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A novel approach to sensitivity evaluation of laser-induced breakdown spectroscopy for rare earths elements determination

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We report the potentials of Laser-Induced Breakdown Spectroscopy (LIBS) for the determination of lanthanum and yttrium in soils and rocks. Since the main problems to quantify rare earth elements by LIBS is their rich spectra and, consequently, often spectral interferences with matrix elements, we demonstrated how thermodynamic modeling of spectra can assist the spectroscopists in the estimation of LIBS sensitivity. The theoretical LOD for La was close to the one retrieved from experimental data (6 ppm), while the theoretical LOD for Y was one order of magnitude higher than the experimental LOD (6 ppm *vs* 0.4 ppm). The possible reasons for such discrepancy are discussed.

Laser-Induced Breakdown Spectroscopy (LIBS) uses a laser ablation for generation the plasma, which emission serves for analysis of a sample. In recent years, LIBS has proved to be efficient for rapid real time in situ analysis of environmental samples including a variety of geological samples such as soils, rocks or even gemstones.[1-4] The specific feature of LIBS analysis in geochemical studies consists in obtaining the fingerprints of geological objects. Different classes of minerals can be discriminated[5] on the basis of the emission lines of major components, while it is more difficult to identify correctly particular mineral within the same type of sample with a fixed major element composition and a high degree of trace element variability. Moreover, geological samples contain ten to twelve major elements including elements with rich emission spectra (iron, titanium, *etc.*) providing strong spectral interferences. Thus, accurate trace element analysis is quite a challenge.

Rare earths elements (REE) are among the main markers in geochemistry . REE are members of group 3 of the Periodic table and all of them have similar physical and chemical properties, but these elements may be partially separated by some petrological and mineralogical processes.[6] To our best knowledge there are no works on quantitative REE determination by LIBS in geological solid samples due to significant spectral interferences and relatively low content of REE in the main geochemical materials (soils, sediments and rocks). And there are only few works on REE quantitative LIBS analysis in aqueous solutions[7,8] or in synthetic simple matrix.[9-12] Thus, the evaluation of achievable sensitivity of LIBS determination of the REE in solid natural samples is highly beneficial.

We present an approach to estimate the limit of detection (LOD) with the use of thermodynamic modeling of LIBS spectra. This method is based on a generating of synthetic spectra calculated under local thermodynamic equilibrium (LTE) conditions and sensitive to the Doppler and Stark broadenings of emission lines in laser plasma. Spectral slit width as well as diffraction function of a spectrometer, and detector instrumental function (combination of an image intensifier resolution and spectral CCD pixel width) are fixed to an instrument specification. Assuming that detection capability is restricted mainly by two factors, namely signal-to-noise ratio (SNR) and spectral interferences, we estimated LODs with the use of experimental noise and synthetic spectra calculated for various ratios of analyzed to the interfering species. This also enables estimation of accuracy of LIBS analysis with the use of small number of certified samples. We examined light REE (yttrium, and lanthanum) in soils and rocks by LIBS to validate our approach.

In our previous work,[13] we use the simple model of optically thin homogeneous plasma under LTE conditions to calculate emission spectra. Although, condition providing optically thin plasma is preferable for LIBS analysis,[14] it is difficult to realize them for species of main components especially for intense lines.[15] Overlapped wings of such broadened self-absorbed lines significantly influence the shape of a spectrum, making a pseudo- background and masking weak lines of trace components. In the current study the possible self-absorption of the emission lines was accounted for to provide more realistic synthetic spectra. We used so-called transport equation and assumption of a homogenous plasma rod for calculation. In this case light intensity

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corresponds to the energy emitted per unit time, surface and wavelength by the rod of certain length. The equation for calculation of the absorption coefficient as a function of wavelength and plasma rod length, which takes into account both the absorption by lower level atoms and the stimulated emission of the upper level atoms under the effect of the radiation, was taken from Ref.[16]. Thus, in the current study we used static model of homogeneous plasma under LTE condition, accounting, accounting instrumental function, Stark and Doppler broadening as well as self-absorption.

Table 1. CRM samples composition.

