Spark Discharge-LIBS: Evaluation of One-Point and Multi-Voltage Calibration for P and Al Determination

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ABSTRACT: Spark discharge (SD) laser-induced breakdown spectroscopy (LIBS) is a technique suitable to overcome the low energies of lasers by reheating the plasma, increasing the emission intensities and to perform single-standard calibration. A calibration method called one-point and multi-voltage calibration (OP-MVC), which requires two different voltages applied to both the standard and the sample, is proposed for use with SD-LIBS. The performance of this method was compared to that of the one-point and multi-lines calibration (OP-MLC) and the slope ratio calibration (SRC) methods for LIBS determination of Al in certified reference plant leaves and P in commercial fertilizers. No statistical differences at the 95% confidence level were observed between the Al and P concentrations determined by OP-MVC LIBS for the Al certified values and the P values measured by high-resolution continuum-source flame atomic absorption spectrometry (HR-CS FAAS). The limit of detection (LOD) for P was 0.60 wt% P₂O₅ and 35.1 mg kg⁻¹ for Al. The relative standard deviation (n=3) was typically 7% for Al and in the 4 - 10% range for P.

OP-MVC LIBS

INTRODUCTION

The interest in laser-induced breakdown spectroscopy (LIBS) for elemental analysis has increased greatly in recent years due to its capability to analyze a wide range of samples.¹ However, despite its advantages, the low sensitivity and calibration of this technique are still challenging.²⁻⁴

Among several approaches attempted to achieve LIBS signal enhancement,^{2,3,5,6} spark discharge (SD) was found to be simple and relatively low-cost.⁷ Since its first proposal in 1962,⁷ SD-LIBS has been used to analyze a variety of samples⁸ in various sectors of agriculture⁹, such as soil,¹⁰⁻¹⁷ phosphate rock,^{10,18} rice,¹⁹ honey,²⁰ coal^{21,22} and onion leaves.²³ For instance, when using the SD method, the signal-to-background (S/B) ratio increased up to 7 times in the analysis of Pb and As in soil,¹¹ up to 3 times for As, Al, Ba, Ca, Co, Fe, Mg, Pb, Si, Sr, Ti and V in soil,¹³ and up to 12 times for P in fertilizer.¹⁸ Furthermore, the detection limit

decreased 10 times for Pb, Mg and Sn in soil¹⁵ and improved to 0.028 ppm for Cu in onion leaves.²³

Besides sensitivity, calibration is also considered a main issue in LIBS analysis due to the matrix effects.^{9,24} Several univariate and multivariate calibration methods have been applied to overcome these effects, including partial least squares (PLS),^{9,25} artificial neural networks (ANN),^{9,25} principal component regression (PCR),^{9,25} external calibration (EC),^{18,24} internal standardization (IS),²⁴ calibration-free (CF),^{26,27} one-point calibration (OPC),^{27,28} CF inverse,^{27,29} C-sigma,^{27,30} and single-sample calibration (SSC).³¹ In particular, the SSC method does not require the calculation of plasma temperature, electron number density or other experimental parameters.²⁶⁻³⁰

The use of a single standard to produce several signal intensities (multi-points), which avoids the preparation of a set of solid standards with a similar matrix to test the samples at different

analyte concentrations, is very attractive. The one-point and multi-line calibration (OP-MLC) method proposed by Hao *et al.*³² used several wavelengths of Mn, Cr, Ni and Ti to analyze alloy steel, achieving the relative errors of 9, 22, 21 and 36%, respectively. Nunes *et al.*³³ used the slope ratio calibration (SRC) method³³ to determine B, Ca, Cu, Mg, Fe, Mn, P and Zn in plant leaves with an equation equivalent to single-point calibration. An increase of the emission intensities as a function of the applied voltage was observed in the SD-LIBS analysis of Al and Cu in air,³⁴ As, Pb, Si and Mn in soil,^{11,35} Si in silicon crystals,³⁶ P in fertilizers¹⁸ and Pb and Fe in copper alloys.³⁷ Quantitative analysis by SD-LIBS usually employs calibration with a fixed single voltage and standards at various concentrations,⁹⁻²³ whereas the use of a single standard and various applied voltages has rarely been reported in the literature.

