Т. 88, № 3 **ЖУРНАЛ ПРИКЛАДНОЙ СПЕКТРОСКОПИИ** МАЙ — ИЮНЬ 2021
V. 88, N 3 **JOURNAL OF APPLIED SPECTROSCOPY** MAY — JUNE 2021

EVALUATION OF THE CALIBRATION-FREE AND MULTIVARIATE METHOD FOR QUANTITATIVE ANALYSIS IN LASER-INDUCED BREAKDOWN SPECTROSCOPY

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The calibration-free laser-induced breakdown spectroscopy (CF-LIBS) method is used to obtain the concentration of the constituents of samples because it overcomes the limitation of matrix-matched standards in the calibration curve method of quantification. However, there are often doubts that remain about the efficiency of the CF-LIBS method. Hence, in the present work, different certified reference materials (CRMs) of plants and soil were employed to check the capabilities of the CF-LIBS method. If the emission lines of an element are missing in the LIBS spectra, its contribution in the CF-LIBS result will be missing as well, which leads to incorrect quantification. Therefore, in order to overcome this problem in CF-LIBS, instead of only determining the elemental concentrations, an additional step to calculate the concentration ratio of all elements with respect to the concentration of a major element was added. The calculated concentration ratios for different elements are more accurate than the elemental concentration obtained by CF-LIBS. Along with the CF-LIBS method, the partial least square regression (PLSR) approach was also applied for the prediction of the concentration.

Keywords: *calibration-free laser-induced breakdown spectroscopy, certified reference materials, analytical accuracy, partial least square regression.*

ОЦЕНКА БЕСКАЛИБРОВОЧНОГО И МНОГОМЕРНОГО МЕТОДА КОЛИЧЕСТВЕННОГО АНАЛИЗА В ЛАЗЕРНО-ИСКРОВОЙ ЭМИССИОННОЙ СПЕКТРОСКОПИИ

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УДК 543.42

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(Поступила 1 апреля 2020)

Бескалибровочный метод лазерно-искровой эмиссионной спектроскопии (CF-LIBS) используется для определения концентрации компонентов образцов, поскольку преодолевает ограничение, связанное с необходимостью соответствия матриц стандартного и исследуемого вещества при построении калибровочной кривой. Эффективность такого подхода часто ставится под сомнение. Для проверки возможностей методологии CF-LIBS использованы различные сертифицированные стандартные образцы растений и почвы. Если эмиссионные линии элемента отсутствуют в спектрах LIBS, его вклад в результат CF-LIBS также отсутствует, что приводит к неправильной количественной оценке. Для преодоления этой проблемы в CF-LIBS вместо определения только концентраций элементов вводится дополнительный этап — расчет отношений концентраций всех элементов к концентрации базового элемента. Расчетные отношения концентраций для различных элементов более *точны, чем концентрации элементов, полученные с помощью CF-LIBS. Для предсказания концентрации наряду с CF-LIBS применен подход частичной регрессии наименьших квадратов.*

Ключевые слова: *бескалибровочный метод лазерно-искровой эмиссионной спектроскопии, аттестованные стандартные образцы, аналитическая точность, частичная регрессия методом наименьших квадратов.*

Introduction. Laser-induced breakdown spectroscopy is a useful analytical method for the identification and determination of trace, minor, and major elements in a variety of samples. In this technique, a powerful laser pulse is focused on the sample surface, resulting in the ejection of its material, which leads to the formation of a plasma plume. The emitted radiation from the plasma plume is recorded, and the composition of the sample is determined from the measured spectra by identifying the observed spectral lines [1–7]. This technique is getting more and more attention compared to other elemental analytical methods because it provides *in situ*, rapid, simultaneous multi-elemental analysis. Another major advantage of this technique is its informativity irrespective of the phase of the samples (solid, liquid, or gas). Moreover, it can be performed without any elaborate sample preparation, which is one of the limitations of the conventional techniques, such as AAS, ICP-AES, ICP-MS, etc. [8–13].

