Quantitative multiple-element simultaneous analysis of seaweed fertilizer by laser-induced breakdown spectroscopy

QINGYU LIN,[1] PENGKUN YIN,[1] YIXIANG DUAN,[1,3] YING WANG,[2] LIN ZHANG,[2] AND XIAOHUI WANG[2,4]

[1] College of Life Sciences, Research Center of Analytical Instrumentation, Key Laboratory of Bio-resource and Eco-environment, Ministry of Education, Sichuan University, 610064 Chengdu, China
[2] Ministry of Agriculture Key Laboratory of Seaweed Fertilizers, Qingdao Brightmoon Seaweed Group Co Ltd, Qingdao, China
[3] yduan@scu.edu.cn
[4] xiaohui.wang@bmsg.com

Abstract: Laser-induced breakdown spectroscopy, coupled with advanced chemometric methods, was used to quantitate multiple elements in a seaweed-based fertilizer. The influence of important parameters was determined using partial least squares regression (PLSR), support vector regression (SVR) and random forest (RF) optimizations. Optimal results for Mg, K and P were obtained using PLSR, whereas RF yielded the best results for Mn, Cu, Sr and Ca. The best predictions for Ba levels were obtained with SVR. The lowest root mean square errors in the prediction sets for Mn, Cu, Sr, Ba, Mg, K, P and Ca were 48.27 µg/g, 36.90 µg/g, 0.37 mg/g, 40.32 µg/g, 1.99 mg/g, 2.03 mg/g, 4.81 mg/g and 14.08 mg/g, respectively, with average relative standard deviations of 13.65%, 2.68%, 19.80%, 5.17%, 3.32%, 2.98%, 1.82% and 5.81%. The results showed that the optimal multivariate model depended on the specific element being analyzed. The proposed method provides a rapid means of determining multielement concentrations in seaweed-based fertilizers.

1. Introduction

The demand for high-quality agricultural products continues to grow with the world population. The fertilizer industry, which supplies essential nutrients for crop growth, is predicted to grow as a result of this demand [1,2]. The ability to rapidly determine the elemental content in a given fertilizer is key to improving its quality and performance [3]. The most common techniques used to determine elemental concentrations in fertilizers are atomic absorption spectrometry and atomic emission spectrometry. However, these techniques require complicated and time-consuming sample pre-treatment procedures. Alternatively, laser ablation-inductively coupled plasma mass spectrometry (LA-ICP-MS) and X-ray fluorescence (XRF) can be used to directly analyze solid samples. Unfortunately, LA-ICP-MS requires expensive equipment, rendering it impractical for widespread industrialization, and XRF cannot accurately detect lighter elements [4]. Therefore, there is an urgent need for a reliable and direct analytical method that can provide rapid, high-quality information about the elemental composition of solid fertilizers.

Laser-induced breakdown spectroscopy (LIBS) is an elemental analysis technique that measures the spectral emission from elements in a laser-induced plasma. LIBS has been widely applied in a variety of fields over the last decade [5]. The main advantages of LIBS techniques include minimal sample preparation, rapid response and simultaneous multielement identification [6]. These features are ideally suited for direct qualitative and quantitative analyses of fertilizers, as demonstrated in several published reports [7–10]. However, the properties of solid fertilizers, such as particle size and heterogeneity introduce special matrix effects, posing a great challenge

for the laser plasma stability and detection accuracy [11]. The matrix effects in a LIBS plasma are often complex and inevitably non-linear, which leads to inaccurate results when using a univariate calculation method [12]. The precision and accuracy of LIBS techniques are primary concerns in direct analyses. Internal standardization is one of appropriate methods used to minimize fluctuations in LIBS techniques. However, it is difficult to select an adequate internal standard in LIBS analysis [13]. Multivariate regression methods that eliminate interference factors can be used to extract useful information from LIBS spectra and obtain effective calibration curves for quantitative analyses [14,15].

