Review

Calibration Strategies Applied to Laser-Induced Breakdown Spectroscopy: A Critical Review of Advances and Challenges

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Over the years, laser-induced breakdown spectroscopy (LIBS) has been reported in the literature as an alternative to traditional methods of analysis, becoming well established among spectroanalytical techniques. LIBS is a technique widely used for qualitative approaches; however, it is necessary considerable effort for use in quantitative analysis, mainly due to severe matrix effects. These limitations make it difficult to broaden the application of LIBS in quantitative analysis. In this sense, this review discusses recent advances in calibration strategies applied in LIBS for minimizing matrix effects and enabling determination with satisfactory accuracy and precision. Applications, advantages, and limitations of the calibration strategies, such as matrix-matching calibration (MMC), internal standardization (IS), standard addition (SA), multi-energy calibration (MEC), one-point gravimetric standard addition (OP GSA), one-point and multi-line calibration (OP MLC), slope ratio calibration (SRC), two-point calibration transfer (TP CT), single-sample calibration (SSC), multiple linear regression (MLR), principal component regression (PCR), partial least squares (PLS) and artificial neural networks (ANN) are discussed.

Keywords: LIBS, calibration strategies, quantitative analysis, matrix effects

1. Introduction

Currently, laser-induced breakdown spectroscopy (LIBS) has been reported[1-3] as the most prominent spectroanalytical technique due to its attractive set of advantageous analytical characteristics. LIBS is versatile, presenting several features, such as high analytical frequency, minimal sample preparation and reagent consumption, and the ability to provide information for practically any type of sample.[4-6]

After advances and the establishment of the use of LIBS in several applications, it seems reasonable to repeat the words once said by Winefordner *et al.*:[7] they stated in 2004 that LIBS would be the "next superstar" within the group of spectroanalytical techniques. This statement can be evidenced by the number of scientific publications in the last 39 years (1981-2019) regarding LIBS with approximately 5,000 papers according to the Web of Science database, where in the last 12 years (2008-2019) account for approximately 80% of the total publications. These data exemplify the community interest in LIBS, as it is currently possible to find a wide variety of studies[8-19] proposing innovations and improvements to this technique.

For qualitative analysis purposes, LIBS is well established. However, for quantitative goals, LIBS require considerable effort due to difficulties in preparing and obtaining calibration standards and the absence of commercial certified reference materials (CRM) with mass fractions on the order of µg. In addition, there are problems with matrix effects, which are currently the main challenge in quantitative LIBS analysis.[20-28]

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To minimize possible matrix effects normally observed in LIBS analysis, some calibration strategies have been reported in the literature[29-35] over the last few years to improve its figures of merit. The main calibration strategies employed in LIBS can be divided into three groups: (*i*) traditional calibration, (*ii*) nontraditional calibration, and (*iii*) multivariate calibration. Our intention is to provide to the reader a clear guide about how to apply each calibration strategy correctly and in which situation to use each one. In addition, we present the advantages and limitations related to each approach.

2. Description of the Main Matrix Effects in LIBS

One of the inherent challenges in LIBS is quantitative analysis due to the complexity of laser-sample interaction processes, involving laser parameters, sample properties, and plasma chemistry, and due to plasma-particle interaction processes that depend on both space and time.[3,36] For quantitative aspects, it has always been reported[3,36,37] that traditional calibration strategies applied to LIBS suffer severe matrix effects.

Besides matrix effects, there is also spectral effects that occur when a strong line interferes with the emission region of a weak line for a monitored element. This problem can easily be circumvented by selecting an alternative line of the element, carefully adjusting the peak area of the analytical signal, or switching the spectrometer arrangement for a high spectral resolution system.[38] On the other hand, problems related to matrix effects are more challenging and difficult to detect and solve when compared to spectral interferences.[39]

Matrix effects depend on the physical characteristics and chemical compounds in the sample, and there are many possibilities for how the matrix may influence the emission phenomenon during LIBS analysis.[38] Physical matrix effects are directly correlated to the different physical properties of samples, e.g., irregular surface, heterogeneity, sample moisture content, compressive pressure for sample pelleting (when applied), heat of vaporization, thermal conductivity, and absorption coefficient, which affect the transport of the ablated sample mass in the plasma.[3,22]

Chemical matrix effects occur due to fluctuations of the plasma parameters related to the predominant organic and inorganic composition of the sample or the content of easily ionized elements.[40,41] In addition, the interaction of the laser or sample with atmospheric conditions (e.g., ambient gas or reactive gas) may affect the plasma temperature and density, resulting in changes in the emission intensity of constituent elements.[42] These matrix effects may contribute to the nonstoichiometric ablation of the sample and thus reduce the ability of quantitative analysis by LIBS.

