QUANTITATIVE ANALYSIS OF NITROGEN IN COMPOUND FERTILIZERS USING LASER-INDUCED BREAKDOWN SPECTROSCOPY COUPLED WITH MULTIVARIATE REGRESSION

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Quantitative analyses of the nitrogen concentration in compound fertilizer were performed using laser-induced breakdown spectroscopy (LIBS). Thirty-two samples were used as a calibration set, and eight samples were used as a validation set. To eliminate the matrix effect, partial least-squares regression (PLSR) and least-squares support vector regression (LS-SVR) were used to establish models. For the partial least-squares regression model, the correlation coefficients for the calibration and prediction sets were 0.837 and 0.794, respectively. While using the LS-SVR method, the correlation coefficients for the calibration and prediction sets were improved to 0.994 and 0.993, respectively. Therefore, the LS-SVR method improved the analysis accuracy. The prediction mean absolute error was 0.023%. The results indicate that LIBS coupled with LS-SVR is a reliable and accurate method for determining the nitrogen concentration in compound fertilizer.

Keywords: *Laser-induced breakdown spectroscopy, compound fertilizer, nitrogen, multivariate regression.*

КОЛИЧЕСТВЕННЫЙ АНАЛИЗ АЗОТА В СЛОЖНЫХ УДОБРЕНИЯХ С ИСПОЛЬЗОВАНИЕМ ЛАЗЕРНОЙ АТОМНО-ЭМИССИОННОЙ СПЕКТРОСКОПИИ В СОЧЕТАНИИ С МЕТОДОМ МНОГОМЕРНОЙ РЕГРЕССИИ

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С помощью лазерной атомно-эмиссионной спектроскопии (LIBS) проведен количественный анализ концентрации азота в сложных удобрениях. Тридцать два образца использованы в качестве калибровочного набора, восемь образцов — в качестве проверочного набора. Для построения моделей и устранения матричного эффекта использованы частичная регрессия методом наименьших квадратов и регрессия опорных векторов методом наименьших квадратов (LS-SVR). Для модели частичной регрессии методом наименьших квадратов коэффициенты корреляции для наборов калибровки и прогнозирования составили 0.837 и 0.794. С использованием метода LS-SVR коэффициенты корреляции для наборов калибровки и прогнозирования улучшены до 0.994 и 0.993. Таким образом, метод LS-SVR повышает точность анализа. Средняя абсолютная ошибка прогноза 0.023%. Показано, что LIBS в сочетании с LS-SVR является надежным и точным методом определения концентрации азота в сложных удобрениях.

Ключевые слова: *лазерная атомно-эмиссионная спектроскопия, комплексное удобрение, азот, многомерная регрессия.*

Introduction. In China, compound fertilizers are used extensively in agriculture to increase crop yields. According to statistics, China is the largest user of compound fertilizer in the world. If the compound fertilizer is applied in excessively, it can cause accumulation of heavy metals in soil. Currently, the methods used by fertilizer manufacturers for compound fertilizer testing are national standard methods [1], atomic absorption spectroscopy [2], flame atomic absorption spectrometry [3], and inductively coupled plasma-atomic

emission spectroscopy [4]. All of these methods require on-site sampling and analysis after laboratory pretreatment, and are time-consuming, expensive, and use a number of consumables. These methods cannot provide real-time information during the production process. The rate of qualification of compound fertilizer products is approximately 97% [5], and unqualified products need to be processed, which causes huge economic losses. Thus, a rapid and accurate technique for determining the elemental composition of compound fertilizer is urgently needed.

