Comparative Study on the Determination of heavy metals in Soil by XRF and ICP-MS

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Abstract: The contents of Cr, Ni, Cu, Zn, As, Pb and Cd in standard soil for composition (GBW07403) and two soil samples were determined by XRF and ICP-MS, respectively. The results showed that XRF had higher precision than ICP-MS in the determination of seven metals in standard soil, but the relative errors of Ni, As and Cd were larger, up to -33%~22.7%. XRF and ICP-MS were used to determine contents of seven kinds of heavy metals in 2 soil samples, respectively. Both methods had high precision. F test showed that there was no significant difference in precision between the two methods except for Cd in No.2 soil. The t test showed that there were significant differences by the two methods for the determination of other heavy metals except for Cd and Cu (P ≤0.05). Although the method of XRF was fast and simple, its accuracy and comparison with other experimental methods need to be further studied due to the sample matrix effect.

1. Introduction

In recent years, with the rapid development of industry and agriculture, the emission of heavy metals has maintained a certain growth. Soil contaminated by heavy metals affects the growth and development of plants and causes serious impacts on the human health through the transfer and enrichment of biological chain. Therefore, the accurate determination of heavy metal content in soil is of great significance for soil monitoring and treatment[1-2].

Methods for the determination of heavy metals in soil mainly include flame atomic absorption spectrometry (FASS), graphite furnace atomic absorption spectrometry (GF-AAS), atomic fluorescence spectrometry (AFS), inductively coupled plasma-mass spectrometry (ICP-MS)[3-4]. These methods have accurate detection results and high reproductivity. But these methods usually require digestion with strong acid, and the pre-treatment steps are complex and take a long time, which will pollute the environment.

The basic principle of X-ray fluorescence spectroscopy (XRF) is that atoms in the ground state absorb radiation at a specific frequency and are excited to a high energy state, and then emit fluorescence at characteristic wavelengths in the form of light radiation [5]. This is a method for quantitative analysis of the fluorescence intensity emitted by atomic vapor of the element to be measured under the excitation of radiation energy of a certain wavelength. This method can be used for the determination of heavy metal content in soil samples without digestion. The determination is fast, but the accuracy is poor. It is mainly used for heavy metal pollution on-site screening in the early stage.
There are many factors that lead to uncertainty in the analysis of heavy metal in soil by XRF, such as sample size, sample uniformity, voltage and current changes of X-ray tube, spectral line overlap and matrix effect, etc.

In recent years, there has been continuously improved and developed on XRF, and its accuracy has been greatly improved. In this study, XRF instrument produced by a certain technology company was used to determine the content of heavy metals in soil, and compared with ICP-MS method. The result may support for the application of XRF in the determination of soil heavy metal content.

2. Materials and methods

2.1. Reagents and instruments

X-ray fluorescence spectrometer, Microwave Digestion Instrument, ICP-MS (Thermo ICAPQ). The standard soil for composition analysis (GBW07403), the superior pure solution such as HClO₄, HNO₃, HF and HCl, external standard solution of Cr, Ni, Cu, Zn, As, Cd and Pb with the concentration of 100mg/L, internal standard solution of rhodium and rhenium with the concentration of 100mg/L, ultrapure water.

2.2. Soil sample collection and preparation

Two surface farmland soils (0-20cm) were collected, and put at laboratory for natural air drying. Plant residues and stones remaining in the soil were removed, grounded, and 100 mesh were screened for use.

2.3. Determination of heavy metal in soil samples

XRF method: the instrument was calibrated with the standard before determination, and then the contents of Cr, Ni, Cu, Zn, As, Pb and Cd in the standard soil for composition (GBW07403) for 7 times respectively, and two soil samples were determined for 6 times.

ICP-MS method: the standard soil and two soil samples were weighed in seven portions and six portions respectively, and were digested by microwave with acid, expelled acid, and fixed volume with ultrapure water, and determined by ICP-MS.

3. Results and analysis

3.1. Comparison of the results of standard soil samples

Precision is expressed in terms of the relative relative standard deviation (RSD), which is equal to the standard deviation (SD)/ measurement average multiplied by 100. Precision refers to the reproducibility of measurement, which is a prerequisite to ensure accuracy. It can be seen from the table 1 that the RSD of XRF ranged from 1.2% ~35.9%, and that of ICP-MS ranged from 7.1%~35.9%. The RSD of the recommended values for standard soils ranged from 12.9% to 225% by AAS. In terms of the RSD value, the precision of the two methods was better than that of the recommended value. The RSD value of Cd measured by XRF, ICP-MS and recommended value was similar, reaching 35.9%, 35.9% and 37.3% respectively. The RSD value of Cd was large, which may be due to the lower content in the standard soil, only being 0.059mg/kg. Low content was easy to cause large fluctuations owing to the existence of random error. The precision value of XRF was lower than that of ICP-MS in the determination of other 5 heavy metals except for nickel.

| Method and value | Cr   | Ni  | Cu  | Zn  | As  | Pb  | Cd  |
|------------------|------|-----|-----|-----|-----|-----|-----|
| XRF n=7 Avg. mg/kg | 33.1 | 8.1 | 10.7 | 29.0 | 5.4 | 22.6 | 0.07 |
Relative error (RE) refers to the ratio of the absolute error to the recommended value multiplied by 100, expressing as a percentage. In general, the relative error is a better indicator of the reliability of the determination. It can be seen from the table 1 that the relative errors of XRF in the determination of Cr, Ni, Cu, Zn, As, Pb and Cd in standard soil (GBW07403) ranged from -33% to 22.7%, the relative errors of Ni and As were higher, and the relative errors of Cr, Cu and Zn were smaller and less than 10%. The relative errors of ICP-MS were about ±10% except for As and Cd. The relative error of Cr, Cu and Zn by XRF were lower than that of ICP-MS. However, The relative error of Ni and As were higher than that of ICP-MS. The relative errors of different metals show great differences by the same method.