3. Traditional Calibration Strategies Applied to LIBS

3.1. Matrix-matching calibration (MMC)

Among the traditional calibration strategies applied in LIBS, MMC is the most widely used. The calibration standards in MMC are prepared in the sample matrix, usually employing certified reference materials (CRMs). However, very few CRMs that are suitable for LIBS applications are commercially available. In addition, the reference values for available CRMs are only valid for applications involving a minimum material mass (typically 100 mg), which is usually incompatible with the amounts required for LIBS calibration (typically a few µg).[2,20,21]

MMC can also be based on a set of samples with reference values that are obtained from well-established analytical techniques or the use of solid standards with the concomitants that present interference. This strategy is very interesting and, in many cases, solves matrix effects problems because the samples themselves are used to obtain calibration curves.[43] The MMC method has been effectively applied to elemental determination in different types of matrices.[44-51]

3.2. Internal standardization (IS)

The IS method consists of adding an element as the internal standard to all samples, calibration standards and analytical blank and using the analyte/internal standard signal ratio to obtain a calibration curve. The internal standard has a known concentration and, ideally, both internal standard and analyte must be affected by the same processes during instrumental measurement.[52]

Therefore, the IS method is often applied to minimize pulse-to-pulse variations and matrix effects. Two different types of internal standards can be used; however, in both cases, the ionization and excitation energies and emission line intensity must be similar for the internal standard and the analyte. In the first approach, the emission line of the element selected as IS must be already present in the sample spectra which its intensity remains constant for all standard samples. The second approach is applied to samples with very variable composition, in which an emission line of an added element that is not present in the unknown and standard samples can be used.[53-56]

3.3. Standard addition (SA)

Standard addition is also a calibration strategy widely used in LIBS,[20] minimizing matrix effects in complex samples. The SA method consists of adding known quantities of the element to be determined in the unknown sample, producing a similar behavior in the calibration series to that of the unknown sample.[43,52]

For using the SA method is important to point out that the sample itself is used to prepare the calibration solutions or mixtures. Thus, the matrix effects are naturally corrected, and no prior knowledge of the sample matrix is required. On the other hand, the main limitations associated with SA are the time consuming required to construct a calibration curve for each sample and the need for a considerable amount of sample. These problems become more critical for analysis of large number of samples and if a limited sample amount is available.[12,43,52] Several studies[57-60] have successfully quantified analytes using SA and LIBS.

4. Nontraditional Calibration Strategies Applied to LIBS

In this section, we present calibration strategies that were recently developed for LIBS. These strategies explore the physicochemical properties of laser-induced plasma species, the use of analyte emission lines with different sensitivities, and a limited number of standards (one or two standards) to obtain a linear model or calibration curve.

4.1. Multi-energy calibration (MEC)

MEC is one of the most recent calibration strategies reported in the literature[61,62] for minimizing matrix effects in different analytical techniques of atomic spectrometry. MEC is based on different transition energies (wavelengths) for analytical signal acquisition from the analysis of two standards: pellet 1, containing 50% m m^{-1} sample and 50% m m^{-1} standard and pellet 2, containing 50% m m^{-1} sample and 50% m m^{-1} blank. Analytical signals acquired from pellets 1 and 2 are plotted on the *x*-axis and *y*-axis (see Figure 1), respectively. Using the slope of the linear model and the analyte concentration of the standard ($C^{Standard}$) added in the pellet 1, it is possible to obtain the analyte concentration in the sample (C^{Sample}).[61] As shown in the Boltzmann equation (equation 1), the analyte concentration (C_s) and excited-state transition energy (E_k) are related to the instrument response at a given wavelength (λ_i). F is the experimental factor, A_{kj} the transition probability, g_k the degeneration of the upper level, $U_s(T)$ the partition function of the species
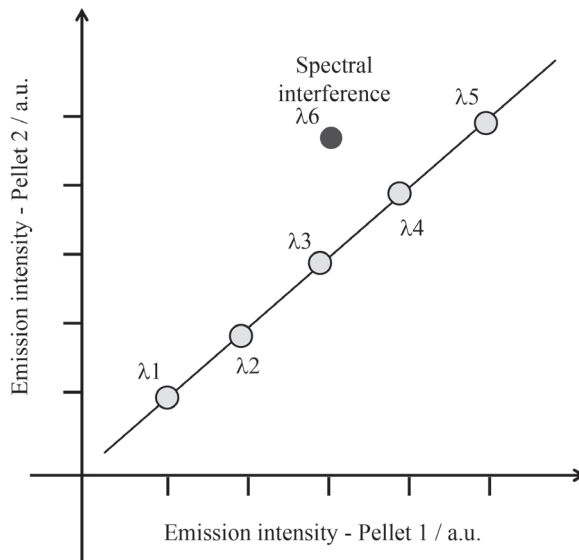
Figure 1. MEC plot and spectral interference at wavelength 6 (outlier).

present in the plasma, T the temperature of the plasma and K_B the Boltzmann constant. If C_s is fixed and E_k is changed by using different wavelengths during the analytical signal acquisition, the instrument response is a dependent variable of both parameters.

