Guest Forum

Lecture by a Jury Member for the 2006 Masao Horiba Awards

Material History — The Past of Materials Read with X-Ray

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By using fluorescent X-ray, we can read out the past information hidden in a material. This lecture explained X-ray fluorescence analysis using synchrotron radiation by referring to the identification for the Wakayama Poisoned Curry Murder Case, presumption of origins of ceramic ware, and research on plants that absorb and accumulate toxic arsenic from the environment, as examples.

Introduction — X-ray and X-ray Fluorescence Analysis

I am specialized in X-ray analysis using synchrotron radiation, and these days, I use portable X-ray fluorescence analyzers or X-ray devices designed for on site analysis. My work is primarily about X-ray fluorescence analysis and I am engaged in research for the purpose of extracting past information out of materials. Synchrotron radiation is a very strong X-ray source and one of the most representative facilities, SPring-8 (Super Photon ring 8 GeV) is a very big synchrotron radiation facility about 1.5 km around. SPring-8 emits ultraviolet rays and visible rays, but mainly used is X-rays in the region devoid of laser light and partly infrared light. The characteristics of synchrotron radiation are below; (1) it is extremely bright light, (2) it is highly collimated parallel beam, and (3) it covers very wide wavelength range from infrared to X-ray. How bright is synchrotron radiation? As taking SPring-8 for instance, it is 10 raised to the 10th power brighter than the light of the sun in terms of the number of photons per unit area. One of the advantages you get from using synchroton radiation in X-ray fluorescence analysis is that you can see very minute things because of the brilliant X-ray intensity, and therefore, it is suitable for analysis of trace components and minute samples.

Since X-rays are short in wavelength and high in energy , they interact with inner-shell electrons in atoms and cause photoelectron emission. When applying X-rays to atoms, if the X-rays have higher energy than the binding energy of electron to nucleus, electrons are knocked out by the photoelectric effect. X-rays of high energy are necessary to cause photoelectron emission of the K-shell electrons, the innermost shell. This unstable condition with lack of an electron is excited state. The excited atom releases the extra energy as X-rays when an electron in upper orbit falls down to the orbit of missing electron (Figure 1). The energy of this X-ray is unique to elements and called fluorescent X-ray. When X-ray is irradiated to a sample, fluorescent X-rays with the energies unique to the component elements are generated. The intensity of the emitted X-rays is proportional to the amount of the element exist in the sample as a first approximation. By using this mechanism, we can analyze the kind and quantity of elements contained in the sample. This is X-ray fluorescence analysis. Next, I am going to show you some application examples.

