

QUANTITATIVE ANALYSIS OF MAGNESIUM IN SOIL BY LASER-INDUCED BREAKDOWN SPECTROSCOPY COUPLED WITH NONLINEAR MULTIVARIATE CALIBRATION****J. Yongcheng^{1,2*}, S. Wen¹, Z. Baohua³, L. Dong³**

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Laser-induced breakdown spectroscopy (LIBS) coupled with the nonlinear multivariate regression method was applied to analyze magnesium (Mg) contents in soil. The plasma was generated using a 100 mJ Nd:YAG pulsed laser, and the spectra were acquired using a multi-channel spectrometer integrated with a CCD detector. The line at 383.8 nm was selected as the analysis line for Mg. The calibration model between the intensity of characteristic line and the concentration of Mg was constructed. The traditional calibration curve showed that the concentration of Mg was not only related to the line intensity of itself, but also to other elements in soil. The intensity of characteristic lines for Mg (Mg I 383.8 nm), manganese (Mn) (Mn I 403.1 nm), and iron (Fe) (Fe I 407.2 nm) were used as input data for nonlinear multivariate calculation. According to the results of nonlinear regression, the ternary nonlinear regression was the most appropriate of the studied models. A good agreement was observed between the actual concentration provided by inductively coupled plasma mass spectrometry (ICP-MS) and the predicted value obtained using the nonlinear multivariate regression model. The correlation coefficient between predicted concentration and the measured value was 0.987, while the root mean square error of calibration (RMSEC) and root mean square error of prediction (RMSEP) were reduced to 0.017% and 0.014%, respectively. The ratio of the standard deviation of the validation to the RMSEP increased to 8.79, and the relative error was below 1.21% for nine validation samples. This indicated that the multivariate model can obtain better predicted accuracy than the calibration curve. These results also suggest that the LIBS technique is a powerful tool for analyzing the micro-nutrient elements in soil by selecting calibration and validation samples with similar matrix composition.

Keywords: laser-induced breakdown spectroscopy, soil, magnesium, nonlinear multivariate calibration.

КОЛИЧЕСТВЕННЫЙ АНАЛИЗ СОДЕРЖАНИЯ МАГНИЯ В ПОЧВЕ С ПОМОЩЬЮ ЛАЗЕРНО-ИСКРОВОЙ СПЕКТРОСКОПИИ С НЕЛИНЕЙНОЙ МНОГОПАРАМЕТРИЧЕСКОЙ КАЛИБРОВКОЙ**J. Yongcheng^{1,2*}, S. Wen¹, Z. Baohua³, L. Dong³**

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Для анализа содержания магния в почве применена спектроскопия лазерно-искровой плазмы (LIBS) с использованием метода нелинейной многомерной регрессии. Для генерации плазмы применен

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импульсный Nd:YAG-лазер мощностью в импульсе 100 мДж, а регистрация спектров осуществлена с помощью многоканального спектрометра с ПЗС-детектором. Для анализа содержания Mg выбрана линия на длине волны 383.8 нм. Зависимость интенсивности характеристической линии от концентрации Mg определялась с помощью созданной калибровочной модели. Построение традиционной градуировочной кривой показывает, что на интенсивность выбранной линии влияет не только концентрация Mg, но и содержание других элементов в почве. Поэтому в качестве входных данных для нелинейного многопараметрического расчета использована интенсивность характеристических линий магния (Mg I 383.8 нм), марганца (Mn I 403.1 нм) и железа (Fe I 407.2 нм). В соответствии с результатами применения нелинейной регрессии наиболее приемлема из изученных моделей трехмерная нелинейная регрессия. Наблюдалось удовлетворительное совпадение величины, полученной расчетом по выбранной нелинейной регрессионной модели, со значением концентрации, измеренной с помощью масс-спектрометрии с индуктивно-связанной плазмой (ICP-MS). Коэффициент корреляции между рассчитанной и измеренной концентрацией 0.987, причем среднеквадратичная ошибка калибровки (RMSEC) и расчета (RMSEP) снижены до 0.017 и 0.014 %. Отношение стандартного отклонения валидации к RMSEP возросло до 8.79, а относительная ошибка оказалась ниже 1.21 % для девяти образцов проверки. Это подтверждает, что многомерная модель может обеспечить лучшую прогнозную точность, чем калибровочная кривая. Полученные результаты также свидетельствуют о том, что метод LIBS является мощным инструментом для анализа микроэлементов в почве путем выбора калибровочных и валидационных образцов со схожими по составу матрицами.

