Multi-elemental Analysis by Energy Dispersion X-ray Fluorescence Spectrometry and Its Application on the Traceability of Soybean Origin

Hanqing Lai,^{†a,b} Jialin Xi,^{†c} Jianchun Sun,^d Weizhong He,^e Zhaohui Wang,^{*a,f} Chuangmu Zheng,^{b,d} and Xuefei Mao^{*b}

^a College of Food Science and Engineering, Jilin Agricultural University, Changchun 130118, China

^b Institute of Quality Standard and Testing Technology for Agro-products, Chinese Academy of Agricultural Sciences, and Key Laboratory of Agro-food Safety and Quality, Ministry of Agriculture and Rural Affairs, Beijing 100081, China

^c Municipal Station of Agro-Environmental Monitoring, Beijing 100029, China

^d Inspection and Testing Center of Agricultural and Livestock Products of Tibet, Lhasa 850000, China

^e Institute of Agricultural Quality Standard and Testing Technology, Xinjiang Academy of Agricultural Sciences, Urumqi 830091, China

^f Division of Soybean Processing, Soybean Research & Development Center, Chinese Agricultural Research System, Changchun 130118, China

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ABSTRACT: In this work, a commercial energy dispersion X-ray fluorescence (ED-XRF) spectrometer was utilized to measure the trace elements in soybean samples. After optimizing the radiation time and calibration strategy, ED-XRF was able to successfully measure 9 elements (Mg, K, Ca, Mn, Fe, Ni, Cu, Zn, and Rb) in 296 soybean samples from five producing areas of northern China (Henan, Inner Mongolia, Xinjiang, Heilongjiang, and Liaoning). Since principal component analysis (PCA) is not able to distinguish all growing areas completely, the multi-layer perceptron (MLP) procedure was employed which demonstrated to have a powerful classification capacity with an accuracy rate of 96.2%. XRF is a type of solid sampling analytical method, which is fast, accurate and partly portable for multi-elemental analysis. The combination of MLP and ED-XRF overcomes the analytical disadvantages found with ICP-MS or wavelength dispersion XRF analysis, and provides a novel and fast testing method for on-site recognition of food origin traceability.

INTRODUCTION

The origin of foods is often associated with food quality; therefore, safety, authenticity, and traceability are receiving considerable interest for research. Moreover,

consumers prefer to pay more for high-quality food products with known and guaranteed origin. So, the tracing and confirmation of food origin, such as geographical indication of products or regionally famous

products, has become a research hotspot involved in various technical fields.¹ The basic and effective analytical methods used include multi-elemental analysis,² isotope ratio analysis of light or heavy elements,³ near infrared spectroscopy,⁴ and organic constituents analysis⁵ or integrated analysis.

Multi-elemental analysis has mostly been used due to the popularity of atomic spectrometers in analytical laboratories, such as atomic absorption spectrometry (AAS),^{6–9} inductively coupled plasma optical emission spectrometry (ICP-OES),^{2,10–12} inductively coupled plasma mass spectrometry (ICP-MS),^{13–16} and X-ray fluorescence spectrometry (XRF), *etc.* While AAS, ICP-OES, and ICP-MS can measure a variety of micro and trace elements, they suffer from complex, labor-intensive, and environmentally unfriendly sample preparation procedures, such as sample digestion, considering the instrumental sampling system for liquids.¹⁷ Thus, they are not competent methods for the fast and on-site detection of multi-elements in food samples.

By contrast, XRF is a favorable tool of solid sampling analysis for multi-elements without sample digestion, and has been frequently utilized in geological,¹⁸ environmental,¹⁹ archeological²⁰ and food sample analysis^{21–24} involved in the food origin traceability. For example, Wang *et al.*²⁵ employed wavelength dispersion XRF (WD-XRF) spectrometry to measure the contents of Mn, Fe, Cu, Zn, Mg, P, S, K, and Ca in 30 rice samples from three Chinese areas (Hubei, Sichuan, and Heilongjiang provinces). The detection limits (LOD) for the elements were almost at $\mu\text{g/g}$ level with the relative standard deviations (RSD) less than 5.8%. Combined with principal component analysis (PCA) and cluster analysis, the origin of the rice samples was successfully traced. Mohamed *et al.*²⁶ also used WD-XRF to measure K, Ca, Mg, Al, Si, P, S, Cl, Fe, Mn, Cu, Zn, Rb, Sr, and Ni in 47 coffee samples grown in four Ethiopian regions. Combined with the δC^{13} value for linear discriminant