In general, the calibration curve method is used for quantitative analysis. In this method, a plot between the known concentration of elements and the respective intensity is drawn for a particular emission line of the element. For the calibration curve, it is necessary to have standard samples of a similar matrix to that of an unknown sample. However, it is not always feasible to prepare matrix-matched standards to that of the unknown sample. To overcome the limitations of matrix-matched standards, a mathematical algorithm is proposed by Ciucci et al. [14], named calibration-free laser-induced breakdown spectroscopy (CF-LIBS). This approach is capable of yielding precise and accurate elemental composition of materials without using calibration curves and internal standards. CF-LIBS has also been reported for the quantitative analysis of a variety of samples [15–18] in which different constituents in the laser-induced plasma are used for determining the concentration of the various elements of the sample.

The spectrum obtained from LIBS contains a large number of variables in the form of intensities corresponding to each pixel. The LIBS spectra of soils and plants are complex, as they contain numerous spectral lines. It is difficult to compare the analytical results for each element using every possible emission line for that element in such a chemically complex matrix. In the analysis of such complex and large variable data, multivariate analysis (MVA) is useful as it allows the analysis of all possible variables, removes the redundant ones, and correlates different variables without losing any useful spectral information. Nowadays, MVA is widely used on LIBS data to utilize the abundant spectral information from the elemental compositions of the sample [19, 20]. Multivariate techniques like principal component analysis (PCA) and partial least square regression (PLSR) are also useful methods to compensate the data points for different deviations [21–23]. The PLSR model on LIBS data can be used to build calibration models and thereafter predict the concentrations of different elements for unknown samples of a similar matrix.

In the present manuscript, an attempt has been made to assess the capability of the CF-LIBS method by computing the concentration ratios of the constituents. A chemometric analysis of LIBS data was also performed using PLSR. The predicted concentrations obtained using the PLSR model of all CRMs were compared with the results obtained from CF-LIBS and the certified values.

Experimental. Six reference materials, namely, three environmental standards (SL1 [IAEA], 1632A, and 2704 [NIST certified]) and three certified reference materials (tea leaf (NCSZC73014), cabbage leaf (NCSZC73012), and milk powder (NCSZC73015) from the China National Analysis Center for Iron and Steel), were used for the analysis. For recording the LIBS spectra, triplicate pellets of each standard (reference material) were prepared using a hydraulic H-Br press machine.

The second harmonic (532 nm) of a Nd:YAG laser (Continuum, Surelite III-10) was focused on the surface of pellets of different certified reference materials using a 15 cm converging lens, which produces plasma on the sample surface. The emission from the plasma was collected using a collimator and finally fed to the spectrometer through an optical fiber. A spectrometer (Mechelle 5000, Andor Technology) equipped with ICCD (iStar, 735DH, Andor Technology) camera was employed to obtain spectra in the region 200–850 nm. LIBS spectra of each pellet (triplicate of each) were recorded under optimized experimental conditions, i.e., at a 50 mJ laser energy, a 1 Hz repetition rate, and a 4 ns pulse width. The position of the collimator (CC 52, Andor Technology) was set to get the maximum emission signal from the plasma plume. Fifty accumulations were employed for recording each spectrum of different standards.

Algorithm of CF-LIBS. A mathematical program in the MATLAB environment was used to calculate the concentrations of different elements. The steps in this program are (1) analysis of LIBS spectra, (2) calculation of the plasma temperature using the Boltzmann plot for each element (species), (3) calculation of the partition function, and (4) calculation of the experimental factor 'F.' For the calculation of the experimental factor, it is assumed that the sum of the concentration of all elements (species) of the sample is 100%.