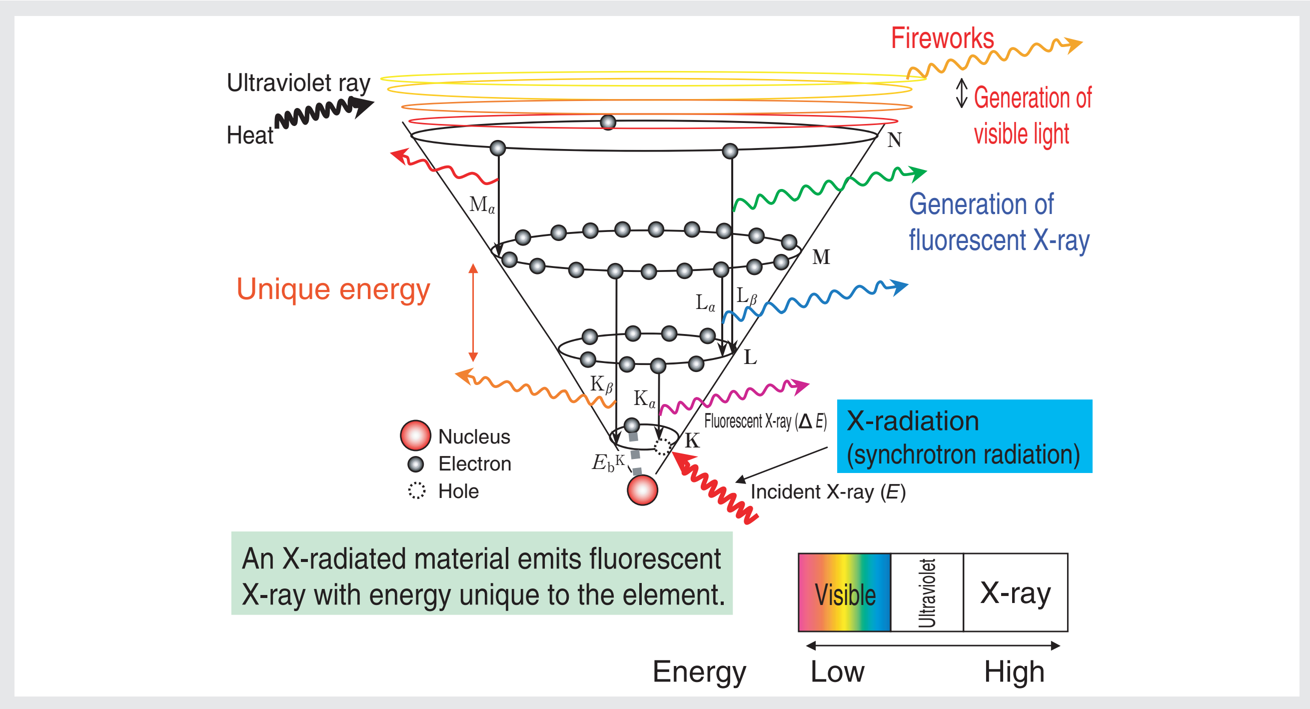


Figure 1 Generation of fluorescent X-ray and visible light (schematic diagram showing electron energy level and light emission)

Reading the Past with X-Ray

Application of X-ray Fluorescence Analysis to Forensic Science (Scientific Criminal Investigation)

The crime is an event or a fact conducted or caused in the past by people. Forensic science is a method to rationally prove a crime by verifying the human behavior in the past with depositions by people and physical evidences left in the crime scenes. In forensic science, physical evidences are particularly important.

I am telling you about the Wakayama Poisoned Curry Murder Case; caused on July 25, 1998 at a summer festival venue in Sonobe, Wakayama City, killed 4 people and 60-some people poisoned with arsenic; as an actual example.

The samples were for forensic comparison; taken from the five locations related to the case. It is the role of forensic comparison to make sure whether the substances are identifiable or not. Arsenic trioxide is generally produced as a byproduct from refining of copper, but the trace components contained in the final product vary depending on the mine or the refining process. If the arsenic trioxide related to the case had the same trace components, the substances are proven to be the same. Then, we analyzed substances focusing on the impurities of arsenic trioxide.

Analysis was conducted using synchrotron radiation at SPring-8 in Hyogo Prefecture and at the Photon Factory (PF) in Tsukuba City. For a heavy element such as Bi, high energy is necessary to excite the innermost K-shell electrons and SPring-8 is the only synchrotron radiation facility in Japan that can produce such high energy. Even though the outer L-shell is excited, the result is that the L-line peak of trace bismuth becomes invisible by large K-line peaks of arsenic that coexists in large quantities. That is why high energy is required to excite the K-shell.

Figure 2 shows the configuration of the high-energy X-ray fluorescence analysis system. In principle, the mechanism is very simple as measuring fluorescent X-ray from the sample excited by SR. X-rays of 116 keV. The high-energy X-rays from an elliptical multipole wiggler were used as an excitation source. Monochromatic X-rays of 116 keV were obtained from a doubly bent Si (400) monochromator. Energy dispersive XRF system utilizing, a pure-Ge solid-state detector was used. In 1998, no facility was conducting high-energy X-ray fluorescence analysis by using the third-generation synchrotron radiation, and so we assembled the equipment on the spot.

Figure 3 shows an example of spectra obtained from the measurement of one tiny grain of arsenic trioxide crystal by using the system. We should just pay attention to the three peaks; tin (Sn), antimony (Sb), and bismuth (Bi). The height of the peak is basically proportional to the concentration.

Unlike police identification, our identification was conducted totally in a non-destructive manner. Thus, the sample remained intact and therefore we could put it to

