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ORIGINAL ARTICLE

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Establishment and evaluation of a quantitative analysis model for potentially toxic metals in wet soil samples by LIBS

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Abstract

Fast on-site detection of potentially toxic metals in soils is crucial for soil remediation and contamination monitoring. The moisture in soils is a challenge for quantitative analysis of potentially toxic metals. Here, we used laser-induced breakdown spectroscopy (LIBS) and partial least squares regression (PLSR) for fast on-site quantitative analysis of potentially toxic metals in wet soil samples. The model offered direct measurement of the moisture content in soil samples: the coefficient of determination (R^2) value and the root-mean-square error of prediction (RMSEP) of predicted moisture content were 0.98% and 1.3%, respectively. The correlation between laser ablation factor and moisture content of the samples was determined by analysing the influence of sample moisture content on laser ablation. Quantitative analysis of wet soil samples based on ablation factor was established with an R^2 of 0.97. Potentially toxic elemental Cu and Cr in sample 4# were verified by the quantitative analysis model through weighing and direct measurement. The relative error of concentration was within 10%, and the accuracy was improved by over 80%. The preliminary results show that the quantitative analysis model of potentially toxic metals in wet soil samples based on LIBS technology can detect potentially toxic metals in wet soil samples quickly and accurately on-site. This has important guiding significance for real-time and on-site monitoring of contaminated soils.

Highlights

- Fast on-site quantitative analysis of potentially toxic metals in wet soil samples
- Quantitative analysis of wet soil samples based on ablation factor was established

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- The relative error of concentration was within 10%, and the accuracy was improved by over 80%
- The model can detect potentially toxic metals in wet soil samples quickly and accurately on-site

KEYWORDS
ablation factor, coefficient of determination, contamination monitoring, laser-induced breakdown spectroscopy, moisture content, on-site, partial least squares regression

1 | INTRODUCTION

Potentially toxic metal pollution in soil has become a global problem and has seriously affected human health, survival and development (Eugenio et al., 2020; Hu et al., 2020; Y. Liu, Wu, & Zhao, 2020). Real-time monitoring and prevention of potentially toxic metal contamination in soil is urgent, but traditional methods are complicated, time-consuming and laborious to operate, and cannot meet current demands for on-site analysis (Borges et al., 2020; Jindy et al., 2020; M. Liu, Zhang, et al., 2020). Laser-induced breakdown spectroscopy (LIBS) technology has been used widely in soil remediation, food safety, biomedical analysis and potentially toxic metal detection in crops. It offers rapid, nondestructive sample preparation with simultaneous detection of multiple elements (Ilhardt et al., 2019; Khajehzadeh et al., 2016; Mingyin et al., 2017; Rehan et al., 2018; Jabbara, 2020; Wang et al., 2020; Zhang et al., 2013; Zhao et al., 2019). However, the detection of potentially toxic metals in soil by LIBS technology is currently performed in a laboratory after drying and pressing the sample; the effect of soil moisture is not considered. Thus, LIBS is not suitable for the rapid detection of potentially toxic metals in wet soil samples in the field due to the long pre-treatment time (Badday et al., 2015; G. Chen et al., 2021; Sun et al., 2019; Yu et al., 2018).

