

Feature Article

The Winner's Article of 2006 Masao Horiba Awards

Development of Microbeam in the High-Energy X-Ray Region and the Application to X-Ray Fluorescence Analysis

Yasuko Terada

X-ray fluorescence analysis that directly detects K-lines of heavy metal elements was conducted using high-energy X-ray of 100 keV or more obtained from SPring-8. The analysis showed that it could detect rare earth elements at ppm level and some heavy metal elements such as tungsten. As a result of applying this method to various fields, it was found that the method was very useful as a means of identification using heavy metals in glass or ceramic shards as the indicators. Moreover, the X-ray focusing element was designed and developed in an effort to realize microbeam in the unprecedented field of high-energy X-ray region, and it was demonstrated that microbeams about 1 μm could be obtained in the 30 to 100 keV regions with a total reflection mirror.

Introduction

Today we have various analytical techniques. And detection and re-assessment of heavy metal elements existing around us, such as lead (Pb), arsenic (As) or cadmium (Cd), are gathering attention. Featuring advantages including simple measurement environment and non-destructiveness, the X-ray fluorescence (XRF) analysis is one of the analytical techniques that can sufficiently satisfy the recent needs. But the conventional XRF analysis mostly uses X-rays below about 50 keV as probes and is mainly applied to analysis of elements around the 4th group of the periodic table. Therefore, L-lines have to be used if we want to analyze heavy metal elements with larger atomic numbers. But since K-lines of transition metal elements also exist in the energy region of those L-lines, there are disturbances by coexisting elements in large quantities, and even if there is no coexisting element, it is often very difficult to discern which element the peak of any given L-line belongs to because of the complicated status of existence. When X-rays of 120 keV are used, heavy metal elements that can only be seen with L-lines can be analyzed with K-lines (in this case up to the uranium (U) K absorption edge). In such a high-energy X-ray region, although XRF analysis was being known to be possible in principle, no sufficient results could be obtained due to various

restrictions such as X-ray sources or the capability of detectors until around 1987, when successful analysis results began to be published in the literature^[1, 2].

In research, we attempted to apply SPring-8, a third-generation synchrotron radiation facility that produced high-energy and high-brilliance X-rays, to XRF analysis. It also involved development of an X-ray focusing element to realize microbeams, which could make the most effective use of the properties of synchrotron radiation, in the high-energy X-ray region.

High-energy X-ray Fluorescence Analysis

The greatest feature of this method is direct analysis of K-lines of heavy metal elements. A basic experiment was conducted using X-rays of 116 keV obtained from SPring-8 BL08W, and the spectra as shown in Figure 1 were produced. This figure shows the fluorescent X-ray spectra of standard sample NIST612 glass, to which rare earth elements were added by 40 ppm. The experiment proved the method was capable of measuring rare earth elements and heavy metal elements such as tungsten from a glass shard about 300 μm in size. Next, I measured a rock standard sample, JG-1, and calculated the minimum detection limit (MDL) in order to evaluate the sensitivity of the method. It was then found that the method could

analyze metal elements in low ppm level such as 3.8 ppm of barium (Ba), 1.1 ppm of neodymium (Nd), 1.1 ppm of gadolinium (Gd), 1.0 ppm of ytterbium (Yb), or 0.1 ppm of tungsten^[3].

Now as an example to show the utility of the method, some applications to forensic science and cultural property science are shown below.

Samples taken from crime scenes are often very minute, such as glass shards, paint chips, waste textile or stone particles. In forensic science, we conduct analysis to clarify the correlation; in other words, forensic comparison; which is between those samples and samples found away from the crime scene, for example, found around the suspect. Commodities in our surroundings may be the subjects of analysis and, surprisingly, they often contain heavy elements and are supposed to serve as good indicators for forensic comparison. In addition, materials for investigation require storage as evidence and can never be consumed for analysis.