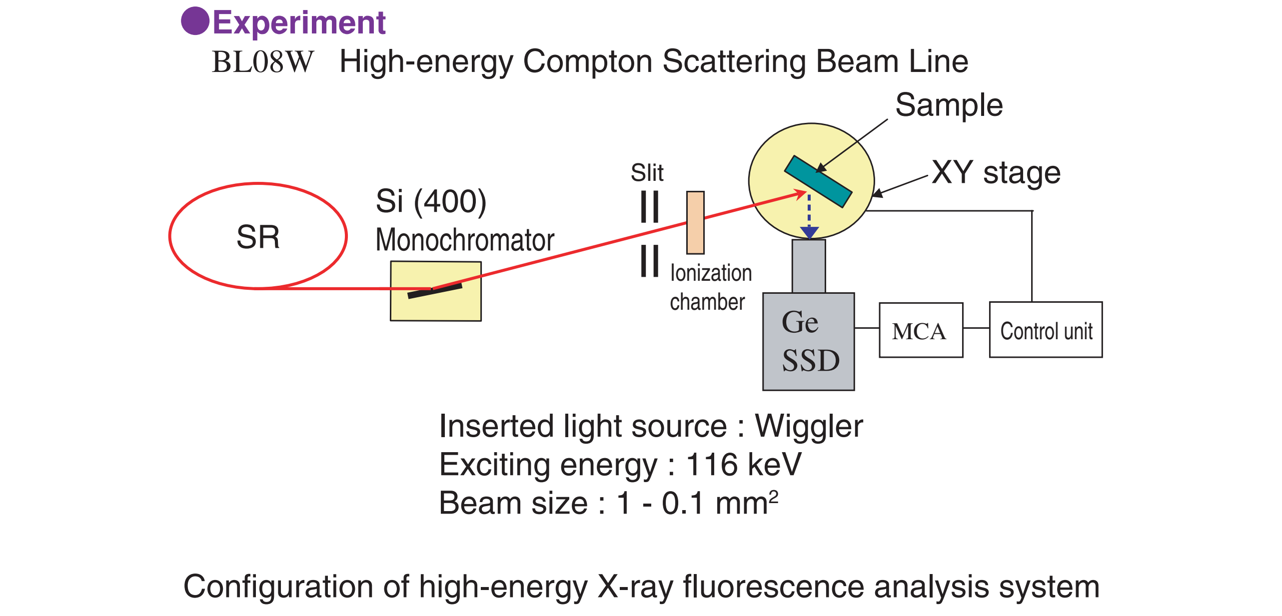


Figure 2 Configuration of high-energy X-ray fluorescence analysis system

re-identification by Prof. Kazuo Taniguchi. Based on our results of the high-energy X-ray fluorescence analysis of arsenic trioxides, all the identified samples related with the crime agree with each other in trace heavy element compositions.

"If the judge has a conviction (certainty) that the evidence is true to the degree where no ordinary person has reasonable doubt, the suspect is judged guilty." The identification for this case was based on the result of the high-energy synchrotron radiation X-ray fluorescence analysis. And the obtained data were the world's first forensic data obtained by high energy XRF analysis utilizing the world's finest facility. But in the trial, the point of contention was "whether or not the evidence provided for chemical analysis has the probative force with respect to court deliberations." In other words, "the method of request," "delivery, acceptance and storage of samples," "reason why it was found in the curry," and "the photos of