Soil collected on-site contains water that will affect the characteristics of the plasma produced during laser ablation, thus impacting the precision of quantitative analysis. Some researchers have studied the moisture content of samples, as well as the plasma excitation characteristics of wet soil samples, using LIBS. However, quantitative analysis of potentially toxic metals in wet samples is rarely reported. Y. Liu et al. (2012) investigated the moisture content in cheese using LIBS and established a mathematical model that used the O intensity and moisture content to predict the moisture content of samples with a coefficient of determination, R^2, of 0.99. However, the study mentioned above has not offered relevant data for quantitative analysis. M. Chen et al. (2015) studied the effect of moisture content in coal powder on the characteristics of laser-induced plasma. They compared the plasma properties of two samples with moisture contents of 1.19% and 22.25%. The results showed that the plasma temperature was consistent, and that the electron density increased first and then remained constant with increasing moisture content. This work only analysed the effect of moisture on sample sputtering. It did not study sputtering in detail. Paris et al. (2015) found that the effect of moisture content of limestone on emission intensity and line ratio was inconsiderable. Conversely, the plasma electron density clearly increased with cooling of rock samples to Martian conditions. This effect was assigned by Rauschenbach et al. (2008) to ice cementation because the intensities of O and H lines did not monotonically change near the triple point of water. Popov et al. (2018) showed that neither plasma temperature nor electron density correlates with moisture although the emission intensities were strongly dependent on its content. Peng et al. (2017) investigated LIBS for quantitative analysis of potentially toxic metals in plant samples. This work predicted the moisture content of samples via a model built with background intensity and quantitative analysis to deduct moisture content. Finally, chemometric methods were used to compensate for prediction deviations. This model ignored the sputtering effect of water on the weight of sample ablation. Kim et al. (2013) investigated the effect of moisture content and particle size of soil samples on LIBS. The intensity of LIBS emission lines reduced from 59% to 75% when the moisture content increased from 1.2% to 7.8%. The effect of moisture content on the LIBS emission line was more obvious than that of particle size. It was recommended that all samples collected from abandoned mining areas and military camps should be ground and sieved to ensure similar moisture contents and particle size before LIBS analysis via chemometric methods. This method increased the pretreatment time, and it could not, therefore, meet the requirements for on-site real-time analysis.

This work established a quantitative analysis model of potentially toxic metals in wet soil samples based on LIBS to solve problems in real-time analysis of wet soil samples. The correlation between the laser ablation factor in wet soil samples and moisture content in the sample was determined, and a quantitative analysis model of wet soil samples based on an ablation factor was established. Finally, the quantitative analysis model was verified by weighing and direct measurement. These results showed that this method could be used for rapid on-site analysis of soil moisture content and elemental concentration.

2 | THEORETICAL SECTION

2.1 | Ablation factor

Laser excitation in wet soil samples can change the quality of ablated samples because the moisture can affect the accuracy of quantitative analysis (M. Chen et al., 2015; Paris et al., 2015). Here, an accurate quantitative analysis of wet soil samples was performed using the intensity of the elemental spectral line including the effect of the ablation factor. We analysed the ablation factor from two perspectives. First, the presence of water is equivalent to adding a diluent to a dry sample. This means that the actual ablation amount of the sample is the total ablation mass minus the water mass when exciting a wet soil sample with the same mass. Second, some of the sample was splashed out of the sample before it could be ablated when the laser was applied to the sample because the water was vaporised in a very short time. The phenomenon mentioned above would ultimately lead to a reduction in the actual amount of ablation. We show here that the sputtering factor K is introduced to represent the ratio of the sputtered mass to the actual ablated mass of the sample. Therefore, the ablation factor θ of wet samples can be calculated by Equation (1):

$$\theta = \frac{m_{\mathrm{w}}}{m_{\mathrm{d}}} \cdot \frac{m_a}{m_{\mathrm{w}}} = \frac{m_{\mathrm{w}}}{m_{\mathrm{d}}} \cdot \frac{1}{\frac{m_{\mathrm{a}}+m_{\mathrm{s}}}{m_{\mathrm{a}}}} = \frac{m_{\mathrm{w}}}{m_{\mathrm{d}}} \cdot \frac{1}{1+\frac{m_{\mathrm{s}}}{m_{\mathrm{a}}}} = \frac{1-\varepsilon}{1+K(\varepsilon)}, \qquad (1)$$

where m_{a} is the actual sample ablation mass of the laser ablated wet soil sample, m_{d} is the mass of the laser ablated dry sample under the same conditions, m_{w} is the mass of the sample in the wet soil sample, $\mathrm{m_s}$ is the weight of the unablated sample splashed beyond the sample, ε is the moisture content of the sample, and $K(\varepsilon)$ is the sputtering factor related to the moisture content. The expression should be validated experimentally.