Considering $C^{Standard}$, C^{Sample} and a simple mathematical treatment used for elemental determination, it is possible to obtain equations 2 and 3:[61]

$$I_{\lambda_i} = FC_s \frac{A_{kj}g_k}{U_s(T)} e^{-E_k/K_B T} \qquad (1)$$

$$I(\lambda_i)^{Sample+Standard} = K_p \left(C^{Sample} + C^{Standard} \right) \qquad (2)$$

$$I(\lambda_i)^{Sample} = K_p C^{Sample} \qquad (3)$$

where the terms $C^{Standard}$ and C^{Sample} were defined previously, $I(\lambda_i)^{Sample+Standard}$ and $I(\lambda_i)^{Sample}$ are the instrument response at a given wavelength (λ_i) for both pellets, and K_p is a proportionality constant. After reorganization of equations 2 and 3, it is possible to calculate C^{Sample} from equation 4:

$$C^{Sample} = \frac{Slope \times C^{Standard}}{(1 - Slope)} \qquad (4)$$

The main advantages of MEC are related to the matrix-matching capability due to the presence of the sample in the standards (pellets 1 and 2) and the possibility of identifying spectral interferences, as shown in Figure 1. Emission line number 6 (λ_6) is an outlier, where its signal is shifted from the proposed linear model plot, indicating that λ_6 is an emission line with spectral interference and must be removed and the model calculated again.

In this sense, Babos *et al.*[29] applied MEC as a calibration strategy, for the first time, for the analysis of cattle mineral supplements by LIBS. The authors used different salts to prepare solid stock standards containing the analytes. High-purity sodium carbonate (Na_2CO_3) was used as a blank (and as a diluent) to simulate the matrix of the analyzed samples due to the presence of carbonates. To build the linear models, several atomic (I) and ionic (II) emission lines were selected from the most sensitive lines for each analyte.

In addition, the authors also evaluated the influence of different standard mass (that is, different $C^{Standard}$ values) added to pellet 1 on the accuracy of the results. The precision, described as the relative standard deviation (RSD), ranged from 2 to 32%, and the trueness varied from 85 to 102% using MEC-LIBS. According to the *t*-test, at the 95% of confidence level, no significant difference was observed between the reference results obtained by inductively coupled plasma optical emission spectrometry (ICP OES) or reference materials and MEC-LIBS.

Some important aspects should be highlighted: (*i*) the selection of a blank material is a challenge because it must be a high-purity reagent to avoid contamination during the analysis, contributing to better method precision, and, at the same time, must have a similar composition to the matrix of the samples to be analyzed; (*ii*) the homogenization of the standard and blank material with the samples is a crucial aspect because a failure to do so can compromise the precision and the accuracy of the proposed method.

Some studies in the scientific literature[30,33,63-66] have reported elemental determination in different samples using the MEC-LIBS method with good analytical performance parameters (Table 1).

4.2. One-point gravimetric standard addition (OP GSA)

SA is a calibration strategy that consists of increasing the analyte concentration in the samples, which are then plotted on the *x*-axis, and the analytical signals (S) are plotted on the *y*-axis. Thus, in an unknown sample, the analyte concentration can be calculated using equation 5 proposed by Bader:[67]

$$C_x = \frac{intercept\ V_s C_s}{slope\ V_x} \tag{5}$$

where the intercept and the slope were obtained from the calibration curve, V_s is the fixed unit volume of the standard, V_x is the fixed unit volume of the unknown sample, C_s is the stock standard concentration and C_x is the unknown sample concentration.

For direct analysis of solids, a new gravimetric approach (G) was introduced to SA that considers masses instead of volumes. In 2008, Kelly *et al.*[68] reformulated equation 5, considering the mass of the standard (m_s), the unknown sample mass (m_x) and the mass of the diluent (m_D).