Statistical treatment. A matrix of the variables (spectral emission lines corresponding to various wavelengths) in the LIBS spectra of different samples was arranged for statistical treatment. The Unscrambler-X software (CAMO Software India Pvt. Ltd.) was used to perform the multivariate analysis on the LIBS spectral data matrix. In the present work, two types of samples (plants and soil) were used; therefore, the data sets were further divided into two matrices, a matrix of 30×23847 for plants and another matrix of 30×24046 for soil samples. PLSR works on the principle of partial least square (PLS), which is widely employed for the analysis of large data. PLS residuals in the calibration model can be minimized by effectively utilizing the spectral information, which reduces the possibility of overfitting and thus improves the accuracy of the model. The dependent variables and independent variables are linearly related in PLSR, which works well, especially when independent variables carry common information, and simplifies the interpretation of the relationship between them. The performance of the PLSR calibration model is validated using a set of unknown samples. Based on the prepared PLSR model, the concentration of the constituent elements of unknown samples can be predicted. Validation test sets are used to compare the effectiveness of the PLSR model. The aim is to develop quick and robust calibration models based on the concentration of different elements in a sample and to use the developed calibration model to predict the concentrations of these elements in unknown samples of the similar matrix. The use of MVA in extracting and analyzing the LIBS spectral information improves the quantitative analytical capability of LIBS and makes it more applicable.

Results and discussion. *Elemental identification.* A typical LIBS spectrum of the tea leaf CRM is shown in Fig. 1. Figure 1 shows the prominent lines of the major elements Mg, Ca, Na, K, Al, Fe, C, etc. present in the plant CRM. Similarly, in the CRMs of soil, Ti, Si, Ba, Mg, Cr, Ca, Na, K, Al, Fe, etc. are observed. The different atomic and ionic species in the spectra were identified using the atomic spectroscopy database of NIST [24].

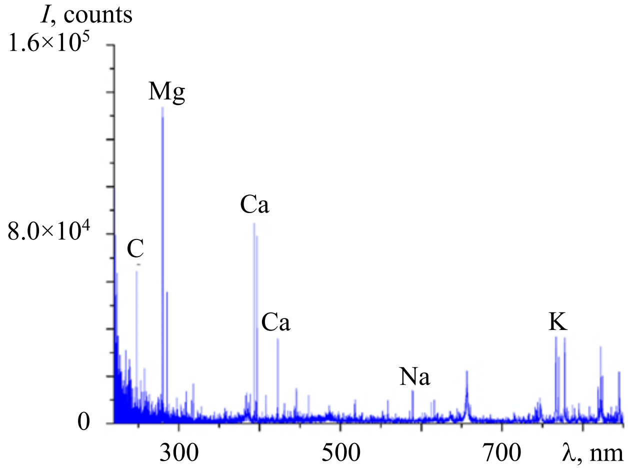

Fig. 1. A typical LIBS spectrum of the tea CRM sample.

Quantitative analysis using CF-LIBS. To employ CF-LIBS for the quantitative analysis of the constituents of the sample, three assumptions must be fulfilled by the laser-induced plasma, namely i) the laser-induced plasma should be stoichiometric, ii) the plasma should be optically thin, and iii) local thermodynamic equilibrium is observed [15–18].

In the present experiment, the laser irradiance at the sample surface was calculated to be ~10^{12} W/cm^2, which is sufficient for the stoichiometric ablation [25]. The optical thinness condition of the plasma was verified using the Ca(II) 315.8 nm and Ca(II) 317.9 nm emission lines. The values of the intensity ratios of two lines (I'/I'') for different samples (Table 1) are close to the values obtained $(A_{ki}'g_k'\lambda'')/(A_{ki}''g_k''\lambda')$, which satisfy the criterion for an optically thin plasma.

For the plasma to be in local thermodynamic equilibrium (LTE), there are two conditions; one is necessary and the other sufficient [25–28]. For the necessary condition, the electron density of plasma calculated from the experimental results using the stark broadening of the suitable emission lines should be higher than the lower limit given by the McWhirter relation [27, 28]:

$$N_e \geq 1.6\times10^{12}[T]^{1/2}[\Delta E]^3, \tag{1}$$

where N_e (cm^{-3}) is the electron density, T (K) is the plasma temperature, and ΔE (eV) is the largest energy difference between two adjacent levels for the allowed transitions.

