Application of Energy Dispersive X-ray Fluorescence Analysis in the detection of heavy metal element content

Lingyun Liu¹, Xiaoping Zeng² and Jianchuan Deng¹
¹Industrial Crops Research Institute, Yunnan Academy of Agricultural Sciences, Kunming, 650205, China
²The Key Laboratory of Chemistry for Natural Products of Guizhou Province and Chinese Academy of Sciences / Guizhou Provincial Engineering Research Center for Natural Drugs, Guiyang, 550014
Corresponding author: e-mail: Jianchuan Deng, lly@yaas.org.cn

Abstract. The method of food safety testing is usually to use different testing methods to determine the various elements contained in the food to obtain whether its content meets human health standards compared with international standards. At the same time, it can be judged its origin by the content of elements detected in the food, and analyze the impact of environment pollution on its growth. Commonly used methods for detecting heavy metals in food include ICP-AES/MS, flame atomic absorption method, graphite furnace atomic absorption spectrometry and so on. The introduction of physical rapid detection methods into the field of food safety detection can greatly reduce the time required for food detection. Among them, EDXRF is a non-destructive analysis method, which can simplify the analysis process while achieving detection accuracy, and does not require chemical steps to make it more than traditional detection methods. For the purpose of environmental protection, so this article will use EDXRF to detect the content of K and other trace elements in the sample.

1. Introduction
With the development of society, food safety has gradually become a central topic of people’s attention, and food safety issues have also become diversified. Among them, heavy metal pollution in the soil caused by industrial pollution or factory wastewater discharge leads to excessive heavy metal content in crops. As a result, heavy metal poisoning of consumers is a relatively high incidence of accidents in the field of food safety in recent years. Potato, which is rich in a variety of nutrients and has various uses, is the main food crop and has become the second staple food in most European and American countries. The content of K element and other heavy metals in it is closely related to the soil environment where it is grown, and environmental pollution will have a greater impact on its composition. With the advancement of testing instruments and methods, the current methods used in food safety testing are gradually diversified. For example, in 2008, Guo Hui studied potatoes grown in red soil containing heavy metals Cd and Zn, and its physiological, biochemical and quality indicators as well as tubers The influence of the nutrient elements K, Ca, Mg, Fe, Cu, Zn in the content of [1], using the pot experiment method, it is concluded that different concentrations of Cd and Zn have an effect on the nutrient elements K, Ca, Ca and Zn in the tubers of two varieties of potato. Mg, Fe, Cu, and Zn can all have an impact. With the increase of Zn treatment concentration, the content of Ca, Mg, Fe, Cu, and Zn in potato tubers all show an upward trend. When the Zn treatment concentration is less than 40 mg/kg, the K content in
The tuber of Zhongshu No. 3 shows an upward trend, and when the Zn treatment concentration is greater than 40 mg/kg, it shows a gradually decreasing trend. The K content in the Atlantic tuber is less than 80 mg when the Zn treatment concentration is less than 80 mg. It showed an upward trend under the condition of Zn/kg, and showed a downward trend when the Zn treatment concentration was greater than 80 mg/kg. In addition, it is concluded that under the experimental conditions, there are differences between varieties in the absorption of nutrients K, Ca, Mg, Fe, Cu, and Zn in potato tubers by Cd and Zn. In 2011, Han Hongping et al. used FAAS detection method to determine 8 kinds of trace elements in black potatoes. In this experiment, the detection limit of K element was 0.002mg/L, the recovery rate was 100.3%, and the RSD was 2.76% [2]. Also in 2016, Wang Ningfang used the flame atomic absorption method to determine the trace elements in potatoes. The recovery rates of the trace elements Cu, Zn, Fe, Mn, Ca, K, and Mg were 97.00%~99.70%, and the relative standard deviation was 1.17%~2.75%[3]. However, the flame atomic absorption method to determine the trace elements contained in potatoes is accurate, but the operation process is relatively complicated. In the field of food inspection, extremely high inspection accuracy is usually not required, and the accuracy obtained by common food inspection methods such as flame atomic absorption method is often surplus in food safety analysis, and the inspection process is not simple and fast enough. In contrast, EDXRF inspection has the characteristics of fast and non-destructive, Applied in the field of food inspection can not only simplify the process and reduce the time required, but also achieve higher accuracy. Therefore, this paper uses EDXRF to detect the content of K and other heavy metal elements in potatoes, and analyzes its relationship with soil pollution in the growing environment.

