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Technical note

Concentric multipass cell enhanced double-pulse laser-induced breakdown spectroscopy for sensitive elemental analysis

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ABSTRACT

Although double-pulse laser-induced breakdown spectroscopy (DP-LIBS) is regarded as a promising technique in trace element analysis, its limit of detection (LOD) is not sufficient for some applications. The enhancement of spectral signal is the key to further improve the sensitivity of DP-LIBS. To further increase the sensitivity of DP-LIBS, a concentric multipass cell (CMC) enhanced DP-LIBS (CMC-DP-LIBS) technique is proposed for the first time, which makes full use of the energy of reheating laser by multi-reflection in CMC to enhance the spectral signal and lower LOD. 2.3 times signal enhancement of Mn I 403.08 nm line and 2.3 times decrease of LOD of Mn on the surface of zinc bulk compared with traditional orthogonal reheating DP-LIBS were attained. The signal enhancement factor can reach to 3.6 theoretically with the increase of reflectivity and the sizes of mirrors of CMC. This CMC-DP-LIBS provides a new approach to further improve the sensitivity of DP-LIBS and promotes its application in trace element detection.

1. Introduction

Laser-induced breakdown spectroscopy (LIBS) is a promising method for determining the elemental content of target samples rapidly [1]. Due to its real time, capability of multi-elemental analysis and little sample preparation requirement, LIBS shows great potential in space exploration [2], industrial monitoring [3], agricultural or biological analysis [4,5], environmental protection [6] and other fields. However, conventional LIBS using single laser pulse suffers from a relatively poor sensitivity for several elements in some applications against other spectrometric methods [7], which greatly limits its use. Therefore, the double-pulse LIBS (DP-LIBS) has been developed to improve both spectral signal and signal-to-noise ratio, which result in a lower limit of detection (LOD) for certain use [4,8–15].

In general, the configuration of DP-LIBS setup can be designed to be collinear [16], orthogonal reheating or orthogonal pre-ablation [17]. The orthogonal reheating DP-LIBS completely separates the use of the two laser pulses for ablating the sample to generate plasma and reheating the plasma, which can improve sensitivity without further ablation of the sample [4] or lower the pulse energy requirement for special use [10]. The spectral signal enhancement is significant using this setup. Choi et al. reported an enhancement of 8 times on Mg II (280.27 nm) line from Al alloy samples [18]. Ahmed and Baig reported enhancements of Cu I lines up to 15 times on copper samples [19]. On the other hand, higher plasma temperature and longer plasma lifetime were detected, which contribute to the enhancement of spectral signal by orthogonal reheating DP-LIBS [18].

Despite the use of DP-LIBS approaches, the LODs of some elements are still poor for further applications. For example, the reported LOD of As from Kwak et al. using DP-LIBS system is 85 ppm [20], which is at least twice over the applicable LOD for assessment of pollution risk of soil for agriculture. On the other hand, the experiment of An et al. indicated that the second laser pulse in DP-LIBS suffers from a significant decrease of absorption rate to as much as 10% after certain delay [21]. The remaining energy of second laser pulse is wasted in the conventional reheating DP-LIBS with only one pass through the laser-induced plasma. Therefore, optimization of the absorption rate of the second laser pulse is a breakthrough to further improve the analytical performance of reheating DP-LIBS.

Here, by combining the previous studies on multipass cell [22] and laser-induced plasma [23,24], we propose a new orthogonal reheating design, concentric multipass cell (CMC) enhanced DP-LIBS (CMC-DP-

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LIBS), to make almost full use of the second laser pulse energy and greatly improve the detection sensitivity of trace elements. In this design, the incident laser pulse can be reflected in the CMC for several times passing through the laser-induced plasma to generate higher spectral signals. The LODs of Mn on the surface of self-made zinc bulk samples were determined for both CMC-DP-LIBS and orthogonal reheating DP-LIBS for analytical performance comparison. And the reflection effects in the CMC was discussed.