In gravimetric SA, the *x*-axis is represented by equation 6, the *y*-axis is represented by equation 7, and C_x is calculated using equation 8:[68]

$$x\ axis = \frac{m_s C_s + m_D C_D}{m_x} \tag{6}$$

Table 1. MEC-LIBS methods applications

Sample	Analyte	Sample/standard or blank ratio / (% m m⁻¹)	RSD / %	Trueness / %	Highlight	Reference
Mineral supplements for cattle	Ca and P	80:20	4 to 26	80 to 109	Na_2CO_3 was used as the blank (and diluent); identified one spectral interference for P	30
Hard disk magnets	Fe, B, Dy, Gd, Nd, Pr, Sm and Tb	42:58	3 to 44	80 to 120	Na_2CO_3 was used as the blank, cellulose was used as a binder, and a sample was selected as the standard	33
Dietary supplements	Ca, K and Mg	50:50	< 56	60 to 120	microcrystalline cellulose was used as the blank and diluent; evaluation of the influence of different proportions of the analyte in the stock solid mixture on analytical signals	63
Nickeliferous ores	Ni and Cr	50:50	1 to 9	89 to 114	Na_2CO_3 as the blank and diluent	64
Liquid crystal display	In	40:60	12 to 20	80 to 120	SiO_2 was used as the blank and cellulose as a binder; identified one spectral interference for In	65
High-silicon-content samples	Al, Fe and Ti	50:50	4 to 7	88 to 115	fused glass disks were prepared from CRM (brick clay and sediment), SiO_2 and a lithium borate flux mixture; after the fusion procedure, fused samples were analyzed considering five emission lines for Al, seven for Fe and five for Ti; B and Li were evaluated as internal standards	66

RSD: relative standard deviation; CRM: certified reference material.

$$y \text{ axis} = \frac{m_x + m_s + m_D}{m_x} S \tag{7}$$

$$C_x = \frac{|\text{intercept}|}{\text{slope}} \tag{8}$$

where C_D is the analyte concentration in the diluent, and the term $m_D C_D$ can be neglected in equation 6 because the diluent is usually of high purity, and S is the analyte signal. In addition to its advantages, SA usually requires five points, which causes long preparation of solid calibration standards for each sample.

Moreover, for the first time, Babos *et al.*[30] proposed OP GSA for direct solid analysis by LIBS. This strategy uses two calibration standards (sample + blank and sample + standard), similar to the standards prepared when using MEC, and only one wavelength is monitored. Figure 2 shows an example of the calibration curve employing OP GSA by LIBS, in which the unknown concentration of analyte in the sample is calculated by extrapolation of the calibration curve, according to equation 8.
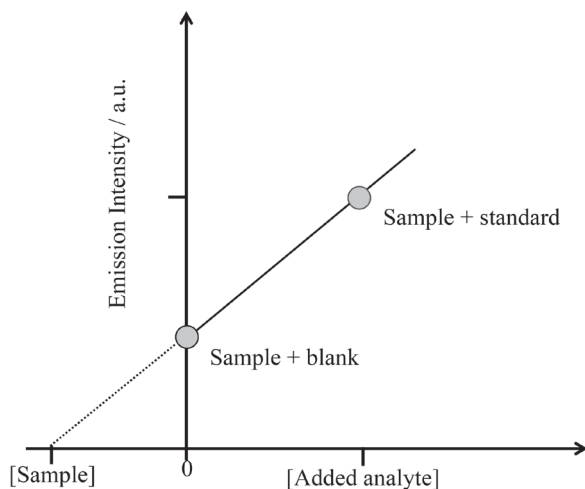

Figure 2. OP GSA calibration curve.

In the literature, only two studies are available employing OP GSA, including one for determination of Ca and P in solid mineral supplements[30] and one for determination of B, Fe, Dy, Gd, Nd, Pr, Sm and Tb in hard disk magnets.[33] In general, the authors obtained sufficient RSD values (ranging from 1 to 39% in mineral supplement and 2 to 44% in hard disk magnet determinations, in addition to adequate trueness).

The OP GSA method has an advantage over conventional SA because it requires a small amount of sample to prepare the standards which only one SA point is used, and, consequently, there is a higher analytical throughput.

4.3. One-point and multiline calibration (OP MLC)

OP MLC is a new calibration strategy based on a single matrix-matched standard sample and multiple lines of determined elements. The main idea is that from the local thermodynamic equilibrium (LTE) in the temporal window of signal acquisition, the measured integral line intensity can be expressed according to the Boltzmann equation, as shown in equation 1.[31]

Therefore, measuring the intensity of spectral line I_{λ_1} is proportional to I_{λ_2} from the same species under the same plasma conditions. Moreover, if two emission lines λ_1 and λ_2 are emitted from the same element but in different samples, their intensity ratio can be expressed by equation 9:

$$\frac{C_s^a}{C_s^b} = \frac{I_{\lambda_1}^a}{I_{\lambda_1}^b} \tag{9}$$

where a and b indicate two different samples and C_s^a and C_s^b are the concentrations of species in samples a and b. Therefore, the unknown concentration of the determined species can be obtained by employing only one sample as a standard in which the concentration of the analytes must be certified or known.