3.2. Comparison of the heavy metal contents of soil samples

The Table 2 showed the contents of heavy metals in soil sample 1 measured by two methods. It can be seen from the table 2 that the average value of Cr, Ni, Cu, Zn and As determined by XRF were higher than those by ICP-MS, while the contents of Pb and Cd determined by XRF were lower than those by ICP-MS. RSD values of both methods were less than 10.0%, which showed that the precision of both methods were high. The precision of seven kinds of heavy metal by XRF was better than those by ICP-MS.
The table 3 showed the contents of heavy metals in soil sample 2 determined by two methods. It can be seen from the table 3 that the average value of Cr, Ni, Cu, Zn and As determined by XRF were higher than those by ICP-MS, while the contents of Cu, Pb and Cd determined by XRF were lower than those by ICP-MS. RSD values of both methods were less than 10.0% except for that of As, which showed that the precision of Cr, Ni, Cu, Zn, Pb and Cd were high, and the precision of As was lower. The precision of six kinds of heavy metal by XRF was better than those by ICP-MS except for As.

### The tab. 3 the result of heavy metals in No.2 sample soil

| Method  | Cr     | Ni     | Cu     | Zn     | As     | Pb     | Cd     |
|---------|--------|--------|--------|--------|--------|--------|--------|
| XRF     | Avg. mg/kg | 43.9   | 10.1   | 7.6    | 40.3   | 2.7    | 20.5   | 0.42   |
|         | SD     | 0.71   | 0.24   | 0.41   | 1.18   | 0.46   | 0.64   | 0.02   |
|         | RSD%   | 1.6    | 2.4    | 5.4    | 2.9    | 17.0   | 3.1    | 4.8    |
| ICP-MS  | Avg. mg/kg | 31.0   | 9.5    | 7.9    | 38.0   | 1.4    | 24.8   | 0.47   |
|         | SD     | 1.07   | 0.52   | 0.34   | 1.40   | 0.22   | 0.79   | 0.05   |
|         | RSD%   | 3.5    | 5.5    | 4.3    | 3.7    | 15.7   | 3.2    | 10.6   |

### 3.3. F test and t test of the heavy metal contents of soil samples

F test is often used to compare the precision of the results determined by the two methods. The formula for F is as follows:

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F = \frac{S_{\text{max}}^2}{S_{\text{min}}^2}
\]

In the formula, \(S\) means the standard deviation, \(S_{\text{max}}\) and \(S_{\text{min}}\) indicates the maximum and minimum of two groups of every kind of heavy metal. \(F_{0.05(5,5)} = 5.05\) by checking F table. If the calculated value of F is less than 5.05, there is no significant difference in the precision of the two methods, and If not, there is a significant difference. The calculated value of F of two soil sample were shown in table 4.

The t test results can represent the difference between the results by two methods. SPSS22.0 was used to calculate the value of t. The calculated value of t of two soil sample were shown in table 4.

As can be seen from the table 4, the F values calculated by the two methods for the seven kinds of metals in the soil sample 1 were all less than \(F_{0.05(5,5)} = 5.05\), indicating that the precision of the results by the two methods was not significantly different. The t-test showed that there were significant differences between the two methods for the determination of 6 other metals except Cd (P<0.01).

### The tab. 4 The value of F and t of two methods

| Heavy metal | Soil sample1 | Soil sample2 |
|-------------|--------------|--------------|
|             | F           | t            | F       | t      |
| Cr          | 1.76        | -44.54**     | 2.28    | -23.90** |
| Ni          | 2.19        | -8.02**      | 4.68    | 2.66*  |
| Cu          | 1.26        | -7.19**      | 1.50    | 1.23   |
| Zn          | 1.04        | -22.18**     | 1.40    | -3.28** |
| As          | 1.11        | -12.52**     | 4.32    | -6.23** |
| Pb          | 3.19        | 8.62**       | 1.48    | 4.34** |
| Cd          | 2.03        | 1.29         | 5.88*   | 2.41*  |

Note: * and ** indicate significant difference P<0.05 and P<0.01, respectively
As can be seen from the table 4, the F value of Cd determined by the two methods in the soil sample 2 was 5.88, and more than $F_{0.05(5,5)}=5.05$, indicating that there was a difference in the precision of the two methods for the determination of Cd, while there was no significant difference in the precision of other six kind of metals. The t-test showed that there were significant differences between the two methods for the determination of 6 other metals except Cu ($P \leq 0.01$).

4. Conclusion
The content of Cr, Ni, Cu, Zn, As, Pb and Cd in standard soil (GBW07403) and two soil samples were determined by XRF and ICP-MS respectively. The relative error, precision and accuracy of the two methods were compared and studied. The conclusions are as follow:

(1) The contents of Cr, Ni, Cu, Zn, As, Pb and Cd in standard soil (GBW07403) determined by XRF and ICP-MS respectively showed that the precision of the two methods could meet the requirements of the determination standard, and the relative error of XRF in the determination of Ni, As, Pb and Cd was larger than that of ICP-MS.

(2) The contents of Cr, Ni, Cu, Zn, As, Pb and Cd in two soil sample were detected by XRF and ICP-MS respectively. There was no significant difference in the precision of the two methods except for Cd. There were significant differences in the determination results of other metals in two soil samples except for Cd in soil sample 1 and Cu in soil sample 2.

(3) XRF does not require digestion of sample in the determined of soil heavy metals, and the instrument is simple to operate, high efficiency. However, the sample matrix effect is large, the accuracy and comparison with other experimental methods need to be further studied.

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