2. Materials and methods

2.1. Materials and instruments

| Material (Instrument) | Brand (Source) | Instrument | Source |
|-----------------------|----------------|------------|--------|
| Potatoes              | A,B,C area     | BSA224 Analytical balance | Sartorius, Germany |
| Hydrogen peroxide     | Tianli         | UPT−1—10T ultrapure water machine | Sichuan Youpu Ultrapure Technology Co., Ltd. |
| Nitric acid (HNO3, GR)| Shandong Xuchen Chemical Technology Co., Ltd. | PC-12 Powder Pressing Machine | Tianjin Jingtuo Instrument Company |
| K Standard Solution   | National Nonferrous Metals and Electronic Materials Analysis and Testing Center | HK-02A100g Portable crusher | Guangzhou Xulang Machinery Equipment Co., Ltd. |
| Ammonium Dihydrogen Phosphate (NH4H2PO4) | Tianjin Third Chemical Reagent Factory | EDX8300HEDXR fluorescence spectrometer | Suzhou Sanvalue Precision Instrument Co., Ltd. |
| ZEEnit650P atomic absorption spectrometer | Jena Analytical Instruments AG | EH45 adjustable temperature electric heating plate | LabTech |

The working parameters of the EDXRF instrument are: tube pressure 45Kv, tube flow 300μA, temperature 16°C, vacuum degree 93.0Kpa.
2.2. Sample pretreatment
(1) Selection of raw materials: Choose varieties with large tubers, thin skins, low reducing sugar content, and less protein and fiber. In this experiment, potatoes grown in Chaozhou were used.
(2) Cleaning: Wash the silt and dust on the selected potato skin with clean water.
(3) Peeling: It can be done by artificial peeling or lye peeling. For manual peeling, a knife can be used to peel off the outer skin of the potato and trim its surface to a smooth surface. The potato samples were dried and crushed, passed through different mesh sieves, mixed thoroughly, and reduced to 50g by the quarter method [4]. Dry for 4-6 hours at 80°C to make the moisture content less than 0.1%, cool it a little and place it in a desiccator for later use.

2.3. Selection of EDXRF testing conditions
After Ma Jiangyuan et al. [5] conducted an experiment on the best detection conditions for EDXRF, 4 g of potato powder sample passed through a 140 mesh sieve was pressed under a pressure of 25 MPa for 30 s and then made into flakes. The detection time is At 90 s, the measured count rate is the highest. The precision and stability under this condition are 0.03% and 0.19%, respectively, indicating that the precision and stability of the method are relatively high, and this experimental condition is used for the determination in this experiment.

3. Experimental part
3.1. The detection limit
Among the elements determined by EDXRF, the detection limit varies with the body and component content of the sample. The detection limit varies from element to element, and the calculation method is usually calculated according to formula (1)

\[ L_D = \frac{3S}{R\sqrt{t}} \]  

Where S is the sensitivity of the analytical element (S-1·mg·kg⁻¹); R is the background count rate(s-1); t is the background measurement time (s).

3.2. Actual relative error
The actual relative error is the percentage of the absolute error to the true value. In the EDXRF test, the actual relative error is used to reflect the accuracy of the measurement result. The actual relative error is calculated by formula (2)

\[ RE = \frac{\Delta C}{C} \times 100\% \]  

Among them, \( \Delta C \) is the difference between the measured content and the true content in mg·kg⁻¹ (take the absolute value); C is the true content value in mg·kg⁻¹, in this method is the element content value measured by the flame atomic absorption method.