The Lomakin-Scheibe formula shows that the intensity of the elemental spectral line is linearly related to the concentration of the analyte without self-absorption (Musazzi & Perini, 2014). Therefore, the ablation factor θ of wet samples could be characterised by the intensity of the elemental spectral line, which was shown in Equation (2)

$$\theta = \frac{I_{\mathrm{w}}}{\overline{I_{\lambda}^{\mathrm{ki}}}}, \qquad (2)$$

where I_{w} is the measured intensity of elemental spectral line of the wet sample, and $\overline{I_{\lambda}^{\mathrm{ki}}}$ is the measured intensity of the elemental spectral line of the dried sample.

2.2 | Modelling of quantitative analysis of wet samples

The equation for the intensity of the elemental spectral line (Ciucci et al., 1999) was derived as Equation (2) under the assumption that the laser-induced breakdown plasma satisfies the local thermal equilibrium (LTE) condition and the optical thin plasma condition.

$$\overline{I_{\lambda}^{\mathrm{ki}}} = \mathrm{FC_s A_{ki}} \frac{\mathrm{g_k} \mathrm{e}^{-(E_{\mathrm{k}}/k_{\mathrm{B}}T)}}{U_{\mathrm{s}}(T)}, \qquad (3)$$

where $\mathrm{g_k}$, A_{ki}, F, C_{s}, $U_{\mathrm{s}}(T)$, E_{k}, k_{B} and T are the upper-level degeneracy factor, the Einstein transition coefficient, the experimental constant, the concentration of elements to be measured, the partition function, the upper-level energy of spectral lines, the Boltzmann constant and the plasma excitation temperature, respectively.

In Equation (2), $\overline{I_{\lambda}^{\mathrm{ki}}}$ is the intensity of the characteristic spectral line obtained by laboratory excitation of dry samples with the same mass. However, the original spectral line intensity measured in the experiment is derived from the wet soil sample. The ablation quality changes with the different moisture content. Therefore, the intensity is modified by the introduction of the ablation factor. When substituting Equation (2) into Equation (1), we obtain the following:

$$\overline{I_{\lambda}^{\mathrm{ki}}} = \frac{I_{\mathrm{w}}}{\theta} = \frac{I_{\mathrm{w}} K(\varepsilon)}{(1-\varepsilon)}. \qquad (4)$$

Substituting Equation (4) into Equation (3), we obtain the following:

$$C_{\mathrm{s}} = \frac{I_{\mathrm{w}} K(\varepsilon)}{(1-\varepsilon)} \cdot \frac{U_{\mathrm{s}}(T)}{\mathrm{FA_{ki} g_k} \mathrm{e}^{-(E_{\mathrm{k}}/k_{\mathrm{B}}T)}}, \qquad (5)$$

where the experimental parameter F is constant for a given experimental condition, the plasma temperature was shown to be independent of the moisture content in the sample (Yu et al., 2018).

Thus, the relationship between the intensity of elemental spectral lines in wet samples and the concentration of elements can be expressed by Equation (5). Other atomic parameters are fixed values and are related to the characteristic spectral lines of elements; they were obtained from the National Institute of Standards and Technology (NIST) Database.

3 | EXPERIMENTAL SECTION

3.1 | System construction

A schematic of the LIBS system is shown in Figure 1a. The system consists of a laser, an optical system, a spectrometer, a computer and a mobile power supply. The laser was a Q-switched Nd:YAG solid-state laser (CFR200, Quantel, Paris, France) with a laser wavelength of 1064 nm, a beam diameter of 7.1 mm, a pulse width of 7.1 ns, a working frequency of <22 Hz, and a single pulse energy of <200 mJ. The spectrometer was a seven-channel fibre optic spectrometer (LIBS2500+, Ocean Insight, Dunedin, FL, USA) with 190–900 nm wavelength range and better than 0.1 nm optical resolution. The laser beam expander was a Galilean telescope structure consisting of a concave lens ($f = -200$ mm) and a convex lens ($f = 300$ mm); the focal length of the focusing lens is 50 mm. The system benchtop is shown in Figure 1b.