TABLE 1. Verification of an Optically Thin Plasma

Sample	I'/I'' Ca(II)317.9/Ca(II)315.8nm	$(A_{ki}'g_k'\lambda'')/(A_{ki}''g_k''\lambda')$
NCSZC73014	1.69	1.73
NCSZC73012	1.71	1.73
NCSZC73015	1.73	1.73
IAEA-RM SL1	1.81	1.73
SRM-1632A	1.69	1.73
SRM-2704	1.68	1.73

The plasma temperature for the different species were calculated using the Boltzmann plot shown in Fig. 2. The plasma temperature was obtained between 14000–15000 K for the different standards (Table 2). The lower limit of electron density calculated from Eq. (1) is ~10^{16} (cm^{-3}), and the calculated electron density by measuring the FWHM of the Stark broadened line was found to be ~10^{17} (Table 2), which confirms the existence of the necessary condition for laser-induced plasma in LTE. For the sufficient condition, the ionization temperature should be within 10% of the Boltzmann temperature [27, 28]:

$$\ln\frac{I_{mn}^{\text{ion}}A_{ki}^{\text{atom}}g_k^{\text{atom}}}{I_{ki}^{\text{atom}}A_{mn}^{\text{ion}}g_m^{\text{ion}}} = \ln\left(\frac{2(2\pi kT^{\text{ion}}m_e)^{3/2}}{N_e h^3}\right) - \frac{E^{\text{ion}} - dE + E_m^{\text{ion}} - E_k^{\text{atom}}}{k_B T^{\text{ion}}}, \tag{2}$$

where I_{ki}^{atom} and I_{mn}^{ion} are the integrated emission intensity of the atomic and ionic lines, m_e is the electron mass, h is Planck's constant, T^{ion} is the ionization temperature (K), E^{ion} is the ionization potential of the atom, E_m^{ion} and E_k^{atom} are the upper energy levels of the ionic and atomic species of the elements having transition probabilities A_{mn}^{ion} and A_{ki}^{atom} with statistical weights g_m^{ion} and g_k^{atom}, dE is the lowering correction parameter, and k_B is the Boltzmann constant [27, 28].

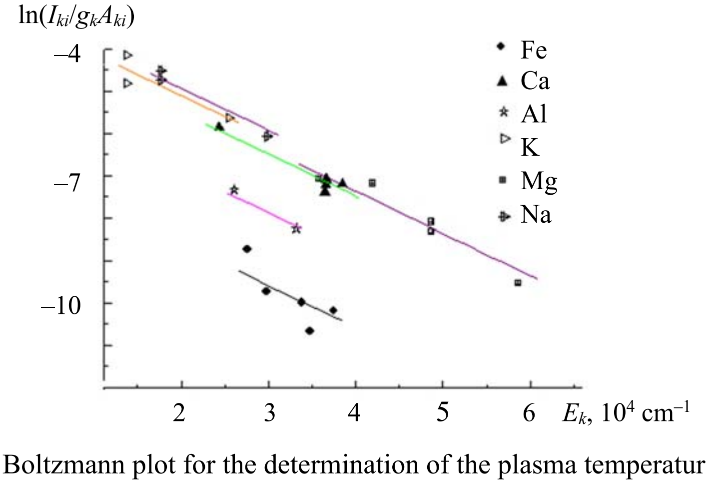

Fig. 2. The Boltzmann plot for the determination of the plasma temperature for the tea CRM sample.

The ionization temperature was calculated using Eq. (2) for all samples, and the values are presented in Table 2. Table 2 confirms that the sufficient condition for laser-induced plasma to be in LTE is also satisfied. As all the assumptions are fulfilled by the laser-induced plasma, the spectral line intensity (integrated intensity) of an element can be used to calculate the constituent concentration in the sample with the CF-LIBS approach. The CF-LIBS algorithm written in MATLAB software was used to evaluate the concentration of the constituent elements of the sample.