LIBS technique coupled with partial least squares regression could be a reliable and accurate method in the quantitative determination of element in compound fertilizers matrix [16]. Yao et al. employed partial least squares regression method to accurately detect P and K content in fertilizer with LIBS [3]. A commercial analytical strategy employing partial least squares regression has been used to quantitatively analyze mineral fertilizers [17]. A method combined LIBS with Derringer's desirability function was also used to direct analysis the pelletized samples [18]. An ensemble learning algorithm, named Adaboost backpropagation artificial neural network, was used to develop multivariate analysis models in agricultural biochar [11]. Nicolodelli et al. reviewed the last decade of LIBS applications focused on fertilizer characterization. Multivariate algorithms are beneficial to improve the accuracy of the quantitative results by eliminating interference factors and extracting useful information from spectra. LIBS coupled with multivariate chemometric methods is an attractive technique for the direct analysis of solid fertilizer samples [19]. Importantly, multivariate regression methods could be used to reduce redundant information and make a breakthrough in analytical capabilities [20]. However, no LIBS application has been performed on seaweed fertilizers and quantitative measurement in complex matrix fertilizers is still a challenge in LIBS analysis. Therefore, it is important to define the most appropriate experimental conditions, including various spectral preprocessing and multivariate models, for the quantitative analysis of different elements in seaweed fertilizer with LIBS.

The main goal of this study was the development of a LIBS analytical method for multielement simultaneous analysis of seaweed fertilizer samples. Principle component analysis (PCA) was applied to LIBS data to help discriminate and quantitate elemental emission peaks. To our knowledge, no prior study has addressed the multielement, rapid analysis of seaweed-based fertilizers using LIBS combined with various multivariable algorithms. Here, LIBS data were processed using several advanced chemometric methods, including partial least squares regression (PLSR), support vector regression (SVR) and random forest (RF) algorithms, to predict the multielement content in seaweed fertilizer. The data pre-treatment methods and input variables used in the regression analyses were optimized and quantitative methods were constructed for each target element.

2. Experiment

2.1. Sample preparation

Eight seaweed fertilizer samples were supplied by the Ministry of Agriculture Key Laboratory of Seaweed Fertilizers (Qingdao, China). The samples were oven-dried at 50°C for 1.5 h to attain a constant weight. Dried samples were ground in a blender. The obtained powder was selected through a sieve to obtain a uniform particle size (100 mesh, 150 μm) and stored at 4°C before use. For LIBS measurements, 500 mg of dried sample was put into a tableting press (FW-5, Botian, Tianjin, China) and pressed at 10 atm for 120 s. The resulting thickness and diameter of each pellet was about 2 mm and 12 mm, respectively. Five pellets were prepared for each sample. Thus, 40 pellets of eight seaweed fertilizer samples were obtained. For reference, the concentrations of Mn, Cu, Sr, Ba, Mg, K, P and Ca in each sample were measured by inductively coupled plasma-optical emission spectroscopy (ICP-OES) with a model OPTIMA 8000 (PerkinElmer,

Shelton, CT, USA). To prepare for ICP-OES analysis, 200 mg of each fertilizer sample was digested in a boiling mixture of 4 mL of aqua regia ($HNO_3 + 3HCl$) and 1 mL of 30% H_2O_2 to obtain a clear solution.

