Study on enrichment characteristics of Chinese herbal medicine based on LIBS technology*

WANG Chun[1,2,3], LI Honglian[1,2,3], SUN Jiaxing[1,2,3], LÜ Heshuai[1,2,3], WANG Fan[1,2,3], and ZHANG Rongxiang[4]****

1. School of Quality and Technology Supervision, Hebei University, Baoding 071000, China

2. National & Local Joint Engineering Research Center of Metrology Instrument and System, Baoding 071002, China

3. Hebei Key Laboratory of Energy Metering and Safety Testing Technology, Hebei University, Baoding 071002, China

4. College of Physics Science and Technology, Hebei University, Baoding 071002, China

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To improve the accuracy of laser induced breakdown spectroscopy (LIBS) measurement and investigate the enrichment characteristics of trace elements in different parts of Chinese herbal medicine, the original spectral data of different Chinese herbal medicines were preprocessed by combining median absolute deviation (MAD), segmented feature extraction, and wavelet denoising, and the enrichment laws of trace elements in different parts of Chinese herbal medicine were studied based on the calibration free laser induced breakdown spectroscopy (CF-LIBS). For these experimental samples, the contents of K, Ca, Mg, and Fe in chrysanthemum and its roots, stems, and leaves, Iris lactea roots and leaves, Salvia miltiorrhiza and corresponding planting soil were obtained by CF-LIBS. By calculating the element enrichment coefficient, it was found that chrysanthemum had strong enrichment ability of K element, and the enrichment ability of K element was flower > leaf > stem > root. The roots and leaves of Iris lactea showed strong enrichment of Ca and Mg. The enrichment ability for Ca is leaf > root, and for Mg is leaf > root. The enrichment coefficient of Ca and Mg in Salvia miltiorrhiza is higher. The results show that the combination of multiple data preprocessing methods can effectively improve the accuracy of LIBS measurement results. The calculation method of trace element enrichment law in different parts of Chinese herbal medicines provides guidance for the cultivation and fertilization of Chinese herbal medicines and the identification of high-quality Chinese herbal medicines.

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Trace elements in Chinese herbal medicines play a very important role in regulating the body's functions and protecting against foreign viruses. The types and contents of trace elements are closely related to the nature, aptitude and efficacy of the herbs[1]. Studies have shown that trace elements are first absorbed by the roots of herbal plants, some of which accumulate in the roots and some are transported to different organs and enriched, resulting in differences in the distribution of trace elements in different parts of the root, stem, leaf and flower. Therefore, the rapid and efficient analysis of trace elements in different parts of herbs is of great importance to study the enrichment pattern of different parts of herbs.

Laser induced breakdown spectroscopy (LIBS) is a laser induced plasma based atomic emission spectroscopy composition analysis technique that allows for rapid, non-destructive, in-situ, real-time detection. It is widely used in the metallurgical industry[2], coal mining[3], geological exploration[4], mineral development[5], biomedicine[6] and herbal medicine detection[7], but its repeatability is poor. To improve the accuracy of measurement results, researchers have investigated the pre-processing of LIBS spectral data. SHEN et al[8] used the LIBS technique for the rapid and quantitative detection of nutrient elements in Panax ginseng samples. The wavelet transform was used to pre-process the raw spectral data collected from Panax ginseng to eliminate or reduce the errors and noise introduced during the experiment. ZHAO et al[9] used wavelet transform and normalization methods to pre-process the LIBS spectral data of Chuanbeiji samples to reduce the spectral noise. XU et al[10] collected LIBS spectral data of different varieties of tea samples and used a pre-processing method combining window translation smoothing and peak shift function correction to eliminate background radiation and correct drifting spectral peaks. FENG et al[11] investigated

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** E-mails: lihonglian@hbu.edu.cn; zrx@hbu.edu.cn

the effects of the LIBS spectral pre-processing method with multivariate scattering correction, wavelet transform and smoothing filter on the measurement results. The noise effects were effectively reduced.

