

Guest Forum

Lecture by a Jury Member for the 2006 Masao Horiba Awards

Present Status and Future of Advanced Scientific Instrument using X-ray



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X-rays have attracted a lot of attention as a form of electromagnetic radiation that enable us to see objects through materials. And they are also a great contributor to clarification of physical phenomena. In the field of analysis, X-rays have drawn the attention from their initial stage as a method of non-destructive simultaneous analysis. Scientific measurement using X-rays is supported by three elemental technologies; generation of X-rays, spectroscopy and detection. Recent years, we have seen further advancement in those technologies. I am going to explain the present status and the future of advanced scientific measurement obtained by combinations with those evolving elemental technologies.

Introduction

X-rays were found by Röntgen in 1896. After the news of the finding spread worldwide, a transmission X-ray image of a three-month-old infant was taken in the same year. Detailed images of the head clearly showing blood vessels were also taken in 1902. They found applications of X-rays rapidly in medical science and then, in physics and chemistry, and their development was accelerated. I am going to talk about X-ray spectroscopy, application of compact X-ray devices to archaeology, application of synchrotron radiation light to forensic science, development of elemental technologies of the X-ray device and the development project of next-generation X-ray fluorescence analyzer.

Drawing Information from Materials

Interaction between X-rays and Materials

When X-rays are irradiated to a material, one part of the X-rays is scattered or reflected, other part is absorbed, and the rest part penetrates the material. X-rays scattered without losing energy interfere with each other and they

are observed as diffraction lines. Inner shell electrons escape from the area exposed to X-rays. Measuring this kinetic energy of electrons is photoelectron spectroscopy. Holes are formed after emission of electrons, and electrons fall from the upper orbit into the empty holes. Then, X-rays (fluorescent X-rays) equivalent to the energy difference are generated, and then, they are used for qualitative and quantitative analysis of elements. If the orbit, from which electrons fall, is in the valence band, not in the inner shell, generated X-rays directly give us the information on the valence band.

X-ray Spectroscopy

In a compound, the electron orbits of different kinds of atoms interact with each other and separation of those orbits into some finer ones is caused, or transfer of energy levels is caused. Because of the selection rule that restricts movement of electrons among orbits, by measuring X-ray spectra and comparing some spectral peak positions, we can express the energy levels of those electron orbits experimentally. As an example, figures on the next page are the spectra from measurement of compounds, in which the composition ratios of oxygen (O) are increasing