This study aimed to evaluate the performance of one-point and multi-voltage calibration (OP-MVC) for the SD-LIBS determination of Al and P in plant leaves and fertilizers, respectively, in comparison with high-resolution continuum source atomic absorption spectrometry (HR-CS AAS), OP-MLC and SRC. This method required the measurement of the intensities (*I*) of the standard (*C*^{std}) and the unknown sample (*C*^{sample}) at two voltages, so that *C*^{sample} can be calculated (see Equation 3 below).

EXPERIMENTAL

Samples, standards, reagents and procedures

Six fertilizer samples containing different P concentrations (P₂O₅ wt%) were obtained at a local market in Araraquara city (São Paulo State, Brazil). An amount of 1000 g of each sample was quartered, and aliquots of 250 g were ground manually with a pistil in an agate mortar to obtain a fine powder, which was then dried at 105° C for 12 h. Calcium carbonate and NIST SRM 1568a Rice Flour were employed as blanks for P and Al, respectively, and to calculate the limit of detection (LOD) and the limit of quantification (LOQ). The 1515 Apple Leaves, 1570a Spinach Leaves, 1573a Tomato Leaves and 120c Phosphate Rock standard reference materials (SRM) from the National Institute of Standards and Technology (NIST, Gaithersburg, MD, USA) were employed for the evaluation of calibration and accuracy. Disc pellets of 250 mg powdered fertilizer samples, SRM plant leaves and blanks were prepared daily using the SL-10/15 hydraulic press (Solab, Piracicaba, Brazil), operating at a pressure of 7.5 ton cm⁻² for 3 min.

For comparative purposes, P was determined by HR-CS AAS after acid digestion of the sample. In particular, 200 mg of each fertilizer sample and phosphate rock SRM was accurately weighed, transferred to a microwave flask, and 3 mL of HCl and HNO₃ solution at a ratio 1:3 (reverse *aqua regia*), 2 mL of deionized water and 1 mL of hydrogen peroxide were added. High purity de-ionized water (resistivity 18.2 MΩ cm) was used to

prepare all solutions, obtained with a Millipore Rios 5® reverse osmosis and a Milli-Q Academic® deionizer system (Millipore Corporation, Bedford, MA, USA). Hydrochloric acid, nitric acid, and 30 wt% hydrogen peroxide were purchased from Merck (Darmstadt, Germany).

Digestion was performed in a Multiwave microwave oven (Anton Paar, Graz, Austria). The optimized program involving power/ramp time/hold time consisted in the following steps: step 1, 1000 W/15 min/0 min; step 2, 1000 W/0 min/10 min; step 3, 0 W/0 min/20 min (ventilation). After cooling, the digests were transferred into polypropylene flasks and diluted with deionized water to a final volume of 30 mL.

Instrumentation

The LIBS system used for Al and P determinations consisted of a Q-switched ND:YAG laser (Big Sky Ultra 50, Quantel USA, Bozeman, MT, USA), operating at 1064 nm, 9 ns of pulse duration, 10 Hz repetition rate, energy power of 48.7 ± 0.4 mJ, measured by laser power and energy meter (FieldMaxII-P, Coherent, Inc., Santa Clara, CA, USA). The laser beam was focused onto the sample surface by a plano-convex lens (12-cm focal length), thus producing a spot diameter of about 300 μm, resulting in a laser fluence of *ca.* 69 J cm⁻² and an irradiance of 0.59 GW cm⁻² delivered to the sample. The emission spectra were collected by an optical fiber bundle at an angle of 45° with respect to the laser beam and transferred to four spectrometers of the HR2000+ (Ocean Optics, Dunedin, FL, USA), operating at a spectral range from 200 to 620 nm, with optical resolution of 0.5 nm full width at half maximum (FWHM). The analysis was performed using 1-ms integration time and 1-μs Q-switched delay. The LIBS system included an automatic x-y direction sample holder and a video camera inside the sampling chamber in order to help the analyst to control the sample position. The laser was rasterized over a sample surface of about 3 mm² and broadband spectra from 10 single-pulse ablations were collected and mapped on discrete XY spatial coordinates. All measurements were performed at atmospheric air pressure.

The SD-LIBS system employed two cylindrical, pure tungsten electrodes of 100-mm length and 2.6-mm diameter, with tips arranged at a distance of 4 mm between them and 2 mm above the sample surface. The electrodes were connected to a single-spark generator operating in the voltage range from 2.0 to 4.5 kV. More information about the SD system can be found elsewhere.¹⁸ The peak heights of the atomic lines of Al I at 308.22 nm and P I at 214.91 nm were obtained using Excel spreadsheet “Chromatograms and Spectra Handling”³⁸ and Microsoft Excel for data processing and calculating the concentrations. A scheme of the experimental setup is shown in Fig. 1.