In the field of herbal medicine detection, WANG et al[12] used the LIBS technique to collect the spectra of Doklam root and Dendrobium for qualitative analysis of the elements contained, and quantitative analysis of Ca, Mg, Al and K in the two herbs by external standard method. WANG et al[13] built an LIBS experimental setup to measure the relative content of trace elements in Radix et Rhizoma ginseng and compared the results with inductively coupled plasma emission spectrometry (ICP-OES) measurements, which were in good agreement. AL-DAKHEEL et al[14] verified the reliability of CF-LIBS for the qualitative and quantitative determination of elements in Rhamnus roots by ICP-OES, and the results were in good agreement with the LIBS data with a high relative accuracy. YAN et al[15] used inductively coupled plasma mass spectrometry (ICP-MS) and ICP-OES to determine the contents of 20 elements, including Li, Be, Cu and Zn, in the roots and leaves of Songlan and Malan and in the soil of the planting site. The results showed that the nutrient contents in the leaves of Songlan and Malan were higher than those in the roots. LV et al[16] also used ICP-MS and ICP-OES to determine the contents of 13 elements in different parts of bitter bamboo, and the results were analyzed by one-way ANOVA, clustering and principal component analysis to analyze the distribution of elements in different parts of bitter bamboo. In addition, most of the studies on the Chinese herbs of chrysanthemum, Iris lactea and Salvia have focused on the analysis of organic chemical composition and medicinal mechanisms[17-19].

In summary, a single method is commonly reported for data pre-processing of elemental spectroscopic detection, which cannot solve the problems of high baselines, abnormal spectral lines and background noise at the same time. In addition, there are fewer studies on the trace element contents and their enrichment patterns in different parts of chrysanthemum, Iris lactea and Salvia herbs. Given the above problems, this study proposes a combined method of multiple data pre-processing based on LIBS technology and free calibration method to qualitatively and quantitatively analyze the common trace elements in different parts of chrysanthemum, Iris lactea and Salvia and their planting soils, calculate the trace element enrichment coefficients in different organs of herbal plants, and study the element enrichment patterns in different parts of herbal medicines, so as to provide guidance for cultivation, fertilization and identification of high-quality therapeutic Chinese medicines, which is conducive to improving the quality of Chinese herbal medicines.

The LIBS system used in the experiment is the same as that in the previous studies of our group[20]. As shown in Fig.1, the laser beam was emitted by a Nd:YAG laser (Beijing Radbao Optoelectronics Technology Co. Vitle 200) with an output wavelength of 1 064 nm, passing through a 45° reflector and acting vertically through a focusing lens on the surface of a sample placed on a carrier table. The position of the fibre optic probe was adjusted to ensure adequate reception of the plasma signal, which was received by the spectrometer (Ocean Optics Corporation, USA, MAX2500+) and transmitted to the computer for presentation of the spectral data. The pulsed laser energy of 87.5 mJ, delay time of 1.9 μs, repetition frequency of 5 Hz and pulse width of 6.4 ns were set.

The samples of chrysanthemum, Iris lactea and Salvia miltiorrhiza were collected in Anguo City, Hebei Province. The corresponding planting soil and the corresponding roots, stems, leaves, and flowers of the chrysanthemum, the roots and leaves of Iris lacteal, and the roots of Salvia miltiorrhiza were collected.

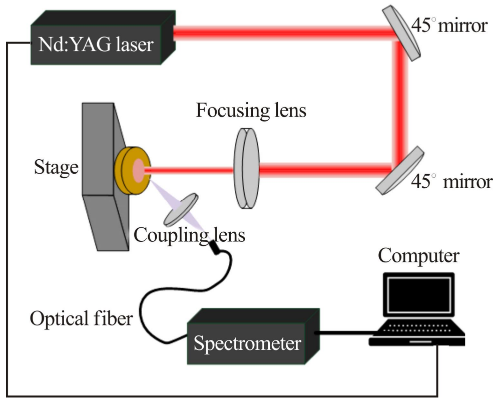


Fig.1 Experimental system diagram

All the samples were placed outdoor for natural air drying after cleaning, and then the samples were crushed by a grinding mill, after which the samples with large particles were removed by a 200 mesh sieve. The soil, root, stem, leaf, and flower parts of chrysanthemum, Iris lactea, and Salvia miltiorrhiza were treated by adding heavy metal elements. The same amounts of Chinese herbal medicine samples were weighed by electronic balance, and the same amount of cadmium chloride ($CdCl_2$) was added to each sample. The sample containing 300 mg/kg Cd was configured. The Chinese herbal medicine samples and metal salt powder were fully mixed and evenly ground. All the above-mentioned processed samples were pressed by tablet press for 10 min under 15 MPa pressure to prepare round flake samples. The pressed samples were placed in a drying oven at 60 °C for drying. The samples for LIBS experimental testing are shown in Fig.2.