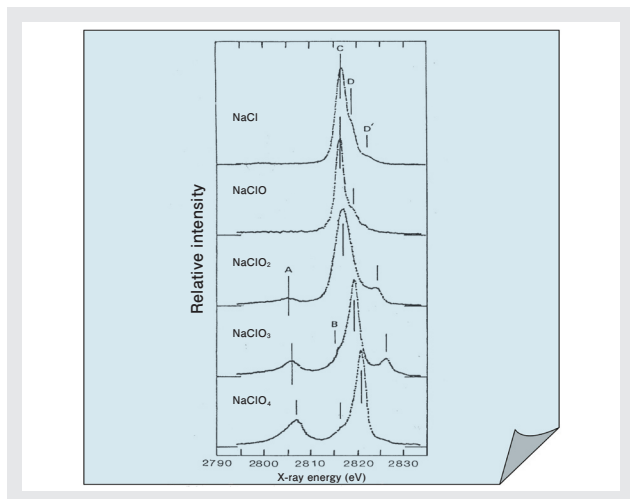


Figure 1 Cl Kβ spectra

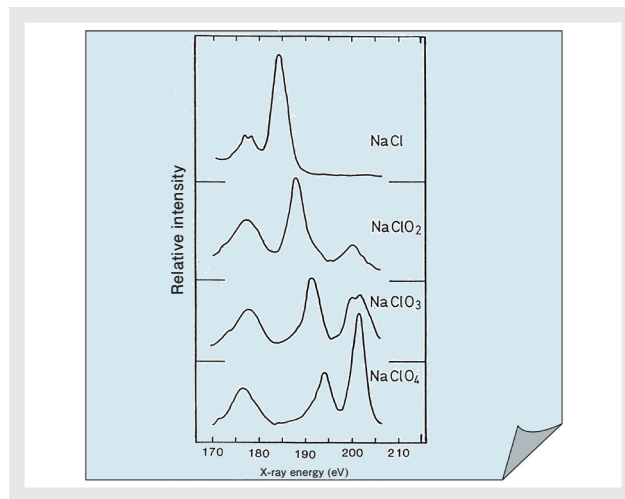


Figure 2 Cl L_{II,III} spectra

in the ascending order from salt (NaCl) to sodium perchlorate (NaClO₄). For Cl Kβ fluorescence (about 3000 eV), generated by moving of electrons from the 3p orbit of the M-shell of chlorine (Cl) to the K-shell (1s orbit), the peaks shift to the high energy side with the rise of oxygen and new peaks are appearing and disappearing (Figure 1). For the Cl L_{II,III} fluorescence line (about 200 eV) generated from movement of electrons from the 3s and 3d orbits of the M-shell to the 2p orbit of the L-shell, the higher energy peak shifts to the high energy side, and highly powerful peak suddenly appears at the high energy side for NaClO₄ (Figure 2). For O Kα fluorescence generated by movement of electrons from the 2p orbit of the L-shell of oxygen (O) to the K-shell (1s orbit), there are not many changes in peak positions (Figure 3). Using these data, we can draw a diagram showing the electron structure of the valence band (Figure 4). This kind of analysis can be used in case that we want to create a material for a certain purpose, which we would desire, for example, to have a good electric conductivity but, at the same time, to have a poor thermal conductivity.

In this way, we carried out research to elucidate the electronic structure of materials with X-ray spectroscopy. But it was impossible to experiment using commercial equipment without changes. To measure the peak shift of Cl Kβ, we had to make a high energy resolution spectroscope with combination of crystals to obtain high resolution. We had to solve the problems on spectroscopic devices or detectors by ourselves in order to detect Cl L_{II,III} of about 200 eV while dispersing it. This was the reason we got involved in making some of

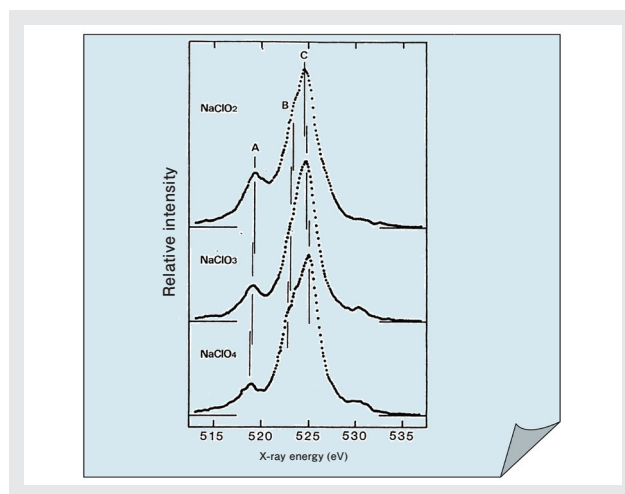


Figure 3 O Kα spectra

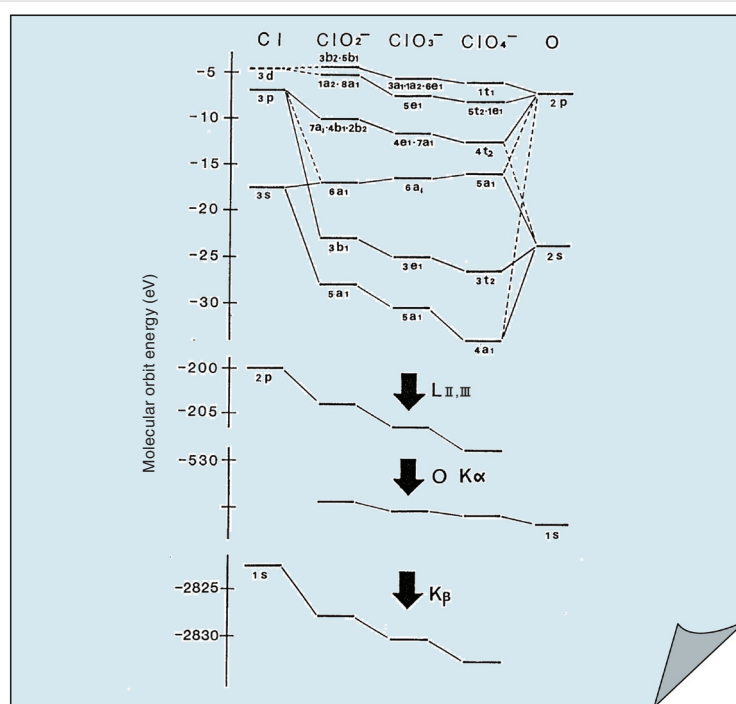


Figure 4 Electronic structure in the valence band

the elemental technologies such as X-ray tubes or detectors by ourselves.