The concentrations of the sample digests, prepared as described above, were determined by HR-CS AAS using an Analytik Jena ContrAA 300, equipped with a xenon short-arc lamp XBO 301

Fig. 1 Scheme of the experiment.

(GLE, Berlin, Germany) and operating in hot-spot mode as the continuum radiation source was used. The instrument was equipped with a high-resolution double-Echelle grating monochromator (< 2 pm per pixel in the far ultraviolet range) and a charge-coupled device (CCD) array detector. All measurements were performed in triplicate using optimized operating conditions.³⁹

Fundamental aspects

In atomic emission spectrometry, the emission response at a given wavelength ($I_{(\lambda_{ij})}^{ji}$) is directly related to the analyte concentration (C) and the excited-state transition energy (E_j),³² according to:

$$I_{(\lambda_{ij})}^{ji} = \frac{FCA_{ji}g_j}{Q(T)} e^{-E_j/k_B T} \quad (\text{Eq. 1})$$

where F , A_{ji} , g_j , $Q(T)$, k_B , and T are, respectively, the instrumental proportionality constant, transition probability, excited-state degeneracy, partition function, Boltzmann constant and temperature.

Based on this equation, for a certain analyte with the concentration C in a given medium, the emission intensity, I , at a given wavelength, can be described as:

$$I = mC \quad (\text{Eq. 2})$$

where m is the proportionality constant of the LIBS instrument.

If a calibration standard with a similar matrix is measured by the same instrument in identical plasma conditions, the ratio between the intensities is proportional to the ratio between the respective concentrations, then the concentration of the analyte in the sample can be calculated according to:

$$C^{sam} = C^{std} \frac{I^{sam}}{I^{std}} \quad (\text{Eq. 3})$$

The proposed OP-MVC method requires that both the standard and the sample be submitted to SD using two different voltages (V_1 , V_2) consecutively, so that the two measured intensities, I_1 and I_2 , define a rectangular trapeze with an area A , given by:

$$A = \frac{(I_1 + I_2) \cdot (V_2 - V_1)}{2} \quad (\text{Eq. 4})$$

If the emission intensity is proportional to the concentration, then also its area is. Thus, if the ratio between the intensities in Eq. 3 is replaced by the ratio between the corresponding areas, the concentration of the analyte in the sample can be calculated according to:

$$C^{sam} = C^{std} \frac{(I_1 + I_2)^{sam}}{(I_1 + I_2)^{std}} \quad (\text{Eq. 5})$$

The LOD and LOQ can be calculated according to:

$$\text{LOD} = C_{\text{Blk}} + 3S_{\text{Blk}} \quad (\text{Eq. 6})$$

$$\text{LOQ} = C_{\text{Blk}} + 10S_{\text{Blk}} \quad (\text{Eq. 7})$$

where C_{Blk} and S_{Blk} are, respectively, the average concentration and the standard deviation of 10 measurements of the concentration in the blank samples.⁴⁰

In OP-MVC, the uncertainties of the analyte concentration ($S_{C^{sam}}$) depend on the errors associated to the intensities of both the sample ($S_{I^{sam}}$) and the standard ($S_{I^{std}}$), and on the confidence interval of the CRM standard ($S_{C^{std}}$), which can be estimated by the error propagation according to:

$$\frac{S_{C^{sam}}}{C^{sam}} = \sqrt{\left(\frac{S_{C^{std}}}{C^{std}}\right)^2 + \left(\frac{S_{I^{sam}}}{I^{sam}}\right)^2 + \left(\frac{S_{I^{std}}}{I^{std}}\right)^2} \quad (\text{Eq. 8})$$

Comparative strategies based on single-standard calibration

The performance of OP-MVC was compared to that of the SRC³³ and OP-MLC³² methods in determining P in fertilizers and Al in plant materials. In particular, the following equation was used for SRC:

$$C^{Sample} = C^{Std} \frac{b^{Sample}}{b^{Std}} \quad (\text{Eq. 9})$$

where b_{sample} and b_{std} are the slopes of the standard and the sample, which were obtained using the 5, 10, 15, 20 and 30 cumulative laser pulses with the SD-LIBS operating at 4.5 kV. The analytical lines P I at 214.91 nm and Al I at 308.22 nm were used for P and Al, respectively.