According to the authors,[31] the use of a single line cannot be guaranteed due to background of the spectrum and intensity errors that can affect the unknown concentration. An alternative for this problem is to use the intensities of multiple lines of a standard or certified material and unknown samples to build a linear model, as shown in Figure 3. In addition, equation 9 was reformulated by replacing the intensity ratio $I_{\lambda_1}^a \big/ I_{\lambda_1}^b$ with the slope of the linear model. Therefore, equation
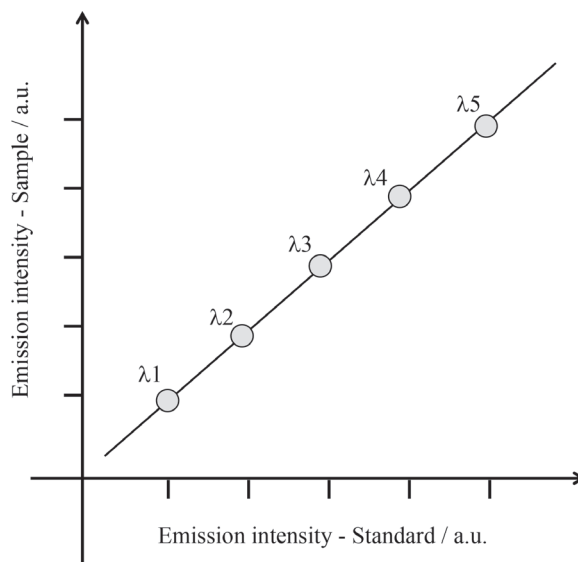

Figure 3. OP MLC linear model for five spectral lines of an analyte.

10 can be used to calculate the concentration of the analytes in the unknown samples.

$$C_{analyte} = slope \times C_{standard} \qquad (10)$$

Using OP MLC for quantitative determination by LIBS simplifies the analysis because it does not require a large number of standards and complicated calculations. In the literature, only one study[31] has reported the use of OP MLC for Mn, Cr, Ni, Ti and Fe determination in standard low-alloy steel samples with average relative errors for determination in the range of 9-36%.

4.4. Slope ratio calibration (SRC) and two-point calibration transfer (TP CT)

The SRC method is a calibration strategy recently proposed by Nunes *et al.*[32] This strategy is related to the increase of the ablated sample mass with the number of accumulated laser pulses on a single calibration standard. The emission intensity (I) is directly proportional to the analyte amount in the ablated sample mass (m), which, in turn, is proportional to the number of laser pulses (Np). Process related to sample ablation (k_1), and analyte atomization and excitation efficiency (k_2) are shown by proportionality (K) between I and Np, according to equation 11.

$$\left\{ \begin{array}{l} I = k_1 m \\ m = k_2 N_p \\ I = K N_p \\ K = k_1 k_2 k_n \end{array} \right\} \qquad (11)$$

Two linear models are generated in SRC, one for a sample with an unknown analyte concentration and the other for a calibration standard, which can be a CRM or reference sample. These two models are obtained by plotting the analyte emission intensity as a function of the number of accumulated laser pulses in the sample and in the standard, as shown in Figure 4a. The analyte mass fractions in the sample with unknown concentrations are determined from the ratio of the corresponding slopes of these linear models.

Using the reference concentration ($C_{standard}$) of the analyte in the calibration standard and the slope ratio obtained in the linear models for the sample ($slope_{sample}$) and calibration standard ($slope_{standard}$), the analyte concentration ($C_{analyte}$) can be obtained using equation 12.

$$C_{analyte} = \frac{slope_{sample}}{slope_{standard}} \times C_{standard} \qquad (12)$$

SRC was employed for the determination of B, Ca, Cu, Fe, Mg, Mn, P and Zn in plant leaves using between 5 and 30 laser pulses *per* site for calibration. Analysis of CRMs and comparison with the results obtained by ICP OES were used to verify the accuracy of the SRC calibration strategy, with agreement at the 95% confidence level.