2.2. LIBS measurement

A schematic diagram and detailed description of the experimental LIBS setups used in this study has been published previously [21]. Briefly, a Nd:YAG laser was selected as the excitation source (wavelength 1064 nm, pulse duration 6 ns, Litron Lasers, Rugby, UK). The laser beam was perpendicularly focused onto the surface of the sample pellets with a 10× objective lens, producing a spot ~200 μm in diameter. The vertical position of the sample was monitored using two crossed red laser beams at oblique incidence on the sample surface. A collimating lens (74-UV Ocean optics, 5 mm diameter, 10 mm focal length) was held on a micro *xyz*-translation stage at an accident angle of 45° to the target surface for collimating the plasma signal into a coupling fiber (400 μm core diameter). The fiber was connected to an echelle spectrometer (Aryelle200; Lasertechnik Berlin GmbH, Berlin, Germany; 193-840 nm, spectral resolution: $\lambda/\Delta\lambda = 9000$) equipped with an ICCD camera (iStar, Andor Technology, Belfast, UK). The wavelength calibration of the spectrometer and spectral response of the detection system were performed with mercury argon lamp and a certified deuterium halogen tungsten light source (AvaLight-DH-BAL-CAL, Avantes), respectively. The overall linear dispersion of the spectrometer camera system ranges from 24 pm (at 220 nm) to 83 pm per pixel (at 750 nm). The widths of spectral lines were determined by the mercury argon lamp source. The laser pulse energy was fixed to 80 mJ with a repetition rate of 5 Hz. In order to compensate for the decreasing emission signals due to the rapid decay of the plasma and obtain good signal-to-noise ratio (SNRs), an optimized delayed detection window and an adjusted for gate width were used. LIBS spectra were acquired with a delay of 1.0 μs, and the gate width of the camera was set to 100 μs. To obtain a sufficient SNRs, each spectrum represents the accumulation of ten ablation events, and a total of 20 spectra were collected for each sample.

2.3. Multivariate regression algorithm

PLSR, SVR and RF were used to construct an optimal quantitative method for each of the target elements in the seaweed fertilizer. Before modelling, five samples (seaweed organic fertilizer 100%, seaweed organic fertilizer powder 100%, seaweed organic-inorganic compound fertilizer, water-soluble fertilizer and macro-element water-soluble fertilizer) were randomly selected as the calibration set. Three additional samples (seaweed organic fertilizer 50%, seaweed extract powder and compound fertilizer) were selected as the prediction set to evaluate the performance of the established models. Thus, 100 spectra were used to construct the calibrate model and 60 spectra were used to test model. The linear correlation coefficient (R) between the ICP-OES-measured value and the LIBS-predicted value was used to evaluate the predictive ability of each model. The root mean square error (RMSE) was used to evaluate the prediction accuracy of the calibration model and the relative standard deviation (RSD) was used to evaluate the precision of the model. The formulae used to calculate RMSE and RSD are as follows:

$$RMSE = \sqrt{\frac{\sum_{i=1}^{n} (y_i - y_{ip})^2}{n-1}} \tag{1}$$

$$RSD(\%) = \frac{S}{X_m} \times 100\% \tag{2}$$

where y_i is the reference value (ICP-OES-measured value) of sample i, y_{ip} is the prediction value (LIBS-predicted value) of sample i, n is the number of spectra, S is the standard deviation and X_m is the mean of the predicted values. The root mean square error of calibration (RMSEC) and the

root mean square error of prediction (RMSEP) represent model performance with regard to the calibration samples and test samples, respectively. MATLAB R2018a software (MathWorks, Natick, MA, USA) was used to perform the data analysis and statistical multivariate analysis.

3. Results & discussion

3.1. Qualitative spectral analysis

Averaged LIBS spectra of seaweed fertilizer samples are given in Fig. 1. Figures 2(a–d) show representative elemental emission spectra from the seaweed fertilizer samples. Stronger emission lines, including those from Mn, Mg, Ca, K, Na, and Sr, could be visibly differentiated in this spectrum. From these spectra, we also can see that emissions from certain numbers of trace elements like Si (288.15 nm, 390.53 nm), and Fe (371.99 nm, 373.49 nm, 373.71 nm, 374.56 nm, 374.83 nm, 374.95 nm, 375.82 nm, 382.04 nm) are still observable with satisfying SNRs. The identification of these lines was performed by comparison with reference data in the National Institute of Standards and Technology (NIST) database. However, eight elements (Mn, Cu, Sr, Ba, Mg, K, P and Ca) were studied in this experiment, so only the characteristic peaks of these eight elements were listed. A total of 75 characteristic spectral lines belonging to the eight target elements, with no interfering peaks from other elements, were selected for numerical analysis. These lines were extracted from the data as shown in Table 1.
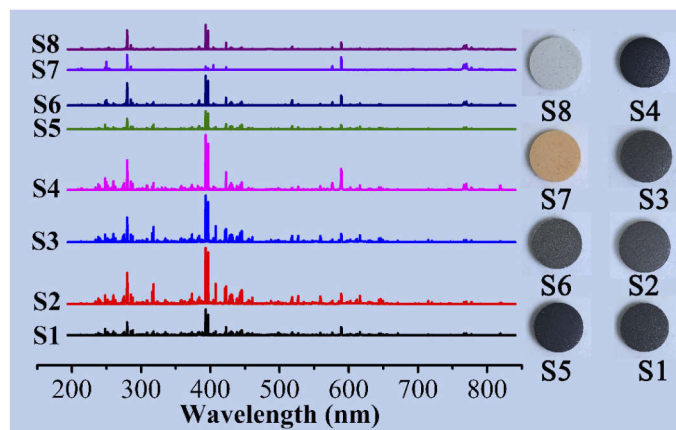