The following equation was used for OP-MLC:

$$C_{Sample} = C_{Std} \alpha^{Sample.Std} \quad (\text{Eq. 10})$$

where $\alpha^{Sample.Std}$ is the slope obtained by plotting the intensities of the sample (y-axis) versus those of the standard (x-axis) measured for different emission lines of the analyte. In particular, the emission lines of P I at 213.62 nm, 214.91 nm and 215.41 nm, and the line of Al I at 308.22 nm, which was selected after considering its lower interference, were employed. However, as OP-MLC requires multiple lines, different wavelengths located at the wing of the Al I core line at 308.22 nm, i.e., 308.01, 308.07, 308.12, 308.17, 308.22 nm, were also used. The SD-LIBS employed 4.5 kV because the Al signals were very low when only LIBS is used.

RESULTS AND DISCUSSION

The P lines profile in the spectra of NIST SRM 120c Phosphate Rock (33.34 ± 0.06 wt% P_2O_5) and the Al lines profile in the spectra of NIST SRM 1515 Apple Leaves (284.5 ± 5.8 mg kg^{-1} Al) acquired by LIBS and SD-LIBS are showed in Fig. 2. Based on

Fig. 2 LIBS (dashed line) and SD-LIBS (continuous line) spectra for (a) P in NIST SRM 120c Phosphate Rock and (b) Al in NIST SRM 1515 Apple Leaves. The voltage applied in SD-LIBS was 4.5 kV.

earlier information,¹⁸ the P I line at 214.91 nm was selected for P determination in fertilizers, and the Al I line at 308.22 nm was chosen for Al determination in plants. Despite the higher intensity observed for the line of Al I at 309.27 nm, this line was not used due to possible spectral interferences caused by the Mg I lines at 309.10, 309.29 and 309.68 nm.⁴¹ These lines might become critical for samples rich in Mg, such as NIST SRMs 1573a and 1515 which contain $12,000$ mg kg^{-1} (not certified) and 2710 ± 120 mg kg^{-1} of Mg, respectively.

The effect of the applied voltage at the values of 2.0, 2.5, 3.0, 3.5, 4.0 and 4.5 kV on the emission intensities of the P I line at 214.91 nm and the Al I line at 308.22 nm was evaluated for the NIST SRM 120c and NIST SRM 1515 samples, respectively (Fig. 3). In both cases, the plots of the line intensity against the applied voltage were linear with correlation coefficients (r) of 0.989 and 0.999 for Al and P, respectively. The NIST SRM 1570a and 1573a in the case of Al (Fig. 3a) and all fertilizer samples in the case of P (Fig. 3b) were analyzed only at higher voltages, i.e., 3.5, 4.0 and 4.5 kV, at which the highest line intensity of the analyte, i.e., a greater sensitivity, was achieved. In all cases, for both Al and P, the intensity versus voltage curves were linear with $r > 0.97$.

The extended temporal evolution of the plasma, and the increase of plasma temperature and electronic density achieved by reheating the plasma, improved the atomization and excitation processes.¹⁰ In particular, the highest increase in the signal intensity for both elements, i.e., 6.7-fold for P (NIST SRM 120c) and 4.4-fold for Al (NIST SRM 1515), was achieved at the maximum applied voltage, i.e., 4.5 kV, which yielded a satisfactory relative standard deviation (RSD) for both Al and P. Thus, further experiments aiming to optimize data collection were carried out at the voltage of 4.5 kV.

Notwithstanding the high content of P in fertilizers and the re-excitation with 4.5-kV high voltage discharge, no self-reversal effect was observed for the peak profiles of P in the concentration range from 4.8 to 33.34 wt% P_2O_5 (Fig. 4a). Furthermore, the plots of the intensity of the emission lines of P I at 213.62, 214.91 and

Fig. 3 Plots of line intensity vs. voltage ($n = 3$) for (a) line Al I at 308.22 nm in three NIST SRM plant leaves and (b) line of P I at 214.91 nm in NIST SRM 120c and fertilizer samples. The error bars represent the standard deviation of the measurements.

Fig. 4 SD-LIBS spectra of solid standards containing 0 (black), 4.8 (red), 11.9 (light blue), 22.9 (magenta), 27.8 (green) and 33.34 wt% P_2O_5 (dark blue) at an applied voltage of 4.5 kV (a), and (b) linear working range of P I lines at 213.62, 214.91 and 215.41 nm.