The spectral data are preprocessed by the combination of the median absolute deviation (MAD) method, segmented feature extraction method, and wavelet transform. In the obtained LIBS spectral data, the plasma transition is random, and some maximum or minimum values may exist in the series of spectra. In addition, due to the influence of experimental operation, experimental environment, the sample itself, and other factors, there will be some abnormal spectra that are quite different from other spectra. Each spectrum needs to be optimized before modeling and eliminating the spectrum under abnormal conditions can improve the stability of the spectral signal. The MAD method is used to eliminate outliers in this study.

Fig.2 Physical drawing of the samples for LIBS experimental testing

The series of spectra after eliminating the outliers are shown in Fig.3. There is no large deviation in the 14 series after eliminating the abnormal value, and the overall spectrum is relatively stable, which can improve the accuracy of LIBS measurement results, indicating the feasibility of the method of eliminating abnormal spectral data by MAD.

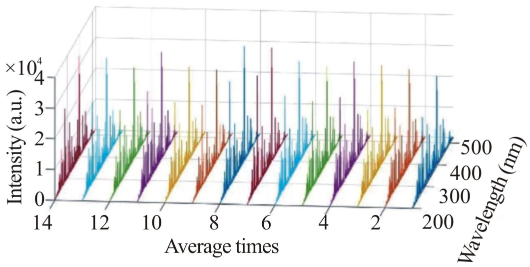


Fig.3 Series of spectra after excluding abnormal values

In addition to the influence of abnormal spectral data, there is usually a continuous background spectrum in the measurement process, due to the complexity of the plasma-inducing process, which is shown in the form of baseline height. Therefore, when using LIBS for qualitative and quantitative analysis, it is usually necessary to preprocess the original baseline correction. In addition, the multi-channel spectrometer is used in this experiment, and the characteristics of each channel are different. Therefore, the spectral baseline in the overlapping region is not at the same horizontal line. The baseline correction method used in this study is the segmented feature extraction method.

The spectrum collected by LIBS technology is not only affected by the continuous background, but also by the noise from the light source and environmental fluctuations. From the spectral data obtained by the LIBS technology, the characteristic peak of the spectral signal is at different positions of the spectrum and the number is small, and the noise is not regularly distributed. In this study, wavelet transform is used for spectral denoising, and the SURE threshold function is selected to distinguish between useful spectral signals and noise. The useful spectral signal is higher than the threshold, and the useless noise signal is lower than the threshold. When wavelet noise reduction is adopted, db5 wavelet SURE value method is selected, and three decomposition layers are selected.

To investigate the effect of the combination of various preprocessing methods on the spectral signal, the 290—293 bands and 409—413 bands are selected for analysis as shown in Fig.4. By combining a variety of data preprocessing methods, the baseline is significantly reduced, and the spectral line is smoother.

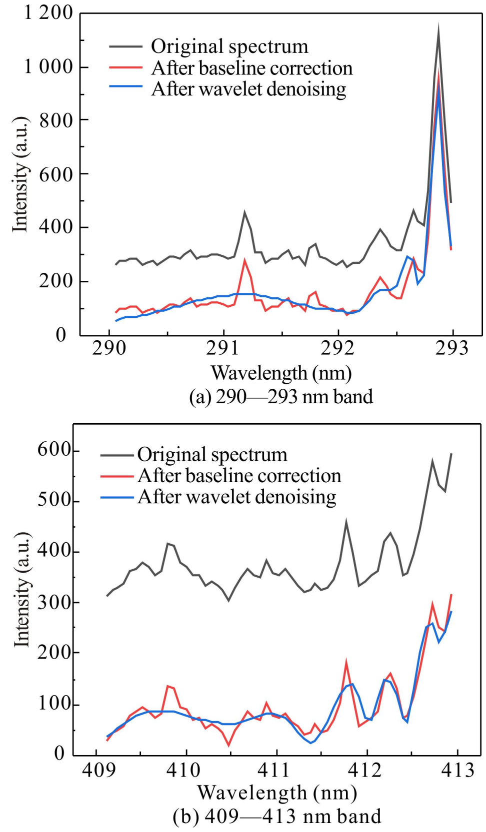


Fig.4 Spectral intensity of partial bands before and after pretreatment

In order to further study the effect of various data preprocessing methods on the spectral signal, the relative standard deviation (*RSD*) and signal-to-noise ratio (*SNR*) of four elements Fe, Al, Cd and Pb were analyzed under conditions of no data preprocessing and multiple data preprocessing methods.