TABLE 2. Verification of the Necessary and Sufficient Conditions for a Laser-Induced Plasma

Sample	Plasma temperature (Boltzmann equation)	Ionization temperature (Saha-Eggert equation)	Electron density using the McWhirter criterion	Electron number density with the stark broadened line
NCSZC73014	14691±328	16144±385	7.22×10^{15}	2.12×10^{17}
NCSZC73012	14100±352	15469±341	7.07×10^{15}	2.47×10^{17}
NCSZC73015	14390±470	15807±350	7.15×10^{15}	2.87×10^{17}
IAEA-RM-SL1	14017±412	15278±462	7.05×10^{15}	2.21×10^{17}
SRM-1632A	14352±349	15572±378	7.14×10^{15}	2.53×10^{17}
SRM-2704	14837±402	16090±380	7.26×10^{15}	2.25×10^{17}

In the CF-LIBS method, the evaluation of the concentrations of the different elements is based on the assumption that the sum of the concentration of each of the constituents of the sample is 100%. The concentrations of the constituents of plant and soil CRMs are shown in Tables 3 and 4. It is possible that a few of the minor constituents are present, which either could not be detected or the presence of the spectral lines corresponding to them are below the LOD of the method. In such a case, it is possible that the information regarding the concentrations of the components considered for CF-LIBS may give an inaccurate result. Moreover, when a sample with widely varying concentrations of individual components is analyzed, it is not always possible to ascertain that the experimental condition of the analysis is suitable for all the samples under study. It can be observed in Tables 3 and 4 that the concentrations obtained by CF-LIBS are not very close to the certified values.

TABLE 3. Concentration (mg/kg) of the Constituents in the Plant CRM Calculated Using the CF-LIBS Method and the Certified Values

Element	NCSZC73012		NCSZC73014		NCSZC73015	
	Certified	CF-LIBS	Certified	CF-LIBS	Certified	CF-LIBS
Al	166	300±33	940	1100±112	30	–
Ca	7000	9000±700	3260	3760±380	9400	11968±1230
Fe	98	150±18	57	–	–	–
K	15500	17500±1380	16300	16800±1580	12500	15000±1620
Mg	2410	2644±350	1860	2360±200	960	1257±138
N	28000	30000±3100	51000	53256±5587	38000	48046±4512
Na	10000	12000±950	90	150±13	4700	5986±483
Si	240	300±21	990	1447±150	–	–
Mn	–	–	500	687±72	–	–

To overcome these shortcomings, we considered the option of obtaining the concentration ratio of each of the constituents with respect to one of the major constituents present in the sample, which have significant emission characteristics in the wavelength region of study. The concentrations of each of the constituent elements were calculated using CF-LIBS, and then the concentration ratios were calculated with respect to the major element (preferably having the highest concentration). Tables 5 and 6 represent the ratio of the concentration of the different elements with respect to potassium (K) for the plant samples and with respect to aluminum (Al) for the soil samples. For CRM 2704, the ratio was calculated with respect to silicon (Si). It can be seen that the ratio for the different elements is consistent with that of the certified value up to 20% for most of the elements. It should be noted that although phosphorus (P) was present in significant amounts in the plant samples, the emission intensity was poor and hence could not be used for determining the concentration. This problem led us to calculate the concentration ratio instead of the absolute concentration. The results in Tables 3–6 reveal that better accuracy was obtained when the concentration ratio was computed.