Sample	Type	La (ppm)	Y (ppm)
SChT-1 (2507-83)	soil	36±5	31±6
BIL-1 (7126-94)	sediment	45±6	30±4
NIST 2710a	soil	30.6±1.2	n/a
NIST 2711a	soil	38±1	n/a
SSV-1 (6104-91)	rock	108±17	25±5

For experimental study we used USA and Russian certified reference materials listed in Table 1 and their full composition is available elsewhere.[17] The experimental setup was the same as that described earlier by us.[18] Second harmonic Q-switched Nd:YAG laser was focused on pelleted samples, providing power density ~3-6 GW/cm^2 on the surface. Spectra were recorded by Czerny-Turner spectrometer equipped with ICCD camera. The best signal-to-noise ratio was achieved at time delay 1.5 μs and gate 1.5 μs.

Initially we assessed the La determination in soils and rocks as a relatively simple case due to the presence of isolated ionic line of La II at 433.37 nm in LIBS spectrum of SSV-1 sample (Figure 1, a). We prepared the series of the synthetic spectra of plasma (430.60-435.60 nm) with the same elemental composition as for the SSV-1 sample. The plasma parameters were varied over the intervals $0.5 < T$, eV< 1.0 and $15 < \lg(N_e$, cm$^{-3})$ <18. The best matched pair of the model and experimental spectra (Figure 1, a) was found by maximal value of Pearson's correlation coefficients between them as described in Ref.13. We normalized both spectra by La line intensity to compare synthetic and experimental data. The plasma parameters for the best correlated synthetic spectrum were T=0.72 eV and $\lg(N_e$, cm$^{-3})$=16.5, and they are in a good agreement with experimental data on soil ablation.[19] We
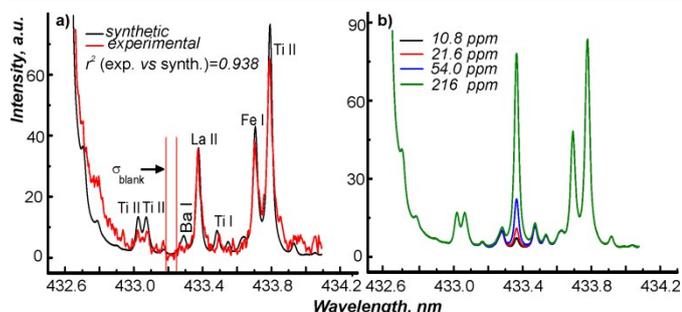
Figure 1. Emission spectra near La II 433.37 nm: (a) comparison between experimental spectrum for SSV-1 sample and the best fitted synthetic spectrum; (b) a set of synthetic spectra with the La content variations.

Table 2. Limits of detection of La and Y in soils and ores

Element	LOD (theoretical), ppm		LOD (experimental), ppm	
	peak	integral	peak	integral
La	6.5	4.1	8.0	4.8
Y	6.0	6.0	0.6/3.0*	0.4/2.5*

* The noise level was calculated on symmetrical wing of Si I 410.29 nm line

prepared a common linear calibration curve for La (r^2=0.968) to estimate the sensitivity in terms of LOD with the use of 3σ-criterion. The noise level was estimated in the spectral range without emission lines near the La II line at 433.37 nm, which was indicated in Figure 1, a. We used both the integral and peak intensity of the La line to achieve experimental values of LODs (see Table 2). We used the synthetic spectra (Figure 1, b) and experimental value of noises to estimate the theoretical LOD values also with the use of 3σ-criterion. As expected, experimental LODs and theoretical ones are close to each other. It means that the background emission is negligible and La II line occurs to be well isolated without spectral interferences. Slightly lower values of LOD in case of synthetic spectra can be related to a more correct presentation of line shape at low intensities.

