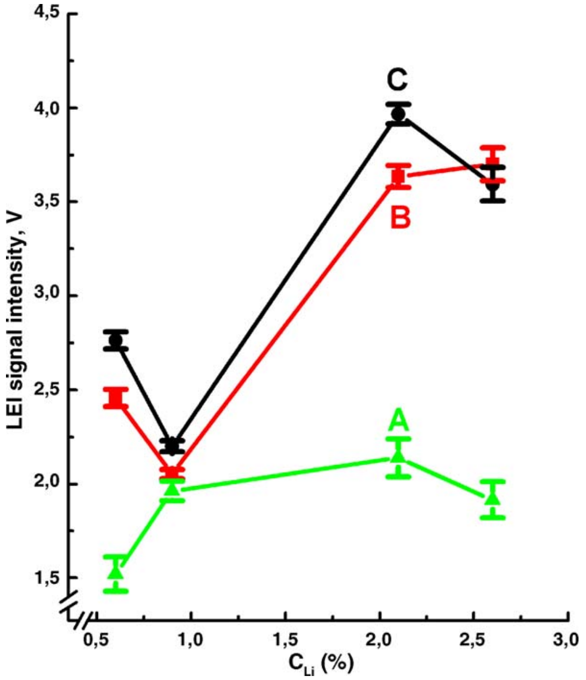

Fig. 1. LEI signal vs. lithium content for the different E_{las} (A, 47 mJ; B, 60 mJ; C, 70 mJ).

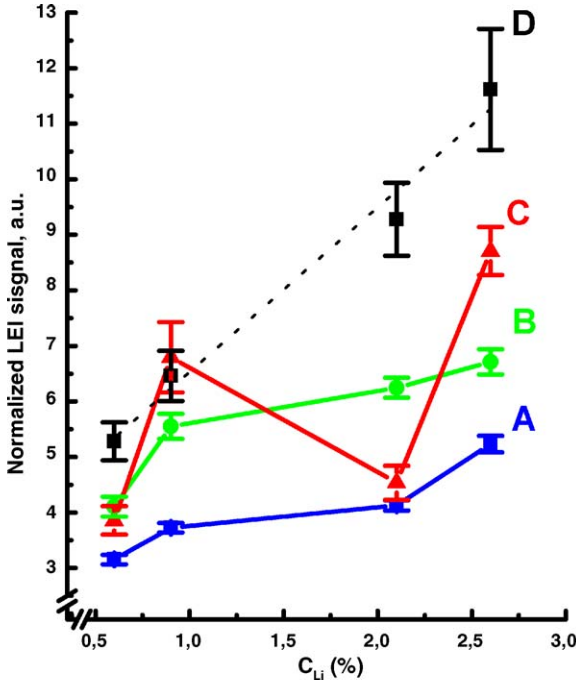

Fig. 2. Normalized LEI signal vs. lithium content with the use of different normalization methods: (A–C) direct normalization for the different E_{las} (A, 47 mJ; B, 60 mJ; C, 70 mJ) and (D) correlative normalization.

using direct normalization (curves A–C in Fig. 2), the influence of both laser energy and matrix composition on the normalized LEI signal are retained. The calibration curve is linear for the correlative normalization (curve D in Fig. 2) and the copper influence on the LEI signal is negligible. Using the proposed normalization method, the detection limit (3σ-criterion) was equal to 0.002 wt.%, which is 10 times lower than previously achieved one [16].

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References

[1] J.D. Winefordner, I.B. Gornushkin, T. Correll, E. Gibb, B.W. Smith, N. Omenetto, J. Anal. At. Spectrom. 19 (2004) 1061.
[2] R.E. Russo, X. Mao, H. Liu, J. Gonzales, S.S. Mao, Talanta 57 (2002) 425.
[3] C. Chaleard, P. Mauchien, N. Re, J. Uebbing, J.L. Lacour, C. Geertsen, J. Anal. At. Spectrom. 12 (1997) 183.
[4] V. Kanicky, V. Otruba, J.-M. Mermet, Fresenius J. Anal. Chem. 366 (2000) 228.
[5] J.-F.Y. Gravel, M.L. Viger, P. Nobert, D. Boudreau, Appl. Spectrosc. 58 (2004) 727.
[6] D. Günther, R. Frischknecht, H.-J. Müschenborn, C.A. Heinrich, Fresenius J. Anal. Chem. 359 (1997) 390.
[7] V. Kanicky, V. Otruba, J.-M. Mermet, Fresenius J. Anal. Chem. 363 (1999) 339.
[8] U. Panne, C. Haisch, M. Clara, R. Niessner, Spectrochim. Acta B 53 (1998) 1957.
[9] G. Chen, E.S. Yeung, Anal. Chem. 60 (1988) 2258.
[10] O.V. Borisov, X.L. Mao, A. Fernandez, M. Caetano, R.E. Russo, Spectrochim. Acta B 54 (1999) 1351.
[11] A. Fernandez, X.L. Mao, W.T. Chan, M.A. Shannon, R.E. Russo, Anal. Chem. 67 (1995) 2444.
[12] D.P. Baldwin, D.S. Zamzow, A.P. D'Silva, Anal. Chem. 66 (1994) 1911.
[13] T.A. Labutin, A.M. Popov, A.A. Gorbatenko, N.B. Zorov, European Conference on Analytical Chemistry "Euroanalysis XIII", Salamanca, Spain, 2004.
[14] J.-S. Huang, K.-C. Lin, J. Anal. At. Spectrom. 20 (2005) 53.
[15] T.A. Labutin, A.M. Popov, A.A. Gorbatenko, N.B. Zorov, Spectrochim. Acta B 60 (2005) 775.
[16] A.A. Gorbatenko, N.B. Zorov, T.A. Labutin, J. Appl. Spectrosc. 69 (2002) 932.