TABLE 4. Concentration (mg/kg) of the Constituents in the Soil CRM Calculated Using the CF-LIBS Method and the Certified Values

Element	SRM-1632 A		SRM-2704		IAEA-RM-SL-1	
	Certified	CF-LIBS	Certified	CF-LIBS	Certified	CF-LIBS
Al	31000	38720±3800	61100	60915±5210	89000	93870±8010
C	–	–	33000	35267±3525	–	–
Ca	2300	3484±352	26000	32061±3360	2500	3754±385
Fe	11100	14713±1250	41100	48091±4380	67400	72279±6472
K	4200	5808±640	20000	22442±2252	15000	16896±1589
Mg	1000	1161±	12000	16030±1590	29000	3285±320
Na	–	–	–	–	1720	938±93
Si	–	–	290800	320610±2500	–	–
Ti	1800	2323±225	4570	9618±895	5170	5632±572
Ba	–	–	414	–	639	750±80
Cr	34.4	38±4	135	–	104	93.8±10
Mn	28.0	–	555	641±52	3460	4693±445
V	44.0	77±10	95	–	170	187±20
Zn	28.0	–	438	641±45	223	281±25

TABLE 5. Concentration Ratio of Different Elements in Plant CRMs

Element	NCSZC73012		NCSZC73014		NCSZC73015	
	Certified[*]	CF-LIBS	Certified[*]	CF-LIBS	Certified[*]	CF-LIBS
Al	0.011±0.002	0.017±0.004	0.058±0.008	0.065±0.002	0.002	–
Ca	0.452±0.030	0.514±0.061	0.200±0.013	0.224±0.017	0.752±0.05	0.798±0.064
Fe	0.006±.001	0.009±0.001	0.003	–	–	–
Mg	0.155±0.016	0.151±0.031	0.114±0.012	0.140±0.021	0.077±0.01	0.084±0.009
N	1.806±0.199	1.714±0.081	3.129±0.318	3.170±0.043	3.040±.28	3.203±0.051
Na	0.645±0.025	0.686±0.093	0.006±0.001	0.009±0.001	0.376±.04	0.399±0.057
Si	0.015±0.004	0.017±0.001	0.061±0.008	0.086±0.006	–	–
Mn	–	–	0.031±0.003	0.041±0.002	–	–

[*] The concentration ratios in the standards were calculated using the concentrations of the different elements in the certificate.

Verification of the methodology. The method was also verified for a bronze sample containing Cu, Al, Fe, and Ni. LIBS spectra of bronze were recorded, and the concentration of the constituents was calculated using the CF-LIBS method. In column A, the concentration of all the elements is reported; in column B the concentration of the constituents is calculated, ignoring one element; and in column C, the concentration is calculated, ignoring two elements (Table 7). It is clear from Table 7 that once we ignore any element, it affects the concentration value of the other constituent elements. However, the concentration ratios in each case of A, B, and C with their highest values remain unchanged. Thus, the proposed method reports the concentration ratio instead of reporting the constituent concentration obtained from CF-LIBS.

Quantitative analysis using the PLSR model. To draw the calibration models using PLSR, the concentrations of different elements and wavelength regions containing the majority of the emission lines of the corresponding elements are chosen for each sample. PLSR calibration models for different elements like Al, Ca, Mg, N, and Na of the plant and Al, Ca, Fe, K, Mg, Si, and Ti of soil are prepared. A typical regression calibration curve of the soil sample for Cr is shown in Fig. 3. Figure 3 shows the predicted vs. reference plot of the PLSR model, in which the predictor is the wavelength range for a particular element and the reference is the concentration value of that element. The coefficient of determination (R^2) and root mean square error (RMSE) assess the performance of the PLSR model. The values of R^2 in different models are nearly 1, while RMSE is very close to 0, which indicates a strong correlation between the predictions and references. Ideally, both the predicted and the reference values should be equal. For the PLSR model, 20 spectra are arbitrarily chosen as a training set, and 10 spectra are arbitrarily chosen as a test set. The prediction of the test sets using the PLSR model gives indications about the strengths and weaknesses of the model. The correlation between the predicted and reference values of these samples is shown in Fig. 3. It is clear that the calibration (blue one) and the validation (red one) deviate very little from the target line due to the high value of R^2, showing that R^2 for the calibration is close to the validation.