3.2 | Sample preparation

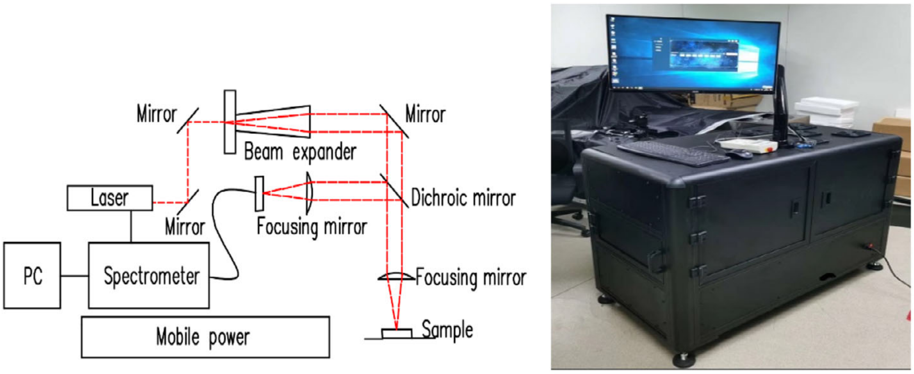
Soil collected from a rice field in Songyuan City, Jilin Province, China was used as the experimental sample. The soil was air-dried, sieved, ground and dried, and the standard sample was prepared via standard addition method. Six portions of dried soil numbered 1#–6# were weighed separately to 2.5 g (2 g for pressing the sample and 0.5 g for analysis by inductively coupled plasma-optical emission spectroscopy [ICP-OES]). Cu (1000 mg/L) and Cr (1000 mg/L) standard solutions (Beijing Institute of Non-Ferrous Metals, Beijing, China) were mixed and diluted with pure water to form a mixed solution containing 250 mg/L of Cu and 250 mg/L of Cr, respectively.

0, 1, 3, 5, 7 and 9 ml of the mixed solution was added to dry soil (0 means no standard solution). This was stirred and soaked for 24 h after bringing to constant volume. The sample was then dried in an oven at 60°C for about 30 h until the samples attained constant weight; sample 4# was used for the model's quantitative analysis of wet samples. The sample was dried for about 15 h to maintain moisture. A 0.5-g sample was taken from each of the six samples and analysed by ICP-OES. Elemental Cu and Cr concentrations were obtained as shown in Table 1.

The remaining samples (~2 g) were ground with an agate mortar and then pressed into cylindrical samples with a diameter of about 40 mm. Six soil standard samples with different Cu and Cr contents were thus prepared.

Wet soil samples were prepared by weighing seven dry soil samples (3 g each) into 100 ml beakers and adding about 3 g of water to each breaker. The samples were then sealed and left for 24 h to allow the soil samples to absorb as much water as possible. The samples were then left open for natural water loss in the laboratory, and the open time of each beaker was controlled to obtain soil samples with different moisture contents.

The moisture content of the samples was measured in two ways: the first calculated the moisture content in the soil by weighing according to the Chinese national standard HJ613-2011 (Ministry of Environmental Protection, 2011); this is hereafter referred to as the standard moisture content. The second is a mathematical model of spectral intensity and moisture content using chemometric methods, leading to direct measurement of the moisture content



(a) (b)

FIGURE 1 Laser-induced breakdown spectroscopy (LIBS) system: (a) schematic diagram and (b) benchtop image

TABLE 1 Amount of sample spiking solution and the content of potentially toxic metal elemental Cu and Cr

Sample no.	1#	2#	3#	4#	5#	6#
Volume of standard solution (ml)	0	1	3	5	7	9
Cu concentration (mg/kg)	20	90	259	426	649	733
Cr concentration (mg/kg)	29	114	341	549	732	865

TABLE 2 Comparison of moisture content calculated by weighing and direct measurement

Sample no.	A#	B#	C#	D#	E#	F#	G#
Standard moisture content (%)	8.98	23.65	32.34	18.35	29.36	14.26	2.09
Predicted moisture content (%)	7.39	21.87	31.29	19.32	30.67	15.68	2.79
Difference between the two moisture contents (%)	−1.59	−1.78	−1.05	0.975	1.308	1.419	0.7

(Y. Liu et al., 2012), hereafter referred to as the predicted moisture content.