Laser-induced breakdown spectroscopy (LIBS) is a rapid and practical method for elemental analysis. This technique is based on atomic emission spectroscopy, but has many advantages. LIBS involve minimal sample preparation, is nondestructive, can be used for multi-element analysis and applied in situ, and provides rapid detection. This method can be used for qualitative and quantitative analysis of matter in any state [6]. LIBS has been widely applied in the areas of water pollution, soil monitoring, coal combustion, agriculture, industrial metallurgy, and archeology [7–12]. A number of studies have used LIBS to determine the elemental compositions of compound fertilizers. Farooq et al. used LIBS to determine the concentrations of P, Mg, and Mn in fertilizer, but the detection limit was not provided [13]. Andrade et al. used LIBS to analyze liquid fertilizer after conversion to a solid. The elements Cu, K, Mg, Mn, Zn, As, Cd, Cr, and Pb were analyzed and the absolute errors ranged from 0.02 to 0.06%, which indicated that LIBS could be used for liquid fertilizer analysis [14]. Yao et al. analyzed phosphorus and potassium in compound fertilizer, and a calibration model was constructed using the partial least squares method in Unscrambler software [15]. Marangoni et al. used LIBS to analyze phosphorus in 26 organic and inorganic fertilizers [16]. However, there were only two verification samples and the absolute error was close to 5%. Nicolodelli et al. analyzed phosphate rock and organic phosphate fertilizer using single-pulse and dual-pulse LIBS. Principal component analysis and partial least squares regression (PLSR) methods were used to classify samples, and the classification results reached 95% confidence, which demonstrated that LIBS could be used to rapidly classify phosphate fertilizer *in situ* [17]. Zhang et al. used LIBS coupled with linear multivariate calibration to analyze nitrogen in ammonium phosphate fertilizer, and obtained a maximum relative error for eight validation samples of 4.32% [18]. All of the above studies have shown that LIBS can be used to analyze the components of chemical fertilizer. However, application of LIBS in the field for quantitative analysis has been limited by its accuracy and stability.

LIBS is seriously affected by the matrix effect, especially with complex samples. In addition, compound fertilizer contains multiple elements, which can result in mutual interference between characteristic spectral lines. Thus, the results of a traditional calibration model using univariate analysis may not be reliable. In recent years, multivariate regression methods had been used in LIBS quantitative analysis. These methods can eliminate interfering factors to a certain extent and extract features from the spectra. Yang et al. applied LIBS coupled with PLSR to detect Cu and Zn in soil. For the prediction set, the correlation coefficient (R^2) was 0.94 [19]. Gao et al. used LIBS to analyze different soil types [8], and the concentrations of Ca, Na, K, Si, Al, Mg, Mn, Ba, Ti, Cr, Cu, Sr, and P in the soil were quantitatively analyzed by constructing PLSR models. The prediction results were compared with those from standard detection methods, and the relative errors for Si, Sr, and Al were less than 10%. He et al. analyzed nutrient elements in soil by single-pulse and double-pulse LIBS with PLSR and support vector regression (SVR) for quantitative analysis [20]. For all of the nutrient elements the R^2 for both the calibration and prediction sets were greater than 0.95. These results demonstrated that LIBS coupled with PLSR and least-squares support vector regression (LS-SVR) methods could be used to detect nutrient elements in soil [20]. Liu et al. used LIBS with PLSR and LS-SVR to quantitatively analyze Cd in soil [21]. The root-mean-square error of calibration (RMSEC) and root-mean-square error of prediction (RMSEP) were only 0.026 and 0.034, respectively. The results showed that the LS-SVR model performed better than the PLSR model. Shi et al. used LIBS for quantitative analysis of sedimentary rock samples, and results for Si, Ca, Mg, Fe, and Al obtained by the PLSR and SVR methods were compared. For the SVR model, the parameter optimization method was a genetic algorithm. The results of SVR model were more accurate and robust under the optimized conditions than those using in the PLSR method [22].

In China, nitrogen in soil cannot meet the nutrient requirements of green vegetables. The purpose of this paper was to evaluate LIBS for determination of the nitrogen concentration in compound fertilizer for real agricultural applications. Forty compound fertilizer samples were provided by the Red Sifang Group (Bengbu, Anhui Province, China). The nitrogen concentrations in these samples were first determined by inductively coupled plasma mass spectroscopy to provide reference values. The multivariate calibration methods, PLSR and LS-SVR, were used to establish analysis models for all samples. The quantitative analysis results obtained using the two models were compared to evaluate their performance.