TABLE 6. Concentration Ratio of Different Elements in Soil CRMs

Element	SRM-1632 A		SRM-2704		IAEA-RM-SL-1	
	Certified[*]	CF-LIBS	Certified[*]	CF-LIBS	Certified[*]	CF-LIBS
Al	1.000	1.000	0.210±0.006	0.190±0.002	1.000	1.000
C	–	–	0.113±0.001	0.110±0.009	–	–
Ca	0.074±0.010	0.090±0.001	0.089±0.001	0.100±0.003	0.028	0.040±0.001
Fe	0.358±0.006	0.380±0.002	0.141±0.004	0.150±0.007	0.757±0.023	0.770±0.009
K	0.135±0.006	0.150±0.012	0.069±0.002	0.070±0.001	0.169	0.180±0.021
Mg	0.032	0.030±0.001	0.041±0.001	0.050±0.002	0.326	0.035±0.004
Na	–	–	–	–	0.019±0.001	0.010±0.002
Si	–	–	1.000	1.000	–	–
Ti	0.058	0.060±0.005	0.016±0.001	0.030±0.002	0.058±0.004	0.060±0.002
Ba	–	–	0.001	–	0.007±0.001	0.008±0.001
Cr	0.001	0.001	–	–	0.001	0.001
Mn	0.001	–	0.002	0.002	0.039±0.002	0.050±0.001
V	0.001	0.002	–	–	0.002	0.002
Zn	0.001	–	0.002	0.002	0.003	0.003

[*] The concentration ratios in the standards were calculated using the concentrations of the different elements in the certificate.

TABLE 7. Proof of the Concept for Better Accuracy Using the Concentration Ratio

Element	Concentrations (w.%) by CF-LIBS			Concentration ratio with respect to the corresponding highest concentration value		
	A	B	C	A/78.64	B/84.89	C/85.13
Cu	78.64	84.89	85.13	1	1	1
Al	13.73	14.82	14.86	0.174	0.174	0.174
Fe	0.25	0.27	–	0.003	0.003	–
Ni	7.36	–	–	0.093	–	–

N o t e. (A) with all constituent elements; (B) after ignoring one element; and (C) after ignoring two elements.

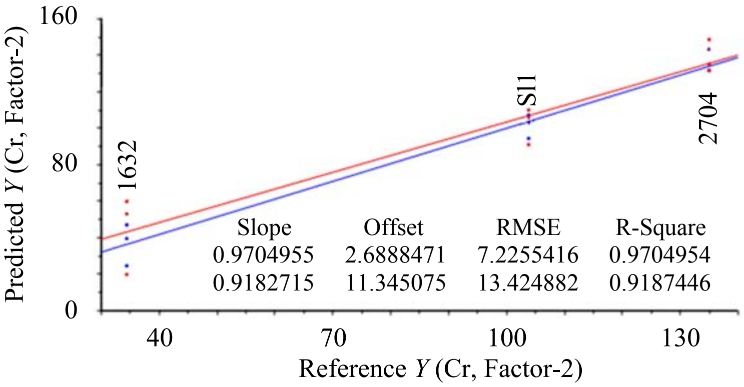

Fig. 3. The prediction vs reference plot of the soil sample.

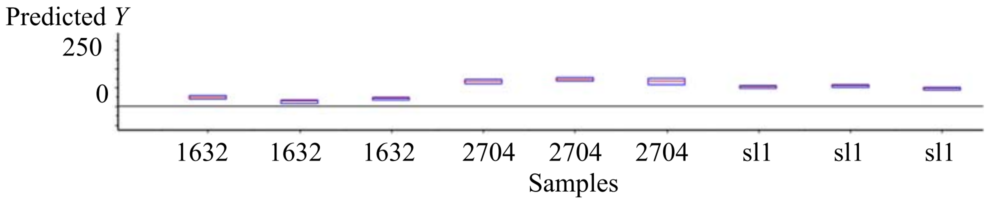

Fig. 4. The predicted values of Cr in the soil samples.