2. Experimental

Fig. 1 illustrates the scheme of the proposed CMC-DP-LIBS setup. The ablating laser (laser 1) was a Nd: YAG laser (Quanta-Ray INDI-40) operating at 1064 nm, 2 Hz and 20 mJ per pulse. This ablating laser was reflected by a silver coated mirror and focused through a plano-convex lens (F = 50.8 mm) perpendicularly to the target surface. The focal point was about 2 mm below the sample surface for generating a plasma larger in lateral size. The spot diameter is 0.7 mm and the fluence is 5 J/cm^2. Another 1064 nm Nd:YAG laser (laser 2, Quanta-Ray INDI-40) was used for reheating, focused by a convex lens (F = 200 mm) and the height of the laser pulse was about 1 mm over the sample surface. The laser pulse from laser 2 was first expanded 3 times by a beam expander, and then restricted by a diaphragm (12 mm in diameter) to match the incident aperture of the CMC with an output energy of 20 mJ, which generating sub-plasma while reheating. The pulse delay between two lasers was adjusted by a digital delay generator (DG535, Stanford Research Systems, 50 ps rms jitter), the jitter of laser triggering is 10 ns. The optical emission from the plasma was collected directly into the spectrometer (AvaSpec-ULS2048, 196–468 nm, resolution 0.20–0.28 nm) by an optical fiber, and the integration time was 1.05 ms.

The principle of the optical path in the CMC is shown in Fig. 2, seen from the direction of the ablating laser. The cell consists of two concentric concave mirrors, one of which has a 3 mm-diameter aperture to enter the reheating laser, while the ablating laser pulse was incident vertically to the center of the CMC. The two concave mirrors were silver coated with reflectivity r of 95%, and curvature radius R of 50 mm. r_b is the beam radius of the reheating laser entering the CMC, which was designed to be equal to the aperture radius. r_c is the radius of the round gap in the center of the CMC where no beam passes, and l is the arc

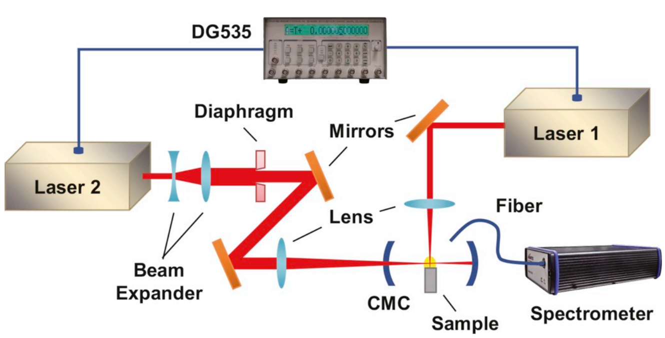

Fig. 1. Scheme of CMC-DP-LIBS setup.

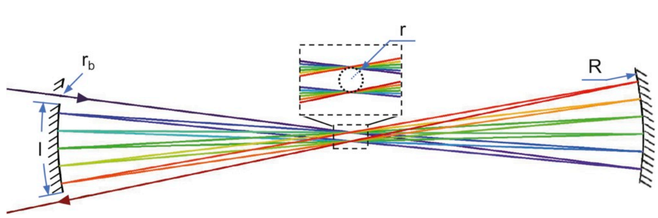

Fig. 2. Scheme of optical path in the CMC.

$$r_c = 1/2r_b. \quad (1)$$

Table 1
The surface contents of Mn for the samples.

Sample no.	1	2	3	4	5	6	7
Mn content ($\mu g/cm^2$)	13.50	9.53	8.76	5.43	3.41	2.56	1.69

length of the effective reflection area. 11 times of reflection can be achieved in our setup with r_c of 0.75 mm, which is the minimal value for the laser pulse to totally reflecting in the cell before it came out from the edges of the mirrors. When $2r_b$, which is the beam size when entering the cell, is enough small compared to R ($R \approx 16(2r_b)$ in our case), the relation between the minimal r_c and the structure parameters can be determined roughly through geometry:

The ideal reflection times N_m of the CMC is limited by the ratio of l to r_b:

$$N_m = 2 \times \lfloor l/(2r_b) \rfloor + 1. \quad (2)$$

To evaluate the analytical performance of CMC-DP-LIBS, seven samples for LOD determination of Mn were prepared by dropping different concentrations of $MnCl_2$ solutions onto the surface of high purity zinc bulks and drying them regularly. Here, the Mn contents on the zinc surfaces were calculated from the concentrations of $MnCl_2$ solutions, the drop volume and the covered area on the zinc surfaces (see Table 1). The LOD was calculated according to the IUPAC (International Union of Pure and Applied Chemistry) method [25]. The same setup and instrumental parameters were used for orthogonal reheating DP-LIBS experiments for comparison.