Experimental. The LIBS system (Fig. 1) used in this experiment contained a Nd:YAG pulsed laser (ICE450, 1064 nm; Quantel Laser, Morgan Hill, CA, USA), a sample stage that could rotate along the *x*–*y* axis for the compound fertilizer sample, and a grating spectrometer with a charge-coupled device detector. The laser energy was 100 mJ, and the laser was focused by a plano-convex lens (ø25.4 mm, focal length 40 mm) onto the compound fertilizer sample. The peak power density on the compound fertilizer sample was approximately 2.2 GW/cm^2, and the diameter of the spot was 0.5 mm. Plasma light was collected using a quartz lens with a focal length of 3.5 cm and focused onto an optical fiber (ø200 μm). Then, the plasma light was transported to the spectrometer (Avantes-ULS2048-USB2, Avantes, Apeldoorn, the Netherlands), which could simultaneously record spectra within the ranges of 190–510 and 690–890 nm. The spectral resolution was 0.1 nm. A digital delay generator in the spectrometer was used to control the gate delay time. The delay time was 1.28 μs, and the integration time was 1.05 ms (spectrometer minimum integration time) [23]. Because of the presence of nitrogen in air, any air in the cylinder was replaced with an argon atmosphere to protect the surface of the compound fertilizer sample (Fig. 1).

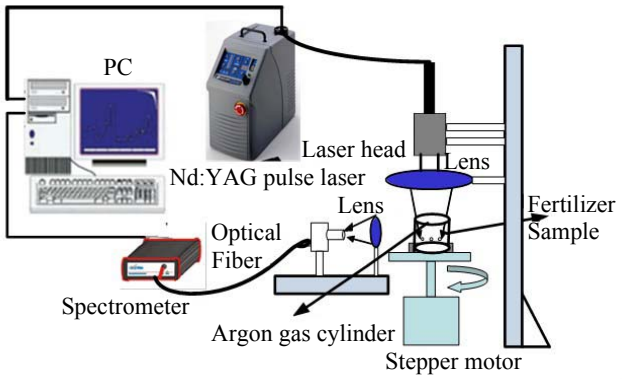

Fig. 1. LIBS detection system for compound fertilizer samples.

Forty compound fertilizer samples were collected and placed into sealed plastic bags to avoid contamination. Because the compound fertilizer samples were pelletized, we first ground these samples into powders. Then, a quantity of powder (5 g) from each of the 40 samples was weighed and pressed into a tablet (ø25 mm) under a pressure of 2 MPa for 60 s (769YP-40C, KQ, Tianjin, China) [23]. The nitrogen concentrations (C_{min} = 9.62%, C_{max} = 10.96%, C_{mean} = 10.39%, standard deviation SD = 0.35%) in these samples were determined by inductively coupled plasma mass spectroscopy (ICP-MS) as reference values. The samples were then analyzed by LIBS, with eight measurements recorded for each sample. Each measurement was collected with an average of 20 laser shots. In this paper, Lorentzian line fitting was used to calculate the line height. The experimental data were analyzed using MATLAB software and graphed using Origin 8.0 software (OriginLab).

The commonest and simplest quantitative analysis method in LIBS is the traditional calibration method. The spectral line intensity is proportional to the concentration of an element in the sample if there is no self-absorption effect and the plasma is under local thermal equilibrium. A calibration curve can be established using the intensity of the spectral line and concentration of the corresponding element. The concentrations of unknown samples can be determined by using the calibration curve. Because of the matrix effect, interference of spectral lines among elements, and many other factors, quantitative analysis of LIBS results is complicated. The traditional calibration curve method, which focuses on only a single line of an element, may miss some useful information. Multivariate calibration that uses chemometrics to improve the accuracy of quantitative analysis can overcome these limitations.

Multivariate calibration has been widely used for quantitative analysis of LIBS results. This method can consider the signals of the analytical element and other related elements in the sample. Thus, it can improve the accuracy of quantitative analysis. PLSR, as a classical linear modeling method, is widely used in quantitative analysis of LIBS results. This method can incorporate principal component analysis, canonical correlation analysis, and multivariate linear regression. The best latent variables are obtained by decomposing the spectral and concentration matrix. Information that is not useful is eliminated by linear transformation. Then, a linear relationship between the spectral properties and the concentration of the target element is established

as a basis for quantitative analysis. This calibration model can later be used to predict the concentration of the target element in unknown samples.