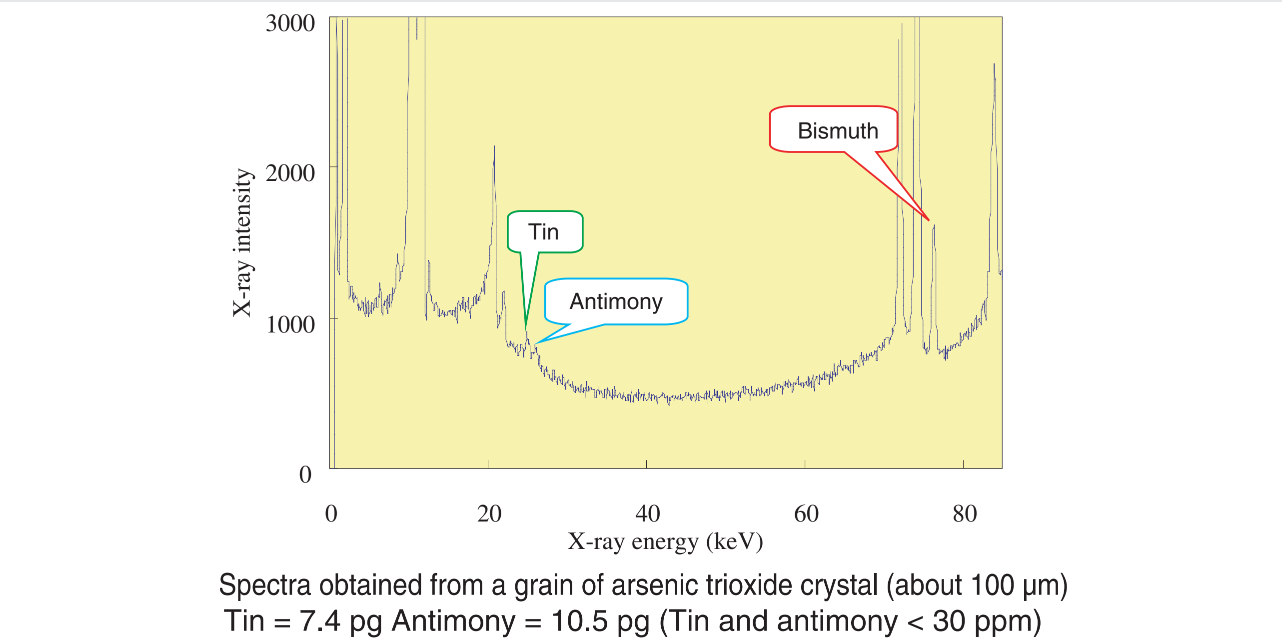


Figure 3 An example of spectra obtained from arsenic trioxide crystal

the analyzed samples" were the point of contention. Considering about the accuracy of those judgments, it can be expressed as in the way of Figure 4. It is natural that scientific measurements, results, interpretations and judgments all have a margin of error. But one thing certain is that the material itself is the truth. On the contrary, the criteria of judgment based on social common sense are vague and the reports by the mass media may aggravate the error. With the development of science and technology, crime also becomes more advanced, diversified and complex. Analytical technique is being advanced and improved day by day. I think we need judges, prosecutors and lawyers, who are good with science and technology and can appropriately understand and evaluate the results of advanced scientific measurement. Universities in Japan are offering forensic medicine courses only and lacks courses of forensic science. In addition, forensic science departments of the Japanese police are very busy with daily identification services and therefore I think university researchers, like us, should cooperate with them.

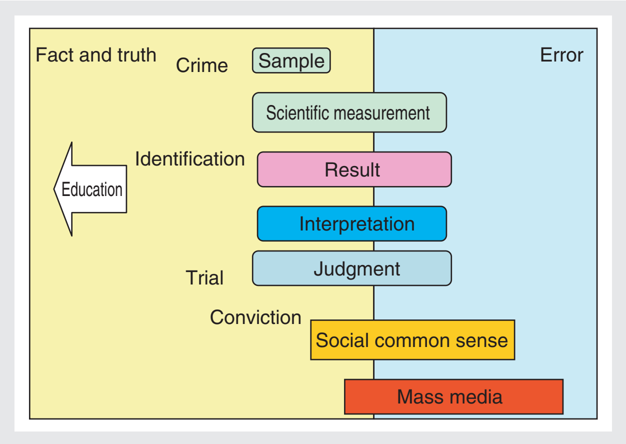


Figure 4 Social common sense and trial

Application to Archaeology

Each material has its own history and we call it material history. All materials are historical presences born at a certain point in the past. The information of the origin, the record of the material and the environment where it exists in the material. This is the information of the material history. High-sensitivity analysis allows us to read the material history. Application of synchrotron radiation deciphers the past of the material.
Forensic science and archaeology are very alike. Archaeology investigates things unearthed from ruins to find out about people, facts or trading in the past. And forensic science traces the crime from the evidence samples left in the crime scene. These activities are the same. In this light, archaeology is the subject of research of the material history and can be the subject of chemistry. Every material is the historical presence and the truth. What do the materials unearthed from ruins tell? With excellent analytical technique, we can open up the past information hidden in the material.

Estimation of Production Area of Ceramic Ware

Ceramic ware is made in places where good clay exists. Clay reflects the geology of the place and analysis of the clay used to make ceramic ware reveals the production area. Since it is unacceptable to destroy an expensive pottery, use of the X-ray fluorescence technique, that can analyze the sample in a non-destructive manner as shown in Figure 5, is necessary. Conventionally, archaeologists study unearthed artifacts based on typological infomation such as checking the shape of the item, patterns on the item and the type of the item. Whereas, in chemistry, we analyze the information of the material history which the unearthed artifacts hold (such as chemical composition, structure, texture, or physical property) to provide various findings. And chemistry is very useful for research of fine arts archaeology. In my lecture, I talked about the attempt to presume the production area of Old Kutani heirloom by using high-energy X-ray fluorescence analysis with synchrotron radiation of SPring-8.
Trace-element components of archaeological sample often reflect its origin. Heavy elements are particularly useful as fingerprint elements in provenance analyses of archaeological samples, as heavy elements are trace elements in nature and exhibit unique geochemical behavior because of their large ionic radii and relatively high valency. XRF analysis is suitable for nondestructive analysis of precious cultural heritages. However, conventional XRF analysis is not suitable for the analysis