To evaluate the effect of reflected pulses on the enhancement of CMC, we changed the reflection times by blocking the laser pulses in the CMC and collected the corresponding plasma spectra of zinc bulk. The peak intensity of Zn I 334.50 nm line was monitored in this experiment for characterizing the enhancing ability of the CMC.

3. Results and discussion

The interpulse delay was optimized according to the spectra of zinc bulks using this CMC-DP-LIBS setup. The peak intensities of the strongest line Zn I 334.50 nm at different interpulse delays are shown in

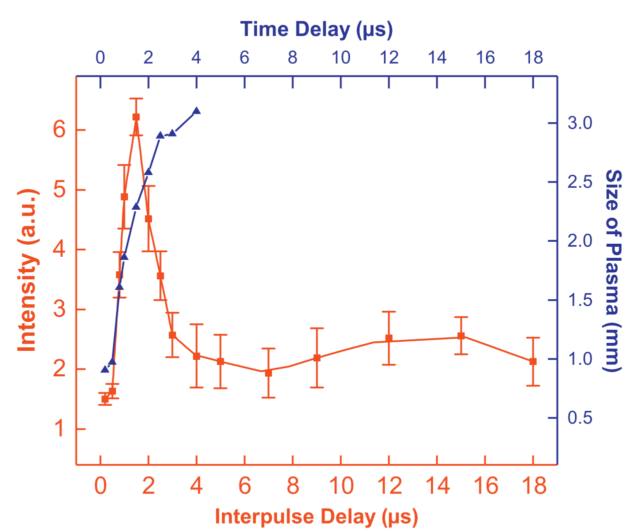

Fig. 3. Interpulse delay effects in CMC-DP-LIBS (red) and temperal evolution of plasma size when only ablating pulse works (blue). Each intensity point is an average of 20 shots and the error bars are their standard derivation. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.) (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

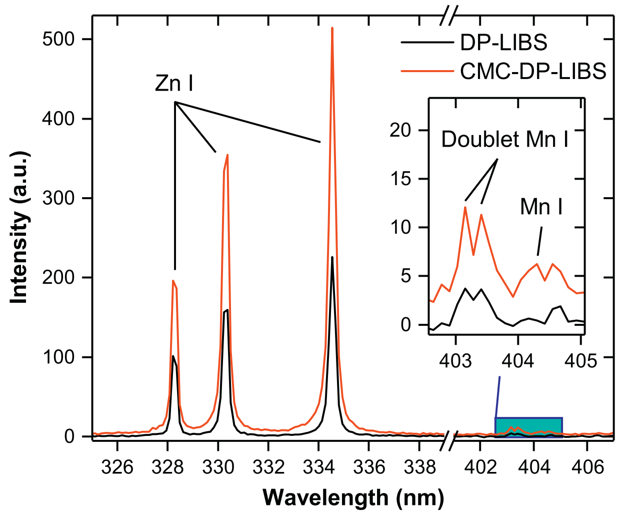

Fig. 4. CMC-DP-LIBS and orthogonal reheating DP-LIBS signals of sample 7.

Fig. 3. The highest point appeared at 1.5 *μs*, which was selected to be the optimal interpulse delay for the following measurements. The blue line in Fig. 3 shows the temporal evolution of zinc plasma diameter estimated from the ICCD images captured after ablating laser hit the sample. It can be seen that at the optimal interpulse delay, the size of the plasma is about 1.5 times larger than the diameter of the round gap in the CMC, which indicates enough density of emitting plasma reaches the reheating zone at this time.

The most sensitive resonant doublet lines of Mn I at 403.08 nm and 403.31 nm in our spectral range were selected to determine the LOD of Mn, as shown in Fig. 4, from sample 7. The integral intensities over the two lines are used for evaluating LOD. In addition, Fig. 4 also indicates that CMC-DP-LIBS achieved a 2.3 times enhancement of Mn I 403.08 nm to orthogonal reheating DP-LIBS and the enhancement factor of Zn I 334.50 nm achieved 2.3.