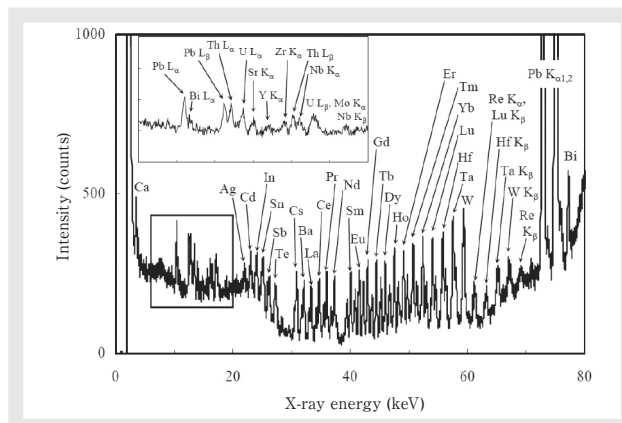


Figure 1 Fluorescent X-ray spectra of standard sample NIST612 glass

That is why those materials have to be analyzed in a non-destructive manner. From this viewpoint, application of high-energy X-ray fluorescence (HE-XRF) analysis is very effective as one of the means for forensic science. Figure 2 is an example of comparing the spectra of four kinds of glass shards. For glass samples, it is known that their refractive index serves as an indicator for forensic science, but identification was impossible for those samples in Figure 2 because they had the same refractive index. But, in HE-XRF analysis, even if each glass shard