Fig.5(a) and (b) are the *RSD* and *SNR* of emission spectra of Fe, Al, Cd, and Pb in the absence of data preprocessing and multiple data preprocessing methods. It can be seen that the *RSD* of the four elements is larger in the absence of data preprocessing. After multi-data preprocessing, the

RSD of the four elements decreased to varying degrees. The *RSD* of Cd, Fe, Al, and Pb decreased from 18.47%, 14.82%, 10.07%, and 19.38% to 14.53%, 10.81%, 7.33%, and 15.90%, respectively, indicating that the combination of multiple data preprocessing methods can improve the repeatability of measurement results. After multi-data preprocessing, the *SNR* of the spectra of the four elements increased to varying degrees. The *SNR* of Cd, Fe, Al, and Pb increased from 7.01, 91.19, 44.73, and 9.36 to 12.53, 121.69, 83.79, and 18.11, respectively, which further proved that the spectral quality was effectively improved by the combination of multiple data preprocessing. The analysis shows that the influence of abnormal spectrum is eliminated and the spectral signal tends to be stable after multi-data processing. Second, the influence of baseline on spectral signal is reduced. Third, the influence of noise on spectral signal is reduced.

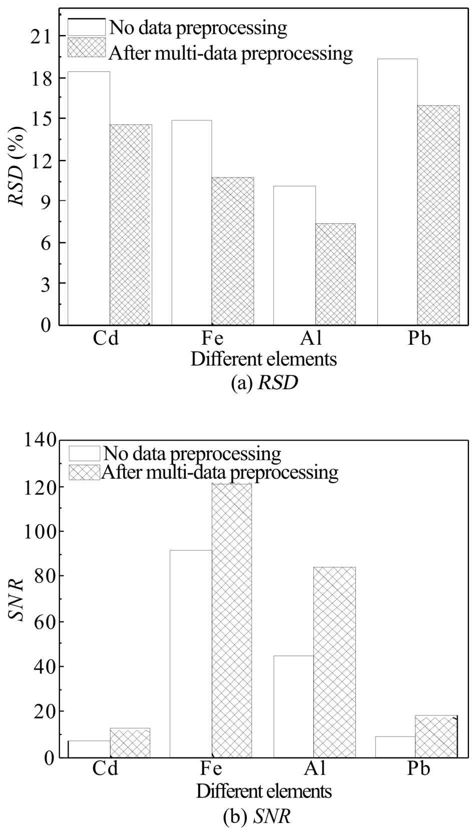


Fig.5 Evaluation indexes of four elements before and after data preprocessing

Studies have shown that by using a variety of data preprocessing methods to process the LIBS spectral signal, the abnormal spectrum elimination, baseline correction, and noise reduction are realized, and the reliability of the LIBS spectrum for sample detection and recognition is improved.

CF-LIBS can effectively reduce the influence of the matrix effect. Therefore, based on CF-LIBS, the enrichment rules of trace elements in different parts of chrysanthemum, Iris lactea, and Salvia miltiorrhiza were studied to detect the LIBS spectra of the tested samples.

The qualitative analysis of the elements contained in Chinese herbal medicine was carried out by LIBS spectrum, the plasma electron density was calculated, and the electron temperature of each element in the plasma was calculated. The atomic quantities of Cd, Fe, Ca, Mg, and K elements in the plasma were calculated by Saha-Boltzmann curve, and the ratio of atomic number to ion number of Cd, Fe, Ca, Mg, and K elements in the plasma was calculated by Saha equation. The total content and the ratio of each element in the sample were obtained by the calculation results. Because the content of Cd added is known, the relative content of elements can be calculated according to the ratio of elements. The enrichment coefficients of different elements were calculated according to the formula.

The LIBS spectra of chrysanthemum, Iris lactea, and Salvia miltiorrhiza in the range of 200—517 nm were obtained by experiments. After collecting the spectral data, the qualitative analysis of chrysanthemum, Iris lactea, and Salvia miltiorrhiza was carried out to study the types of elements in Chinese herbal medicines.