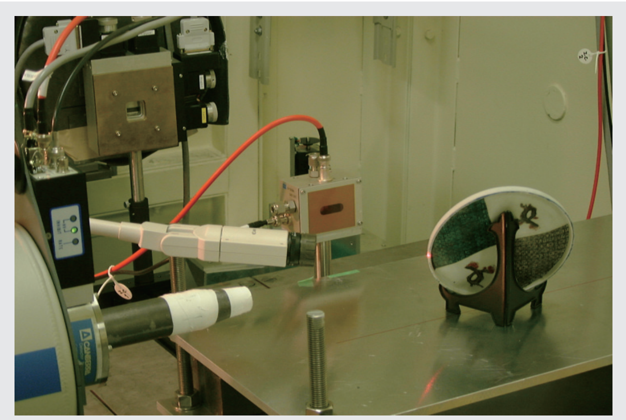


Figure 5 Picture of non-destructive X-ray fluorescence analysis of a heirloom dish of old Kutani at SPring-8

of heavy elements. A typical Energy Dispersive (ED)-XRF spectrum of a multi-component material in energy regions of less than 20 keV is usually complicated by an overlap of the L, and M emission lines of heavy elements with K lines of the light elements. Therefore, trace heavy elements cannot be measured by conventional XRF technique due to the presence of intense K-line peaks of the light elements. In contrast, the XRF spectrum above 20 keV contains only K line peaks; thus the spectrum becomes very simple.

SPring-8 is suitable to obtain high energy X-rays up to 300 keV. As introduced above, we for the first time used 116 keV X-ray as an excitation source of XRF analysis for the forensic analysis of the arsenic murder case and developed a new technique suitable for sensitive analysis heavy elements. This technique was successfully used to reveal locality of the Old Kutani china wares.

Kutani china wares were first produced in the late 17th century in the Kaga Province, which is now Ishikawa Prefecture, Japan. China wares from this early period is known as Old Kutani, which is painted china wares with beautiful color and is extremely precious because of the high quality art and limited number of production. In 1710, however, after half a century of continuous production of the china wares the Old Kutani kiln suddenly closed. Many museums exhibit Old Kutani and we appreciate the quality of the art. Recently, however, it is said that the Old Kutani might come from Arita, another world famous production place of painted china wares since 17th century in Japan. Because pottery shreds excavated from the Old Kutani kilns scarcely contained painted work. On the other hand, Arita produced many beautiful colored painted china wares till now. Therefore, identification of Old Kutani and Arita is an important and mysterious problem in Japanese art history. The high-energy SR-XRF analysis of porcelain clay bodies is expected to reveal the origin of the source materials of museum grade work.

China wares excavated from old kilns dated 17th to 19th century in Kutani and Arita districts in Japan were used as reference samples. Himetani, Hiroshima prefecture in Japan is also known as famous production of painted china wares during the same periods. Therefore, the excavated samples from Himetani were also included in the samples. Several “original works” of the old dishes in museum grade were also nondestructively analyzed (see Figure 5). They were very precious so-called Old-Kutani and Arita wares, which were borrowed from several collectors and artists. This was the first nondestructive analysis of museum grade samples of Old Kutani.

The analysis confirmed that the irradiation of 116 keV X-rays caused practically no damage on the samples. So this technique is suitable for nondestructive characterization of precious historical samples as is demonstrated in Figure 5. The XRF peak intensities of the heavy elements were used as the parameters of some statistical treatments for the provenance analysis. It is found that the Ba / Ce-Nd / Ce plot is the most useful to estimate the origin of the wares. The result is given in Figure 6, which shows that Kutani, Arita, and Himetani