Ключевые слова: лазерно-искровая спектроскопия, почва, магний, нелинейная многопараметрическая калибровка.

Introduction. Accurate analysis of the nutritious elements in soil is of great importance in precision agriculture. In particular, the reduction of agricultural production costs is important for crop fertilization. Precision agriculture is a farming management concept based on observing, measuring and responding to inter and intra-field variability in crops. Precision fertilization is a key component of precision agriculture based on division of the field into grids using GPS, then testing for soil nutrients and computing the fertilizer input needed using the fertilization model, before finally applying fertilizer using a variable rate applicator. Quantitative detection of the element concentrations in soil is important to improve precision fertilization. Compared with traditional chemical analysis methods, LIBS is faster and more effective in the quantitative detection of element concentrations.

The LIBS technique is an atomic emission spectroscopy technique that uses a pulsed laser as an excitation source [1]. Spectrochemical analysis using LIBS is determined not only by the concentration of the analyte in the sample, but also by the experimental conditions, e.g., delay time, laser characteristics, sample characteristics, atmosphere gas, and other parameters [2]. Thus, a detailed analysis of the experimental parameters is required to obtain a reliable quantitative result. The most common approach to performing quantitative LIBS analysis is the calibration curve method with matrix-matched standards. The LIBS technique has been used in various fields [3–7] and the application of LIBS in agriculture for heavy metal pollution, soil fertility, plant materials, and fertilizer is of particular interest to precision fertilization [8–11]. The determination of nutrient elements in soil has been examined in the literature because of its importance to the continued improvement of precision fertilization [12–15]. The analyses conducted in these studies have focused on total carbon (C), inorganic C, organic C, total nitrogen (N), and total phosphorus (P) in soil. However, few investigations have been devoted to the research of analyzing the Mg element in soil [16–18]. Moreover, most of these studies have carried out qualitative analysis, and only a few studies have been reported in the literature dealing with quantitative analysis. This may be attributed, in part, to the limited attention paid to the role of the Mg element in plant growth. However, Mg element in soil has a major function in the photosynthesis and metabolism of plants and can promote growth, strengthen disease resistance, and increase yield. The oxide and hydrate forms of Mg have good surface activation and degrading functions on the organic pollution in soil. Therefore, experimental parameters for LIBS analysis of Mg in soil should be estimated, together with the investigation of new strategies of calibration for LIBS analysis of Mg in soil.

Many researchers have recently used the multivariate calibration method for quantitative analysis of LIBS. Taking into account the properties of samples and accuracy of prediction, we see that the characteristic chemometric algorithms include different approaches, such as multiple linear regression, principal components regression, partial least squares, and nonlinear multiple regression, all which have been used in LIBS analysis [19–22]. In the present study, we applied the LIBS technique to determine the concentration

of Mg in soil for the goal of precision fertilization. Soil samples collected from a rice field containing various amounts of Mg were used to construct the relationship between LIBS intensity and the Mg concentration. In addition, linear regression and nonlinear multivariate regression were used to predict the concentration of Mg in soil samples, and a suitable nonlinear multivariate regression model with Fe and Mn as inter-element interference with lower RMSEC and RMSEP was obtained. This means that the results of this study can measure the Mg content in soil more accurately.