Fig.6(a) is the LIBS spectrum of chrysanthemum, (b) is the LIBS spectrum of Iris lactea, and (c) is the LIBS spectrum of Salvia miltiorrhiza. Through calibration, it is found that the three Chinese herbal medicines all contain four main elements K, Ca, Mg and Fe, and the spectral lines of the spectral intensities of the three Chinese herbal medicines are roughly the same.

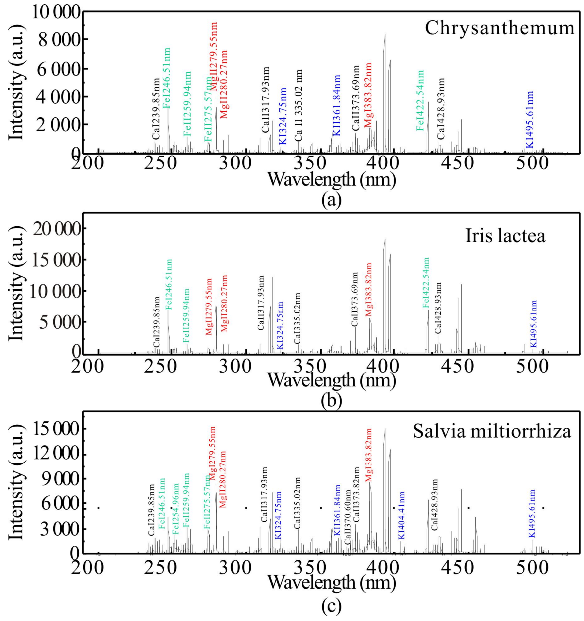
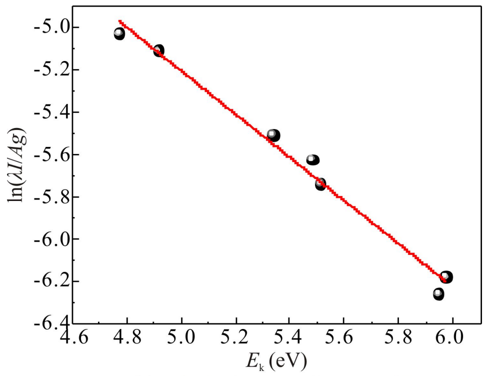


Fig.6 Spectra of three Chinese herbal medicines: (a) Chrysanthemum; (b) Iris lactea; (c) Salvia miltiorrhiza

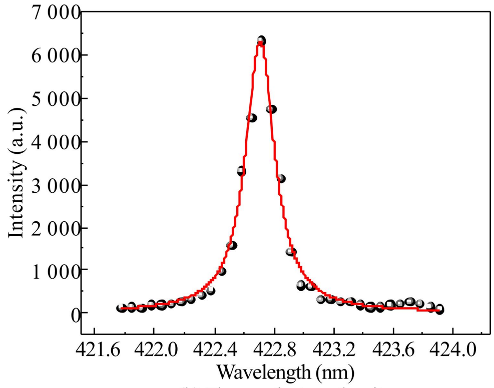
The FeI 422.74 nm spectral line was analyzed, and the plasma electron density was calculated according to Stark broadening method with this spectral line information. Fig.7(a) shows the Saha-Boltzmann diagram obtained from the atomic and ion spectral parameters of Fe.

The plasma temperature of other elements is also calculated by this method. The average plasma temperature obtained by different elements is taken as the plasma electron temperature, and the plasma electron temperature is finally obtained as 11 032 K.

The FeI 422.74 nm spectral line has good independence, which is not affected by adjacent spectral lines and has no obvious self-absorption effect. The FeI 422.74 nm spectral line is fitted by Lorentz, as shown in Fig.7(b). According to the full width at half maximum, the plasma electron density is 8.17×10^{15} cm^{-3}.



