Quantitative analysis of heavy metal pollution in surface soil along the Funan River by XRF

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Abstract. With the development of urbanization and industrialization, the excessive use of metals leads to a sharp decrease in soil resources. Funan River runs through the whole urban area of Chengdu, and the surrounding population density is large, and environmental governance needs exist all the year round. It is of great significance to test the soil heavy metal content in this area. Under current environmental pollution, heavy metals mainly refer to biotoxic materials such as lead, cadmium, mercury and chromium, which are widely distributed in the atmosphere, water, soil and other substances in nature. They will react with proteins and enzymes in the human body, thus losing their original activities and even causing chronic poisoning. In this paper, reasonable sampling, sample treatment, X-ray fluorescence analysis and other methods were carried out for the surface soil along the Funan River, and the quantitative analysis of heavy metals was carried out. Results show that the heavy metal content of surface soil Chendu Funan river coast are not more than the soil environment quality standard "regulation of the secondary standard, however, As, Cu and Zinc are found in the experiment of different degrees of pollution, including the As affected by natural factors, pollution is not obvious, the Cu and Zn pollution is more obvious, and concentrated in the industrial zone, highway interchange, namely industrial pollution and traffic pollution are more serious.

1. Introduction

Heavy metals are a kind of environmental pollutants with a cumulative effect and strong toxicity. They cannot be removed by self-purification of water, but can accumulate in water and enter the food chain, thus threatening human health and ecological environment. In recent years, with the rapid acceleration of China, the aggravation of industrial pollution and urban waste discharge, and the application of pesticides, and the extremely difficult degradation of heavy metals, soil environmental problems are very serious. Analysis of heavy metal pollution has become a hot topic in today's world [1].

The problem of soil pollution follows closely behind that of air pollution and water pollution. Because soil is a mixture of man-made factors and natural pollutants on earth, most of the pollutants in the world end up on the land [2]. Therefore, China's land and environmental problems are centralized, complex and explosive. Severe soil pollution and high-risk areas occur in local industrial and mining areas and surrounding areas, urban and suburban areas, and heavily polluted companies or industrial intensive areas [3]. As early as the early 1960s, the Dumping of chemical wastes in the United States and the Netherlands caused serious soil pollution [4].The presence of significant toxic waste at the United States Lavrov Kana landfill poses an extremely serious safety risk for soil contamination at the site and directly affects the health of the surrounding population. Hooker Enterprises has invested more
than $400 million to solve the problem of environmental pollution. In the process of real estate development in the Netherlands, waste materials containing toxic chemicals such as xylene and toluene were used as soil filling materials, causing serious soil pollution along the lakeside, so much so that 188 million Guilders were spent to clean and remediate the contaminated soil[5]. Early mining activities in Fukuyama prefecture in Japan resulted in the release of large amounts of cadmium into the natural world, posing a huge safety hazard to local residents and leading to increased soil pollution in many places. Therefore, the detection of urban soil pollution is urgent.

2. Research design

2.1. Principle of XRF quantitative analysis

![Figure 1. Schematic diagram of characteristic X-ray excitation detection.](image)

Calculation formula of characteristic X-ray fluorescence count rate ($I_k$) can be considered as the integral of the maximum energy $E_{\text{max}}$ of the main spectrum and the absorption limit of the element to be measured (less than $K_{ab}$ when excited by multiple small energy regions of the tube's main spectrum).

$$I_k(E_i) = \frac{K\tau_A(E_i)I_0(E_i)C_x}{E_i\left(\frac{u_{ij}}{\sin\alpha} + \frac{u_k}{\sin\beta}\right)}[1-e^{-\left(\frac{u_{ij}}{\sin\alpha} + \frac{u_k}{\sin\beta}\right)M}]$$

$$K = \frac{\Theta}{4\pi}\cdot E_k\cdot \omega_k\cdot g\cdot \bar{e}\cdot (1-\frac{1}{\xi_k})$$

(1)

(2)