Li K Absorption Spectra

The ultimate is measurement of Lithium (Li). With X-rays, we were able to analyze elements of smaller atomic numbers but only down to carbons (C) or borons (B) in those days. Li, which has an atomic number of 3, does not get along with X-ray, but we get a lot of information by measuring the X-ray spectra of Li. For example, we get the information on electronegativity from the peak position. In the past, when you wanted to analyze a Li battery, you had to start from checking what the partner element of the Li battery was. With the total electron yield method using synchrotron radiation, we successfully measured the Li K absorption spectra. As shown in Figure 5, even just a little bit of change in the structure greatly changes spectra. We were engaged in study of charging or discharging processes by reading those spectra through molecular orbit calculation. It was the world's first attempt to directly measure Li inside the battery using X-rays, and our achievement enjoyed a high reputation.

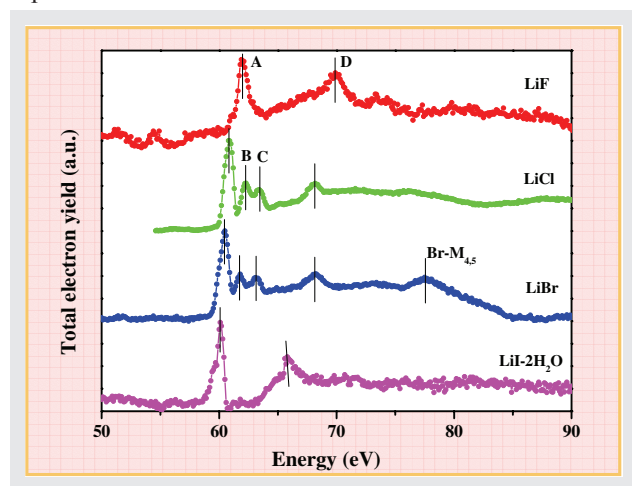


Figure 5 Li K absorption spectra in various kinds of lithium halides

Portable X-ray Fluorescence Analyzer

While I was involved in this kind of basic research, I was asked about the feasibility of an X-ray fluorescence analyzer operable on the spot. If we could improve an excited X-ray source, dispersing/focusing device, and detector circuit, we would be able to downsize the X-ray analyzer. So we decided to start development of a portable

X-ray fluorescence analyzer.

After the development of a portable device which could be taken to a site for measurement, the Egyptian Archaeological Agency got interested at first. They had plenty of things to analyze without damaging them at all, and the portable X-ray analyzer was the very thing they needed. Thus, our portable analyzer got busy analyzing valuable archaeological materials including the wooden coffin of Nepsen or the paint on the stela of Amenemhat. Figure 6 is a photo showing field analysis of the wooden coffin of Nepsen.

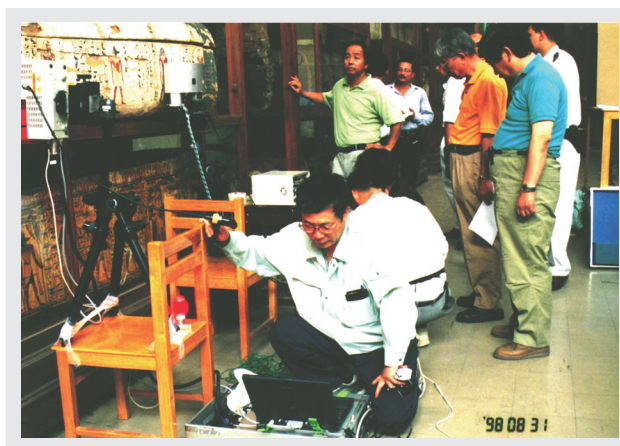


Figure 6 Nepsen's wooden coffin being analyzed

Application to Forensic Science

The defense lawyers of the Wakayama Curry Case protested against the identification by Prof. Nakai from the viewpoint of decent evidence preservation. In order to establish the conditions that make the evidence worth being valid in court, we decided to analyze it again. The major contention was whether arsenic trioxide found in the plastic container in the suspect's kitchen, the paper cup left at the summer festival venue, and the curry served for the festival participants were identical or not. The three parties — the lawyers, judges and prosecutors — attended all the processes of analysis from sampling to measurement. We got on processes in the circumstance like holding court in the synchrotron radiation facility; we were in such a condition that we answered any questions if there were any problems there. The paper cup was disinfected by boiling and cleaned at the public health center it was first taken to, but a trace remnant of arsenic was found in the joint of the bottom. For the curry, we carried out CT-scan to look for arsenic and found crystals of arsenic trioxide. Those samples were put to X-ray fluorescence analysis using synchrotron radiation to

analyze impurities. The conclusion reached from this reanalysis was that the arsenic trioxide found in the plastic container and that in the paper cup were of the same kind, and that the arsenic trioxide found in the curry was of an allied substance.