3.3. Relative standard deviation
The relative standard deviation is used to characterize the reliability of the repeatability test results, which can reflect the precision of the EDXRF measurement. The relative standard deviation is calculated by formula (3)

\[ RSD = \frac{1}{N-1} \sqrt{\sum_{i=1}^{N} (x_i - \bar{x})^2} \times 100\% \]  

In the formula, N is the number of tested samples (a natural number); \( x_i \) is the test content of the i-th sample; \( \bar{x} \) is the average test content of N samples.
4. Results and discussion

4.1. Standard curve and element detection limit

To quantitatively analyze the elements contained in potatoes in group A, it is necessary to use the basic parameter method to establish a standard curve. Figure 1 is a schematic diagram of the standard curve of K element. It is the relationship between the concentration of K element and the measured intensity. The element intensity of each group of samples is converted into the concentration in the sample.

![Figure 1. Measured intensity of K's main peak and the standard curve of the theoretical intensity.](image)

The potato standard samples of group A were measured. According to formula (1), the average detection limit of K element mass fraction in standard potato was 1.25 mg·kg⁻¹ and the average detection limit of Fe element mass fraction was 1.50 mg·kg⁻¹, the average detection limit of the mass fraction of Zn element is 1.25 mg·kg⁻¹, and the average detection limit of the mass fraction of Pb element is 1.00 mg·kg⁻¹. The average detection limit of the four element mass fractions is 1.25 mg·kg⁻¹, which is taken as the average detection limit of metal elements in potatoes under this background condition.

4.2. Actual relative error and relative standard deviation

In this experiment, the accuracy of the EDXRF method was determined by comparing the measurement results of the potato sample by the flame atomic absorption method. In order to ensure that the accuracy of the experimental data is not affected by random factors, five parallel experiments were performed on the potato standard samples of group A, the average count rate was calculated, the metal element content was converted, and the actual relative error of the metal content detected by the EDXRF method was calculated. The results are shown in Table 2.

| sample | EDXRF method measurement results | Flame atomic method measurement results | RE/% |
|--------|----------------------------------|----------------------------------------|------|
|        | Parallel group 1                 | Parallel group 2                       | Parallel group 3 | Parallel group 4 | Parallel group 5 | Average value | RE/%   |
| K      | 16.87                           | 19.01                                  | 17.11            | 18.03            | 18.34            | 17.87         | 17.34  | 3.07  |
| Zn     | 26.55                           | 26.98                                  | 27.10            | 27.26            | 27.62            | 27.10         | 25.81  | 5.01  |
| Pb     | 4.99                            | 3.78                                   | 4.67             | 3.69             | 5.57             | 4.54          | 4.33   | 4.85  |

The comparison chart of the measured values of EDXRF and flame atomic absorption method is shown below.
Figure 2. The results of 5 parallel experiments on group A potatoes and the comparison of the average values by the EDXRF method and the flame atomic absorption method.

It can be seen from Table 2 that the actual relative error between the metal element content value measured by the EDXRF method and the content value measured by the flame atomic absorption method is less than 6%, and the relative error of the K element is 3.07%. The t test was performed to obtain p>0.05, indicating that the EDXRF method and the flame atomic absorption method are not statistically significantly different, that is, the results of the two methods are consistent, and the EDXRF method can be effectively applied to the detection of metal element content in potatoes.

Then by repeating the measurement of the potato standard samples of group A for 10 times, the average value, standard deviation and relative standard deviation of each sample are calculated by formula (3), and the repeatability of EDXRF is analyzed. The results of the precision test are shown in Table 3.