Fig. 1. The averaged LIBS spectra of seaweed fertilizer samples (S1 seaweed organic fertilizer 50%; S2 seaweed organic fertilizer 100%; S3 seaweed organic fertilizer powder 100%; S4 seaweed extract powder; S5 Seaweed organic-inorganic compound fertilizer; S6 Water soluble fertilizer; S7 Macro element water soluble fertilizer; S8 Compound fertilizer).

Based on spectral patterns, it was possible to classify the samples into different groups [22]. PCA was applied to all of the acquired LIBS data. Figure 3 presents the resulting score plot using PC1, PC2 and PC4. Each group is shown with a different color for better visualization. PC1 accounted for 88.48% of the total variability, where PC2 (7.24% of the total variability) and PC4 (0.88% of the total variability) provided supplemental information. Seaweed organic fertilizer 50%, seaweed extract powder, water-soluble fertilizer, macro-element water-soluble fertilizer, and compound fertilizer could be distinguished, as illustrated in Fig. 3. However, seaweed organic fertilizer 100%, seaweed organic fertilizer powder 100%, and seaweed organic-inorganic compound fertilizer were clustered together, suggesting that these fertilizers were similar in elemental composition and matrix. A previous study found that flours with similar LIBS spectral patterns tended to cluster together in PCA plots [22]. Thus, PCA alone is suitable for the
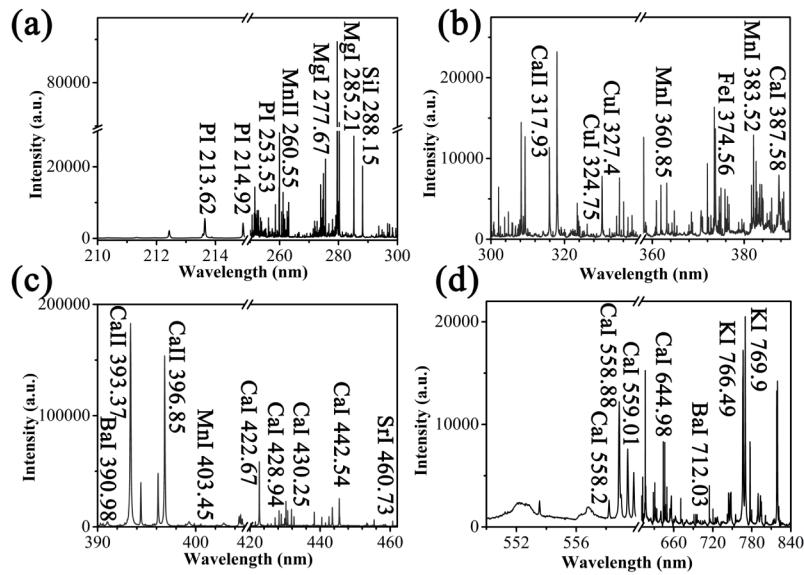
Fig. 2. Representative LIBS spectra of macro element water soluble fertilizer sample.

Table 1. Spectral lines of the target elements.