If the sample is infinitely thick ($M \to \infty$):

$$I_k(E_i) = \frac{K\tau_A(E_i)I_0(E_i)C_x}{E_i\left(\frac{u_{ij}}{\sin\alpha} + \frac{u_k}{\sin\beta}\right)}$$

(3)

When excited by a tube, the total X-ray fluorescence count rate ($I_k$) can be considered as the integral of the maximum energy $E_{\text{max}}$ of the main spectrum and the absorption limit of the element to be measured (less than $K_{ab}$ when excited by multiple small energy regions of the tube's main spectrum).

$$i_k = \int_{E_{\text{max}}}^{E_{\text{max}}} I_k(E) \cdot dE$$

(4)

In this calculation, the primary fluorescence between $K_{ab}$ and $E_{\text{max}}$ can be subdivided into multiple energy spacing $\Delta E$, and then the strength of all $\Delta E$ can be calculated and summarized, namely:

$$i_k = \int_{K_{ab}}^{E_{\text{max}}} I_k(E) \cdot dE = \sum[\Delta EI_k(E)D_{E_i}]$$

(5)

In formula (2-5), when $E_i < K_{ab}$, $D_{E_i}=0$; when $E_i > K_{ab}$, $D_{E_i}=1$. Substituting equation (2-3) into equation (2-5), the total count rate recorded by the detector:

$$i_k = KC_x\Delta E\sum\left[\frac{\tau_A(E_i)I_0(E_i)}{E_i\left(\frac{u_{ij}}{\sin\alpha} + \frac{u_k}{\sin\beta}\right)}\right]$$

(6)
In the formula, \( I_0(E_i) \) represents the specific intensity distribution of the main spectrum of the tube. As early as the 1920s, Clemmers scholars began to theoretically derive the specific formula (2-6) for the intensity distribution of bremsstrahlung continuum in their research. Kramers’ calculation formula:

\[
I_0(\lambda_i) = I(\lambda_i) = C K Z \frac{1}{\lambda_i^2} \left( \frac{1}{\lambda_{\text{min}}} - \frac{1}{\lambda_i} \right)
\]

(7)

The main purpose of the electron probe is to measure the continuous spectrum of many thick targets. The specific calculation formula of peak and escape peak is as follows:

\[
I(\lambda_i) = 2.72 \times 10^{-6} \left[ \frac{1}{\lambda_i^2} - \frac{1}{\lambda_{\text{min}}^2} \right] f W_{ab}
\]

(8)

In the formula, \( Z \) is the target atomic number, and \( W_{ab} \) is the correction factor for the absorption limit of the beryllium window of the X-ray tube. The definition of \( f \) is:

\[
f = (1 + C \xi_i)^{-2}
\]

(9)

\[
\xi_i = \left( \frac{1}{\lambda_{\text{min}}^{1.65}} - \frac{1}{\lambda_i^{1.65}} \right) u_{\text{tg}} \csc \phi
\]

(10)

In the formula, \( \phi \) refers to the angle between the X-ray tube emission ray and the target; \( u_{\text{tg}} \) is the mass absorption coefficient of the target element. \( C \) represents:

\[
C = \frac{1 + (1 + 2.56 \times 10^3 Z^2)^{-1}}{[1 + (2.56 \times 10^3 \lambda_{\text{min}} Z^2)^{-1}] (0.25 \xi_i + 1 \times 10^3)}
\]

(11)

X-rays have wave-particle duality and can be regarded as either particles or electromagnetic waves. There is a one-to-one correspondence between the energy of particles and the wavelength of electromagnetic waves. So the formula (2-7) can also be used to calculate the energy:

\[
I_0(E_i) = I(E_i) = C K Z \frac{1}{(hc/E_i)^2} \left( \frac{1}{(hc/E_{\text{max}})} - \frac{1}{(hc/E_i)} \right)
\]

(12)

Formula (2-8) can be expressed as:

\[
I(E_i) = 2.72 \times 10^{-6} Z \left[ \frac{hc/E_i}{(hc/E_{\text{max}})_{ab}} - 1 \right] f W_{ab}
\]

(13)

