The application of EDXRF on soil heavy metal analyzation in a planting area

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Abstract. With the increase of heavy metal concentration in soil, serious environmental problems have arisen. At present, heavy metals mainly refer to biotoxic heavy metals, including Lead, Cadmium, Mercury and Chromium, etc., which are produced in large quantities by human activities and difficult to be degraded, resulting in their loss of original activity and chronic poisoning because of the reaction with proteins and enzymes in human body. The soil concentration in the planting area exceeds the standard and is enriched in human beings, animals and plants, which directly endangers the living environment and health. In this paper, the soil in the planting area next to Xiangzhang canteens of Chengdu University of Technology was selected for field investigation, and the data analysis and risk assessment were carried out after testing the concentration of heavy metals in the surrounding soil through reasonable sampling, sample treatment and Energy-Dispersive X-ray fluorescence analysis techniques.

1. Introduction

Human activities such as mining, smelting, and agriculture cause heavy metal pollution in the soil. (Hong Tao et al.,2019) The chemical and metallurgical industries are the most important sources of metals in the environment, which are classified as "heavy metals". From the analysis of the environment of the entire urban, various human activities have brought a lot of heavy metals into the urban soil, causing the accumulation of these heavy metal elements to cause great damage to the ecological environment, especially the pollution of the soil environment(García-Sánchez et al., 2019), which threaten the safety of farmland ecological environment and the quality of agricultural products(Wu Tangfu et al., 2019). The main purpose of this study is to evaluate the soil conditions in the planting area beside the Xiangzhang canteen of Chengdu University of technology. Most of the plants in the planting area can be used. However, it is obvious that eating the vegetables planted in the contaminated soil will damage the health(Liu et al., 2019). Unlike other types of pollution, such as air pollution or ozone exposure, the individual risk associated with soil pollution largely depends on the heavy metal concentration of vegetables, and soil is the most important factor directly determining whether the amount of heavy metal in vegetables exceeds the limit. At present, the commonly used heavy metal detection methods mainly include a new electrochemical based on physical and chemical reactions, biological detection and optical detection method, but the steps are complicated and the detection cost is high. The biggest advantage of EDXRF detection technology based on atomic excitation is its high efficiency. At the same time, it can deal with the above problems simply, and it can also achieve the effect of nondestructive and rapid detection in the field.
2. Materials and method

2.1. Overview of the study area
The sampling point is located in the planting area next to the Xiangzhang canteen of Chengdu University of Technology, Chengdu, Sichuan Province. Due to the planting area next to the Xiangzhang canteen is too large, the area of 40 × 40 m² is selected in this experiment. The sampling interval is 10 m, and the soil below 2 cm in the surface layer is taken (no ground slide, no impactor, and no soil error from other different areas). 25 samples were taken and transferred to the plastic vacuum sample bag, numbered and sealed, about 20g each.

2.2. Experimental instrument
IED-2000T portable X-ray fluorescence analyzer was used in this experiment, which is developed by Chengdu University of Technology. Its specific parameters are as follow: HardGain=2, SoftGain=10000, ShapTime=2, TubeHv=30, Tubel=2, TestTime=100, EgA=0.0346331, EgB=0.0259799.

2.3. Moseley's theorem
The EDXRF system is consisted of an X-ray tube, a sample chamber, a collimator, a detector, a counting circuit and a computer. When the characteristic X-ray of the substance contained in the sample is recorded by the detector, the electron hole pair will be generated immediately. The number is proportional to the energy of the incident photon, and the pulse within a certain energy length will be obtained through a series of circuits. Finally, the types and concentrations of the elements to be measured are obtained through noise reduction, background deduction and separation of overlapping peaks.

Moseley's study found that the calculating photon energy is (Mingtai Yang, et al., 2009):

\[ E = h\nu = h\frac{c}{\lambda} \]

Where, \( E \): energy of the X-ray photon; \( \nu \): frequency of light waves; \( h \): Planck's constant; \( C \): the speed of light.

The energy generated by the electron transition from the different layers is recorded as \( \Delta E \), which is released in the form of X-ray. The calculation formula is

\[ \Delta E = RhC(Z - \sigma) \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \]

Where, \( \Delta E \) is the characteristic X ray energy; \( R \) is Rydberg constant; \( \sigma \) is a constant related to the excited energy level.

According to the formula, the type of elements can be obtained by the wavelength or energy of EDXRF. Since EDXRF intensity is related to the content of elements, the qualitative and quantitative analysis of heavy metal elements can be conducted accordingly.