Element	Spectral lines/nm							
Mn I	360.85	383.52	403.08	403.31	403.45	408.23		
Mn II	257.61	259.37	260.55	293.93	294.92			
Cu I	324.75	327.4						
Sr I	460.73	640.85						
Sr II	407.77	421.55						
Ba I	390.98	399.38	553.55	712.03				
Ba II	252.84	455.4	493.41	585.37	649.69			
Mg I	277.67	277.98	278.15	285.21	294.2	333.21	382.94	383.23
	383.83	516.72	517.27	518.36				
Mg II	279.08	279.55	279.8	280.27	385.04	433.19		
K I	766.49	769.9						
P I	213.62	214.92	253.53					
Ca I	387.58	422.67	428.94	429.9	430.25	430.77	431.87	442.54
	443.50	445.48	487.81	534.95	558.2	558.88	559.01	559.44
	559.85	612.22	643.91	644.98	645.56	646.26	649.38	
Ca II	317.93	393.37	396.85					

qualitative classification of seaweed fertilizers based on the variance of their corresponding LIBS spectra.

3.2. Quantitative analysis

Exploiting the linear relationship between the intensity of a given characteristic elemental peak and the concentration of that element in the sample matrix is the most common quantitative protocol. However, LIBS spectra can be notoriously noisy, inconsistent, scattered, incomplete and
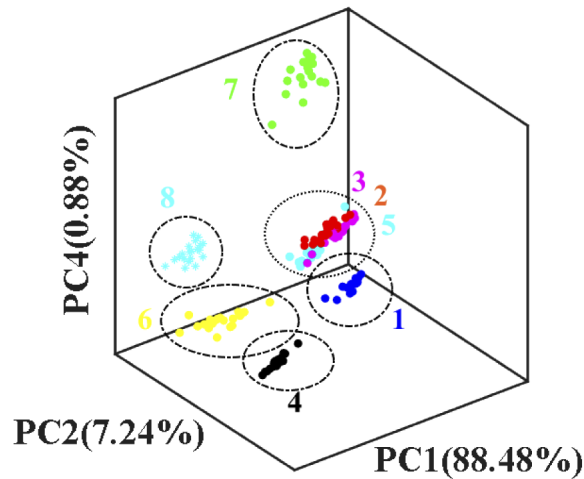
Fig. 3. The 3D PCA score plots. (1 seaweed organic fertilizer 50%; 2 seaweed organic fertilizer 100%; 3 seaweed organic fertilizer powder 100%; 4 seaweed extract powder; 5 seaweed organic-inorganic compound fertilizer; 6 water soluble fertilizer; 7 macro element water soluble fertilizer; 8 compound fertilizer).

uncertain [23]. In addition, matrix effects associated with laser ablation and plasma generation can result in non-linear interactions [20]. Therefore, as a first step in our quantitative analysis, five pre-treatment methods (normalization by maximum, normalization by the sum of all signals, and normalization by vector, scale, and first derivative) were performed to enhance the accuracy of the model. Leave-one-out cross-validation was conducted to avoid over-fitting the model [23]. The results were evaluated according to root mean squared error of cross-validation (RMSECV). Figure 4 shows the resulting RMSECV values obtained with different data pre-treatment methods. Normalization by the sum of all signals yielded the highest RMSECV values for Cu, Sr, K, P and Ca. Normalization by vector yielded the best results for Mn, Ba and Mg.
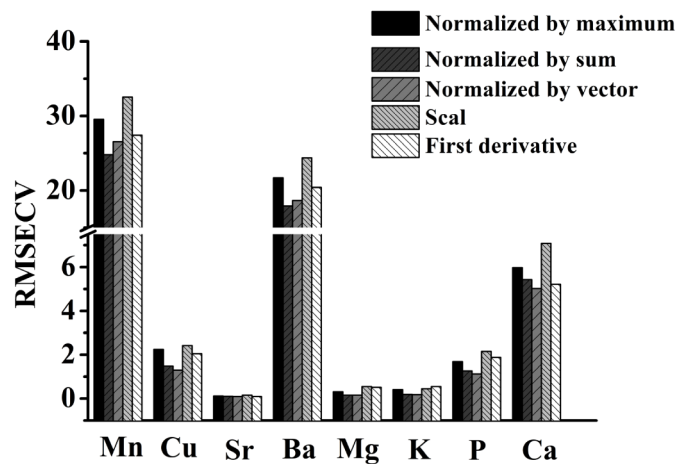

Fig. 4. The RMSECV values obtained with different data pre-treatment methods.