Fig. 5 Effect of the number of replicate spectra on the emission line intensities of Al I at 308.22 nm in NIST 1515 Apple Leaves SRM (○) and P I at 214.91 nm in NIST 120c Phosphate Rock SRM (●) recorded at an applied voltage of 4.5 kV. Circles correspond to the average values and error bars to standard deviations.

215.41 nm versus P concentration yielded straight lines (Fig. 4b) with correlation coefficients ≥ 0.997 . As these results were obtained using the maximum voltage discharge, the OP-MVC method yielded emission intensities in the linear range. Generally, SD-LIBS studies do not investigate the influence of re-excitation by high-voltage discharge on self-absorption. The plasma temperature homogeneity increase achieved by SD-LIBS without changing the ablation rate would explain the reduction of P self-absorption in the plasma periphery. A similar effect was observed by Tang *et al.*⁴² who used microwave to increase LIBS sensitivity.

The effect of the number of replicate spectra recorded at the emission intensities of P I at 214.91 nm and Al I at 308.22 nm was evaluated by acquiring 3, 5, 10, 15, 20, 25 and 30 spectra for the NIST SRM 120c Phosphate Rock and NIST SRM 1515 Apple Leaves at the voltage of 4.5 kV. The results obtained (Fig. 5)

showed that the average intensity for both the Al and P lines remained constant for replicated spectra ≥ 5 and that a satisfactory precision (RSD: 6% for P and 17% for Al) was achieved for replicate spectra ≥ 10 . Thus, the total of 10 replicate spectra was chosen for data acquisition as a compromise between precision, sensibility and sample throughput.

After optimization, the proposed calibration method was applied to determine P in fertilizers and Al in plant leaves using one or two voltages. In particular, the NIST SRM 120c Phosphate Rock was used as the unique standard to determine the P content in the five commercial fertilizer samples, which were also analyzed by HR-CS FAAS. The data in Table 1 show good agreement with the paired *t*-test at the 95% confidence level between the data achieved by OP-MVC LIBS and those obtained by HR-CS FAAS. The RSD values for P were in the 4.3 – 9.6% range.

For Al determinations, the NIST SRM 1515 Apple Leaves was used as the unique standard to analyze NIST SRM 1570a Spinach Leaves and NIST SRM 1573a Tomato Leaves, whereas the NIST SRM 1570a Spinach Leaves was used as the unique standard to analyze NIST SRM 1515 Apple Leaves. The results obtained by OP-MVC LIBS were in good agreement with the certified values with a paired *t*-test at the 95% confidence level (Table 1). The recoveries were in the range of 94 – 107% and the RSD values in the 6.0 – 6.9% interval.

The use of two voltages, V1: 3.5 kV and V2: 4.5 kV applied sequentially, achieved good performance in precision and accuracy, which may be attributed to the linear relationship existing between the line intensity and the applied voltage (Fig. 3). Furthermore, the use of three voltages appeared not to alter the results significantly, but it limited the analytical throughput due to the increased time needed to charge the capacitors. Calibration using only one applied voltage at 4.5 kV, which provided the best signal-to-noise ratio, was also tested. For the P and Al data, the relative standard deviations were in the range of 4.3 – 9.5% and 6 – 11%, respectively (Table 1). However, the precision achieved for both P and Al was improved when calibration was performed using two voltages (3.5 and 4.5 kV), which provided also better discrimination between the nominal and the actual applied voltage.

For comparative purposes, the performance of the SRC and OP-MLC methods was also tested for P and Al determination by LIBS (Table 1). The results obtained for Al by OP-MVC were in agreement with those achieved by SRC and OP-MLC at the 95% confidence level, but the RSD values for OP-MVC (in the range of 6.0 – 7.0%) were better than those for SRC and OP-MLC (in the range of 8.3 – 15.8% and 23.0 – 26.7%, respectively). However, the results obtained for P were in agreement with those achieved by SRC, but not by OP-MLC, at the 95% confidence level. The RSD values of P obtained by OP-MVC, SRC and OP-MLC ranged from 4.3 – 9.5%, 4.0 – 14.1% and 0.6 – 15.8%, respectively. Using OP-MVC, SRC and OP-MLC, the LOQs for P (expressed

Table 1. Comparative Results (Mean $\pm$ Standard Deviation, $n=3$) for the Determination of P (wt% P_2O_5) in Fertilizers and Al (mg kg^{-1}) in Plant Leaves Obtained by OP-MVC (with One and Two Voltages) and SRC and OP-MLC Methods