Table 3. The precision of EDXRF analysis of 10 repeated measurements on the potato standard samples of group A.

| Sample | Repeat times | Average value (mg·kg⁻¹) | SD   | RSD/% |
|--------|--------------|-------------------------|------|-------|
| K      | 10           | 17.49                   | 0.67 | 3.81  |
| Zn     | 10           | 26.72                   | 0.95 | 3.57  |
| Pb     | 10           | 4.39                    | 0.18 | 4.13  |

According to the results in Table 3, it can be seen that the relative standard deviation of the K metal element content in the sample is 3.81%, and the relative standard deviations of the three elements are all below 5%, indicating that the EDXRF method has high precision and can meet the analytical requirements’ need.

4.3. Detection of heavy metal elements in potatoes and soil heavy metal pollution

EDXRF was used to detect potato samples from three different regions of A, B, and C. At the same time, the soil for potato planting in three regions of A, B, and C was tested for heavy metal element content. The average results of the measurement are as follows.
Table 4. Potato heavy metal content and soil heavy metal content detection from the three regions of A, B, and C (mg·kg⁻¹).

| Area | Sample | K    | Zn    | Pb    |
|------|--------|------|-------|-------|
| A    | Potato | 17.49| 26.72 | 4.39  |
|      | Soil   | 42.13| 40.56 | 8.19  |
| B    | Potato | 12.56| 21.34 | 3.56  |
|      | Soil   | 23.89| 36.27 | 6.32  |
| C    | Potato | 19.23| 31.23 | 5.13  |
|      | Soil   | 50.09| 63.25 | 10.25 |

The comparison of the metal element content in potatoes in the three regions and the metal element content in the planting soil is shown in Figure 3.

Figure 3. Comparison of the potato heavy metal content and soil heavy metal content detection from the three regions of A, B, and C (mg·kg⁻¹).

It can be seen from Figure 3 that the content of heavy metal elements in potatoes has a positive correlation with the content of heavy metals in the soil, and soil heavy metal pollution is likely to cause excessive heavy metal content in potatoes.

5. Conclusions

The EDXRF method detects heavy metal elements in potato samples. The method has an average detection limit of 1.25 mg·kg⁻¹ for metal elements in potatoes. Therefore, this method can be used to detect metal elements that are higher than this content in the national standard. And it has a high detection sensitivity for the K element, which meets the requirements for the analysis of the K element content in the potato; at the same time, EDXRF has no special requirements for the detection environment, and it can detect potato samples in real time in the on-site environment, and the results are accurate and reliable. In addition, the use of EDXRF to detect the content of heavy metals in the potato planting environment can analyze that heavy metal pollution in the soil may cause the heavy metal content of the potato to exceed the standard.

The high sensitivity and low detection limit of EDXRF in the detection of heavy metals in potatoes make it more comprehensive in the analysis of the types and contents of elements contained in food.
This technology provides a new idea for the traceability of food origin. In addition, due to the timeliness of the technology, the technology can be used more in the field of rapid detection of food elements.

Acknowledgement
The authors thank for the supported by Yunnan Agricultural Joint Foundation “Study on physiological response mechanism of potassium for potato scab resistance” (No. 2018FG001-077) for this research.

References
[1] Guo Hui. The effect of heavy metals Cd and Zn on potato growth and quality [D]. Hunan Agricultural University, 2008.
[2] Han Hongping, Hu Fengzu. FAAS determination of 8 trace elements in black potato [J]. Spectroscopy Laboratory, 2011, 28(03): 1385-1387.
[3] Wang Ningfang. Determination of trace elements in potatoes by flame atomic absorption method [J]. Journal of Anhui Agricultural Sciences, 2016, 44(34): 46-47.
[4] Yang Xuewen. Rapid determination of cadmium content in grain by X-ray fluorescence spectrometry [J]. Cereals, Oils and Foodstuffs Science and Technology, 2016, 24(3): 62-64.
[5] Ma Jiangyuan, Sang Xiaoxia, Li Yeli, Huang Dengyu. Optimization of tea detection conditions based on energy dispersive X-ray fluorescence spectrometry [J]. Food and Fermentation Industries, 2020, 46(04): 282-286.