To reduce noise, a reduction in the number of variables was performed by selecting only wavelength ranges containing useful peaks [24]. The PCA scores, the peak intensity of featured

lines for each element and different wavelet functions of Daubechies (db1-db8) were investigated. The results of leave-one-out cross-validation were also evaluated by the resulting RMSECV values (Fig. 5). The RMSECV values were lower for Mn, Ba, Mg, Sr and K when using the db4 wavelet function to generate input variables. However, db1, db2 and db8 yielded better results for Cu, Ca and P, respectively.
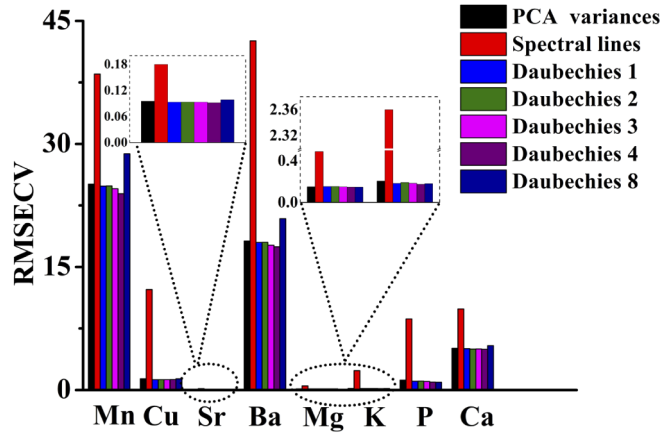

Fig. 5. The RMSECV values obtained with different variable selection methods.

Table 2. Optimal parameters used to construct the multivariable quantitative model.

Element	Pre-treat method	Input variables	Variable numbers	PLSR	SVR		RF	
				Latent variable	c	g	n_{tree}	m_{try}
Mn	Normalized by vector	Wavelet function of Daubechies 4	2730	13	256	48.50	500	910
Cu	Normalized by sum of all signals	Wavelet function of Daubechies 1	21709	14	256	256	500	7236
Sr	Normalized by sum of all signals	Wavelet function of Daubechies 4	2730	16	256	256	500	910
Ba	Normalized by vector	Wavelet function of Daubechies 4	2730	13	256	27.86	500	910
Mg	Normalized by vector	Wavelet function of Daubechies 8	188	11	256	9.19	500	910
K	Normalized by sum of all signals	Wavelet function of Daubechies 4	2730	13	256	256	500	910
P	Normalized by sum of all signals	Wavelet function of Daubechies 8	188	16	256	256	500	62
Ca	Normalized by sum of all signals	Wavelet function of Daubechies 2	2730	14	256	256	500	3621

Table 2 lists the optimal parameters, including pre-treatment method, input variables, and the number of variables used to construct multivariable quantitative models, for the eight target elements. The optimal latent variables in the PLSR model, the significant penalty parameter c and the kernel parameter g in the SVR model, and the random regression tree forest tree (n_{tree}) and characteristics of random variables (m_{try}) of the RF model are also listed in Table 2.