analysis, the classification accuracy reached 89%. In addition to WD-XRF, energy dispersive XRF (ED-XRF) can be used for food origin traceability as well. For example, Otaka *et al.*²⁷ utilized ED-XRF equipped with a three-dimensional polarizing mirror to measure trace elements in 46 domestic and imported soybeans in Japan. By optimizing the selection of the secondary target and measurement time, the instrumental LODs can be improved to below $\mu\text{g g}^{-1}$ level for Cu, Zn, Br, Rb, Sr, Mo, and Ba. After PCA and linear discriminant analysis, eight elements (Mg, P, Cl, K, Mn, Cu, Br, and Ba) were determined as effective parameters, and the final correct discrimination rate for Japanese soybean samples reached 91.3%. However, all of the WD-XRF or desktop ED-XRF instruments mentioned above are still too large for use as vehicle-mounted or portable equipment for real sample analysis.

As a successful commercial instrument, XRF is generally divided into two categories: WD-XRF and ED-XRF.²⁸ Compared with ED-XRF, WD-XRF has a lower background, higher spectral resolution, and better capability of detecting ultra-light elements like Be, C, and F.^{29–31,37} However, WD-XRF always has some disadvantages, such as larger size, higher power consumption, and lower analytical efficiency. Therefore, it cannot be miniaturized for portability.³² By comparison, the ED-XRF apparatus can be made available in a smaller size and using low energy and is extremely suitable for fast and on-site testing.^{33–36} Thus, if the miniaturized XRF, based on energy dispersion, can be used for trace multi-elemental analysis in food, it would also be able to be used for food origin traceability to protect the geographical indication and regional famous products timely and effectively.

Considering the lower analytical sensitivity, numerous ED-XRF manufacturers are committed to improve the instrumental performance.³⁷ For example, the NX-100S ED-XRF from NCS Testing Technology Co., Ltd. (Beijing, China) and the EDX3200S PLUS ED-XRF

from Jiangsu Skyray Instrument Co., Ltd. (Kunshan, China) have been reported to detect Cd in soil and food samples as low as $< 0.1 \text{ mg kg}^{-1}$. These ED-XRF instruments can be attached to a car or be loaded into a special suitcase for on-site use with a battery.

Therefore, in this work, a miniaturized ED-XRF was used for the multi-elemental analysis of soybean samples from five main producing areas in northern China (the Heilongjiang, Liaoning, Inner Mongolia, Xinjiang, and Henan provinces) after establishing instrumental optimization and calibration. To analyze the analytical results, the multi-layer perceptron belonging to artificial neural network was carefully studied and utilized to establish a provenance model. The ED-XRF proved to be effective and efficient to measure micro and trace multi-elements for the fast identification of soybean origin.

EXPERIMENTAL

Instruments. An ED-XRF spectrometer (Model NX-200S, NCS Testing Technology Co., Ltd., Beijing, China), composed of side-window X-ray tubes (max. to 65 kV and 1 mA) and ultra-high performance silicon drift detector (over 1,000,000 cps, Amptek Inc., Texas, USA), was employed to measure multi-elements in soybean samples. For the X-ray tube, silver was used as a target material to excite the X-rays. The size of the XRF instrument is $46 \text{ cm} \times 45 \text{ cm} \times 35 \text{ cm}$, weighing $\sim 25 \text{ kg}$. When establishing the calibration curves for XRF using solid standards, the ICP-MS (Model EXPEC-7000, Focused Photonics Inc., Hangzhou, China) was employed to quantitatively determine the multi-elements in selected soybean samples. The detailed ICP-MS instrumental parameters are shown in Table 1.