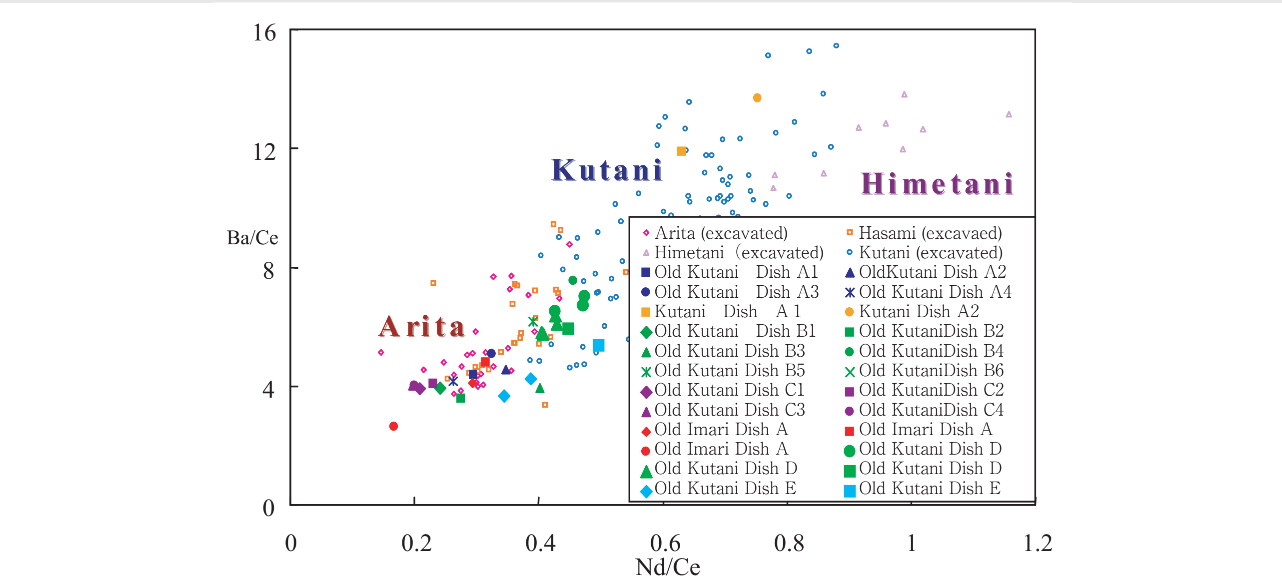


Figure 6 The result of estimation of Kutani, Arita and Himetani wares
A plot of the XRF intensities ratio of Ba/Ce-Nd/Ce for analyzed porcelain shreds excavated from the old kilns at Kutani, Arita and Fukuyama showing that each ware can be distinguished using this plot. The analytical results for the museum grade samples (A -E) are also plotted on the graph.

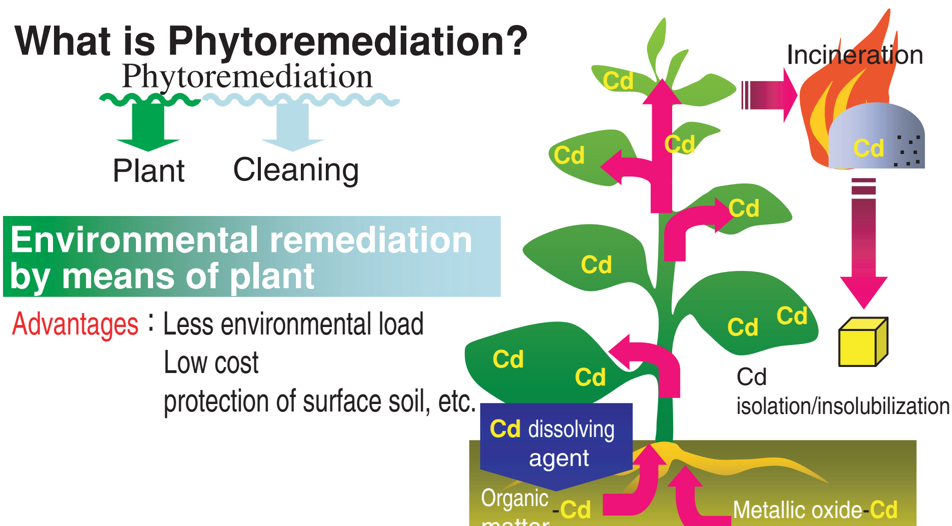
wares can be distinguished using this plot.

Analytical results obtained by the nondestructive analysis of the museum grade heirloom samples (Old Kutani A-E and Old Imari A) were also plotted in the Figure 6. It was found that the data of some samples were located on the region of the Kutani wares in Figure 6 and some were on that of the Arita wares. The data suggest that the former samples were produced using the potter's clay of Kutani area truly and the latter were those of Arita areas. Thus, high-energy XRF is able to reveal the original locality of china wares and is suitable for nondestructive analyses of historical samples.

Application to Environmental Analysis — How Plants Remove Hazardous Arsenic from the Environment

I am talking about the research on plants that accumulate As or Cd as an application of X-ray fluorescence analysis to the environmental field. Phyto-remediation; "phyto" means plants and "remediation" means stopping environmental damage, as shown in Figure 7 ; is technique to clean the environment using plants. In 2003, Ma et al. reported in Nature that a kind of fern, *Pteris vittata L.*, can accumulate As at a high concentration of 20,000ppm. Another fern, *Athyrium yokoscense*, and a mustard plant, *Brassica juncea*, are also known to accumulate Cd and Pb, respectively. These plants are planted in the polluted soil and then they suck up the pollutants from the soil to the above-ground part as they absorb water or nutrients from the soil through the roots. By using this mechanism, the toxic substances can be taken away from the soil. This method is recently drawing attention as an environmental remediation technique for its advantages of less environmental load, low cost, and protection of surface soil, compared with the conventional topsoil replacement. At present, *Pteris vittata L.* has been planted at some fields contaminated by arsenic compounds in an effort to remediate the arsenic-polluted land. The method is already commercialized. But we have got little knowledge on how As, once absorbed by the plant, is distributed in the plant and in what state the toxic element exists. Still, the method of X-ray fluorescence is suitable for tracing heavy metals in the plant because we can analyze the plant as alive, and, particularly by using synchrotron radiation, we can analyze at a spatial resolution of the cellular level.