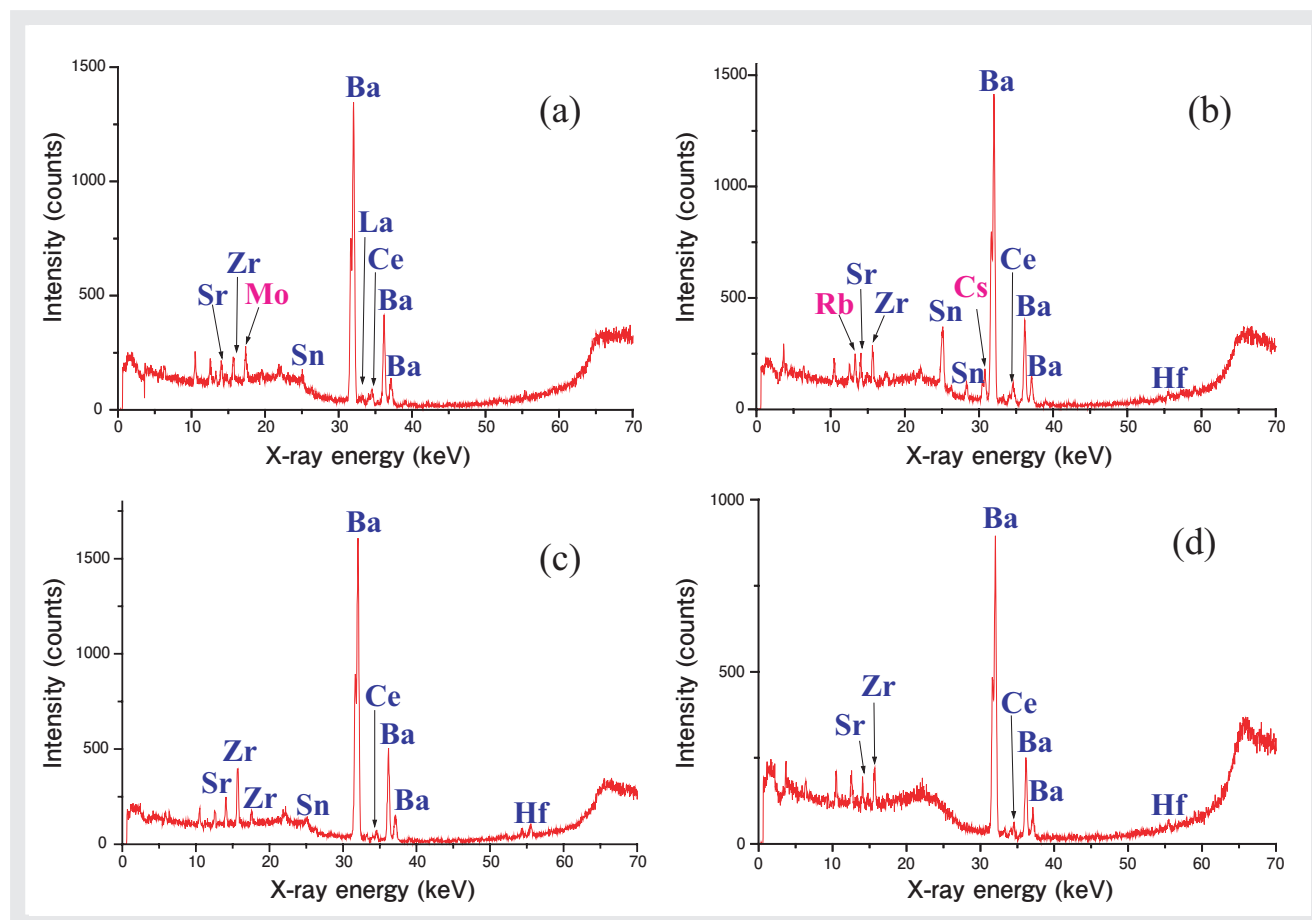


Figure 2 Sample of fluorescent X-ray spectra of four glass shards sharing the same refractive index

has the same refractive index (1.522 as shown in Figure 2), it is possible to identify the differences among products of the same company or production countries by setting molybdenum (Mo), rubidium (Rb) or cesium (Cs) as indicators^[4]. The method is currently applied to actual crime investigation mainly by a group of the Forensic Science Laboratory of the Hyogo Prefecture Police Department and has actually been successful in helping solve some cases^[5]. More and more materials will become the subjects of measurement.

Another example that heavy metal elements were used as indicators is presumption of the origin of Old Kutani ceramics^[6]. "Old Kutani" is one of the brands of china wares made of pottery stone that contains silica, and there have been in a welter of different theories on the original production area; that is in chaos. To straighten out this tangled condition, we tried to attempt to find out the original producer from a viewpoint of materials science. But the conventional technique, radioactivation analysis, needs powdered samples, and therefore invaluable assets handed down from generation to generation are rarely analyzed by this technique. We chose HE-XRF as a research tool to analyze an invaluable sample without destroying it. Firstly, china ware shards of different origins such as Kutani, Arita and Imari etc. were analyzed as the population for presumption of the production area, and then the vessel of Old Kutani was analyzed to presume where it was born. The analyzed spectra detected peaks of rare earth elements ranging from lanthanum (La) to ytterbium (Yb) and other elements of cesium (Cs), barium (Ba), hafnium (Hf) or tungsten (W). Statistical processing was conducted for the spectra of nearly 200 samples and revealed that groups of measured samples were dispersed by barium (Ba), cerium (Ce) and neodymium (Nd). Figure 3 plots the relationship between Ba/Ce intensity ratio and Nd/Ce intensity ratio (Ba/Ce - Nd/Ce). There are formed clusters that well reflect different origins, Arita (red), Kutani (blue) or Himetani (purple). The abundance of those trace elements is greater than ^{55}Cs , ^{57}La or ^{59}Pr , whose atomic numbers are odd, because of the stability of the nucleus according to the Oddo-Harkins' law. Light rare earth elements such as Ce or Nd have a large ionic radius and therefore tend to be limited to a smaller site in which they can be present in minerals compared with heavy rare earth elements. Therefore, use of Ba, Ce and Nd as indicators realized a clear representation of regional characteristics. Using results above, we considered the origins of historical Old Imari and Old Kutani china wares and learned that the origin of the Old Imari product was presumed to be Imari

and that the Old Kutani products were suggested to be divided into two areas, Kutani and Hizen; as some were plotted in the left side of the region of Kaga and others in the region of Hizen.