The calibration curves of Mn using both methods are shown in Fig. 5.It could be calculated that the LOD of Mn by orthogonal reheating DP-LIBS was 0.9 $\mu g/cm^2$. while that by CMC-DP-LIBS was reduced to 0.4 $\mu g/cm^2$. The LOD of Mn using orthogonal reheating DP-LIBS was 2.3 times over the result of CMC-DP-LIBS. The comparison shows that CMC-DP-LIBS can significantly lower the LOD of LIBS measurements.

The relation between the enhancement factor in CMC and the reflection times of the CMC is shown in Fig. 6, where the enhancement factors were calculated by normalizing the intensities with that of 0 reflection. The case of 0 reflection means that the CMC is not working, similar to the conventional DP-LIBS configuration. Note that this is still different from the setup of conventional orthogonal DP-LIBS, whose reheating laser is directed into the center of the plasma plume.

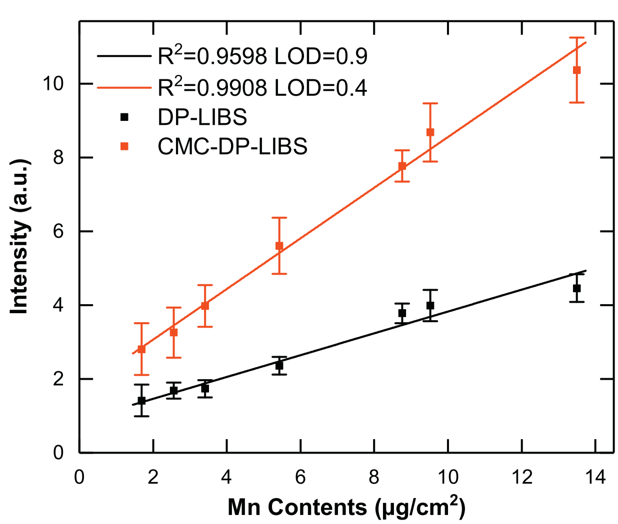

Fig. 5. Calibration curves of Mn content by CMC-DP-LIBS (red) and orthogonal reheating DP-LIBS (black). The error bars are the standard derivation of 17 intensity measurements.

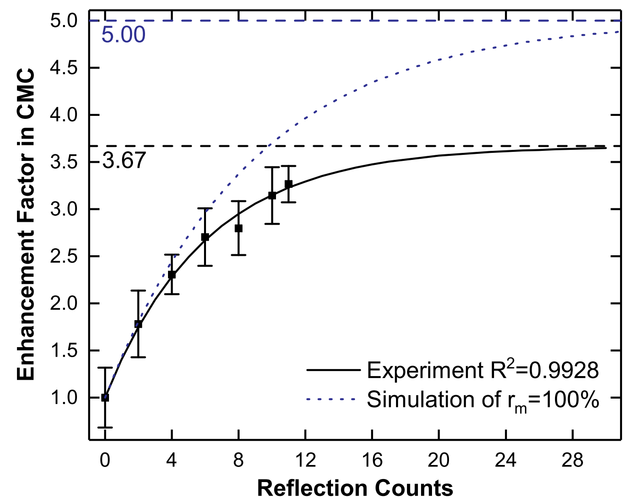

Fig. 6. Effect of reflection times to the enhancement of spectral signal by experiment (black), and simulation of $r = 100\%$ (blue). The error bars are the standard derivation over 24 shots. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

The total optical emission collected into the fiber can be divided into two parts: the emission of the initial plasma generated by the ablating laser pulse, and the emission in the reheating process by the absorption of reheating laser pulse. For the latter part, the reflectivity of the mirrors and the scattering of laser light when passing through the plasma have essential effects on the energy loss besides absorption within once refection in the CMC. Here, using a as the absorptance of the plasma, b as the scattering loss rate when pass through the plasma which can not be recollected by the mirrors, the accumulated absorptance of the reheating laser can be written as a geometric series (marked as R):

$$R = a + r(1 - a - b)a + r^2(1 - a - b)^2 a + ... + r^x(1 - a - b)^x a, \quad (3)$$

where x is the reflection times. Therefore, assuming the optical emission intensity has a linear relation with absorption, the whole optical emission intensity I can be written as:

$$I = I_a + \alpha R, \quad (4)$$

where I_a represents the emission intensity from the ablating plasma, and α is used to convert from absorption to the emission intensity. In normalization process, Eq. (4) is divided by $(I_a + \alpha a)$, where a is the first term of R. Then, normalized emission intensity I_N, which can also be interpreted as the enhancement factor in CMC, is written as:

$$I_N = 1 + \alpha r(1 - a - b)a/(I_a + \alpha a)/[1 - r(1 - a - b)][1 - r^x(1 - a - b)^x]. \quad (5)$$