The TP CT method is another interesting calibration strategy and it was recently proposed by Castro *et al.*[33] It is derived from the SRC approach with the difference of using only two points of accumulated laser pulses. Therefore, the linear model for the sample and standard is obtained
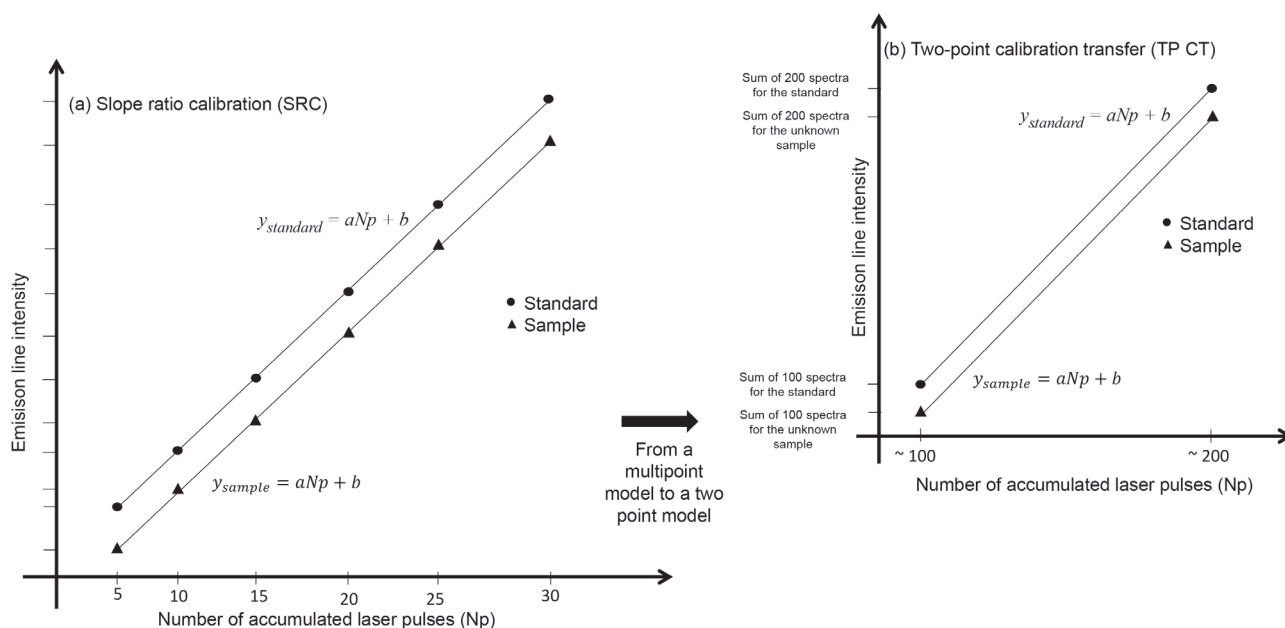

Figure 4. Linear models obtained for the sample and standard using (a) SRC and (b) TP CT for LIBS.

with two analytical signals monitoring only one analyte emission line, as can be seen in Figure 4b. The interest analyte concentration is also calculated as the SRC method (equation 12).

As in LIBS, hundreds of spectra are obtained for representative analysis, so it is easy to obtain two sets of spectra for the linear model plot. In addition, the sum of the intensity of the spectra obtained for each set should be used as data pretreatment.[33] According to the pioneering study,[33] the second set of spectra must be at least twice as large as the first set to obtain good linearity of the models. The linearity is obtained calculating the *F*-values ($F_{experimental}$ and $F_{tabulated}$) from the mean of square of regression and residue (MSR and MSr, respectively). If the ratio of $F_{experimental}/F_{tabulated}$ is $\geq$ 10, the model is considered statistically valid with good linearity.[30,69-71]

A limitation of both methods (SRC and TP CT) is the difficulty in choosing an appropriate standard for obtaining a linear model for subsequent calibration transfer. The laser-to-sample/standard interaction depends on the physicochemical characteristics of the sample, the laser properties and the optical design.[32] Therefore, it is necessary that the unknown sample and the standard have similar characteristics and concentrations of the analyte for a perfect matrix-matching. In addition, the analysis in LIBS should be performed using the same parameters for both samples (unknown and standard).[33]

TP CT was successfully employed for the direct analysis and determination of base and rare earth elements in eight obsolete hard disk magnets. The RSD values varied from 2 to 28%.[33] TP CT has also been successfully used by Gamela *et al.*[70] for the direct determination of Ca, K and Mg in cocoa beans. The last three calibration possibilities presented (OP GSA, SRC and TP CT) require the selection of an emission line free of spectral interference. In this case, a good strategy is to first use MEC, identify the emission lines that are free of spectral interference and apply these lines in the calibration strategies that employ signal from an individual emission line.

4.5. Single-sample calibration (SSC)

The SSC method was recently proposed by Yuan *et al.*[34] This strategy is based on the Lomakin-Scherb formula, where the emission intensity of a spectral line of element j is equal to the multiplication of an experimental factor by the concentration of element j. Thus, to estimate the concentration of the analyte only one sample (CRM or sample with a reference concentration) is used as a calibration standard and subsequent correlation is calculated between the different emission lines of the analyte and other

elements present in the standard and sample (unknown) and the concentration of all these elements present in the calibration standard.