Experimental. A schematic drawing of the experimental setup is shown in Fig. 1. A Q-switched Nd:YAG laser (Ultra ICE 450, USA), which can deliver up to a maximum of 100 mJ/pulse at 1064 nm wavelength with a pulse duration of 6 ns and a maximum repetition of 20 Hz, was used in this experiment. The beam was focused onto the soil sample pellet (soils described below) using a plano-convex K9 lens (25 mm diameter, $f = 50$ mm). The light emitted from the plasma was collected by a fused silica quartz lens of 40 mm focal length. The end of the optical fiber was connected to the entrance slit of a multiple spectrometer (2048-USB2, Avantes, the Netherlands). The spectrometer has three channels containing separate grating and charge coupled device array. This equipment offers a large spectral range from 190 to 510 nm with a spectral resolution of 0.1 nm. The spectra were recorded and processed by a personal computer. A homemade gate pulse generator was employed to trigger the laser and the spectrometer. When triggered, the generator can produce a burst of pulses, which was used to fire the laser and trigger the spectrometer after a set delay time. The operating conditions were laser pulsed energy 90 mJ, repetition rate 1 Hz, detection delay 1.8 μ s, and integration time 1.05 ms.

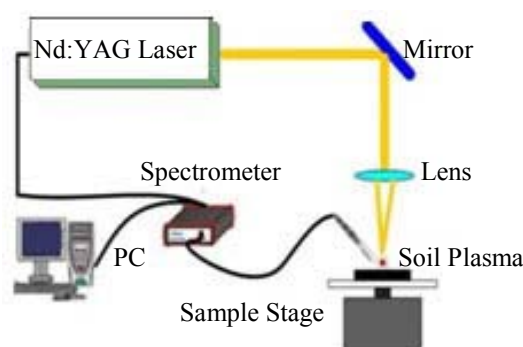


Fig. 1. Schematic diagram of LIBS experimental system.

Thirty soil samples were collected from a rice field (Huaiyuan, Anhui Province). The sampling position was 10–25 cm below the ground, which was considered to be the main area from which the plant roots absorb micronutrients. The collected soil was first dried naturally and then ground into powder. The ground samples were sieved through 100 mesh screens to achieve sample homogeneity. The powdered samples were compressed under 10 tons of pressure for 2 min to improve the stability of LIBS emissions. Pellets were analyzed in duplicate when assessing the element concentration using LIBS. At the same time, traditional inductively coupled plasma mass spectrometry (ICP-MS) was used to measure the concentration of Mg in soil samples (Table 1).

TABLE 1. Measured Mg Concentration in Soil Samples (% dry weight) Using ICP-MS

Sample	Concentration, %	Sample	Concentration, %	Sample	Concentration
1	1.098	11	0.972	21	1.122
2	1.140	12	1.146	22	0.978
3	1.092	13	1.278	23	1.266
4	1.212	14	1.128	24	1.176
5	1.260	15	1.230	25	1.254
6	1.086	16	1.164	26	1.236
7	1.308	17	1.308	27	1.038
8	1.122	18	1.242	28	1.314
9	1.416	19	1.314	29	1.212
10	1.110	20	1.158	30	1.14

During the LIBS experiment, the soil pellet was mounted on an x - y rotary stage, which was constantly rotated with a stepper motor to minimize heterogeneity. Thirty spectra were averaged for each soil pellet to improve the signal/noise ratio and reduce statistical error caused by laser shot-to-shot fluctuation.

Results and discussion. *Selection of characteristic line.* The LIBS spectrum at 270–290 and 380–410 nm of sample 1 (Table 1) is shown in Fig. 2. The laser pulsed energy and delay time were optimized at 90 mJ and 1.8 μ s, respectively. Each spectrum was generated according to a 30 shot average. Figure 2 shows that strong emission lines for Mg, manganese (Mn), and iron (Fe) were apparent in the spectrum. The feature spectral lines of Mg element detected by LIBS were at 280, 285.2, 382.9, 383.2, and 383.8 nm, respectively. According to the National Institute of Standards and Technology (NIST) database, the spectral line at 383.8 nm is observed easily without the interference of other spectral lines, and the relative intensity of this line is the strongest. The feature lines of Mn and Fe were abundant and, based on the relative intensity and the interference of other elements, the emission lines of Mn I at 403.1 nm and Fe I at 407.2 nm were selected as the analytical lines.

