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Quantitative Analysis of Trace Heavy Elements in Geological Samples Utilizing High-energy (116 keV) Synchrotron Radiation X-ray Fluorescence Analysis for Forensic Investigation

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High-energy (116 keV) synchrotron radiation X-ray fluorescence analysis has for the first time been applied to the quantitative analysis of trace heavy elements of geological samples. Calibration curves for the determination of trace heavy elements were obtained by measuring 7 reference rock samples and showed good linearity because of the high penetrating power of the high-energy X-rays. It is found that this method is suitable for rapid and nondestructive quantitative characterization of trace heavy elements in trace amount of soil samples for forensic investigation.

Over the past half century, the X-ray fluorescence (XRF) has become one of the most valuable methods for the qualitative and quantitative analysis of materials in both industry and academic research. However, conventional X-ray sources for XRF analysis in the laboratory are limited by the energy of the generated X-rays, which produce XRF spectrum at energy less than 20–30 keV. In this energy range, the L and M emission lines of trace heavy elements usually overlap severely with the crowded K and L emission lines of the major component elements, causing difficulties in either qualitative or quantitative study of the heavy elements.

In 2001, Nakai and his co-workers reported that such overlapping problems could be overcome by using high-energy synchrotron radiation (HE-SR) X-ray sources.[1] Compared with laboratory XRF techniques, high-brilliance, high-coherence SR X-rays offer a superior light source for XRF that allows high sensitivity (sub ppm level) analysis with smaller samples (less than 1 mg in weight and less than 1 mm in size) and much shorter measurement time than typically possible. Moreover, laboratory XRF cannot analyze heavy elements such as Th and U by their K lines while HE-SR-XRF utilizing 116 keV X-rays allows the analysis of all heavy elements by their K lines. In their pioneering work,[1,2] high-energy X-ray with an energy of 116 keV from third generation SR sources in SPring-8 was used to evaluate the lowest detection limit of geological standard reference sample, JG-1, and a linear calibration curve of Lu was obtained using liquid droplet samples with concentrations from 10 to 0.03 ng. Their results demonstrated the applicability of the technique for the quantitative analysis of heavy elements in relatively pure materials.

This paper reports the first successful application of high-energy (116 keV) synchrotron radiation X-ray fluorescence to the quantitative analysis of geological samples. Trace heavy elements are particularly useful in fingerprinting the origin of geological samples. This newly developed quantitative technique is, therefore, used to construct the database of trace heavy elements derived from stream sediments collected from 3024 sampling points all over Japan. It is expected by the National Police Agency of Japan that the database will be used for real forensic soil investigation. By comparing the trace elements database with the real forensic sample, forensic scientists will be able to determine the likely provenance of the material which in turn provides important clues in aiding or directing an active forensic investigation. The sediment samples were supplied from the Institute of Geology and Geoinformation, AIST, which had been analyzed by ICP-AES/MS and AAS for a nationwide geochemical mapping program at a 1:2000000 scale since 1999.[3]

HE-SR-XRF analysis was carried out at the BL08W beam line in SPring-8. Monochromatic X-rays of 116 keV from an elliptical multipole wiggler obtained from a Si(400) monochromator was used as an excitation source. The size of the incident X-ray beam was 0.5 mm × 0.5 mm. The fluorescent X-rays were measured with a pure-Ge solid-state detector (CANBERRA: GUL0055p). The XRF spectra of the sediment powders were measured in air atmosphere for 600 s (live time) per sample, with a dead time lower than 20%.