More complicated task was Y determination in soils and ores. Following NIST database,[20] Y I 408.37 nm line has the highest relative intensity, but it turned out that it was not sensitive to Y variations in soils and rocks. We have prepared synthetic spectra of soil sample SChT-1 to explain such a behavior (Figure 2, a). We obtain another set of synthetic spectra within the spectral range 408.0-412.7 nm. The plasma parameters (T=0.65 eV and $\lg(N_e$, cm$^{-3})$=16.6) of synthetic spectra provided the highest correlation with experimental one. To recognize possible spectral interferences, the line intensities obtained before the convolution procedure were added to the Figure 2 as the bars. The Y I line is significantly weaker than line of Mn I at 408.36 nm (Mn content in the sample is 612 ppm), which completely suppressed Y signal.
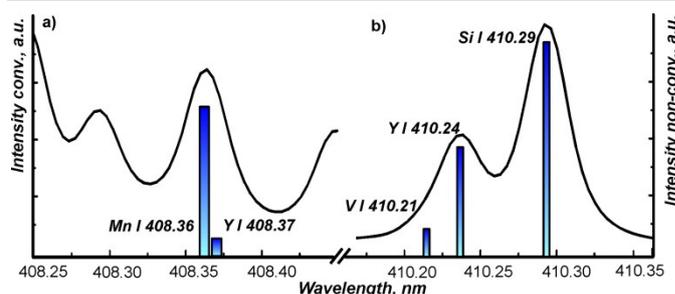
Figure 2. Synthetic spectra for SChT-1 soil near to Y I 408.37 nm (a) and Y I 410.24 nm (b). Position and height of bars indicate the wavelength and intensity of the neighboring lines, respectively.

Thereafter we studied another strong line of Y I at 410.24 nm (Figure 2, b). In spite of possible overlapping with neighboring lines it can be resolved. The experimental spectrum and the synthetic one obtained under the above mentioned plasma parameters are compared in Figure 3, a. It should be noted that synthetic spectrum revealed the significant spectral interferences of Si I line at 410.29 nm

Journal Name

(silicon is the main component of soils) and V I line at 410.21 nm (V content in the sample is 72 ppm) at low concentration of yttrium (Figure 3, b). Similarly to La, we calculated experimental LODs for Y determination (Table 2). We calculated the intensity of Y line after simple subtraction of baseline. This led to the upper estimation of LOD, lowering Y signal. The use of upper limit seems appropriate, since we use the linear extrapolations to the low concentrations. Besides the spectral range without emission lines, the symmetrical wing of Si I line near 410.34 nm was used for the noise estimation to account the fluctuations of both background and interfering line. As one would expect, the LOD's values were much higher (in 5-6 times) in latter case. The theoretical LODs of Y determination in soils and rocks were evaluated close to 6 ppm, when Y signal can be distinguished even without noise consideration. We estimated the equal value of LOD for the peak and integral intensities, since it is impossible to single out Y line and, as a consequence, calculate its integral intensity even with the deconvolution procedure below 6 ppm of Y. The LODs calculated on experimental calibration curve are significantly lower than theoretical LODs. A clear discrepancy between two sets of LODs for yttrium seems to be a result of
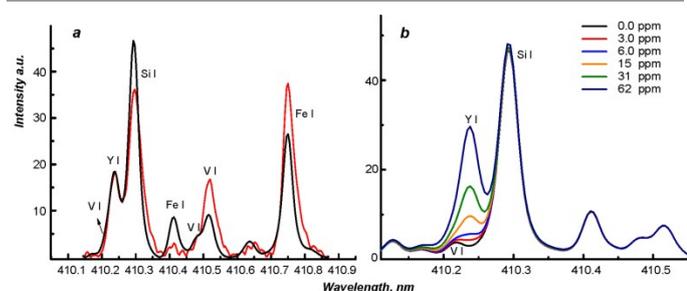
Figure 3. Emission spectra near Y I at 410.24 nm: (a) comparison of the experimental spectrum obtained for SChT-1 (red curve) and the synthetic spectrum (black curve); (b) a set of synthetic spectra near the line of Y I at 410.24 nm with the Y content variations.

an extrapolation to low concentrations that was not allowed the correct consideration of spectral interferences.