(a) Saha-Boltzmann diagram of Fe



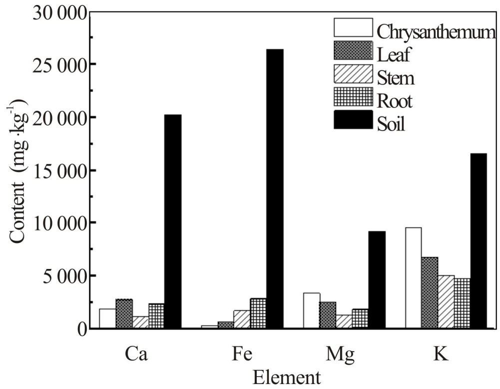
(b) Plasma electron density

Fig.7 Lorentz fitting parameter curve

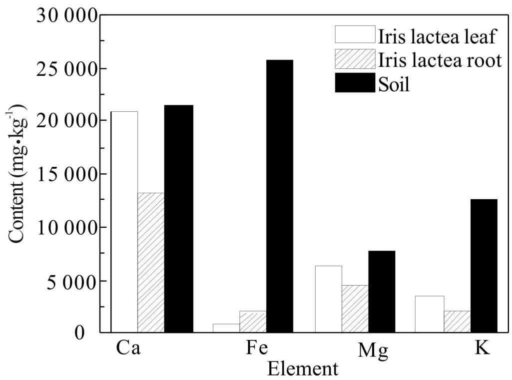
According to the Mcwhirter criterion, this experiment satisfies the local thermodynamic equilibrium (LTE) assumption.

Through the above analysis, it is determined that the plasma is in the state of LTE. The content of Cd in the known sample is 300 mg/kg, so the contents of Fe, Ca, Mg and K elements relative to Cd can be calculated. Fig.8(a) is the content of trace elements in soil, chrysanthemum roots, stems, leaves, and flowers. Fig.8(b) is the content of trace elements in soil and Iris lactea roots and leaves. Fig.8(c) is the content of trace elements in soil and Salvia miltiorrhiza.

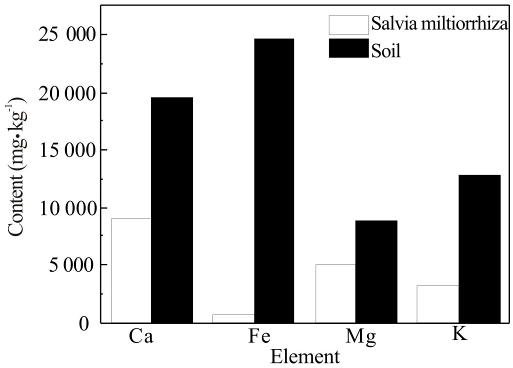
It can be seen that the contents of Ca, Fe, and Mg in the soil where chrysanthemum, Iris lactea and Salvia miltiorrhiza are planted are similar. The K content in the chrysanthemum planted soil is higher than that in the Iris lactea and Salvia miltiorrhiza planted soil. The analysis shows that the demand for trace elements is different for different Chinese herbal medicines in the growing process, and chrysanthemum needs more K elements than the other two Chinese herbal medicines in the growing process. Therefore, more K-containing fertilizers are needed in the soil planted with chrysanthemums, so the K content in the soil planted with chrysanthemums is higher.



(a) Contents of trace elements in soil, chrysanthemum and its roots, stems, leaves



(b) Contents of trace elements in soil, Iris lactea root and leaf



(c) Contents of trace elements in soil and Salvia miltiorrhiza

Fig.8 Contents of trace elements in three different Chinese herbal medicines and their soils

Through the enrichment coefficient study of different parts of chrysanthemum, Iris lactea, and Salvia miltiorrhiza, the enrichment rules of the four trace elements Ca, Fe, Mg, and K were compared and analyzed. The element enrichment coefficient is defined as the ratio of

Chinese herbal medicine (or other parts of the production of Chinese herbal medicine) element content to element content in the soil. Through this method, the Ca, Fe, Mg, and K element enrichment coefficients in chrysanthemum, Iris lactea, and Salvia miltiorrhiza are calculated and shown in Tabs.1, 2 and 3.

Tab.1 Enrichment coefficients of inorganic elements in chrysanthemum and different growth parts

	Ca	Fe	Mg	K
Root	11.6%	10.8%	20.1%	28.8%
Stem	5.8%	6.5%	14.1%	30.4%
Leaf	13.6%	2.5%	27.3%	40.7%
Flower	9.3%	1.0%	36.6%	57.7%

From Tab.1, the enrichment coefficients of different parts are quite different. The enrichment coefficient of Ca in different parts of chrysanthemum is in the order of leaf > root > flower > stem. The enrichment coefficient of Mg is in the order of root > stem > leaf > flower, and the enrichment coefficient of K element is in the order of flower > leaf > stem > root. Compared with the other three elements, the enrichment coefficient of K element is higher, and the flower part of chrysanthemum is 57.7%. The enrichment coefficient of Fe is in the order of root > stem > leaf > flower. Compared with the other three elements, the enrichment coefficient of Fe is lower, and the enrichment coefficient of Fe in chrysanthemum is only 1%.