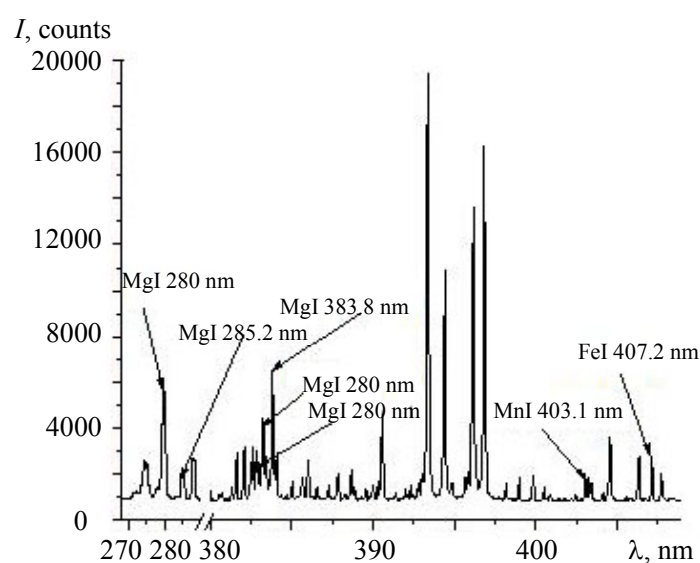


Fig. 2. LIBS spectrum of soil sample.

Quantitative analysis using calibration curve. The average spectrum (30 shot) of each sample was obtained by subtracting the baseline by Lorentz fit using Matlab software. The relationship between the intensity of the LIBS emission line of Mg 383.8 nm and the actual concentration of Mg in soil samples was first determined using the traditional calibration curve. We used 21 of the 30 soil samples as the calibration set to construct the calibration model, with Mg concentration varying from 0.972% to 1.416 (Fig. 3a). It provides a regression model with a correlation coefficient of only 0.766. The remaining nine of the soil samples, with unknown Mg contents, were used to estimate the prediction accuracy of LIBS technique for analysis of the Mg content. Figure 3b shows the LIBS predicted content and the reference content of Mg. The correlation coefficient is 0.831, and the slope of the calibration curve is 1.52. It is worth mentioning that the simple calibration curve only considered the objective element Mg (Mg I 383.8 nm). However, in a LIBS spectrum, there are different atomic and ionic lines emitted from the same element. The intensities of these emitted lines are not only dependent on the emitted elemental species concentration, but they are also affected by the other corresponding elemental species in the plasma. As the soil samples are very complex, the other corresponding elements can obstruct the result of calibration curve. The application of multiple characteristic lines would provide more information to construct the nonlinear multivariate calibration method, making it possible to achieve more accurate modeling of the inter-element interference. In other words, the nonlinear multivariate calibration method can reduce the influence of the matrix effect. Therefore, the measurement accuracy of LIBS can be improved effectively.