The SSC method requires only a correlation between emission line intensity and concentration, eliminating the necessity to construct a calibration curve or linear models. The highlight of this strategy is that the analyte emission line and other emission lines of the elements present in the plasma formed after sample ablation are employed in this correlation to estimate the analyte concentration, which enables good accuracy in the determinations.[34]

Thus, the analyte concentration ($C_{analyte}$) is calculated using equation 13:

$$C_{analyte} = \frac{\dfrac{C_{standard\ analyte} \times I_{analyte\ sample}}{I_{analyte\ standard}}}{\displaystyle\sum_{i=1}^{N} \dfrac{C_{standard\ element}^{N} \times I_{element\ sample}^{N}}{I_{element\ standard}^{N}}} \tag{13}$$

where $C_{standard\ analyte}$ and $I_{analyte\ standard}$ are the concentration and intensity of the emission line of the analyte in the sample used as a calibration standard, respectively; $I_{analyte\ sample}$ is the emission intensity of the analyte in the unknown sample, $I_{element\ sample}^{N}$ is the emission intensity of the element N in the sample of unknown concentration, and $C_{standard\ element}^{N}$ and $I_{element\ standard}^{N}$ are the concentration and the emission intensity of the element N, respectively, in the sample used as a calibration standard.[34]

In SSC there is a direct correlation among the concentration and emission line intensities of the elements present in the plasma. It is important to mention for the concentration estimation that both standard and sample need to have similar physicochemical properties to minimize the matrix effects and, in addition, the selection of emission lines free of spectral interference.

In the study of Yuan *et al.*,[34] SSC was employed to determine Fe, Cu, Zn, Ni, Cr, Nb, and Mo in steel, brass, and nickel-based microalloy samples. The analytical figures of merit obtained using SSC showed better results than those of matrix-matching calibration (multipoint calibration).[34]

5. Multivariate Calibration

Unlike univariate calibration, multivariate analysis is the study of several variables measured in a certain number of samples, of which the aim is to determine all types of variation in the data. This calibration refers as first-order calibration, where a vector is determined for each sample. Therefore, chemometric tools attempt to find the relationship between samples (scores) and variables (loadings).[72-74]

Some advantages of multivariate calibration are noted as follows: (*i*) noise reduction is accomplished using multiple responses, improving the precision and obtaining robustness towards random artifacts; (*ii*) interferents can be handled when these interfering species are included in the calibration model and both signals (interferent and analyte) are not completely identical. On the other hand, if these species are not included in the calibration model, the presence of interference can be detected but not corrected; (*iii*) several parameters are obtained with the models, which can be used to investigate, understand and improve the model. With the scores, it is possible to observe the presence of outliers, for instance, where extreme scores can indicate an extreme sample (possibly an outlier).

To predict samples from validation with the calibration model, one important aspect is that the new sample should contain the same characteristics as those of the samples for which the calibration model was built; otherwise, the deviation can be observed, containing unmodeled variation, where the new samples cannot be accurately predicted with the model.[75-77]

There are many tools for multivariate calibration, such as multiple linear regression (MLR),[78,79] principal component regression (PCR),[80,81] partial least squares (PLS),[82,83] and artificial neural networks (ANN).[84,85] According to Web of Science, since 2000, the number of publications with LIBS and multivariate calibration has presented a systematic increase, and among the methods mentioned, PLS proved to be included in the most published papers, followed by those reporting on ANN, PCR and MLR, as showed in Figure 5. In addition, Table 2 presents some applications of multivariate calibration in LIBS.[59,80,86-93]
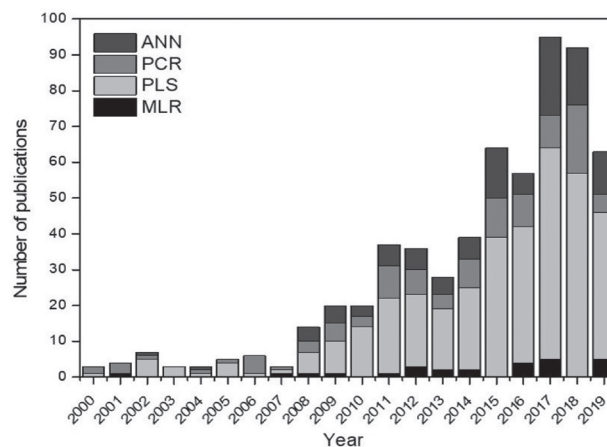

Figure 5. Publications since 2000 about multivariate calibration and LIBS.