Tab.2 Enrichment coefficients of inorganic elements in Iris lactea and different growth parts

	Ca	Fe	Mg	K
Root	52.1%	7.6%	58.1%	15.8%
Leaf	68.9%	3.1%	80.1%	27.3%

As can be seen from Tab.2, the enrichment coefficients of Iris lactea root and leaf also have obvious difference. The enrichment of Ca and Mg is strong in Iris lactea root and leaf. The enrichment coefficients of Ca and Mg in the leaf are higher than that of the root. Compared with the other three elements, the enrichment coefficient of Mg is higher, and the enrichment coefficient of Iris lactea leaves is as high as 80.1%. The K element enrichment coefficient is in the order of leaf > root, and the enrichment coefficient of Fe is in the order of root > leaf. Compared with the other three elements, the enrichment coefficient of Fe was relatively low, and the enrichment coefficient of Iris lactea leaves was only 3.1%.

It can be seen from Tab.3 that the enrichment coefficients of Ca and Mg in Salvia miltiorrhiza are high, and the enrichment coefficients are 45.8% and 55.6%, respectively. The enrichment coefficient of Fe is as low as 2.4% and the enrichment coefficient for K is 24.3%.

The study shows that the enrichment coefficients of inorganic trace elements in different Chinese herbal medicines are quite different, which is related to the nature of Chinese herbal medicines. The element content of different parts of Chinese herbal medicines is obtained by the CF-LIBS method, and then the enrichment coefficient is calculated by the element content between different parts. This method is used to study the enrichment rule and characteristics of Chinese herbal medicine, which provides a simple and efficient way of regulating the quality standards of Chinese herbal medicines.

Tab.3 Enrichment coefficients of inorganic elements in Salvia miltiorrhiza

	Ca	Fe	Mg	K
Salvia miltiorrhiza	45.8%	2.4%	55.6%	24.3%

In this paper, the MAD method, the segmentation feature extraction method, and wavelet transform combined with multi-data preprocessing method were used. After processing, the *RSD* of Fe, Al, Cd, and Pb decreased from 14.82%, 10.07%, 18.47%, and 19.38% to 10.81%, 7.33%, 14.53%, and 15.90%, respectively. The *SNR* increased from 91.19, 44.73, 7.01, and 9.36 to 121.69, 83.79, 12.53, and 18.11 respectively, which realized the function of eliminating abnormal spectrum, baseline correction, and spectral denoising, improved spectral quality of LIBS, the stability of the spectral signal, and the repeatability of experimental measurement results. Based on CF-LIBS, the qualitative and quantitative analyses of trace elements in chrysanthemum, Iris lactea leaves, and Salvia miltiorrhiza were carried out. The relative contents of K, Ca, Mg and Fe in chrysanthemum, Iris lactea leaves and roots, Salvia miltiorrhiza, and the corresponding planting soil were obtained. It shows that the demands for trace elements in the soil are different in the growth process of different Chinese herbal medicines, and the enrichment coefficients of inorganic trace elements in different Chinese herbal medicines are different, which is related to the nature of Chinese herbal medicines. By calculating the enrichment coefficients of different parts of these three Chinese herbal medicines, the enrichment characteristics of different trace elements in Chinese herbal medicines were studied. This research provides a reference for the cultivation and fertilization of high-quality Chinese herbal medicines and a simple and efficient method for standardizing the quality standards of Chinese herbal medicines. It also provides a new scientific basis for the identification method of Chinese herbal medicines.

Statements and Declarations

The authors declare that there are no conflicts of interest related to this article.