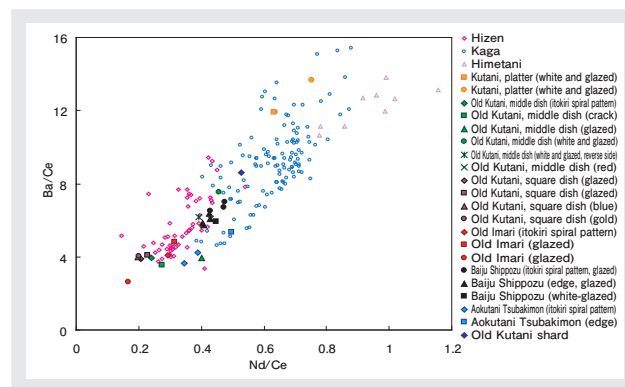


Figure 3 Plot of Ba/Ce-Nd/Ce for China ware shards

Development of High-energy X-Ray Microbeam

In order to further utilize the characteristics, non-destructive and two-dimensional, of XRF analysis, microscopic application combining with X-ray microbeams is actively promoted, and resultantly, the analytical performance level in spatial resolution has now gone up to the nano order^[7]. The material that constituted the total reflective mirror, which was developed in our research, is made of molten quartz finished with Pt coat. The mirror is 100 mm in length, 0.8 mrad in oblique incident angle, and 250 and 100 mm in focal distance, respectively. The spot size in the region of X-ray energy of 30 to 100 keV was evaluated by the knife edge scanning method. Figure 4 shows the measurement result in 37 keV as an example. The transmitted light intensity is shown in a blue line and its differential curve in a red line. The spot size at the focal point was calculated by obtaining the full width at half maximum (FWHM) of the differential curve, and the result was 1.5 μm (vertical) \times 1.3 μm (lateral).

With this microbeam, we analyzed cadmium (Cd) accumulated in the plant. The plant sample was *Arabis gemmifera* hydroponically-cultivated on the Cd-added medium. We made sample cut into section on the eve of measurement and fixed it on an acrylic plate for measurement. The imaging results of the trichomes, fibrous microorganisms dotting the surface of the leaf, are shown in Figure 5. The measurement conditions are 1.5 μm for 0.1 sec. per pixel. From the optical microscopic image, trichome seems the organ with 2 nodes, however, the

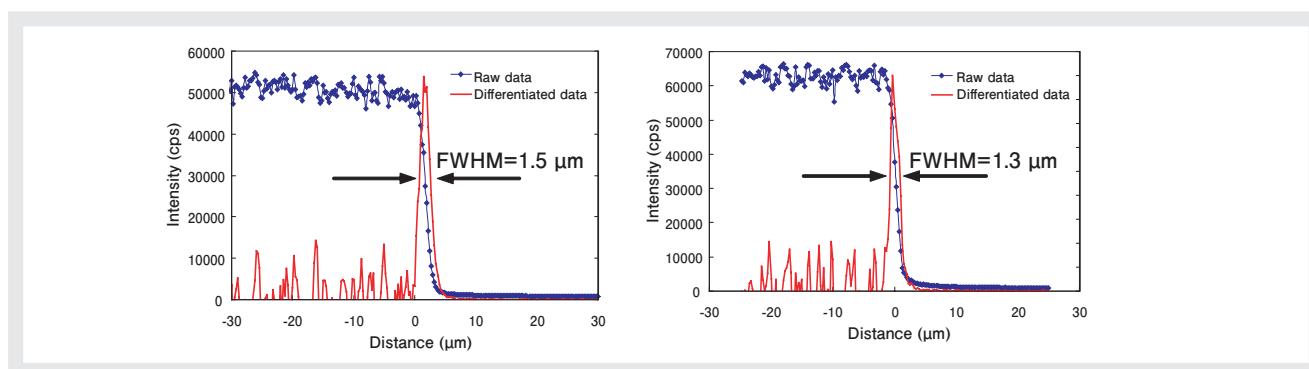


Figure 4 Beam profile at 37 keV

essential elements such as potassium (K) or iron (Fe) are distributed over the trichomes, and that Cd is unevenly distributed around the node near the root^[8]. Since the role of the trichome itself is unknown in terms of plant physiology, the mechanism of uneven distribution of Cd is yet to be identified. But we still continue conducting experiments to ultimately clarify the dynamic behavior of trichomes in the plant using the results of two-dimensional analysis of leaves, stems, roots and other tissues and the known findings on the chemical status by μ -XAFS of Cd. The energy of the Cd K absorption edge is 26.7 keV, and SPring-8 is currently the only facility that can simultaneously analyze calcium (Ca), potassium (K) and transition metal elements at a spatial resolution of 1 μ m.