Pella et al. proposed a detailed formula for calculating the characteristic spectrum of X-ray tube and its continuous spectral intensity ratio:

\[
\frac{I_0(E_i)}{I(E_i)} = \exp \left[ -0.5 \left( \frac{U_0 - 1}{1.17 U_0 + 3.2} \right)^2 \right] \left[ \frac{a}{b + Z^2} + d \right] [U_0 \ln U_0 / (U_0 - 1) - 1]
\]

(14)

At this point, the exposure rate of incident ray is:

\[
I_0(E_i) = I_1(E_i) + I(E_i) = \left[ \exp \left[ -0.5 \left( \frac{U_0 - 1}{1.17 U_0 + 3.2} \right)^2 \right] \left[ \frac{a}{b + Z^2} + d \right] [U_0 \ln U_0 / U_0 - 1] + 1 \right] I(E_i)
\]

(15)

Among them, \( U_0 = \frac{E_{\text{max}}}{E_q} \);

\( \mathit{B, d——Constant;} \)

\( \mathit{E_q——The~critical~excitation~energy~of~the~electron~shell~corresponding~to~the~characteristic~spectrum.} \)

In X-ray fluorescence analysis and related applications, the introduction of relative measurement methods should be considered. For unknown sample and standard sample, the total number rate recorded by the detector can be calculated by the following formula:
$$i_k^s = K_s C_s \Delta E \sum \left[ \frac{\tau_s(E_i)I_0(E_i)}{E_i \left( \frac{u_{0i}^s}{\sin \alpha} + \frac{u_K^s}{\sin \beta} \right)} \right]$$

(16)

$$i_k^u = K_u C_u \Delta E \sum \left[ \frac{\tau_u(E_i)I_0(E_i)}{E_i \left( \frac{u_{0i}^u}{\sin \alpha} + \frac{u_K^u}{\sin \beta} \right)} \right]$$

(17)

\(K_u\) and \(K_s\) are the detection factors of the instrument during the measurement of unknown sample and standard sample respectively. Since the detection conditions of the instrument are the same, there are:

$$K_u = K_s$$

(18)

If the substrate of unknown sample is the same as that of standard sample, the mass absorption coefficients of the primary and characteristic X-rays for each energy are the same. To:

$$\frac{u_{0i}^u}{\sin \alpha} + \frac{u_K^u}{\sin \beta} = \frac{u_{0i}^s}{\sin \alpha} + \frac{u_K^s}{\sin \beta}$$

(19)

By the formula (2-16), (2-17), (2-18) and (2-19) can be obtained:

$$C_u = i_k^u i_s^K C_s$$

(20)

Therefore, quantitative analysis can be carried out by selecting appropriate standard samples and measuring them under the same conditions.

2.2. Data description
This paper mainly analyzed the content and accumulation status of As, Zn, Cu in the surface soil. By selecting the surface soil samples along the river reach, the samples were prepared by means of drying, grinding, laminating and other physical means, and then EDXRF analysis was carried out to compare the obtained data with the national standard soil values. Due to the large number of samples measured in the experiment and the analysis and discussion of heavy metals focused on, the most appropriate means of X-ray fluorescence analysis was selected for this experiment, and the handheld X-ray fluorescence analyzer of Chengdu University of Technology (see Figure 2) was used for experimental analysis, with high efficiency.

![Sample](https://via.placeholder.com/150)

**Figure 2.** Schematic of a hand-held X-ray fluorescence analyser.

Specific experimental technical route (See Figure 3):
In this study, three sections of Funan River basin in the main urban area of Chengdu were selected: from Chengdu 339 to Hejiang Pavilion, from Riverside Park to Hejiang Pavilion, and from Hejiang Pavilion to Wangjiang Lou Park (see Figure 4). The whole journey was about 6km. Soil samples were collected every 100 meters, and a total of 60 samples were taken. As shown in the figure below:

**Figure 4.** Schematic diagram of Funan River section.

3. **Results and discussion**

There are a total of 60 samples measured in this experiment. After element calibration of handheld EDXRF instrument by Zn and Cu peaks, the elements obtained by instrument output results are Mg, Ar, K, Sc, Ti, V, Mn, Fe, Co, Cu, Zn, As, Rb, Sr, Y and Zr in total, including 16 types (see Figure 5). The characteristic peak area of Mg element ranges from 21 to 108, with an average of 59. The characteristic
peak area count range of Ar element is 87–862, and the average value is 372. The characteristic peak area count range of Fe element is 42711–61358, the average value is 50836. The characteristic peak area count range of Co element is 10899–13542, and the average value is 12443. Cu element's characteristic peak area count ranges from 805 to 2911, with an average of 1734. The characteristic peak area count range of Zn elements is 3321–6952, with an average value of 5129. The characteristic peak area count range of As element is 537–1092, and the average value is 693.

In this experiment, the peak area count of Fe element is the largest, far exceeding that of other elements, while the peak area count of Mg element is the smallest. Among 60 samples of Co element, the count was the most stable, and the difference of peak area count in each measurement was not big, and the maximum deviation of relative average value was 4.7%. Among the 60 groups of samples, the count of Ar element fluctuates the most, the peak area count of each measurement varies greatly, and the maximum deviation from the average value is 52%. However, the overall measurement results show high stability and reliability.

Figure 5. Statistical chart of peak area count of 16 elements.

By comparing the experimental data detected by XRF, the analysis of As, Cu and Zn should be emphasized. As element was calibrated according to GSB04–1714–2004 arsenic standard solution (element standard solution). In the 60 samples, the minimum value of As content was 7.83mg/kg, the maximum value was 19.21mg/kg and the average value was 13.35mg/kg. According to the soil properties of the sampling sites, the experimental results showed that the soil PH was 6.9. According to GB15618—2008 "Environmental quality standard for soils", the second-level standard value PH is between 6.5 and 7.5, and the content of As is required to be less than 25mg/kg. The content of As element was compared with the national standard (see Figure 6-A). All the samples did not exceed the national standard.

The Cu elements were also calibrated according to GSBG62024-90 copper standard solution. It was calculated that among the 60 samples, the minimum Cu content was 15.24mg/kg, the maximum was 41.35mg/kg and the average was 28.47mg/kg. According to the second-level standard value stipulated in GB15618-2008 "Environmental quality standard for soils", the Cu content is required to be less than 100mg/kg. The measured content was compared with the national standard (see Figure 6-b), and none of the samples exceeded the national standard.

According to the standard solution of GSBG62025-90, the zinc elements were demarcated. In the 60 samples, the minimum value of Zn content was 82.37mg/kg, the maximum value was 112.91mg/kg and the average value was 97.58mg/kg. According to the second-level standard value stipulated in GB15618-2008 "Environmental quality standard for soils", the content of Zn is required to be less than 250mg/kg. Compared with the national standard (see Figure 6-c), all the samples did not exceed the national standard.
4. Conclusions
The results show that the content of heavy metals in the surface soil along Funan River is stable. In this paper, an X-ray fluorescence analyzer independently developed by Chengdu University of Technology was selected for the experiment. In the analysis process, although the instrument is portable and high efficiency, due to the low detection limit of X-ray fluorescence analyzer and the low content of heavy metals in the soil, such as Hg, Pb, Cr and other elements, specific data cannot be detected. The Fe element with very high content in the measurement is an important plant nutrient element, not a polluting element, so it will not be discussed. However, in this experiment, it was found that there were a lot of elements As, Cu and Zn in the soil. Although they did not exceed the national secondary soil standard value, enough attention should be paid to them. In particular, elements Cu and Zn are already pollutants, which need to be properly controlled to prevent pollution aggravating and exceeding the limit value. Through the comparison of the surrounding environment around the measurement site, it is found that the distribution of As pollution has no fixed rule, which is mainly affected by natural factors, so the pollution is not obvious. The peak value of Cu element is at the junction of traffic arteries, and Zn accumulates in the area adjacent to the commercial district and the old city. Therefore, it is speculated that the pollution of Cu and Zn mainly comes from industrial activities and traffic pollution.

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