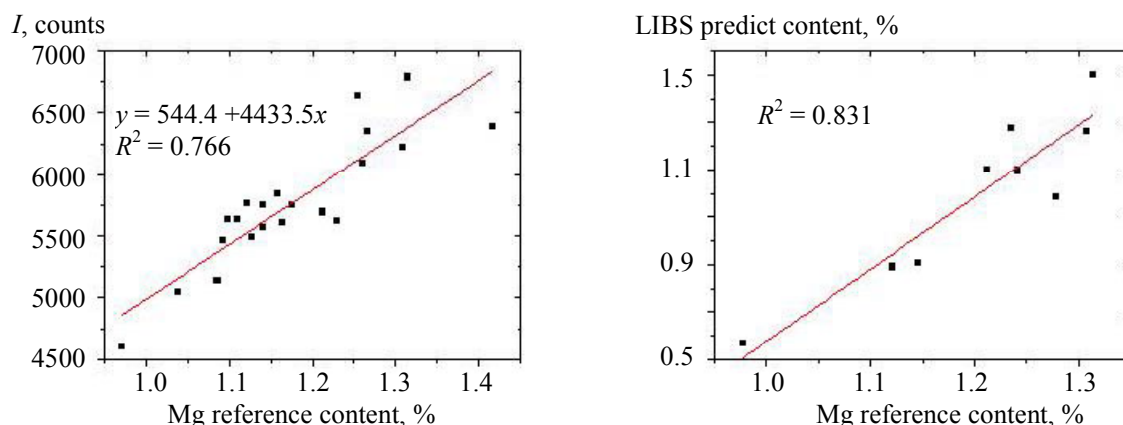


Fig. 3. Spectral intensity as a function of the percentage of Mg in soil.

Nonlinear multiple regression analysis. The nonlinear multivariate model is an advanced analytical tool used in the field of chemometrics, which generally involves the development of mathematical models to analyze complex samples. For the soil sample with the multi-component coexistence, the measuring signal is typically related to many factors. Therefore, in the current application, the intensity of feature spectral lines is taken as the I (independent) variables and the elemental concentrations are the C (dependent) variables. The second order nonlinear multivariate analysis model can be expressed as follows:

$$[C_j] = a_{0,j} + \sum_{i=1}^m (a_{i,j}[I_i] + a_{m+i,j}[I_i]^2) + [e_j], \quad (1)$$

where C_j is the concentration of element j ; e_j is the residual error; j and m are the number of samples and the number of variants, respectively; I_i is the intensity of one of characteristic lines of the corresponding elements; and $a_{0,j}$ and $a_{i,j}$ are the regression coefficients determined by nonlinear multivariate calibration.

During the quantitative analysis using LIBS, the results of determination can be influenced by the concentration of the analyzed elements. Moreover, the other inter-elements contained in the samples play an important role in detecting the object. It can be assumed that the concentration of C_j has a relationship with the intensity of C_j and/or the other interfering elements (I_i), as indicated in the following equation [23]:

$$C_j = f(I_1, I_2, \dots, I_i), \quad (2)$$

where C_j refers to the concentration of the analytical element predicted, and I_i is the integrated intensity of inter-element in the sample.

In the soil, Mg is present in the mineral state, non-exchangeable state, water-soluble state, or exchangeable state. Therefore, it is valuable to consider Mn and Fe as the inter-elements for Mg lines and then

$$C_{Mg} = a_0 + a_1 I_{Mg} + a_2 I_{Mg}^2 + a_3 I_{Fe} + a_4 I_{Fe}^2 + a_5 I_{Mn} + a_6 I_{Mn}^2, \quad (3)$$

where C_{Mg} is the Mg concentration; I_{Mg} , I_{Fe} , and I_{Mn} are the intensities of Mg I at 383.8 nm, Fe I at 407.2 nm, and the characteristic spectrum line intensity of Mn I at 403.1 nm, respectively.

The quality of the nonlinear multivariate model can be evaluated in many ways. In this paper, four indicators were applied to evaluate the accuracy of the model from different aspects: (i) the determination coefficient (R^2), (ii) the root mean square error of calibration (RMSEC) was used to assess the calibration quality, (iii) the root mean square error of prediction (RMSEP) was calculated to compare prediction accuracy, and (iv) the ratio of standard deviation of the validation to RMSEP (RPD) was used to assess the model stability. The following formulas were used to calculate RMSEC, RMSEP and RPD:

$$RMSEC = \sqrt{\sum_{i=1}^{N_c} (y_i - y'_i)^2 / N_c}, \quad (4)$$

$$RMSEP = \sqrt{\sum_{i=1}^{N_p} (y_i - y'_i)^2 / N_p}, \quad (5)$$

$$RPD = \sqrt{\sum_{i=1}^{N_p} (y_i - \bar{y})^2 / N_p} / RMSEP, \quad (6)$$

where y_i is the known elemental concentration; y'_i is the calculated elemental concentration; \bar{y} is the mean elemental concentration; N_c and N_p indicate the number of calibration and prediction samples, respectively. An accurate model should have an R^2 value close to 1, a small RMSEC and RMSEP, and $RPD > 2$.