Least-squares support vector regression is a supervised machine-learning method which is based on the standard SVR objective function with the addition of a squared error term. This method is a multivariate nonlinear correction method, and is particularly suitable for regression analysis of small numbers of samples [24]. Recently, it has been used in quantitative analysis of LIBS results, and shows good learning performance with nonlinear regression problems. In the analysis of this method, the observed value was the sample value, and the theoretical value was defined as the fitting function. The fitting function model was obtained when the objective function was the smallest. The objective function can be set as follows:

$$h_\theta(x_1, x_2, ...x_n) = \theta_0 + \theta_1 x_1 + ... + \theta_{n-1} x_{n-1}, \quad (1)$$

whereas the loss function is set as follows:

$$J(\theta) = \frac{1}{2}(X\theta - Y)^T(X\theta - Y). \quad (2)$$

After deduction and sorting, the parameters were obtained as follows:

$$\theta = (X^T X)^{-1} X^T Y. \quad (3)$$

The above formula shows that the least squares algorithm is simple and efficient. This method can avoid the need for quadratic programming in the fitting function and solve the problems of robustness, sparseness, and large sample sets. However, there are some limitations, for example, the fitting function must be converted before use and linear, and calculation of the inverse matrix is lengthy when the number of samples is too large.

In this study, the multivariate PLSR and LS-SVR methods were used to analyze the concentrations of nitrogen in the compound fertilizer samples. The optimal spectral range was selected for multivariate analysis to avoid over-fitting of the model. Several statistical parameters that determine the capacity of the regression model were used to evaluate the performance of the calibration model. These parameters were the determination coefficients of the calibration set (R_C^2) the validation set (R_P^2), the residual predictive deviation (RPD), the RMSEC, and the RMSEP. For a better model, R^2 should be close to one, RPD should be greater than three, and the RMSEC and RMSEP should be as small as possible.

Results and discussion. *Spectral analysis.* Although compound fertilizer is not as complex as a soil sample, it produces many characteristic lines in LIBS. Because of the relatively high concentration of nitrogen, when selecting the analytical lines, unsaturated lines with high signal-to-noise ratios should be chosen.

The LIBS results for the compound fertilizer pellets (sample No. 1) between 735–780 and 840–885 nm showed nine characteristic emission lines for nitrogen at 742.4, 744.2, 746.8, 856.7, 859.4, 856.7, 870.3, 871.2, and 871.8 nm (Fig. 2). None of these lines suffered from interference and all could be observed easily. The line for nitrogen with the strongest relative intensity occurred at 746.8 nm. The intensities of the characteristic lines for nitrogen were calculated using the Lorentzian function and the line height.

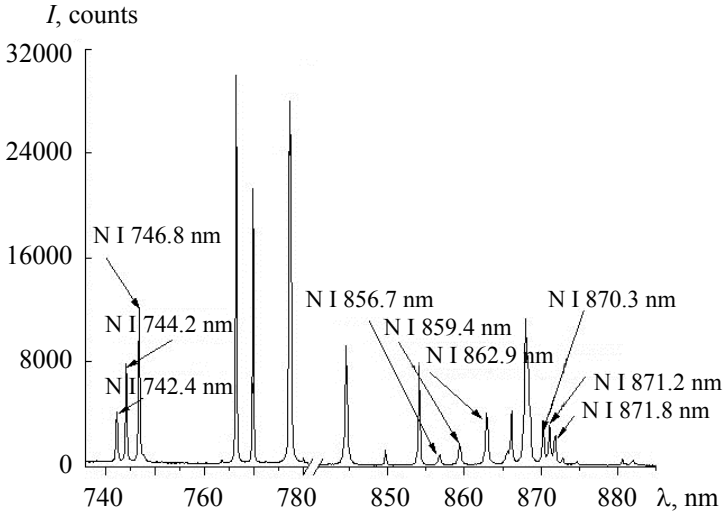

Fig. 2. LIBS results for compound fertilizer in the ranges 735–780 and 840–885 nm.