Samples and their preparation. In 2017, 296 soybean samples were collected from 5 provinces in northern China: Zhengzhou in Henan; Hulunbuir, Chifeng in Inner Mongolia; Harbin, Daqing, Jiamusi, Suihua, Heihe, Hailun

Table 1. Instrumental parameters of ICP-MS

Parameters	Values
RF power (W)	1600
Sampling depth (mm)	5
Cooling Ar flow rate (L min^{-1})	14
Nebulizer Ar flow rate (L min^{-1})	1.19
Auxiliary Ar flow rate (L min^{-1})	1.0
PP (rpm)	30
Dwell time (ms)	10
Isotopes	^{24}Mg , ^{39}K , ^{44}Ca , ^{55}Mn , ^{56}Fe , ^{60}Ni , ^{65}Cu , ^{66}Zn , ^{72}Ge , ^a ^{85}Rb , ^{103}Rh , ^a ^{115}In , ^a and ^{185}Re ^a

^a Internal standards are $50 \mu\text{g L}^{-1}$.

Qiqihar in Heilongjiang; Shihezi in Xinjiang; Shenyang, Tieling in Liaoning. The soybeans were picked from mature crops and packed into clean paper bags, where the corresponding geographic information was recorded in time. After air drying, the soybean samples were crushed into powder with a cyclone mill and sieved with a $150 \mu\text{m}$ nylon sieve. Finally, they were bagged and sealed for later use.

XRF analysis. A 2.0 g powdered soybean sample was weighed and loaded into a plastic sample flask with a polycarbonate film ($2.5 \mu\text{m}$ in thickness, Mylar[®]) at the bottom to ensure that the entire bottom is covered and kept flat. The X-ray tube voltage was set to 30 kV, the tube current was $800 \mu\text{A}$, and the filter was set to 1 mm aluminum for measuring the fluorescence intensity of the multi-elements. After screening, the elements Mg, K, Ca, Fe, Mn, Ni, Cu, Zn, and Rb were determined and utilized for the study of food origin traceability. All parameters were controlled with a tablet computer connected to the XRF apparatus.

Calibration strategy. Matrix matching is most frequently used to establish calibration curves for XRF.^{38,39,40,41} First, ICP-MS was used to quantitatively determine Mg, K, Ca, Mn, Fe, Ni, Cu, Zn, and Rb in a group of soybean samples. Then, the certified samples were employed as matching matrix for XRF calibration.

Under the optimized conditions, the fluorescence intensities of these elements were measured ($n = 3$) by XRF. The quantitative analysis of XRF relies on the following equation:

$$C = k * I + b$$

Where C is the element concentration after calibration, I is the elemental fluorescence intensity, k is the slope of the calibration curve, and b is the intercept.

Microwave digestion ICP-MS analysis. For the calibration by XRF, ICP-MS was employed for the multi-elemental measurement in soybean samples after microwave digestion. The detailed method was modified according to the national standard,⁴² and shown as follows: 0.25 g of powdered sample was weighed into a Teflon® digestion vessel, and then 3 mL HNO_3 and 2 mL H_2O_2 were added. The vessels were closed and loaded into a microwave digestion system (TOPEX, PreeKem Scientific Instrument Co., Ltd., Shanghai, China). The microwave digestion program performed was as follows: step 1, heating to 80°C for 5 min; step 2, 80°C to 120°C for 5 min; step 3, 120°C to 190°C for 5 min and holding for 20 min; step 4, cooling to room temperature. Then, the digested solution was heated at 140°C to remove the acid up to less than 1 mL residue, which was diluted to 25 mL using 2% HNO_3 , then homogenized for the next measurement.

Statistical analysis. The data analysis and model building, including PCA and MLP, were carried out by using the SPSS software (Version 20, IBM Corporation, Armonk, NY, USA). Here, MLP is a kind of “feedforward neural network”, which is the most commonly used model with careful evaluation of data.^{43,44} The main body consists of an input layer, several hidden layers, and an output layer. Unlike PCA, which can only solve linear relationships, feedforward neural networks can solve nonlinear relationships of variables.^{45,46} The input variables of the input layer are the calibration concentration values of Mg, K, Ca, Mn, Fe, Ni,

Cu, Zn, and Rb and the output variables of the output layer are the five producing provinces (Henan, Xinjiang, Inner Mongolia, Heilongjiang, and Liaoning). For the 4 neurons in the hidden layer, the hyperbolic tangent function is selected as the activation function, and the Softmax function is selected as the activation function of the output layer.