Figure 1a demonstrates a typical HE-SR-XRF spectrum of a reference rock powder, JR-2. Figure 1b shows the enlarged spectrum in the energy range of 30 to 60 keV. It is clear from

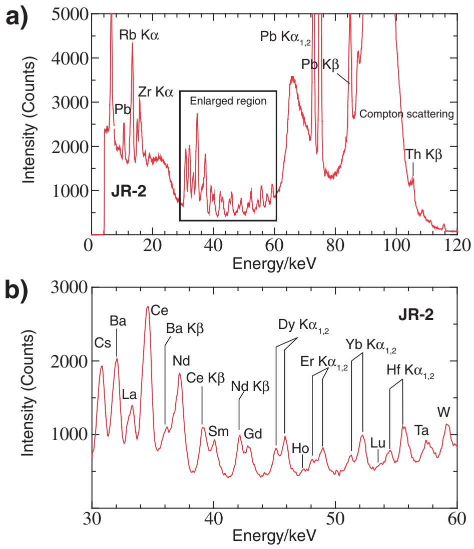

Figure 1. a) Typical HE-SR-XRF spectrum of reference rock powder (JR-2) and b) enlarged spectrum of Figure 1a in the energy range of 30–60 keV.

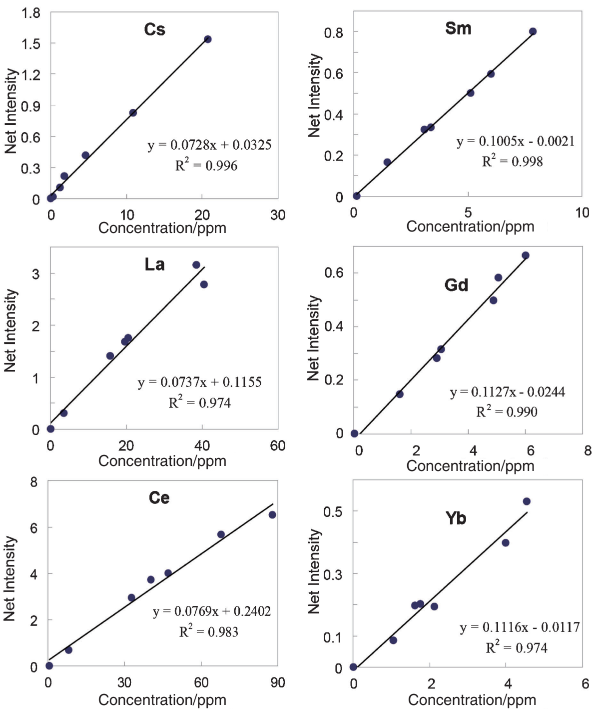

Figure 2. Representative calibration curves for Cs, La, Ce, Sm, Gd, and Yb.

Figure 1a that at lower energy region (5–25 keV), Rb and Zr are detected with a higher background. The K lines of Cs, Ba, REEs (rare earth elements, La to Lu), Hf, Ta, and W are clearly detected in the center of the spectrum, between 30–60 keV, with a low background. At high energy region (>60 keV) the K lines of Th ($Z = 90$) are also detected in both samples with a very high background caused by Compton scattering. The Pb K lines are due to the Pb collimator of the detector. As can be seen from Figure 1b, the K spectra of the H-REEs (Dy (6.63 ppm), Er (4.36 ppm), and Yb (5.33 ppm)) and Hf (5.14 ppm) of JR-2 show a well-resolved $K\alpha_2/K\alpha_1$ doublet, demonstrating the high sensitivity and high resolution of the HE-SR-XRF technique. Besides, this is also the region where the lowest background can be obtained, and it is the most suitable region for quantitative analysis because the background intensity can be subtracted accurately while calculating the net intensity of the elements.

In order to evaluate the quantitative performance of HE-SR-XRF, seven standard reference samples, JLk-1, JLs-1 (Sediment rock powder), JB-1 (Basalt rock powder), JG-3 (Granite rock powder), JA-2 (Andesite rock powder), JR-1 (Rhyolite rock powder), and JGb-1 (Gabbro rock powder) with known concentrations were analyzed to calculate the calibration curves of the trace heavy elements. Figure 2 shows the representative calibration curves for Cs, La, Ce, Sm, Gd, and Yb, together with their coefficient of determination values (R^2). Since X-ray absorption by the sample is not serious for high-energy X-ray of 116 keV, good linearity was observed in these elements with R^2 values exceeding 0.974–0.998. The concentrations of JR-2 (Rhyolite rock powder) were determined by using the calibration curves, and the results were compared with the certified values in Table 1. A good correspondence between the two data was obtained.