3.3 | Experimental parameters

The LIBS system used the spectrometer to trigger the laser. The laser pulse frequency was set to 0.5 Hz, and the measured laser energy focused on the sample was 101 mJ. The integration time of the spectrometer was set to 1 ms to obtain a good signal-to-noise ratio and to reduce the effect of background noise; the integration delay was set to 1 μs, and it produced a relatively stable plasma. The laser beam was focused 2 mm below the sample surface. Three spectra were repeatedly acquired for each sample to reduce the effect of laser pulse energy fluctuations on the intensity of the spectra; each spectrum was the arithmetic mean of 10 replicate laser ablations.

4 | RESULTS

4.1 | Measurement of moisture content

This experiment used a cross-validation method to model and predict seven different moisture content samples (A#–G#) based on LIBS. The spectral data in the 280–320 nm band had characteristic spectral lines representing major elements in soil; these lines were selected as modelling data. The partial least squares regression method was used to model the data and measure the moisture content.

The moisture content pairs calculated via the weighing method and the direct measurement method are shown in Table 2. The results were compared with the moisture content calculated by the weighing method. The moisture content error obtained by the direct measurement method is within 1.8%, which is better than that of the existing on-site moisture content measurement technology. The measurement error of the soil moisture sensor is within 3%.

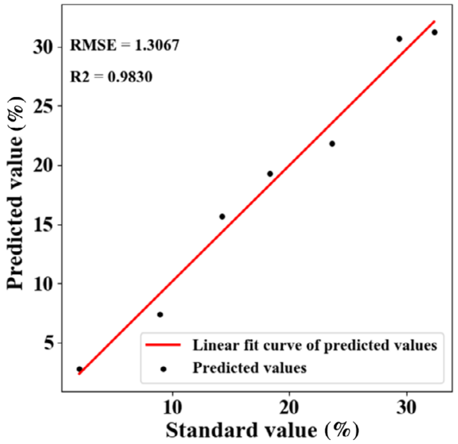


FIGURE 2 Reference vs. predicted value of moisture contents

The moisture content obtained by the two moisture content measurement methods is compared shown in Figure 2. The R^2 of the moisture content obtained by the two methods reached over 0.98, and the RMSEP was only 1.3%. These two results indicate that LIBS combined with chemometric method can accurately predict the soil moisture content.

4.2 | Determination of quantitative analysis model parameters

Here, a quantitative analysis model was established for seven wet soil samples listed in Table 2. Seven samples were excited by the LIBS system under the same conditions to obtain the spectral intensity data of each sample and to make the selected modelling data representative.

The peak intensities of the six characteristic wavelengths (BG: 410 nm, Fe I: 309.819 nm, Al I: 309.271 nm, Al I: 394.401 nm, Ca II: 393.366 nm, Ca II: 396.847 nm) were selected for reference because these six characteristic peak intensities have a certain gradient; intensities from 11,544 (higher peak) to 306 (background) are somewhat representative (Figure 3).

Figure 3 shows that the moisture content of the sample has a great influence on the spectral intensity. The spectral peak intensity decreases rapidly, with the increase of moisture content. The peak intensities of the six characteristic wavelengths extracted from Figure 3 are shown in Table 3.

Each peak intensity needs to be first subjected to standardised pretreatment after extracting the characteristic peak intensity in order to make the different peak intensities on the same order of magnitude. The sputtering factors of the seven samples with different moisture contents were then calculated as in Equation (4), as shown by the black dots in Figure 4a.