RESULTS AND DISCUSSION

Effect of radiation time on XRF analysis. For this XRF apparatus, the X-ray light source, optical filter, light line, detector, and other hardware were designed and installed by the manufacturer. However, X-ray radiation time plays a crucial role in exciting/receiving fluorescence and signal analysis. The more time it consumes, the more stable the final signal. When used in the field or in the laboratory, quickness, high-throughput, and precision have to be considered for the miniaturized XRF, so the key is to find a balance between them. To investigate the optimal analytical precision, different radiation times (60–420 s) were performed to determine the multi-elements in the soybean samples repeatedly ($n = 5$). Here, the RSDs of the repeated measurements indicate analytical precision. As shown in Fig. 1, with increasing radiation time from 60 to 300 s, the RSDs of the Mg, K, Ca, Fe, Mn, Ni, Cu, Zn, and Rb fluorescence intensities

Fig. 1 Effect of radiation time on XRF analysis ($n = 5$). The voltage and the current of the X-ray tube were 40 kV and 800 μA , respectively.

demonstrate an obvious decline trend; when exceeding 300 s, all RSDs are below 1.5%, and their change indicates a plateau, which proved very excellent analytical precision. As a result, 300 s was chosen as the optimized radiation time for the following experiment.

Establishment of calibration curves. XRF is most frequently used to analyze solid samples, and the analytical accuracy depends on the sample matrix.^{48,49} Thus, matrix matching is suitable to establish the calibration curves for XRF. According to the experimental section, the elements Mg, K, Ca, Mn, Fe, Ni, Cu, Zn and Rb were determined by ICP-MS (n=3). Eight of these soybean samples were also employed as certified solid standards for analysis of these elements by XRF (n=3). For each element, the fluorescence intensities were combined with the certified values by ICP-MS, and the established calibration curves are shown in Fig. 2. The correlation coefficient (r) for Ca, Mn, Fe,

Ni, Cu, Zn, and Rb is more than 0.995 for each, while for Mg and K it is below 0.995 as well as higher than 0.991. This is possibly due to the Auger effect during exciting fluorescence, which leads to relatively poorer results for light elements, such as K and Mg. Considering the complication with solid standards, we inferred that the calibration curves of $r > 0.995$ for Ca, Mn, Fe, Ni, Cu, Zn, and Rb and of $r > 0.991$ for Mg and K should be used for the quantitative analysis by XRF.

Real sample analysis and principal component analysis. After establishing the calibration curves, the elements Mg, K, Ca, Mn, Fe, Ni, Cu, Zn, and Rb were measured by ED-XRF in 296 soybean samples from the Henan, Xinjiang, Inner Mongolia, Heilongjiang, and Liaoning provinces. The detailed concentration information of the multi-elements is listed in Table 2. After variance analysis, these elemental concentrations, except for Mg, demonstrate highly significant differences

Fig. 2 Calibration curves of Mg, K, Ca, Mn, Fe, Ni, Cu, Zn, Rb for XRF using certified soybean samples.

Table 2. Multi-elemental analysis by ED-XRF of soybean samples from different provinces