Partial least squares regression model. Before modeling, the 40 compound fertilizer samples were divided using the Kennard–Stone method into a calibration set (32 samples) and a validation set (eight samples). To establish the multiple regression analysis model, the nitrogen concentrations for each calibration compound fertilizer sample were organized for the Y matrix (32×1), and the selected emission line intensities for each calibration sample were organized for the X matrix (32×9). The multivariate calibration model was then used to determine the concentration of nitrogen in the validation set. The prediction results could determine the accuracy of the calibration model. The PLSR and LV-SVR multivariate analysis methods were used to establish the calibration models with respect to the latent variables.

The PLSR regression model was used to establish and analyze the nitrogen concentrations in compound fertilizer. Three principal components were used to build the PLSR calibration model. Most of the calibration data points deviated from the fitting curve, and the R_C^2 was 0.897 (Fig. 3a). For the prediction results of the validation set, the R_P^2 was only 0.794 (Fig. 3b). The minimum and maximum data points deviated far from the fitting curve, whereas the other data points were distributed around the fitting curve (Fig. 3b). Results from the PLSR model for determination of the nitrogen concentration in compound fertilizer were R_C^2 = 0.837, RMSEC = 0.137, R_P^2 = 0.794, RMSEP = 0.136, and RPD = 2.52. Both the R_C^2 and R_P^2 were not close to 1, which indicated that the accuracy of the established PLSR model needed to be improved. When the RPD is larger than 5, the established calibration model is robust enough to be used for quantitative analysis. Thus, the analytical precision and accuracy of the PLSR model need to be improved.

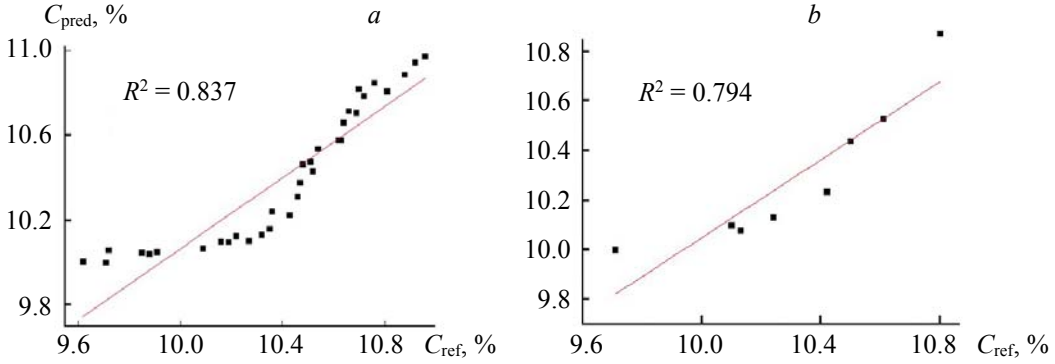

Fig. 3. Comparison of the nitrogen concentrations in compound fertilizer obtained by ICP-MS and LIBS combined with the PLSR method: (a) calibration set, (b) validation set.

Least-squares support vector regression model. The number of compound fertilizer samples used in this study (n = 40) was less than 100, which meant that the characteristic dimension of SVR was decreasing. To establish the calibration model, the least squares method was used to optimize the parameters. The principal components were the same as those for the PLSR method. The data points for both the calibration and validation sets were fitted better by the LS-SVR model than by the PLSR model, which indicated that the LS-SVR model could provide reliable and accurate quantitative analysis of the nitrogen concentration in compound fertilizer (Fig. 4). The results of the LS-SVR model for determination of the nitrogen concentration were R_C^2 = 0.994, RMSEC = 0.028, R_P^2 = 0.993, RMSEP = 0.030, and RPD = 11.33.