Figure 4 shows that curved lines had an obvious exponential form. Seven groups of data together and fit the curve with an exponential function, as shown by the black solid line in Figure 4a. Here, R^2 is 0.92, and the sputtering factor was strongly correlated with the moisture content. The experimentally obtained fitting

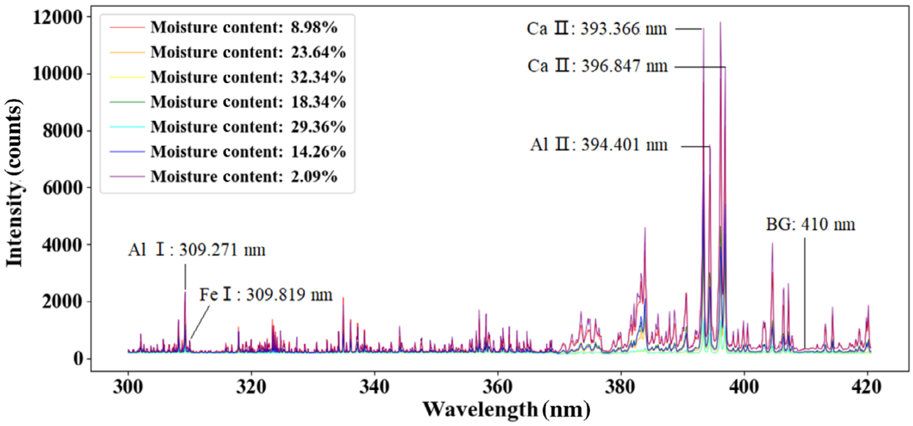
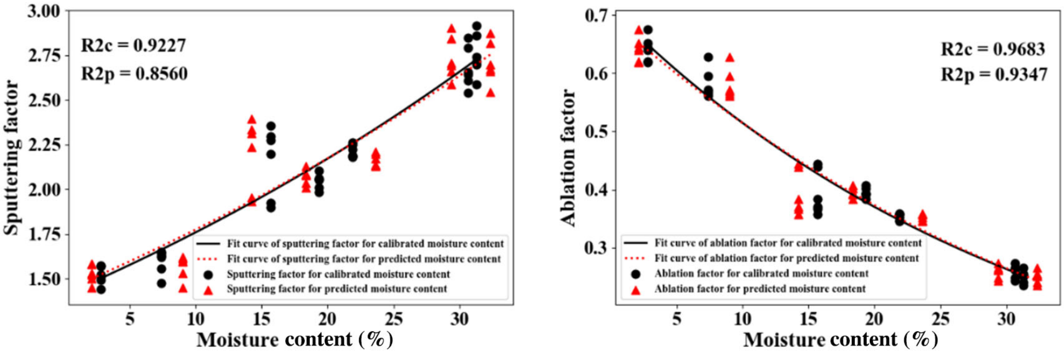


FIGURE 3 Representative spectra of samples with different moisture contents

TABLE 3 Peak intensities of the six characteristic wavelengths

Wavelength	A#	B#	C#	D#	E#	F#	G#
BG: 410 nm	331	225	179	240	182	231	351
Fe I: 309.819 nm	569	284	188	346	204	322	617
Al I: 309.271 nm	2078	935	380	1172	423	988	2329
Al I: 394.401 nm	6445	2306	754	2996	889	2509	7490
Ca II: 393.366 nm	9689	4334	1224	5221	1422	6523	11,587
Ca II: 396.847 nm	8171	3458	951	4350	1136	5410	10,217



(a) (b)

FIGURE 4 Model fitting effects: (a) sputtering factor and (b) ablation factor function is brought into the ablation factor calculation Equation (2) to obtain the ablation factor equation as shown in Equation (6):

$$\theta = (1-\varepsilon)/\left(1.668e^{1.862\varepsilon} - 0.261\right). \tag{6}$$

The ablation factor model is shown by the black curve in Figure 4b, and R^2 reaches 0.97, thus indicating that the actual ablation of laser-induced breakdown of wet soil sample has a strong correlation with the soil moisture content. This model intuitively reflects the influence of water in the sample on the laser-ablated sample.