Provinces	Values	Elemental concentrations								
		Mg (mg g ⁻¹)	K (mg g ⁻¹)	Ca (mg g ⁻¹)	Mn (μg g ⁻¹)	Fe (μg g ⁻¹)	Ni (μg g ⁻¹)	Cu (μg g ⁻¹)	Zn (μg g ⁻¹)	Rb (μg g ⁻¹)
Henan	min	2.42	17.2	3.50	24.2	44.8	2.59	6.53	22.1	1.00
	max	2.67	20.1	4.97	30.7	73.1	7.12	9.44	27.9	11.8
	med	2.56	18.6	4.34	28.3	51.6	4.38	8.71	24.7	1.77
	Mean±SD	2.56±0.07	18.5±0.9	4.33±0.46	27.8±1.9	53.9±8.6	4.69±1.53	8.35±0.89	24.9±2.0	3.41±3.93
Inner Mongolia	min	1.99	13.1	2.27	18.9	57.0	3.10	5.48	17.6	6.29
	max	2.74	21.4	5.47	32.6	102	20.1	11.2	33.7	32.0
	med	2.58	17.5	3.84	23.9	73.5	10.6	6.68	23.0	13.6
	Mean±SD	2.54±0.16	17.4±1.5	3.84±0.75	24.1±2.9	75.6±10.4	10.8±5.4	7.49±1.77	24.3±3.7	16.4±7.8
Xinjiang	min	2.38	13.6	3.53	23.4	44.2	2.41	7.54	17.5	1.58
	max	2.63	21.2	6.10	33.1	94.4	5.28	11.5	26.7	3.58
	med	2.52	19.3	4.63	27.0	55.0	3.23	9.56	22.0	2.70
	Mean±SD	2.53±0.06	18.9±1.6	4.70±0.66	27.3±2.7	57.4±9.9	3.39±0.77	9.60±0.88	22.2±2.3	2.76±0.49
Heilongjiang	min	1.94	9.66	2.56	19.0	51.3	2.11	4.60	18.5	8.89
	max	2.77	22.0	6.50	56.9	100	23.1	9.32	29.5	39.0
	med	2.57	18.3	4.19	24.0	72.7	11.3	5.88	22.8	15.0
	Mean±SD	2.54±0.15	18.0±1.8	4.22±0.71	26.3±6.2	73.1±9.3	10.8±4.6	6.15±0.97	23.1±2.3	19.1±9.0
Liaoning	min	1.37	9.72	3.57	21.2	58.0	7.31	5.83	23.8	14.7
	max	2.73	19.3	6.21	57.3	97.7	26.2	7.88	38.2	37.8
	med	2.63	17.3	4.71	33.5	72.8	17.6	6.90	27.8	27.8
	Mean±SD	2.59±0.23	17.0±1.7	4.78±0.67	35.2±11.2	72.9±8.9	16.0±5.8	6.90±0.52	28.5±3.5	27.7±7.2

Fig. 3 Principal component analysis for soybean samples from different producing areas. (A) PCA for soybean samples plotted using the concentration of the elements (Mg, K, Ca, Mn, Fe, Ni, Cu, Zn, and Rb). (B) Factor loading plot of PC1 and PC2.

($p < 0.01$) among the different soybean producing areas. To further analyze these data and achieve the origin traceability, PCA was utilized to make preliminary classification predictions for the soybean samples. The biggest feature of PCA is that it can project data from high-dimensional space to low-dimensional space and

find linear combinations of variables to reach the best interpretation for the data. Thus, PCA has been one of the most frequently used chemometric tools for food origin traceability.⁵⁰ PCA was used to perform a preliminary analysis of the data to check all classification possibilities of the samples based on geographical sources. According

to the Eigen value > 1 , three principal components were extracted, which contributed 61.0% of the total variance. As shown in Fig. 3, the first principal component (PC1) and second principal component (PC2) accounted for 27.2% and 19.8% of the variance, respectively. The concentrations of Fe, Ni, and Rb largely contribute to PC1, and the concentrations of Mg and Zn contribute to PC2 (Fig. 3B). As shown in Fig. 3, we found that these data can be used to visually separate Xinjiang from Liaoning based on the value of PC1. Henan can be well separated from other provinces except Xinjiang. Henan, Xinjiang, and Liaoning can be separated from Inner Mongolia and Heilongjiang. However, Inner Mongolia vs. Heilongjiang and Henan vs. Xinjiang cannot be separated from each other using PCA, respectively. To separate soybean origins completely, the MLP technique was introduced to further analyze these data.