The 30 soil samples were divided into calibration (21 samples) and prediction (9 samples) sets. Two second-order nonlinear multivariate models were constructed for Mg elements, with the interfering elements of Fe and Mn, respectively. The results of quantitative analysis of Mg element by the nonlinear multivariate model are presented in Table 2. The final nonlinear multivariate was expressed as Eq. (3).

Figure 4 shows the calibration and prediction results of the nonlinear multivariate model with Fe as the interfering element. For the prediction samples, the nonlinear multivariate model showed better accuracy than the calibration curve, which indicates that the consideration of physical background can improve the prediction results. The RMSEC was 0.026%, RMSEP was 0.016%, and RPD was 4.75. However, the correlation coefficient was only 0.944, which is not sufficiently close to 1. The residuals mainly come from the other interfering elements, e.g., Mn.

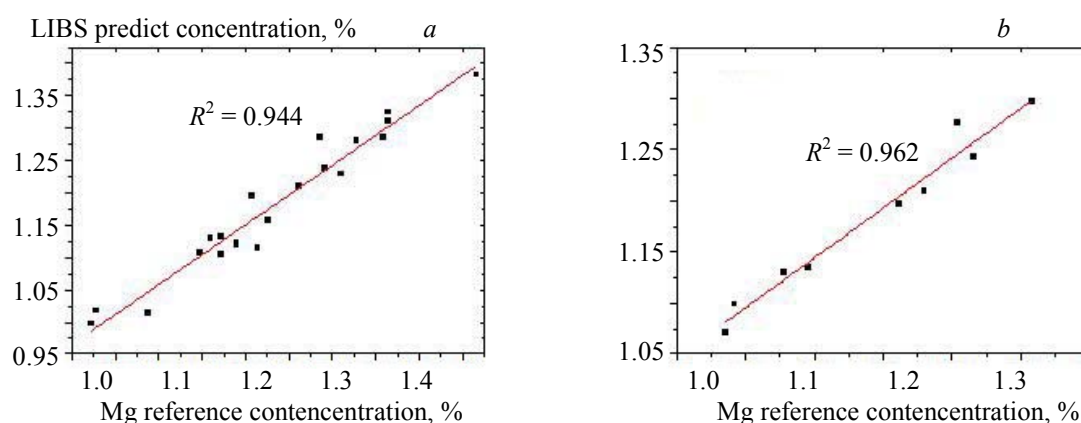


Fig. 4. Models to consider the impact of Fe on Mg: (a) the calibration model and (b) the validation model.

To improve the correlation coefficient, the nonlinear multivariate model with Mg, Fe, and Mn lines input as variables was applied to compensate for the residuals. The calibration and prediction results of the nonlinear multivariate model with Fe and Mn as the interfering elements are shown in Fig. 5. The results in Table 2 indicated that there is a strong relationship between the prediction concentration and the ICP-MS measured concentration, and the correlation was increased to 0.987. The RMSEC decreased from 0.026 to 0.017%, and RMSEP was lowered to 0.014%, as compared with 0.016% for the nonlinear multivariate model with Fe as the interfering elements, and RPD was increased to 8.79. Utilizing multiple lines enables the nonlinear multivariate model to extract more useful spectral information to construct a more accurate model than the above two methods. For soil samples, the second-order nonlinear transformation makes the nonlinear multivariate model capable of handling the nonlinearity more accurately. Hence, the nonlinear multivariate model with Fe and Mn as the interfering elements is supposed to have better accuracy across the wide concentration range, as presented in Table 2.