Ferns reproduce by spores. Among ferns, *Pteris vittata L.* is the only fern that accumulates arsenic in large quantities and can store As in the quantity above 20 g per a kilogram of plant dry weight. X-ray fluorescence imaging, as shown in Figure 8, reveals the distribution of



Examples of heavy metal accumulator plants

Element	Content / ppm	Plant
As[*1]	22,630	*Pteris vittata L.*
Cd[*2]	11,000	*Athyrium yokoscense*
Pb[*3]	34,500	*Brassica juncea*

*1 L. Q. Ma, et al., *Nature*, (2001) , **409**, 579.
*2 T. Honjo et al. The Journal of Phytogeography and Taxonomy (1984), **32**, 68/80.
*3 T. Honjo et al. The Journal of Phytogeography and Taxonomy (1984), **32**, 68/80.

Figure 7 Environmental remediation by means of plant

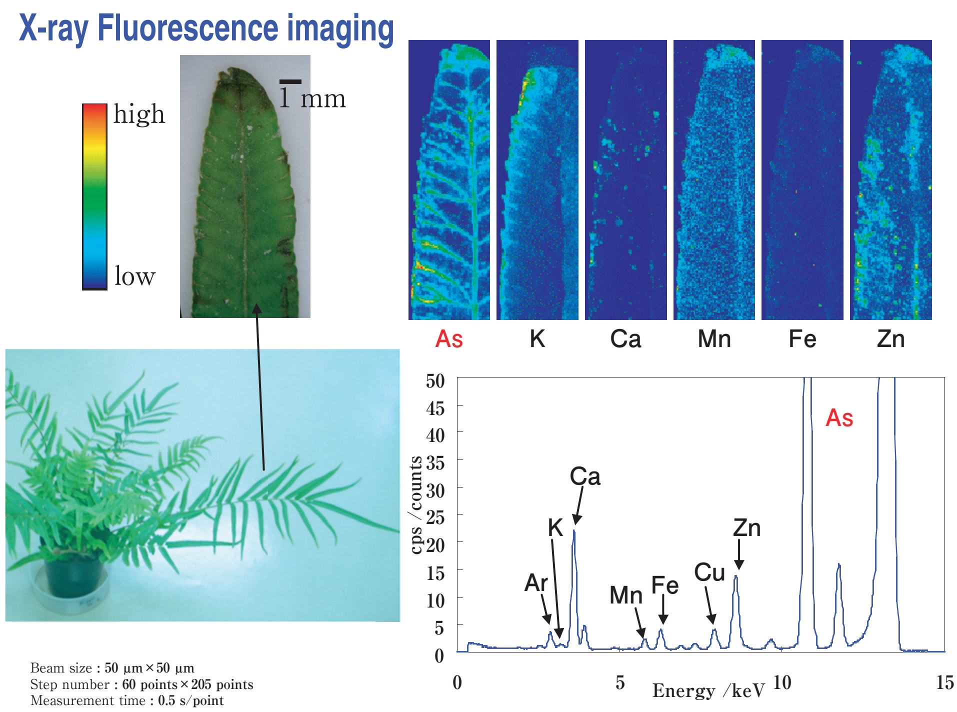


Figure 8 X-ray fluorescence imaging of *Pteris vittata L.*

elements in a leaf. Much As is distributed along leaf veins. A closer look at the withered part reveals that much As is distributed, although, some essential elements such as K were lacking. Compared As distribution in a young leaf with that in a mature leaf, the leaf actively absorbs As as early as in the initial stage and much As is present at the front end of the mature leaf. This distribution is completely different from that of K and others.

From two-dimensional analysis of the pinna of *Pteris vittata L.* cut by the slicer into a thin slice about 200 μm, a strong fluorescent X-ray intensity of As was observed near the area between the capsule part inside the pseudoindusium and the mesophyll. A more detailed measurement of this part using X-ray microbeam revealed that almost no As is transferred to spores (Figure 9). It is found that, although the fern is a lower form of plants, the protective mechanism works not to store As in spores (not to transmit to the descendants) even though it accumulates As in high concentrations.