The data in Table 3 show the predictive performance of the PLSR, SVR and RF models. The PLSR and RF models exhibited the highest correlation coefficients of around 0.99 for all of the target elements, whereas the SVR model exhibited a coefficient of 0.99 for only Mn, Cu, Ba and K. The accuracy of each model was evaluated according to the RMSEP values obtained with the test groups. The RMSEP values obtained for Mn, Sr, Mg, K and P using the PLSR model were lower than those obtained with the SVR and RF models. However, the predicted results for Sr and Mn using the PLSR and SVR models yielded some negative values, which is unacceptable for practical applications. Thus, the RF model was selected as optimal for quantitative analyses of Sr and Mn. Finally, the predicted errors with the best calibration results for Mn, Sr, Mg, K and P were 48.27 µg/g, 0.37 mg/g, 1.99 mg/g, 2.03 mg/g and 4.81 mg/g, respectively. In contrast, RMSEP values obtained using the RF model for Cu and Ca, 36.90 µg/g and 14.08 mg/g, respectively, were significantly lower than those obtained with the PLSR and SVR models. The lowest RMSEP for Ba was 40.32 µg/g, obtained with the SVR model. Therefore, of the three numerical methods, SVR was deemed the most suitable for quantitative analysis of Ba. We hypotheses that is due to difference of the prediction mechanisms between linear and nonlinear algorithms. Moreover, the level of noise, baseline drift and overlapping peaks of target elements are different during the LIBS spectral acquisition process, which may affect the quantitative analysis results. Other authors that studied the quantitative and classification analyses of atmospheric sedimentation also found that each metal in atmospheric sedimentation has its own suitable quantitative analysis method [25].

Table 3. Predictive performance of calibration and test sets of PLSR, SVR and RF models for target elements.

Elem-ents	PLSR				SVR				RF			
	Calibration group		Test group		Calibration group		Test group		Calibration group		Test group	
	R	RMSEC	R	RMSEP	R	RMSEC	R	RMSEP	R	RMSEC	R	RMSEP
Mn µg/g	0.9953	14.02	0.9459	44.26	0.9952	14.16	0.7624	116.38	0.9992	6.00	0.9423	48.27
Cu µg/g	0.9998	0.39	0.9586	37.65	0.9900	3.07	0.9260	37.65	0.9996	0.63	0.7420	36.90
Sr mg/g	0.9992	0.037	0.9045	0.089	0.8136	0.98	0.8391	0.090	0.9978	0.064	0.8733	0.37
Ba µg/g	0.9955	10.23	0.9485	63.78	0.9948	11.01	0.9236	40.32	0.9990	4.85	0.9434	47.84
Mg mg/g	0.9992	0.11	0.9350	1.99	0.9841	0.62	0.8132	2.17	0.9985	0.22	0.1965	2.73
K mg/g	0.9998	0.076	0.8581	2.03	0.9905	4.07	0.9733	2.20	0.9998	0.099	0.9573	2.05
P mg/g	0.9994	0.56	0.9657	4.81	0.8631	16.34	0.9757	7.46	0.9990	0.74	0.4981	6.66
Ca mg/g	0.9990	1.88	0.8954	18.27	0.8195	43.09	0.8053	27.12	0.9989	2.03	0.9306	14.08

Figure 6 and Fig. 7 show optimal scatter plots of ICP-OES data versus LIBS-predicted values for the eight target elements. All of the calibration models for the target elements showed high correlations when applied to the seaweed fertilizer samples. Note that the Cu content in the