Multilayer perceptron analysis. From the PCA results, a large dispersion of elemental concentrations possibly caused by various soil, climate, and production factors in one province with a large geographic size might

lead to a failure of distinguishing the origin, such as for Heilongjiang and Inner Mongolia. In this case, this study decided to use artificial neural networks to further mine and analyze the data. As an artificial neural network, the distributed structure gives MLP the same associative power and fault tolerance as the brain.⁴⁷ Further, it has self-learning and adaptive abilities, which can solve multi-classification problems well. The data were randomly allocated to the training subset (60%), test subset (20%), and holdout subset (20%) at 3: 1: 1. Among them, the training subset is used to train the neural network and build the model; the test subset is used to track the errors in training to prevent overtraining; the holdout subset does not participate in the construction of the model, but is used to evaluate the final neural network and evaluate the model “Real” forecasting capabilities.

The MLP analysis results are shown in Table 3. All 176 samples in the training subset were correctly classified into their respective origin, and the correct prediction rate was 100%. Among the 67 samples in the test subset, one Inner Mongolia sample and one Liaoning sample were

Table 3. Training, test, holdout results for the classification of soybeans according to the model developed by MLP

Subset	Observed	Predicted					Correct (%)
		Henan	Inner Mongolia	Xinjiang	Heilongjiang	Liaoning	
Training	Henan	6	0	0	0	0	100.0%
	Inner Mongolia	0	37	0	0	0	100.0%
	Xinjiang	0	0	21	0	0	100.0%
	Heilongjiang	0	0	0	91	0	100.0%
	Liaoning	0	0	0	0	21	100.0%
	Total (%)	3.4%	21.0%	11.9%	51.7%	11.9%	100.0%
Test	Henan	3	0	0	0	0	100.0%
	Inner Mongolia	0	11	0	1	0	91.7%
	Xinjiang	0	0	6	0	0	100.0%
	Heilongjiang	0	1	0	38	0	97.4%
	Liaoning	0	0	0	1	6	85.7%
	Total (%)	4.5%	17.9%	9.0%	59.7%	9.0%	95.5%
Holdout	Henan	2	0	0	0	0	100.0%
	Inner Mongolia	0	8	0	1	0	88.9%
	Xinjiang	0	0	7	0	0	100.0%
	Heilongjiang	0	1	0	30	0	96.8%
	Liaoning	0	0	0	0	4	100.0%
	Total (%)	3.8%	17.0%	13.2%	58.5%	7.5%	96.2%

misclassified to Heilongjiang, and one Heilongjiang sample was misclassified to Inner Mongolia. Thus, the correct prediction rate was 95.5%. In the holdout subset, one Inner Mongolia sample was misclassified to Heilongjiang and one Heilongjiang sample was misclassified to Inner Mongolia. The correct prediction rate was 96.2%. The current results indicate that MLP can successfully help ED-XRF results to distinguish soybean origin from five places.

CONCLUSIONS

In this work, a commercial ED-XRF spectrometer was employed to measure the trace elements in soybean samples and to characterize their origin. After optimization, the XRF method was improved for precision and accuracy, and then was able to successfully measure 9 elements (Mg, K, Ca, Mn, Fe, Ni, Cu, Zn, Rb) in 296 soybean samples from five producing areas of northern China. This solid sampling analytical method proved to be fast, accurate, and partly portable for food origin traceability. Although PCA is not able to distinguish all producing areas completely, multi-layer perceptron demonstrates a powerful classification capacity through careful evaluation of data, reaching an accuracy rate of 96.2%. It can be stated that MLP is able to help ED-XRF overcome the disadvantages of the analytical performance found with ICP-MS or WD-XRF. Most importantly, it is a novel technical combination of a quick testing method with ED-XRF and MLP data analysis, which has the great application potential for on-site recognition of food origin.

AUTHOR INFORMATION

Corresponding Author

* X. F. Mao.

Email address: maoxuefei@caas.cn.

* Z. H. Wang.

Email address: wzhlndsp@aliyun.com.

Author Contributions

[†] H. Q. Lai and J. L. Xi contributed equally to this work.

Notes

The authors declare no competing financial interest.

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