The sputtering factor and the ablation factor calculated with the predicted moisture content are shown in the red positive triangle in Figure 4. The red dashed line is the line pattern after factor fitting. The R^2 values reached 0.86 and 0.93, which is consistent with the model established by the standard moisture content. These results confirm the effectiveness of the model established by the predicted moisture content.

5 | DISCUSSION

5.1 | Evaluation of quantitative analysis model

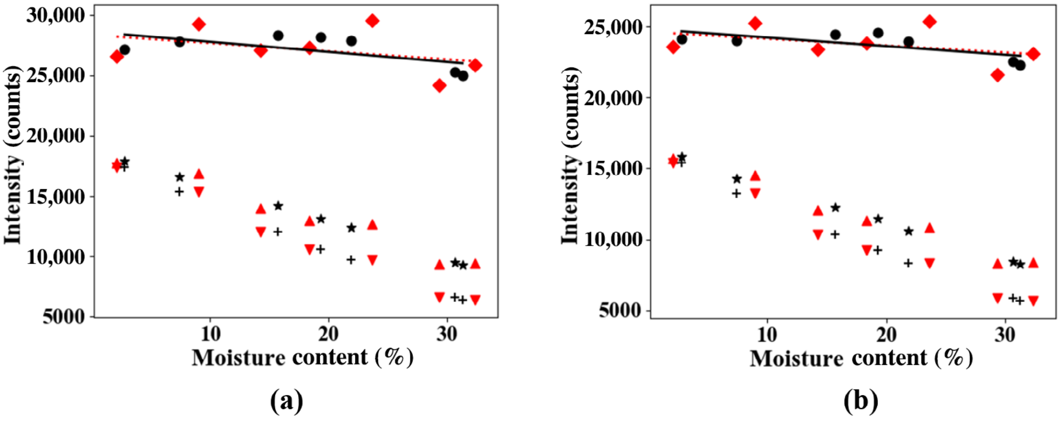
Two characteristic spectra were selected to verify the universality of the model. The peak intensity of the Mg and Fe characteristic spectral lines was gradually modified by the ablation factor calculated using Equation (6). The original intensity of the spectral lines and the modified intensity are shown in Figure 5.

Figure 5a,b shows the correction effect of the quantitative analysis model on the peak intensity of the characteristic spectral lines of Mg I: 383.83 nm and Fe I: 357.03 nm, respectively. The black marked points are the intensities corrected by the model established by the standard moisture content. The red scatter points are the intensities corrected by the model established by the predicted moisture content. The black plus sign and the red inverse triangle scatter points indicate the original intensity of the spectrum. The black asterisk and the red positive triangle scatter points indicate that the intensity is corrected by the moisture content. The black circle and the red diamond scatter points indicate the intensity corrected by the ablation factor.

The intensities of the two spectral lines with different moisture contents are basically on the same straight line close to the horizontal after being corrected by the ablation factor. The RSD of the spectral line intensity (after correction for the ablation factor) calculated by the standard moisture content and predicted moisture content for Mg is 5.16% and 6.89%, respectively, and that for Fe is 3.85% and 5.49%, respectively. The fluctuation corrected by the predicted moisture content is slightly larger, which may be caused by the prediction error regarding moisture content; the difference is not very big. The intensity fluctuation after correction is small, which proves that the model has good universality.