seaweed organic fertilizer 50% test sample was 107.23 μg/g (see Fig. 6(b)), which was beyond the linear range of the calculate curve. Thus, the predicted result for this sample showed a relatively high RMSEP. RSDs were calculated as a measure of precision of the regression models. The average RSDs for Mn, Cu, Sr, Ba, Mg, K, P and Ca were 13.65%, 2.68%, 19.80%, 5.17%, 3.32%,
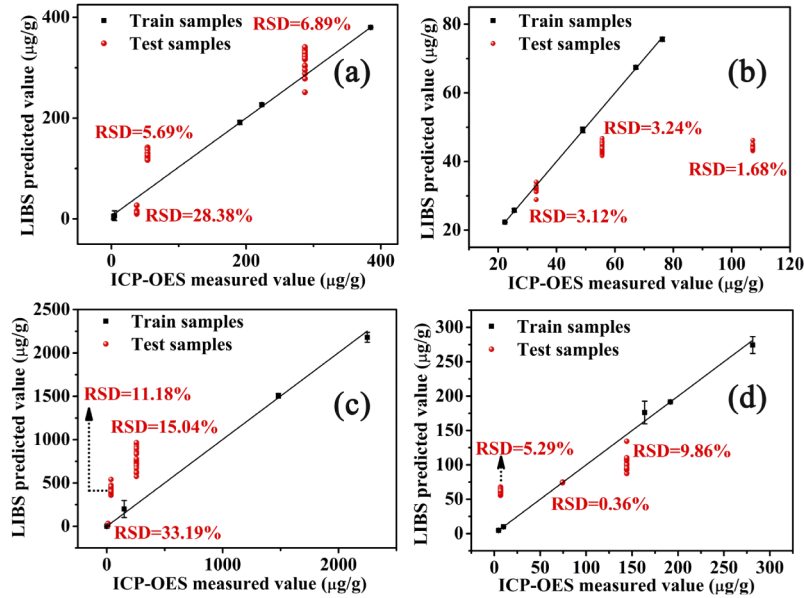

Fig. 6. The performance of each numerical model for determining multielement concentrations in calibration samples: (a) RF model for Mn, (b) RF model for Cu, (c) RF model for Sr and (d) SVR model for Ba.
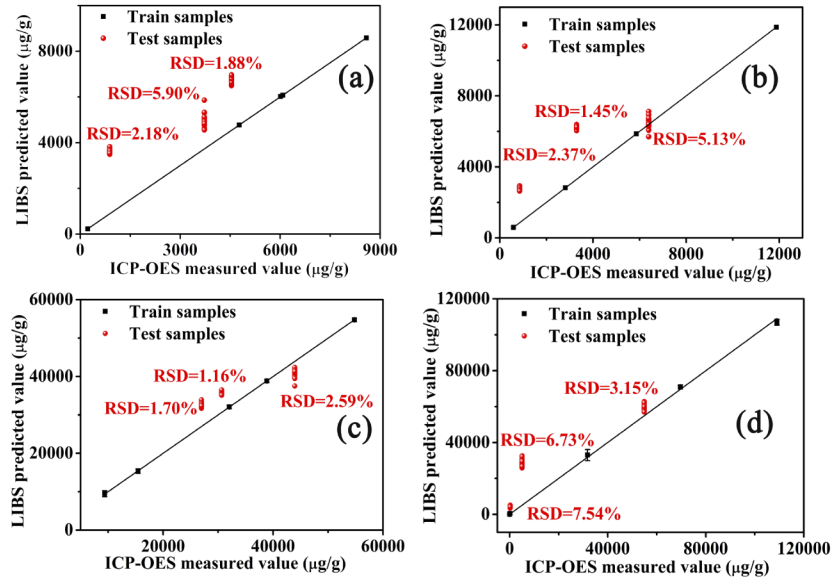

Fig. 7. The performance of each numerical model for determining multielement concentrations in calibration samples: (a) PLSR model for Mg, (b) PLSR model for K, (c) PLSR model for P and (d) RF model for Ca.

2.98%, 1.82% and 5.81%, respectively. These predicted results are satisfactory and confirm that the chemometric methods described herein are applicable to quantitative, multielement detection in seaweed fertilizers.

4. Conclusions

The rapid and direct quantitation of the elemental content of fertilizers is important for quality control. The results presented herein indicate that LIBS coupled with advanced chemometric methods is suitable for quantitative, multielement analysis of seaweed fertilizers. PCA analysis of LIBS spectra can be used to categorize seaweed fertilizers according to the mixture matrix. In addition, multivariable quantitative methods were constructed for direct analyses of Mn, Cu, Sr, Ba, Mg, K, P and Ca. This study shows that a single quantitative algorithm is not suitable for all elements. Instead, it is important to select an optimal multivariate model for each element. In follow-up work, in order to have a better understanding on the characteristics of different algorithms and achieve more precise prediction, more elements in more different kinds of matrix will be studied.

Disclosures

The authors declare no conflicts of interest.

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