Experimental Parameters for XRF Analysis of Soils

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ABSTRACT
Harmful elements (Pb, Se, Cd, etc.) in the soil samples were measured by X-ray fluorescence (XRF) method. We investigated the influence of the thickness of soil layer, the grain size of soils, and the water content in soils on XRF intensity. Since high-energy XRF such as Cd Kα was detected in deep inside of soils, a thickness of 10 mm was recommended. The soil sample with a small grain size gave a relatively strong XRF intensity, especially for low-energy x-rays. Therefore, this grain-size effect should be taken into account for quantitative XRF analysis of the soil. It was also confirmed that water in soils decreased the XRF intensity, especially for low-energy x-rays. Preferably, after the soil sample was dried, the soils should be analyzed by XRF. Otherwise, XRF intensity has to be corrected depending on water content in the soil sample.

INTRODUCTION
X-ray fluorescence (XRF) analysis has been used in various fields, such as material research, environmental research, quality control of products, etc. This is because XRF has unique advantages of rapid non-destructive quantitative analysis in air. In this paper, XRF was applied for analysis of soils. There is a possibility that the soils are polluted with harmful elements, such as Pb, Cd, Hg, As due to the industrial emissions or others.
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Such elements might be eluted into acid rains and introduced in river or sea. Otherwise, they will be directly in-taken by plants or vegetables. Therefore, it is important to know how much harmful elements are included in soils. XRF rapidly gives quantitative information of such elements [1,2]. Other atomic spectroscopic methods such as ICP-AES or AAS are of course useful for quantitative analysis of elements in soils [3]. However, in these methods, soils have to be dissolved into acid solutions. This sample preparation is a time-consuming process. XRF is expected for screening method of harmful elements in soils. However, XRF intensity will be influenced by a size of soil particles and a water percentage in soils. Thus, we have investigated how such experimental parameters will influence XRF analysis of soils in the present paper.

EXPERIMENTAL SETUP
Figure 1 shows our experimental setup for XRF analysis. An x-ray tube with a Rh target (MCBN 50-0.6B, rtw, Germany) was used. An energy dispersive x-ray detector (XR-100CR, Amptec, USA; sensitive area: 7 mm², FWHM at 5.9 keV: 187 eV) was used for the measurement of x-rays. A metallic filter, which was 100-µm-thick titanium or 50-µm-thick zirconium, was attached to the Rh x-ray tube [4]. The aluminum collimators of inner diameters of 6 mm and 3 mm were attached to the x-ray tube and the detector, respectively. The x-ray tube and the detector were tilted to 45 degrees. The detector and the sample holder were placed on a Z-stage and to adjust the distance from the point of the detector to the sample surface. The external diameter of the sample holder was 44.5 mm (inside diameter: 40.5 mm) and height was 25.5 mm. The thickness of soils could be changed by depending its volume put in the sample holder.

SAMPLE PREPARATION
Three types of soil samples were prepared for the XRF analysis. The first type of
samples was the reference soil materials (JSAC0466), supplied by The Japan Society for Analytical Chemistry [5]. The reference soil materials were prepared from a brown forest soil, pulverized to an average grain size of < 4 μm, by spiking 6 elements (Cd, Pb, As, Se, Cr, Hg), as shown in Table 1. The second type of samples was prepared by the authors from a smectic clay collected from a paddy field in Saga prefecture, Japan. A mixed solution of heavy metals (Cd and Pb) were added to the clay, and mixed thoroughly by repeated kneading, rolling on a plastic sheet and folding. The homogenized clay was dried in an electric oven at 105 °C. The hardened block of the clay was crushed in a mortar and fractionated by sieving into 6 different grain sizes of 5-2 mm, 2-0.85 mm, 0.85-0.425 mm, 0.425-0.210 mm, 0.210-0.105 mm, and < 0.105 mm. The third type of samples was a river sediment collected from the bed of Yamato-river in Osaka, Japan. The sample was thoroughly mixed and air-dried for a few days. After drying, the sample was sieved into 4 grain sizes (> 150 μm, 75-150 μm, 45-75 μm, < 45 μm).

Table 1 Certified values of reference soil materials.

<table>
<thead>
<tr>
<th>Elements</th>
<th>Certified value ± uncertainty / mg kg⁻¹</th>
<th>Elements</th>
<th>Certified value ± uncertainty / mg kg⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cd</td>
<td>1199 ± 19</td>
<td>Se</td>
<td>1175 ± 26</td>
</tr>
<tr>
<td>Pb</td>
<td>1214 ± 26</td>
<td>Cr</td>
<td>1483 ± 23</td>
</tr>
<tr>
<td>As</td>
<td>1093 ± 32</td>
<td>Hg</td>
<td>113.5 ± 5.6</td>
</tr>
</tbody>
</table>

RESULTS AND DISCUSSION

**Thickness of soils**

Thickness of soils put in sample holder influences the intensity of x-ray fluorescence. The XRF intensity will saturate at a certain soil thickness. In addition, the thickness of soils for saturation on XRF intensity will be dependent of the energy of x-ray fluorescence. Thus, we investigated how the thickness of soils influenced the XRF intensity and aimed to find the optimum thickness to analyze hazardous metals in soils. We changed the thickness of soils (reference soil material: “JSAC0466”) put in sample holder and investigated the relationship with the XRF intensities. A 50 μm Zr filter was attached to the x-ray tube and the height (h in Fig.1) of the x-ray tube and the detector
from the surface of the sample was adjusted to be 20 mm. The x-ray tube was operated at 40 kV, 0.3 mA, and the measuring time was 500 s.