TABLE 8. Comparison of the Concentration Ratio of Different Elements in Plant CRMs Obtained by CF-LIBS and PLSR

Element	NCSZC73012		NCSZC73014		NCSZC73015	
	CF-LIBS	PLSR	CF-LIBS	PLSR	CF-LIBS	PLSR
Al	0.017±0.004	0.009±0.003	0.065±0.002	0.061±0.005	–	–
Ca	0.514±0.061	0.490±0.050	0.224±0.017	0.215±0.011	0.798±0.064	0.749±0.058
Mg	0.151±0.031	0.163±0.024	0.140±0.021	0.124±0.087	0.084±0.009	0.075±0.005
N	1.714±0.081	1.780±0.073	3.170±0.043	3.137±0.981	3.203±0.051	3.146±0.121
Na	0.686±0.093	0.635±0.091	0.009±0.001	0.008±0.001	0.399±0.057	0.389±0.043

TABLE 9. Comparison of the Concentration Ratio of Different Elements in Soil CRMs Obtained by CF-LIBS and PLSR

Element	SRM-1632 A		SRM-2704		IAEA-RM-SL-1	
	CF-LIBS	PLSR	CF-LIBS	PLSR	CF-LIBS	PLSR
Al	1.000	1.000	0.190±0.002	0.192±0.017	1.000	1.000
Ca	0.090±0.001	0.087±0.001	0.100±0.003	0.091±0.001	0.040±0.001	0.031±0.001
Fe	0.380±0.002	0.391±0.018	0.150±0.007	0.145±0.027	0.770±0.009	0.762±0.051
K	0.150±0.012	0.161±0.075	0.070±0.001	0.073±0.001	0.180±0.021	0.171±0.011
Mg	0.030±0.001	0.027±0.001	0.050±0.002	0.045±0.001	0.035±0.004	0.0315±0.002
Si	–	–	1.000	1.000	–	–
Ti	0.060±0.005	0.058±0.001	0.030±0.002	0.020±0.017	0.060±0.002	0.057±0.003

As the PLSR model shows a good correlation between calibration and validation, it can be applied to predict the concentrations of test samples. The concentration of Cr in soil predicted using the PLSR model is shown in Fig. 4; similarly, the concentration of other elements was predicted. Then the concentration ratios of elements with respect to a major element are calculated for plant and soil samples, and the results are tabulated in Tables 8 and 9. A comparison of the concentration obtained from CF-LIBS and using PLSR analysis is given in Tables 8 and 9. It is clear from Tables 8 and 9 that the concentration ratios obtained from different methods are in good agreement, in comparison with the direct concentration results reported in Tables 3 and 4.

Conclusions. This paper describes the potential of the CF-LIBS approach over the traditional calibration curve method for quantitative measurements since matrix matched certified reference materials are not easily available. A better approach is to determine and report the ratio of concentrations instead of only the constituent concentration. It is interesting to employ this method for a variety of standards (soil, sediment, etc.) since LIBS is an attractive method for *in situ,* real-time analysis in a variety of matrices. CF-LIBS using one of the major elements to calculate the ratio provides more useful information in comparison to employing CF-LIBS for determining the exact concentrations. The results also demonstrate that PLSR is powerful for the implementation of multivariate approaches in analyzing the LIBS spectral data and determining the concentration of constituents in unknown samples. In the case of the CRMs, the predicted concentrations by LIBS are comparable to the values obtained from CF-LIBS and the certified concentrations.

Acknowledgments. UGC-BSR project No. F.30-461/2019(BSR) is acknowledged for the startup grant. The Board of Research in Fusion Science and Technology (BRFST), Institute for Plasma Research, Gandhinagar, Gujarat, India is also gratefully acknowledged for financial assistance under Project No. “NFPDIAG-F11-03”. GSM is thankful to the Indian Institute of Technology, Kanpur for providing financial assistance as an institute postdoctoral fellowship (PDF98).

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