Sample/SRM	Comparative values	OP-MVC		SRC	OP-MLC	Standard used for calibration
		V1 = 4.5 kV	V1 = 3.5 kV V2 = 4.5 kV			
P						
Sample 1	19.0 ± 0.3 ^a	17.3 ± 1.4	17.7 ± 0.9	20.5 ± 2.9	15.0 ± 0.1 ^c	SRM-120c
Sample 2	6.5 ± 0.2 ^a	7.0 ± 0.8	6.9 ± 0.3	6.4 ± 0.4	7.9 ± 0.3 ^c	SRM-120c
Sample 3	17.2 ± 0.4 ^a	16.5 ± 1.6	17.1 ± 1.1	16.2 ± 1.7	14.0 ± 1.3 ^c	SRM-120c
Sample 4	9.2 ± 0.1 ^a	9.1 ± 0.7	9.4 ± 0.9	9.5 ± 1.1	11.4 ± 1.8 ^c	SRM-120c
Sample 5	19.0 ± 0.1 ^a	18.8 ± 1.2	18.5 ± 0.8	19.7 ± 0.8	16.8 ± 1.3 ^c	SRM-120c
Al						
NIST 1570a	310 ± 15 ^b	322 ± 14	316 ± 2	290 ± 46	343 ± 90	NIST 1515
NIST 1515	284.5 ± 5.8 ^b	288 ± 27	280 ± 18	295 ± 25	265 ± 61	NIST 1570a
NIST 1573a	598.4 ± 7.1 ^b	586 ± 56	591 ± 41	579 ± 48	685 ± 183	NIST 1515

^a Comparative value determined by HR-CS FAAS; ^b Certified values; ^c Not in agreement with comparative values at the 95% confidence level.

as wt% P_2O_5) were, respectively, 2.0%, 2.3% and 2.7%, and for Al (mg kg^{-1}) 117, 126 and 269.

Different LIBS configurations may affect the quality of the data obtained for P using OP-MLC, as the emission line of P I at 213.62 nm may be interfered by those of Cu and Zn, which are commonly present in fertilizers, thus deteriorating the calibration curve obtained for OP-MLC. In particular, the correlation coefficients obtained by plotting the P signal for the sample in the y -axis and that of the NIST SRM 120c Phosphate Rock in the x -axis varied from 0.946 to 0.998, with the lower values possibly due to these spectral interferences. The significantly higher RSD values obtained by OP-MLC for Al in plant materials with respect to those for P in fertilizers (Table 1) might be due to the much lower content of Al (mg kg^{-1}) compared to P (wt%). Furthermore, the wavelengths employed for Al were located at the wing of the Al I line at 308.22 nm, i.e., the lines at 308.01, 308.07, 308.12, 308.17, and 308.22 nm. Although this procedure is not commonly used for MLC, it was a strategy adopted to overcome the limited number of non-interfered Al I lines. In conclusion, the differences among the results obtained with these various methods might be due to the different instrumental strategies used to increase the signal intensities, such as cumulative laser pulses (SRC), several lines (OP-MLC) and voltages (OP-MVC).

CONCLUSIONS

In this work, SD-LIBS was successfully used in combination with the SSC calibration method of OP-MVC to determine Al and P in plant leaves and fertilizers, respectively, achieving suitable accuracy, precision and LOQs. The required SD extra device used should not be seen as a serious shortcoming as it is a simple, low cost, and rugged tool capable of enhancing the signal intensities for any LIBS system, thus improving the performance especially of those featuring limited sensitivity.

For comparative purposes, the performance of the OP-MVC

method was also evaluated with respect to the SRC and OP-MLC methods. Although SRC and OP-MLC are simple and performance calibration methods, they need high sensitivity LIBS systems depending on the specific analyte and sample. Further, SRC can be performed with one emission line, while OP-MLC is limited to elements that feature several lines. In general, all of these calibration methods employ a single solid calibration standard, so that difficulties related to the preparation of several solid standards (e.g., external calibration) with physicochemical properties similar to the samples are minimized.

Finally, the proposed OP-MVC method cannot be considered as limited to LIBS analysis of Al and P in plants and fertilizers, but its performance appears promising to be tentatively extended to other analytes and samples in various matrices.

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Notes

The authors declare no competing financial interest.

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