Conclusion

Revealing the Past of the Material by X-ray

Extracting information of the material history with X-ray serves many purposes, including finding a perpetrator from a very minute amount of the evidence at the crime scene or identifying the place of origin, raw materials and production techniques of ceramic ware or archaeological remains. The use of X-ray microbeams can realize cellular level analysis of a plant in a non-destructive manner.

I hope that the readers, who read the outline of the applications in this report, have a better understanding of the magnificence of X-ray analysis. The greatest feature of X-ray analysis is its capability of analyzing all the major attributes of the material. In other words, chemical compositions can be analyzed by XRF (X-ray fluorescence), the chemical status by XAFS (X-ray absorption fine structure) or XPS (X-ray photoelectron spectroscopy), the internal structures by X-ray CT, and the crystal structure by XRD (X-ray diffraction). It is only the X-ray, among the electromagnetic waves, that

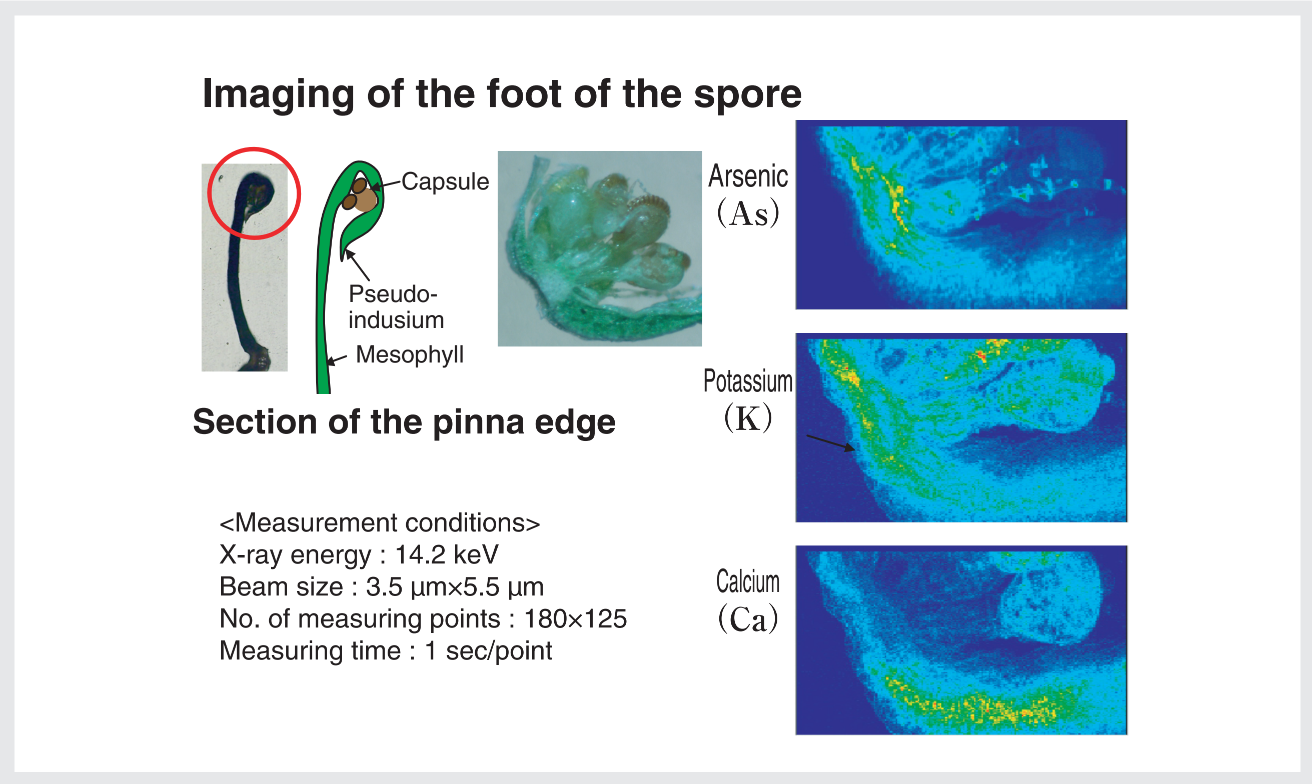


Figure9 XRF imaging of the foot of the spore

can get all the material information in the way as explained above. In addition, it allows microbeam analysis, non-destructive analysis, and multiple-element simultaneous analysis. As the direction into the future, this kind of analysis is more required to obtain multi-dimensional material information from samples with keeping samples as they are, X-ray analysis that matches those needs is expected to develop and more widely spread.

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