5.2 | Quantitative analysis of potentially toxic metal elements

This work used a quantitative analysis model of potentially toxic metals in wet soil samples to measure Cu and Cr in sample 4#. The moisture content of sample 4# was calculated. The predicted moisture content directly measured by the moisture content model is 21.78% for the soil sample with a standard moisture content of 23.26% as



(a) (b)

FIGURE 5 Effect of intensity correction: (a) mg I: 383.83 nm and (b) Fe I: 357.03 nm

TABLE 4 Prediction effect of quantitative analysis model on the content of elemental Cu and Cr

Element	Data source	Intensity (counts)	Concentration calculated by model (mg/kg)	Concentration measured by ICP-OES (mg/kg)	Relative error (%)
Cu	Raw data	1293.99	85.43	426	79.95
	Data corrected for standard moisture content	3616.53	403.44		5.29
	Data corrected for predicted moisture content	3398.1	388.91		8.71
Cr	Raw data	1514.45	123.2	549	77.56
	Data corrected for standard moisture content	4232.72	515.3		6.14
	Data corrected for predicted moisture content	3920.48	495.98		9.66

calculated by weighing. The characteristic spectral lines of the two potentially toxic metals are Cu I: 327.396 nm and Cr I: 425.435 nm, respectively, with reference to the national standard and NIST library. First, dry samples (1#–3#, 5#–6#) were used to establish the calibration curves for Cu and Cr by external standard method. Next, wet soil samples were excited to obtain the original spectral line intensities of Cu and Cr; the intensity data were corrected via an ablation factor. Finally, the concentrations were calculated via the corrected intensities according to the calibration curves shown in Table 4.

Table 4 shows that the concentration error of the intensity prediction without model correction is 79.95% and 77.56% for Cu and Cr, respectively. The relative error of the concentration prediction is reduced to 5.29% and 6.14%, respectively, after intensity correction by the ablation factor and calculations via the standard moisture content. Intensity correction by the ablation factor was calculated via the predicted moisture content and was slightly poor; the relative error of the concentration prediction was 8.71% and 9.66% for Cu and Cr, respectively.

The results show that the relative error of the uncorrected elemental concentration prediction is relatively large in the quantitative analysis of potentially toxic metals in wet soil samples. The relative error of the prediction is significantly reduced after ablation factor correction (within 10%), and the accuracy of the concentration prediction is improved by more than 80%. There is still some error in the prediction, which may be caused by the error in moisture content prediction. Although the sample preparation and analysis process only take a few minutes, the soil moisture content will be affected by the temperature and humidity in the laboratory, thus resulting in changes that affect the accuracy of the quantitative analysis model.

6 | CONCLUSIONS

We show here a quantitative analysis model of wet soil samples based on the ablation factor. The quantitative analysis model was verified by weighing and direct measurements. The results show that the R^2 of the moisture content prediction model established by PLSR for direct measurement of soil moisture content is above 0.98, and the RMSEP is only 1.3%. The sputtering factors of laser-ablated wet soil samples are distributed exponentially. The R^2 of the exponential model is 0.92, the R^2 of the ablation factor model is 0.97 and the RSD values of the model for predicting the intensity of any two spectral peaks are 5.16% and 3.85%. The quantitative analysis model for Cu and Cr in sample 4# was verified by weighing and direct measurement. The relative error in the concentration prediction is within 10%, and the accuracy improved by more than 80%. This quantitative analysis model based on LIBS can quickly and accurately measure toxic metals in wet soil samples on-site. This has value in real-time and on-site monitoring of contaminated soils.

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AUTHOR CONTRIBUTIONS

Yuxing Xu: Conceptualization (equal); data curation (equal); formal analysis (lead); funding acquisition (supporting); investigation (equal); methodology (equal); software (lead); writing – original draft (lead); writing – review and editing (lead). **Bing Han:** Formal analysis (equal); funding acquisition (lead); resources (equal). **Qingbin Jiao:** Methodology (equal). **Zhenyu Ma:** Formal analysis (equal). **Baolin Lv:** Funding acquisition (equal); supervision (equal). **Yuhang Li:** Software (equal). **Hui Li:** Investigation (equal). **Yubo Zou:** Supervision (equal). **Lin Yang:** Validation (equal).

DATA AVAILABILITY STATEMENT

Data available on request from the authors.

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