Eq.(5) can be rewritten as:

$$I_N = A_1(1 - A_2^x) + 1, \quad (6)$$

where A_1 and A_2 are the new independent parameters.

A curve fitting ($R^2 = 0.9928$) of the experimental result using Eq. (6) is shown in Fig. 6. Through the fitting result, the upper limit of the enhancement factor in CMC is 3.67 if the reflection area of the CMC is large enough. On the other hand, the relation between r and the two parameters can be solved from Eqs. (5) and (6). With $A_1 = 2.67$, $A_2 = 0.849$, and $r = 95\%$ (A_1 and A_2 are from the fitting result), Eq. (6) becomes:

$$I_N = 0.425r/(1 - 0.894r)(1 - 0.894^x r^x) + 1. \quad (7)$$

This indicates that the enhancement factor in CMC can be as much as 5.00 when using 100%-reflectivity mirrors in the CMC, also shown in Fig. 6, which will further improve the sensitivity of CMC-DP-LIBS. Using the enhancement factor 2.3 of Mn I 403.08 nm line compared with orthogonal reheating DP-LIBS when CMC-DP-LIBS was working at 11 times reflection and 95% reflectivity, which is mentioned above, the signal enhancement factor compared to orthogonal reheating DP-LIBS can be achieved to 3.6 in this way.

In addition to larger reflection area and higher reflectivity of the mirrors, the optimal laser pulse energy ratio for laser-plasma coupling may also contribute to a better analytical performance of CMC-DP-LIBS, which has already been seen in the optimization to DP-LIBS setups [11,26], so that the signal enhancement factor can be larger.

In the sight of laser-plasma coupling, due to the orthogonal optical configuration of CMC-DP-LIBS, the interaction between laser and plasma occurs at the peripheral edge of the plasma rather than in the central region. Therefore, the distribution of species in the laser-induced plasma has a great influence on the enhancement of elemental emission lines in CMC-DP-LIBS. As shown in Fig. 3, the plasma must be large enough for better laser-plasma coupling. Besides, the species distribution maybe different with different laser parameters [24], which should be considered in the optimization of the laser-plasma coupling. In general, the closer the laser is to the plasma center, the higher the species density and the more obvious signal enhancement. Therefore, reducing r_c is a way to achieve more enhancement. Whereas, it is accompanied with the reduction of r_b, which may limit the pulse energy of reheating laser considering the damage threshold of the mirror. There must be a tradeoff.

4. Conclusions

In summary, we innovatively proposed a method of repeatedly reheating plasma by laser pulse using CMC, which greatly enhances the emission intensity of spectral lines and reduces the LOD of DP-LIBS. The spectral signal enhancement and LOD decrease were examined. The results show that CMC-DP-LIBS enhanced the emission intensity by a factor above 2 and lowered the LOD of Mn by a factor of 2.3 compared to orthogonal reheating DP-LIBS. The effect of reflection times in the CMC was also examined, which confirmed the contributions of the reflected pulses. In addition, the potential of the optimization of CMC-DP-LIBS for higher enhancement was discussed. The CMC-DP-LIBS provides a new approach to further improve the sensitivity of DP-LIBS and strengthen its ability of trace element detection.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper