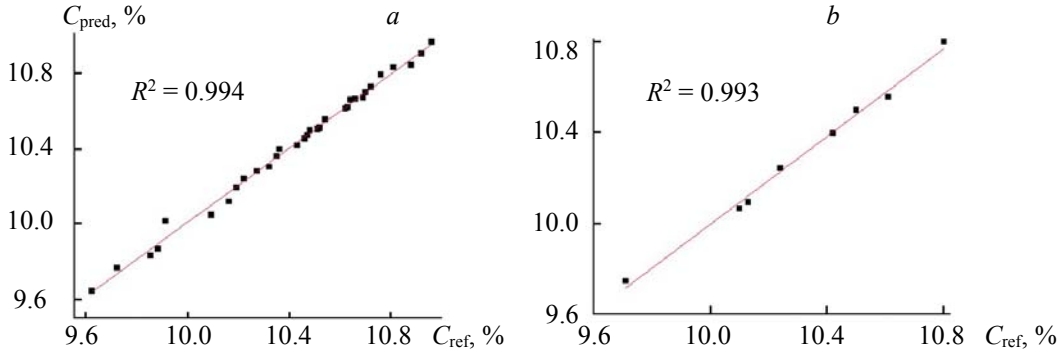

Fig. 4. Comparison of the nitrogen concentrations in fertilizer obtained by ICP-MS and LIBS combined with LV-SVR: (a) calibration set, (b) validation set.

The R^2 for both the calibration and validation sets were obviously improved over those of the PLSR model. The R_C^2 improved from 0.837 for the PLSR model to 0.994 for the LS-SVR model, and R_P^2 increased from 0.794 for the PLSR model to 0.992 for the LS-SVR model. Both the R_C^2 and R_P^2 were greater than 0.99, which indicated that the quantitative regression analysis was good. The slopes for both the calibration and validation sets were close to one, which showed there was a strong correlation between the predicted and reference values. The RMSEC decreased from 0.137 to 0.028 and the RMSEP decreased from 0.136 to 0.030, when the LS-SVR model was used rather than the PLSR model. Predicted and reference values for the validation set are given in Table 1. The mean absolute error was 0.023%. During production of compound fertilizer, the actual nitrogen concentration is qualified if the deviation from the standard value is plus or minus 1.5%. The deviation of the measurement results from different laboratories is not more than 0.5% (ISO 5315: 1984, MOD) [18]. For the LS-SVR model, the RPD increased from 2.52 (PLSR model) to 11.33, which was greater than 5. Thus, the established calibration model could be used for robust and accurate quantitative analysis of compound fertilizer. All these results indicated that the accuracy of LIBS for determining the composition of compound fertilizer improved with use of the LS-SVR model. LIBS is seriously affected by the matrix effect, and there will be some matrix differences among fertilizer samples because they are produced at different times. It will lead to nonlinear effects in the calibration model. The LS-SVR analytical method is nonlinear, whereas the PLSR method is linear. Consequently, for this application, the results of the PLSR model will be inferior to the LS-SVR model. The measurement accuracy of the LS-SVR model meets the required standard [25]. Therefore, LIBS coupled with the LS-SVR model can be used for rapid analysis of compound fertilizer samples.

TABLE 1. Quantitative Analysis of Nitrogen in Validation Samples Using the LS-SVR Model

Validated samples	Reference value, %	Predicted value, %
1	9.71	9.75
2	10.1	10.06
3	10.13	10.09
4	10.24	10.23
5	10.42	10.39
6	10.5	10.49
7	10.61	10.55
8	10.8	10.81

Conclusions. LIBS was applied with multivariate regression to quantitative analysis of nitrogen in compound fertilizer. Forty samples were analyzed using multivariate PLSR and LS-SVR to analysis the nitrogen content. The PLSR model was established using three principal components. The R_C^2 and R_P^2 were 0.837 and 0.794, respectively, and the RPD was only 2.52. All the results indicated that the prediction accuracy should be improved. When the LS-SVR model was used instead, the R_C^2 and R_P^2 greatly increased to 0.994 and 0.993, respectively. In addition, the values of RMSEC and RMSEP decreased to 0.028 and 0.03 respectively, and the RPD increased to 11.33. Therefore, the nonlinear multivariate LS-SVR calibration method improved the accuracy of LIBS. The results in this study provide a basis for quantitative analysis of the nitrogen content in compound fertilizer. Future work will look at methods for improving the accuracy of LIBS in the rapid analysis of compound fertilizer.

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