Conclusions

This work demonstrates that the thermodynamic modeling of emission spectra of laser plasma can be fruitful to plan LIBS analytical studies prior to experimental measurement to evaluate possible spectral interferences both from weak lines of major components and strong lines of minor and trace elements. The comparison of synthetic and experimental data provide more correct evaluation of LIBS sensitivity and LODs calculation, because the spectral interferences from the weak lines should be accounted for the extrapolation to low content of analyzed element. This possibility is very important for analysis of natural solid samples, for which the lack of certified materials is still a serious problem.[21] Finally our study demonstrates that LIBS can be used for determination of light rare earth elements like Y and La under geological exploration since achieved LODs are sufficiently low than their Earth's crustal abundances: 21 ppm for Y and 31 ppm for La.[22]

References

1   R.S. Harmon, R.E. Russo and R.R. Hark, Spectrochim. Acta Part B 2013, **87**, 11.
2   G.S. Senesi, *Earth-Sci. Rev.*, 2014, **139**, 231.
3   S. Qiao, Y. Ding, D. Tian, L. Yao and G. Yang, *Appl. Spectrosc. Rev.*, 2015, **50**, 1.
4   N.B. Zorov, A.M. Popov, S.M. Zaytsev and T.A. Labutin, *Russ. Chem. Rev.*, 2015, **84**, 1021.
5   R.S. Harmon, J. Remus, N.J. McMillan, C. McManus, L. Collins, J.L. Gottfried Jr., F.C. DeLucia and A.W. Miziolek, *Appl. Geochem.*, 2009, **24**, 1125.
6   P. Henderson, *Rare Earth Element Geochemistry* (Elsevier Science, 1983).
7   P. Fichet, M. Tabarant, B. Salle and C. Gautier, *Anal. Bioanal. Chem.*, 2006, **385**, 338.
8   D. Alamelu, A. Sarkar and S.K. Aggarwal, *Talanta*, 2008, **77**, 256.
9   T. Ishizuka, *Anal. Chem.*, 1973, **45**, 538.
10 L.C. Jensen, S.C. Langford, J.T. Dickinson and R.S. Addleman, *Spectrochim. Acta Part B*, 1995, **50**, 1501.
11 A. Weisberg, R.E. Lakis, M.F. Simpson, L. Horowitz and J. Craparo, *Appl. Spectrosc.*, 2014, **68**, 937.
12 M. Martin, R.C. Martin, S. Allman, D. Brice, A. Wymore and N. Andre, *Spectrochim. Acta Part B*, 2015, **114**, 65.
13 T.A. Labutin, S.M. Zaytsev and A.M. Popov, *Anal. Chem.*, 2013, **85**, 1985.
14 D.A. Cremers and L.J. Radziemski, *Handbook of Laser-Induced Breakdown Spectroscopy*, (John Wiley & Sons, Ltd., 2006).
15 C. Aragón, F. Peñalba and J.A. Aguilera, *Spectrochim. Acta Part B*, 2005, **60**, 879.
16 F. Bredice, F.O. Borges, H. Sobral, M. Villagran-Muniz, H.O. Di Rocco, G. Cristoforetti, S. Legnaioli, V. Palleschi, L. Pardini, A. Salvetti and E. Tognoni, *Spectrochim. Acta Part B*, 2006, **61**, 1294.
17 K.P. Jochum, , U. Nohl, K. Herwig, E. Lammel, B. Stoll, and A.W. Hofmann, *Geostand. Geoanal. Res.*, 2005, **29**, 333.
18 S.M. Zaytsev, A.M. Popov, N.B. Zorov and T.A. Labutin, *J. Instrum.*, 2014, **9**, Article No.P06010.
19 I. Rauschenbach, V. Lazic, S.G. Pavlov, H.-W. Hübers and E.K. Jessberger, *Spectrochim. Acta Part B*, 2008, **63**, 1205.
20 A. Kramida, Yu. Ralchenko, J. Reader and NIST ASD Team (2015), NIST Atomic Spectra Database (ver. 5.3), [Online]. Available: http://physics.nist.gov/asd [2016, May 25].
21 O.T. Butler, W.R.L. Cairns, J.M. Cook and C.M. Davidson, *J. Anal. At. Spectrom.*, 2016, **31**, 35.
22 R.L. Rudnick and S. Gao. *Chapter 4.1. Composition of the Continental Crust* In R. L. Rudnick, *Treatise on Geochemistry. Volume 4. The Crust. 2nd Ed.* (Elsevier, 2014).

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