6. Conclusions and Perspectives

After evaluation of this review, the reader is probably asking: what is the best calibration strategy for LIBS? This is a very difficult question and depends on several factors, such as sample type, availability of standards (or reference values), correction or removal of the background signal, besides spectral normalization procedures. Currently, the calibration possibilities for quantitative analysis by LIBS are diverse. However, the optimal calibration will be one that allows determinations with satisfactory accuracy and precision, i.e., one that minimizes matrix effects in the analyte determination. The choice of the calibration strategy employed in the analytical method to be developed will depend on the intrinsic properties of the sample analyzed and the knowledge of the advantages and limitations inherent to each strategy. Table 3 briefly outlines the advantages and limitations of each calibration strategy presented in this review.

Table 2. Applications of multivariate calibration in LIBS

Goal	Sample	Calibration method	Reference
Ti quantification	sunscreen	MLR, PCR and PLS	80
Pb quantification	tea leaves	external standard, IS and MLR	59
Total carbon concentration	soil	MLR	86
Mn quantification	glass matrices	PCR	87
Cu and Zn quantification	brass alloys	PCR and PLS	88
PC and ABS concentration	plastics (PC/ABS) from WEEE	PLS	89
Clay, silt and sand percent	soil	PLS	90
Cu quantification	soil	ANN	91
Quantification of trace levels of uranium	forensic nuclear materials	ANN	92
Cr, Mg, Mn and Cu determination	Al alloys	ANN	93

MLR: multiple linear regression; PCR: principal component regression; PLS: partial least squares; IS: internal standardization; PC: polycarbonate; ABS: acrylonitrile butadiene styrene; WEEE: waste of electrical and electronic equipment; ANN: artificial neural networks.

Table 3. Advantages and limitations of the calibration strategies applied in LIBS

Calibration strategy	Advantages	Limitations
Matrix-matching calibration (MMC)	minimizes matrix effects because the chemical properties of the standards and samples are similar	few certified reference materials are commercially available, as well as samples with reference values
Internal standardization (IS)	minimizes matrix effects and fluctuations in instrumental measurements	difficulty choosing an appropriate internal standard
Standard addition (SA)	minimizes matrix effects in complex samples	requires considerable amount of sample
Multi-energy calibration (MEC)	minimizes matrix effects and identifies spectral interference; requires only two calibration standards for each sample	difficulty choosing an appropriate blank (diluent)
One-point gravimetric standard addition (OP GSA)	minimizes the effects of matrix in complex samples and requires only a small amount of sample	requires effective sample homogenization with blank or standard
One-point and multi-line calibration (OP MLC)	requires only one calibration standard and minimizes matrix effects	difficulty choosing an appropriate calibration standard
Slope ratio calibration (SRC)	minimizes the effects of matrix and only a reference sample or CRM is used as a standard	the concentration of analytes in the samples should be similar to the standard concentration, and the linear model is multipoint
Two-point calibration transfer (TP CT)	minimizes the effects of matrix, only a sample or CRM is used as a standard; simplicity in data processing; linear model is with only two points	the concentration of analytes in the samples should be similar to the standard concentration
Single-sample calibration (SSC)	requires only one calibration standard, and does not require a calibration curve or linear model (only one correlation)	difficulty choosing an appropriate calibration standard
Multiple linear regression (MLR)	calibration in the presence of interferents	the sample number must be greater than the number of variables (collinearity)
Principal component regression (PCR)	calibration in the presence of interferents	requires large number of samples for calibration
Partial least squares (PLS)	calibration in the presence of interferents	requires large number of samples for calibration
Artificial neural networks (ANN)	calibration in the presence of interferents and the capacity to model nonlinear signals	requires large sample sizes for calibration and analyst expertise

CRM: certified reference material.

The authors of this review expect that the information presented here will help readers and LIBS users successfully perform quantitative analysis. Several different calibration methods (univariate and multivariate) were presented, emphasizing their advantages and limitations. Calibration-free (CF) analysis was not mentioned because it is beyond the scope of our intentions. In our opinion, this review can aid users in the selection of a proper calibration alternative, fostering the application of LIBS for several types of samples. The challenges are many, but from the literature, it is possible to conclude that LIBS is already a superstar technique.

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Author Contributions

Vinicius C. Costa, Diego V. Babos and Jeyne P. Castro were responsible for formal analysis, conceptualization, visualization, writing original draft, review and editing; Daniel F. Andrade, Raimundo R. Gamela and Raquel C. Machado for formal analysis, visualization, writing original draft, review and editing; Marco A. Sperança, Alisson S. Araújo and José A. Garcia for formal analysis, conceptualization and visualization; Edenir R. Pereira-Filho for formal analysis, funding acquisition, project administration, resources, supervision, visualization, writing review and editing.

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