3. Results and discussion
A total of 25 samples were measured in this experiment. After calibrating the handheld EDXRF with Zn and Cu peaks, 16 kinds of elements were obtained from the output results of the instrument: Mg, Ar, K, Sc, Ti, V, Mn, Fe, Co, Cu, Zn, As, Rb, Sr, Y and Zr. The output mode is the characteristic peak count of the element (no unit). The range of the characteristic peak area count of Mg element is 0~0, and the average value is 0. The characteristic peak area count of Ar elements ranges from 82 to 783, and the average value is 253. The characteristic peak area count of K element ranges from 425 to 802, and the average value is 570. The characteristic peak area count of Sc elements ranges from 2070 to 5834, and the average value is 3515. The characteristic peak area count of Ti element ranges from 1311 to 1855, and the average value is 1561. The characteristic peak area count of element V ranges from 186 to 541, and the average value is 395. The characteristic peak area count of Mn elements ranges from 210 to 969,
and the average value is 607. The characteristic peak area count of Fe is 63070~81256, and the mean value is 70081. The characteristic peak area count of Co element ranges from 10854 to 13603, and the average value is 12065. The characteristic peak area count of Cu elements ranges from 217 to 737, and the average value is 466. The characteristic peak area count range of Zn is 659~1270, and the average value is 995. The characteristic peak area count of As element ranges from 516 to 1071, and the average value is 689. The range of the characteristic peak area count of Rb element is 2096~4388, and the average value is 2918. The area count of the characteristic peak of Sr elements ranges from 2044 to 5966, and the average value is 3108. The characteristic peak area count of Y element ranges from 567 to 1923, and the average value is 958. The characteristic peak area of Zr elements ranges from 4186 to 7091, with an average value of 5275. In this experiment, the peak area count of Fe element was the largest, far more than other elements, and the peak area count of Mg element was the smallest. The count of Co element was the most stable in 25 groups of samples, and the peak area count of each measurement had a small difference, with a maximum deviation of 5.6% from the average. In the 25 groups of samples, the count of Ar element fluctuated the most, and the peak area count of each measurement varied greatly, with the maximum deviation from the average value being 56%. Nevertheless, the overall measurement results showed high stability and reliability (Qi Zhang, 2019). The concentrations of specific elements are shown in the figure 1 below.

![Statistical figure of peak area count of 16 elements](image)

Figure 1. Statistical figure of peak area count of 16 elements

According to the purpose of this study, heavy metal elements that can be detected by EDXRF and need to be analyzed through this experiment are As, Cu and Zn.

As is calibrated according to As standard solution (elemental standard solution). In the 25 samples, the minimum value of As concentration is 8.67mg/kg, the maximum value is 17.99mg/kg, and the average value is 11.58mg/kg. At the same time, according to the soil properties of the collection site, soil PH = 6.8 is measured according to the experiment, and the As concentration requirement of the secondary standard PH between 6.5 and 7.5 according to GB15618-1995 Soil Environmental Quality Standards is less than 25 mg/kg. The concentration of the As element measured in the experiment and the national standard can be seen in the figure 2(a), and all the samples measured do not exceed the national standard.
The calibration of Cu is also carried out according to Cu standard solution (element standard solution). In 25 samples, the minimum value of Cu concentration is 3.65mg/kg, the maximum value is 12.39mg/kg, and the average value is 7.84mg/kg. At the same time, according to the soil properties of the collected land, the soil PH value is measured as 6.8. According to the GB15618-1995 Soil Environmental Quality Standards, the secondary standard PH value is between 6.5 and 7.5, and the Cu concentration required is less than 100mg/kg. The comparison between the concentration of Cu elements measured in the experiment and the national standard is shown in the figure 2 (b). All the samples measured do not exceed the national standard.

Zn is calibrated according to the Zn standard solution (elemental standard solution). In 25 samples, the minimum value of Zn concentration is 11.09mg/kg, the maximum value is 21.34mg/kg, and the average value is 16.72mg/kg. At the same time, according to the soil properties of the collected land, the soil PH value is measured as 6.8. According to the GB15618-1995 Soil Environmental Quality Standards, the secondary standard PH value is between 6.5 and 7.5, and the Zn concentration required is less than 250mg/kg. The comparison between the concentration of Zn elements measured in the experiment and the national standard is shown in the figure 2 (c). All the samples measured do not exceed the national standard.

![Figure 2](https://example.com/figure2.png)

**Figure 2.** Comparison of the concentration of As(a), Cu(b) and Zn(c) with national standard values

4. Conclusion

According to the comparison of the experimental data with the national standard, the heavy metal concentration near the Xiangzhang canteen of Chengdu University of Technology is stable. Although it is convenient and efficient to use the EDXRF for analysis, the detection limitation is low in this experiment, and the heavy metal concentration in the soil is unavailable, such as Pb, Hg, Cd, Cr and other elements. However, during this experiment, it is found that there are more As elements in the soil. It does not exceed the National second-level soil standard, but it must also attract our attention. It can be inferred that there was groundwater under the soil near the Xiangzhang canteen years ago, and the concentration of arsenic in the natural water body ranged from 0.5 μg /L to 5,000 μg /L. Due to precipitation accumulation effect in the groundwater, in the midst of groundwater As element concentration accumulation. Therefore, it is concluded that there is likely to be groundwater infiltration under the soil years ago near the Xiangzhang canteen of Chengdu University of Technology, resulting in high as concentration in the soil. In addition to the high As concentration, the detected Fe concentration is also higher than other elements. It is speculated that there was precipitation and accumulation of iron ore in the groundwater before.
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