Acknowledgements

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References

[1] S. Musazzi, U. Perini (Eds.), Laser-Induced Breakdown Spectroscopy: Theory and Applications, No. 182 in Springer Series in Optical Sciences, Springer, Berlin ; New York, 2014.
[2] T. Dequaire, P.-Y. Meslin, P. Beck, M. Jaber, A. Cousin, W. Rapin, J. Lasne, O. Gasnault, S. Maurice, A. Buch, C. Szopa, P. Coll, Analysis of carbon and nitrogen signatures with laser-induced breakdown spectroscopy; the quest for organics under mars-like conditions, Spectrochim. Acta B 131 (2017) 8–17, https://doi.org/10.1016/j.sab.2017.02.015.
[3] L. Zhang, Y. Gong, Y. Li, X. Wang, J. Fan, L. Dong, W. Ma, W. Yin, S. Jia, Development of a coal quality analyzer for application to power plants based on laser-induced breakdown spectroscopy, Spectrochim. Acta B 113 (2015) 167–173, https://doi.org/10.1016/j.sab.2015.09.021.
[4] G. Nicolodelli, G.S. Senesi, A.C. Ranulfi, B.S. Marangoni, A. Watanabe, V. de Melo Benites, P.P. de Oliveira, P. Villas-Boas, D.M. Milori, Double-pulse laser induced breakdown spectroscopy in orthogonal beam geometry to enhance line emission intensity from agricultural samples, Microchem. J. 133 (2017) 272–278, https://doi.org/10.1016/j.microc.2017.03.047.
[5] L. Krajcarová, K. Novotný, M. Kummerová, J. Dubová, V. Gloser, J. Kaiser, Mapping of the spatial distribution of silver nanoparticles in root tissues of vicia faba by laser-induced breakdown spectroscopy (LIBS), Talanta 173 (2017) 28–35, https://doi.org/10.1016/j.talanta.2017.05.055.
[6] G. Pan, M. Dong, J. Yu, J. Lu, Accuracy improvement of quantitative analysis of unburned carbon content in fly ash using laser induced breakdown spectroscopy, Spectrochim. Acta B 131 (2017) 26–31, https://doi.org/10.1016/j.sab.2017.03.001.
[7] J.D. Winefordner, I.B. Gornushkin, T. Correll, E. Gibb, B.W. Smith, N. Omenetto, Comparing several atomic spectrometric methods to the super stars: special emphasis on laser induced breakdown spectrometry, LIBS, a future super star, J. Anal. Atom. Spectrom. 19 (9) (2004) 1061, https://doi.org/10.1039/b400355c.
[8] L. St-Onge, M. Sabsabi, P. Cielo, Analysis of solids using laser-induced plasma spectroscopy in double-pulse mode, Spectrochim. Acta B 53 (3) (1998) 407–415, https://doi.org/10.1016/S0584-8547(98)00080-9.
[9] L. St-Onge, V. Detalle, M. Sabsabi, Enhanced laser-induced breakdown spectroscopy using the combination of fourth-harmonic and fundamental nd:YAG laser pulses, Spectrochim. Acta B 57 (1) (2002) 121–135, https://doi.org/10.1016/S0584-8547(01)00358-5.
[10] V. Contreras, M.A. Meneses-Nava, O. Barbosa-García, J.L. Maldonado, G. Ramos-Ortiz, Double-pulse and calibration-free laser-induced breakdown spectroscopy at low-ablative energies, Opt. Lett. 37 (22) (2012) 4591, https://doi.org/10.1364/OL.37.004591.
[11] C. Gautier, P. Fichet, D. Menut, J.-L. Lacour, D. L'Hermite, J. Dubessy, Quantification of the intensity enhancements for the double-pulse laser-induced breakdown spectroscopy in the orthogonal beam geometry, Spectrochim. Acta B 60 (2) (2005) 265–276, https://doi.org/10.1016/j.sab.2005.01.006.
[12] V. Piscitelli, S.M. Martínez, L.A. Fernández, C.J. González, X. Mao, R. Russo, Double pulse laser induced breakdown spectroscopy: experimental study of lead emission intensity dependence on the wavelengths and sample matrix, Spectrochim. Acta B 64 (2) (2009) 147–154, https://doi.org/10.1016/j.sab.2008.11.008.
[13] S. Li, L. Liu, A. Yan, S. Huang, X. Huang, R. Chen, Y. Lu, K. Chen, A compact field-portable double-pulse laser system to enhance laser induced breakdown spectroscopy, Rev. Sci. Instrum. 88 (2) (2017) 023109, https://doi.org/10.1063/1.4975597.
[14] G. Nicolodelli, G.S. Senesi, I.L. de Oliveira Perazzoli, B.S. Marangoni, V. De Melo Benites, D.M.B.P. Milori, Double pulse laser induced breakdown spectroscopy: a potential tool for the analysis of contaminants and macro/micronutrients in organic mineral fertilizers, Sci. Total Environ. 565 (2016) 1116–1123, https://doi.org/10.1016/j.scitotenv.2016.05.153.
[15] A.S. Zakuskin, A.M. Popov, S.M. Zaytsev, N.B. Zorov, M.V. Belkov, T.A. Labutin, Orthogonal and collinear configurations in double-pulse laser-induced breakdown spectrometry to improve sensitivity in chlorine determination, J. Appl. Spectrosc. 84 (2) (2017) 319–323, https://doi.org/10.1007/s10812-017-0470-y.
[16] L. Nagli, M. Gaft, I. Gornushkin, Comparison of single and double-pulse excitation during the earliest stage of laser induced plasma, Anal. Bioanal. Chem. 400 (10) (2011) 3207–3216, https://doi.org/10.1007/s00216-011-4806-9.
[17] A. Safi, M. Bahreini, S.H. Tavassoli, Comparative study of two methods of orthogonal double-pulse laser-induced breakdown spectroscopy of aluminum, Opt. Spectrosc. 120 (3) (2016) 367–378, https://doi.org/10.1134/S0030400X16030024.
[18] I. Choi, X. Mao, J.J. Gonzalez, R.E. Russo, Plasma property effects on spectral line broadening in double-pulse laser-induced breakdown spectroscopy, Appl. Phys. A Mater. Sci. Process. 110 (4) (2013) 785–792, https://doi.org/10.1007/s00339-012-7153-6.
[19] R. Ahmed, M. Baig, A comparative study of enhanced emission in double pulse laser induced breakdown spectroscopy, Opt. Laser Technol. 65 (2015) 113–118, https://doi.org/10.1016/j.optlastec.2014.07.011.
[20] J.-h. Kwak, C. Lenth, C. Salb, E.-J. Ko, K.-W. Kim, K. Park, Quantitative analysis of arsenic in mine tailing soils using double pulse-laser induced breakdown