References

[1] QIN J F. Trace element research in Chinese medicine IV. Trace elements：a bridge between traditional Chinese

medicine theory and modern scientific theory[J]. Guangdong trace element science, 2011, 18(02)：1-13. (in Chinese)
[2] LIAN B G, DENG Z, LAN X S, et al. Development in the application of laser-induced breakdown spectroscopy in recent years：a review[J]. Frontiers of physics, 2021, 16(2)：27-36.
[3] OTTESEN D, WANG J, RADZIEMSKI L. Real-time laser spark spectroscopy of particulates in combustion environments[J]. Applied spectrochimica acta part B：atomic spectroscopy, 2013, 86(6)：31-41.
[4] LAWLEY C J M, SOMERS A M, KJARSGAARD B A. Rapid geochemical imaging of rocks and minerals with handheld laser induced breakdown spectroscopy (LIBS)[J]. Journal of geochemical exploration, 2021, 222(12)：52-57.
[5] ALVAREZ C, PISONERO J, BORDEL N. Quantification of fluotite mass-content in powdered ores using a laser induced breakdown spectroscopy method based on the detection of minor elements and CaF molecular bands[J]. Spectrochimica acta part B：atomic spectroscopy, 2014, 100：123-128.
[6] LI X, YANG S, FAN R, et al. Discrimination of soft tissues using laser-induced breakdown spectroscopy in combination with k nearest neighbors (kNN) and support vector machine (SVM) classifiers[J]. Optics & laser technology, 2018, 102(15)：233-239.
[7] LIU X N, WANG X B, CHE X Q, et al. The application and research progress of LIBS technology in the rapid evaluation of Chinese medicine quality[J]. World science and technology-modernization of Chinese medicine, 2020, 22(04)：1262-1269. (in Chinese)
[8] SHEN T, LI W, ZHANG X, et al. High-sensitivity determination of nutrient elements in panax notoginseng by laser-induced breakdown spectroscopy and chemometric methods[J]. Molecules, 2019, 24(8)：1525.
[9] ZHAO Y, ZHU S, JUAN H E, et al. Identification of fritillaria thunbergii treated by sulfur fumigation using laser-induced breakdown spectroscopy[J]. Spectroscopy and spectral analysis, 2018, 38(11)：3558.
[10] XU X J, WANG X S, LI A Z, et al. Fast classification of tea varieties based on laser-induced breakdown spectroscopy[J]. Chinese journal of lasers, 2019, 46(3)：0311003.
[11] FENG T, ZHANG X, LI M, et al. Pollution risk estimation of the Cu element in atmospheric sedimentation samples by laser induced breakdown spectroscopy (LIBS) combined with random forest (RF)[J]. Analytical methods, 2021, 13(30)：3424-3432.
[12] WANG J, LIAO X, ZHENG P, et al. Classification of Chinese herbal medicine by laser-induced breakdown spectroscopy with principal component analysis and artificial neural network[J]. Analytical letters, 2018, 51(4)：575-586.
[13] WANG Y, SU M, SUN D, et al. Comparative study of magnesium and calcium in Codonopsis pilosula samples detected by CF-LIBS and LCGD-AES[J]. Microchemical journal, 2018, 137：318-323.
[14] ALDAKHEEL R K, GONDAL M A, NASR M M, et al. Quantitative elemental analysis of nutritional, hazardous and pharmacologically active elements in medicinal Rhatany root using laser induced breakdown spectroscopy[J]. Arabian journal of chemistry, 2021, 14(2)：102919.
[15] YAN J, XIE S K, LIU R P, et al. Distribution and enrichment of nutrients in different parts of woad and horse bluestem based on trace element analysis[J]. World nuclear geoscience, 2020, 37(3)：215-218. (in Chinese)
[16] LV J L, WANG M, REN Y, et al. Study on the distribution pattern of 13 elements in multiple parts of bitter bamboo[J]. Journal of pharmaceutical analysis, 2019, 39(3)：426-431. (in Chinese)
[17] YANG Y, SHI J Y, LI M, et al. Study on the phenolic chemical composition of the stems and leaves of Huai Chrysanthemum[J]. Chinese medicinal materials, 2022, (04)：872-875. (in Chinese)
[18] LI Y F, YANG P Y, LUO Y H, et al. Chemical compositions of commercial chrysanthemum tea samples and their anti-inflammatory and antioxidant properties[J]. Abstracts of papers of the American Chemical Society, 2019：258.
[19] CHEN D, MENG Y, ZHU Y, et al. Qualitative and quantitative analysis of C-glycosyl-flavones of iris lactea leaves by liquid chromatography/tandem mass spectrometry[J]. Molecules (Basel, Switzerland), 2018, 23(12)：30567397.
[20] LI H, WANG H, ZHANG S, et al. Study on energy threshold and spectral characteristics with spot radius based on LIBS technology[J]. Optoelectronics letters, 2021, 17(9)：558-563.