Figure 2 shows XRF intensities of Fe Kα (6.4 keV), Se Kα (11.2 keV), Pb Lβ (12.6 keV) and Cd Kα (23.2 keV) as a function of the thickness of soil sample. The intensity of Fe saturated when the thickness of soil was approximately 1 mm. The intensity of Se and Pb was saturated at approximately 2.5 mm and Cd was saturated at approximately 5.3 mm. It was confirmed that the high-energy x-rays saturated at thicker soil thickness than low-energy x-rays. X-rays are easily absorbed as absorption coefficient is large. Absorption coefficient is characteristic of each element and is dependent of energy of x-rays. In generally, absorption coefficient for high-energy x-rays is larger than that for low-energy x-rays. Therefore, it is considered that the result shown in Fig. 2 is caused by difference of absorption coefficient depending on x-ray energy.

When thickness of soils was 1 mm, the incident primary x-rays would reach to the bottom of the soils, while the x-rays would not reach to the bottom when thickness of soils was more than 10 mm. Even if the thickness of soils is enough thick, high-energy x-ray fluorescence generated in the deep soils will be detected on sample surface without serious absorption. In contrast, low-energy x-rays generated at bottom of the sample will be easily absorbed and not detected. In conclusion, the thickness of soils should be more than 6 mm in our experimental setup to analyze all hazardous metals in soil.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig2.png}
\caption{Relationship between the thickness of soils and XRF intensities of different x-ray energies: (a) Fe Kα, (b) Se Kα, (c) Pb Lβ, and (d) Cd Kα.}
\end{figure}
Grain size of soils

It is also expected that the grain size of soil put in sample holder will influence the XRF intensity. Similarly to soil-thickness dependence on x-ray energy, it is considered that the grain-size dependence on XRF intensities depends on energy of x-ray fluorescence. The soil samples of six different grain sizes (5-2 mm, 2-0.85 mm, 0.85-0.425 mm, 0.425-0.210 mm, 0.210-0.105 mm, and < 0.105 mm) were measured. A 50 μm Zr filter and 100 μm Ti filter were attached to the x-ray tube, and the height (h in Fig.1) of the x-ray tube and the detector from the surface of the sample was 25 mm. The x-ray tube was operated at 40 kV, 0.1 mA, and the measuring time was 1000 s. The second type of samples made of clayey soils taken from a paddy field was put in the sample holder in the thickness of 10 mm. This thickness was over the recommended thickness of 6 mm, which was considered the minimum of thickness of soil to analyze hazardous metals in soils.

Figure 3 shows XRF intensities of Ba Lα (4.5 keV), Cr Kα (5.4 keV), Fe Kα (6.4 keV), Pb Lβ (12.6 keV) and Cd Kα (23.2 keV) as a function of the average grain size of soil sample. Average grain size means an intermediate value between maximum grain size and minimum grain size. We used a Ti filter for measurement of low-energy x-rays (Ba Lα and Fe Kα) and a Zr filter for high-energy x-rays (Pb Lβ and Cd Kα). The XRF

![Graphs showing XRF intensities](image)

Fig. 3 Relationship between grain size and XRF intensities of low-energy x-rays (a), and high-energy x-rays (b).
intensities increased as the grain size decreased for low-energy x-rays (Ba, Fe). The same tendency was observed for high-energy x-rays (Pb, Cd), although the statistic error for Cd-plots was relatively large due to its weak intensity.

The XRF intensities decreased for the soils of the larger grain sizes. This is probably because the density of soils near surface decreased. This grain-size effect should be taken into account for the XRF analysis of soils. In contrast, It seems that the grain-size effect was not strongly appeared for XRF intensity of high-energy x-rays (Pb, Cd). This would be related with the fact that the high-energy x-rays generated in deep soils layer were detected without serious absorption.

**Water content in soils**

Since low-energy x-rays are absorbed by water much stronger than high-energy x-rays, influence of water content will show dependence of x-ray energy. The soils were taken near Yamato river in Osaka prefecture, Japan. The size of soils were uniformed by using different size of sieves. The soils having the particle size between 75-100 μm were used for this research. To investigate the influence of water content in soils, the soils were perfectly dried in an oven for 3 hours, 100 degrees C. This soils were put into the plastic sample holder in a height of 10 mm. The weight (W_{dry}) of soils measured by XRF was measured in advance. A certain volume of pure water was added into the soils, then mixed well. Before the XRF analysis, the weight (W_{wet}) of water-added soils was measured. Thus, the water content is given as follows:

\[
\text{Water content (\%) = \frac{(W_{wet} - W_{dry})}{W_{dry}} \times 100}
\]
Figure 4 shows the relative XRF intensities of Sr Kα (14.2 keV), Fe Kα (6.4 keV), Ti Kα (4.5 keV) and Ca Kα (3.7 keV) as a function of water content (%). It was confirmed that XRF intensity, especially for low energy x-rays such as Ca Kα, decreased with the water content. The intensity of Sr Kα decreased 10 % by adding the water in 32 %, while Ca Kα intensity decreased about 70 %. This is because low-energy x-rays are easily absorbed by water.

CONCLUSIONS

We investigated the influence of the thickness of soils, the size of particles of soils and the water content in soils on XRF intensity. The necessary thickness of soils depended on the energy of XRF, because of difference of absorption of x-rays. To analyze all elements from light to heavy elements, the thickness of soils was decided to be 10 mm under our experimental condition. It was also found that the XRF intensity depended on the size of soils. The size of soils should be uniformed for XRF analysis. In addition, it was confirmed that the water content influenced XRF intensity. Preferably, the soils should be dried before XRF analysis. Otherwise, the water content should be evaluated [6], and then XRF intensities have to be corrected with the water content.

REFERENCES