spectroscopy, Spectrochim. Acta B 64 (10) (2009) 1105–1110, https://doi.org/10.1016/j.sab.2009.07.008.

[21] B. An, Z. Wang, L. Yang, G. Wu, J. Zhu, X. Li, Experimental investigation of the shock loss and temporal evolution of hot plume resulting from dual-pulse laser-induced breakdown in quiescent air, J. Appl. Phys. 122 (19) (2017) 193301, https://doi.org/10.1063/1.4990096.

[22] S. Li, L. Dong, H. Wu, X. Yin, W. Ma, L. Zhang, W. Yin, A. Sampaolo, P. Patimisco, V. Spagnolo, S. Jia, F.K. Tittel, μ, Spectrochim. Acta A 216 (2019) 154–160, https://doi.org/10.1016/j.saa.2019.03.025.

[23] J. Hou, L. Zhang, Y. Zhao, X. Yan, W. Ma, L. Dong, W. Yin, L. Xiao, S. Jia, Laser-induced plasma characterization through self-absorption quantification, J. Quant. Spectrosc. Ra. 213 (2018) 143–148, https://doi.org/10.1016/j.jqsrt.2018.04.009.

[24] Y. Zhao, Zhang Lei, Hou Jiajia, Ma Weiguang, Dong Lei, Yin Wangbo, Xiao Lituan, Jia Suotang, Yu Jin, Species distribution in laser-induced plasma on the surface of binary immiscible alloy, Spectrochim. Acta B 158 (2019) 105644, https://doi.org/10.1016/j.sab.2019.105644.

[25] IUPAC, Limit of detection, Blackwell Scientific Publications, 1997, https://doi.org/10.1351/goldbook.L03540.

[26] X. Liu, S. Sun, X. Wang, Z. Liu, Q. Liu, P. Ding, Z. Guo, B. Hu, Effect of laser pulse energy on orthogonal double femtosecond pulse laser-induced breakdown spectroscopy, Opt. Express 21 (2013) A704, https://doi.org/10.1364/OE.21.00A704.