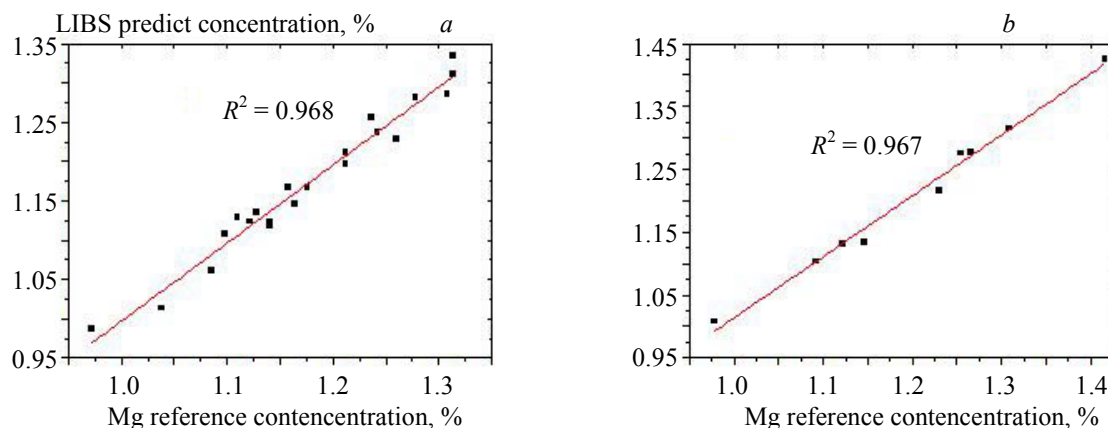


Fig. 5. Models considering the impact of Fe and Mn on Mg: (a) the calibration model and (b) the validation model.

TABLE 2. Results of Multivariate Nonlinear Regression Models

Model	R^2 calibration	RMSEC, %	R^2 validation	RMSEP, %	RPD
Mg with Fe influence	0.944	0.026	0.962	0.016	4.75
Mg with Fe and Mn influence	0.968	0.017	0.987	0.014	8.79

Compared with the above two methods, the present nonlinear method had better calibration and prediction performance. The reduction of the RMSEP in the present nonlinear method was almost 10% of the above two method. In particular, the RPD was increased to nearly 9, which indicated that the practicality of model is good. When using the present nonlinear model, the mean relative error for soil samples was 1.21%. It should be noted that the present model achieved a better accuracy compared with the linear method for the complex soil samples. It may therefore be considered a good-potential method to improve the accuracy of LIBS and promote the development of LIBS for soil analysis.

Conclusion. The potential of LIBS was evaluated for predicting the concentration of Mg in soil samples by coupling with the nonlinear multivariate regression method. The analysis was carried out based on linear and nonlinear regression calibration curves. The results indicated that the unary linear regression method cannot produce a successful quantitative analysis for complex soil samples using only the intensity of Mg as the variable. Indeed, the poor linearity of the conventional calibration curves can strongly affect the accuracy of the prediction. Subsequently, the nonlinear multivariate regression method takes into account the concentration of Mg. For inter-element interference, the intensities of Mg and Fe with nonlinear transformation were considered to establish the nonlinear multivariate regression model. The results showed that the use of characteristic lines in the nonlinear model significantly improved the accuracy compared with the linear regression model. The quantitative analysis results were improved by the introduction of the intensities of Mg, Fe, and Mn as variables in nonlinear multivariate regression analysis. The R^2 between predicted concentration and actual value was 0.987, while the RMSEC and RMSEP were reduced to 0.017% and 0.014%, respectively. Moreover, the RPD was increased to 8.79. Together, these results indicate the good quality of the nonlinear multivariate regression.

Three different regression calibration methods were compared in this paper. The results showed that the nonlinear multivariate regression had better accuracy with Fe and Mn as the inter-element interference. It is reasonable to believe that there is further potential to improve the ability of this nonlinear multivariate method by accounting for more inter-element interference. Our future research is committed to implementing real time and on-line measurement of trace elements in soil for application in precision agriculture.

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