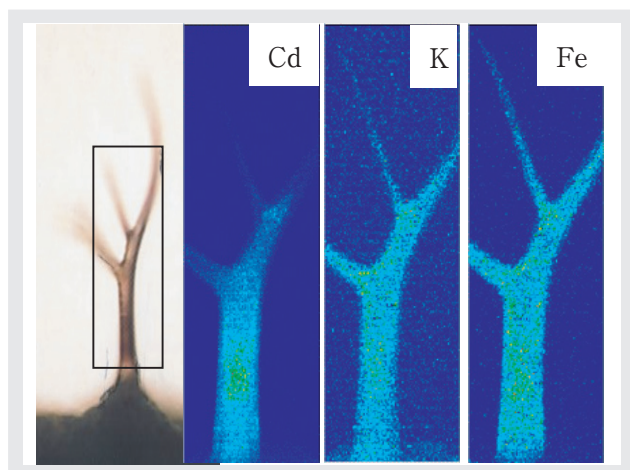


Figure 5 Optical microscopic photo (far left) and XRF imaging results of the trichomes

Conclusion

As explained above, X-ray fluorescence analysis in the high-energy X-ray region using high-intensity light obtained from SPring-8 was conducted, and experiments on generation of microbeam were also conducted. This method can serve as a very powerful tool today as heavy metal elements in the environment are drawing more attention. This report introduces only some examples, but I am delighted if this report would help promote

application of the method to new fields.

In the future, I would like to promote application of nano beams to X-ray microscopes to materialize the technique in nm order. And I hope that “on-the-spot observation” using synchrotron radiation nano beam, by the efforts in micro region analysis using time dissolution in ps order and three-dimensional X-ray fluorescence analysis.

(Publication members have responsibility for the translation)

Reference

- [1] J. R.Chen, E. C. T. Chao, J. M. Back, J. A. Minkin, M. L. Rivers, S. R. Sutton, G. L. Cygan, J. N. Grossman, and M. J. Reed, *Nucl. Instrum. Methods Phys. Res.*, **B75**, 576 (1993).
- [2] K. Janssens, L. Vincze, B. Vekemans, F. Adams, M. Haller, and A. Knochel, *J. Anal. At. Spectrom.*, **13**, 339 (1998).
- [3] I. Nakai, Y. Terada, M. Itou and Y. Sakurai, *J. Synchrotron Rad.* **8**, 1078-1081 (2001).
- [4] T. Nakanishi, Y. Nishiwaki, N. Miyamoto, O. Shimoda, S. Watanabe, S. Muratsu, M. Takatsu, and Y. Terada: *Forensic Science Technology*, **II**, 177 (2006).
- [5] T. Ninomiya, *X-ray Spectrometry: Recent Technological Advances*, Edited by K. Tsuji, J. Injuk and R. V. Griken, John Wiley & Sons, Ltd., 355 (2004).
- [6] Y. Miura, S. Yamato, I. Nakai, Y. Terada, K. Yamana, and N. Terai: *Archaeology and Natural Science*, **46**, 33 (2004).
- [7] T. Ishikawa and Y. Mori, *Applied Physics*, **72**, 439 (2003)
- [8] A. Hokura, R. Onuma, N. Kitajima, Y. Terada, H. Saito, T. Abe, S. Yoshida and I. Nakai, *Chem. Lett.*, **35**, 1246 (2006).



Yasuko Terada

Japan Synchrotron Radiation Research Institute
Research & Utilization Division
Chief researcher
Doctor of Science