Table 1. Comparison of measured values obtained by HE-SR-XRF with the certified values of JR-2 standard sample

Elements	Concentration/ppm		R^2 values
	HE-SR-XRF	Certified values	
Cs	24.60	25.00	0.996
La	12.71	16.30	0.974
Ce	35.78	38.80	0.983
Nd	18.24	20.40	0.989
Sm	4.84	5.63	0.998
Gd	5.39	5.83	0.990
Dy	7.17	6.63	0.970
Yb	5.65	5.33	0.974

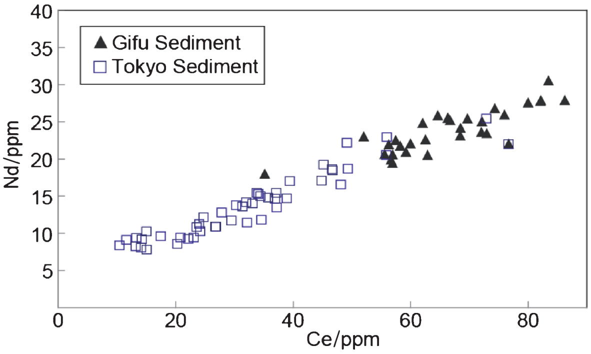

Figure 3. Plot of Nd vs. Ce for 80 sediment samples from Gifu and Tokyo.

To examine the performance of the method, stream sediment samples collected from Gifu and Tokyo were subjected to the quantitative HE-SR-XRF analysis. Approximately 1 g of the sample was crushed directly in an agate mortar to obtain a homogeneous bulk composition. The sample was sealed in pockets prepared by 6 μm thick polypropylene films with a poly sealer and attached to an acrylic sample holder with a 3 cm diameter hole.[4,5] Concentrations of 8 elements (Cs and REEs (La, Ce, Nd, Sm, Gd, Dy, and Yb)) were obtained by the calibration methods. Figure 3 shows the binary plot of Nd vs. Ce for the sediments from Gifu and Tokyo regions. Figure 3 clearly shows that the former sediment can be distinguished from the latter one due to the higher concentrations of Nd and Ce for the former ones. This demonstrates that the heavy element composition is a good fingerprint of the provenance analysis of soil.

In conclusion, this study demonstrates that the HE-SR-XRF technique is suitable for quantitative characterization of geological samples. This method is particularly useful for forensic purposes because we can analyze a sample having a quantity as small as 1 mg, nondestructively. Compared with wet analysis using ICP-AES and ICP-MS, HE-SR-XRF seems possible to offer better accuracy in quantitative results of some heavy elements (REEs and Hf). This is because, one of the disadvantages of wet analysis is that most samples are digested using acid solutions and part of the mineral fractions, e.g., zircon, are usually not satisfactorily decomposed by this method. The incomplete decomposition of these minerals will affect the analytical precision of the immobile elements, especially Hf and other REEs.[6] Such problems can be overcome by using the newly developed quantitative HE-SR-XRF (116 keV) technique. Furthermore, the technique also allows us to measure trace heavy elements with unsurpassed sensitivity which enables us to profile forensic sediment samples based on trace elemental composition that can reflect origins or identify evidence as originating from the same, or different sources.

Apart from the HE-SR-XRF analysis, we have been also studying heavy mineral compositions of the same 3024 samples by using SR X-ray powder diffraction analysis at BL19B2 of SPring-8. Combining these two synchrotron techniques, a nationwide forensic soil database will be constructed in the near future for the first time in the world.

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