Elemental Technology for X-ray Measurement Under Development

Multi-excited X-ray Tube

Synchrotron radiation is used for measurement generally for special cases. We are taking actions in order to realize analysis under the ultimate condition at the laboratory

level with no use of synchrotron radiation. One of them is ongoing development of a multi-excited X-ray tube that can efficiently excite a wide variety of elements. In our plan for this new X-ray tube, targets should be arranged at the anode, and the anode should be moved from outside through the bellows so that targets can be switched to those that excite well depending on the element to measure (Figure 7).

Microfocus Electron Gun

We are trying to develop an X-ray tube that features a small focus size and a high level of luminance (Figure 8). We want to develop an X-ray tube that generate X-rays from a small area and yet has a high intensity of about 50 W.

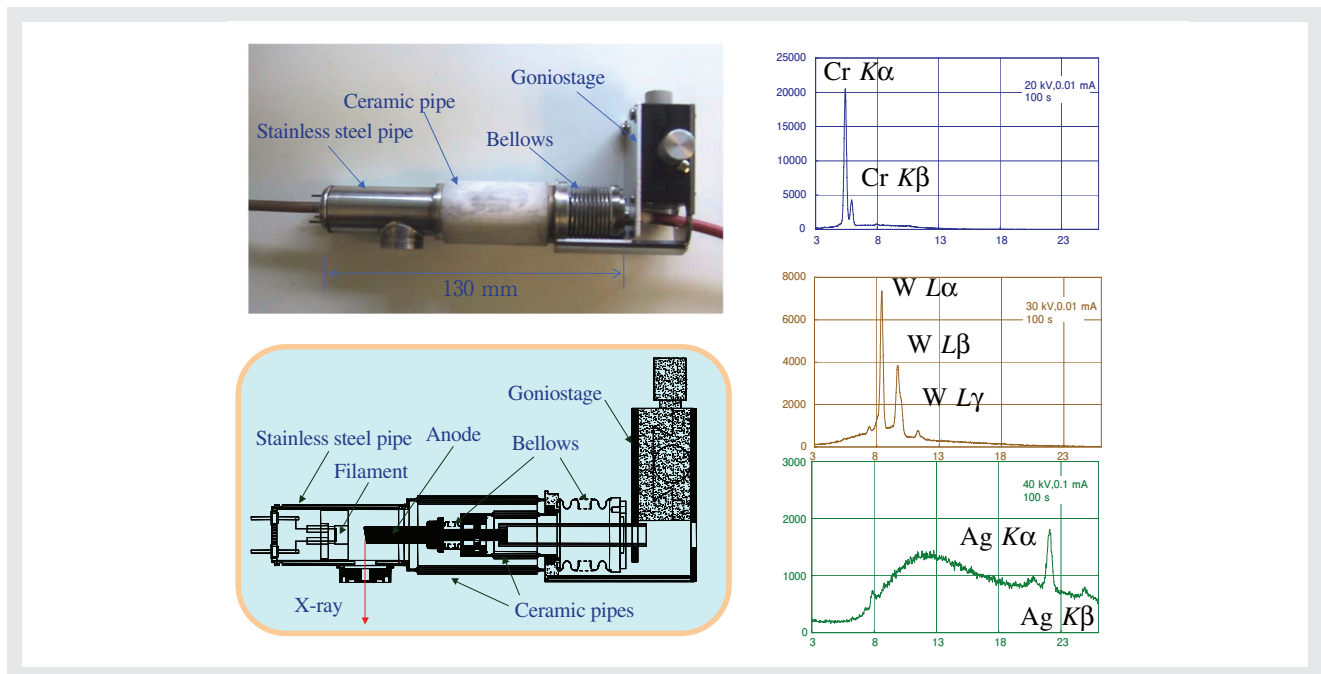


Figure 7 Multi-excited X-ray tube under development
The structure of the X-ray tube and the X-ray spectra emitted from the X-ray tube when the target is switched to Cr, W, and Ag, respectively.

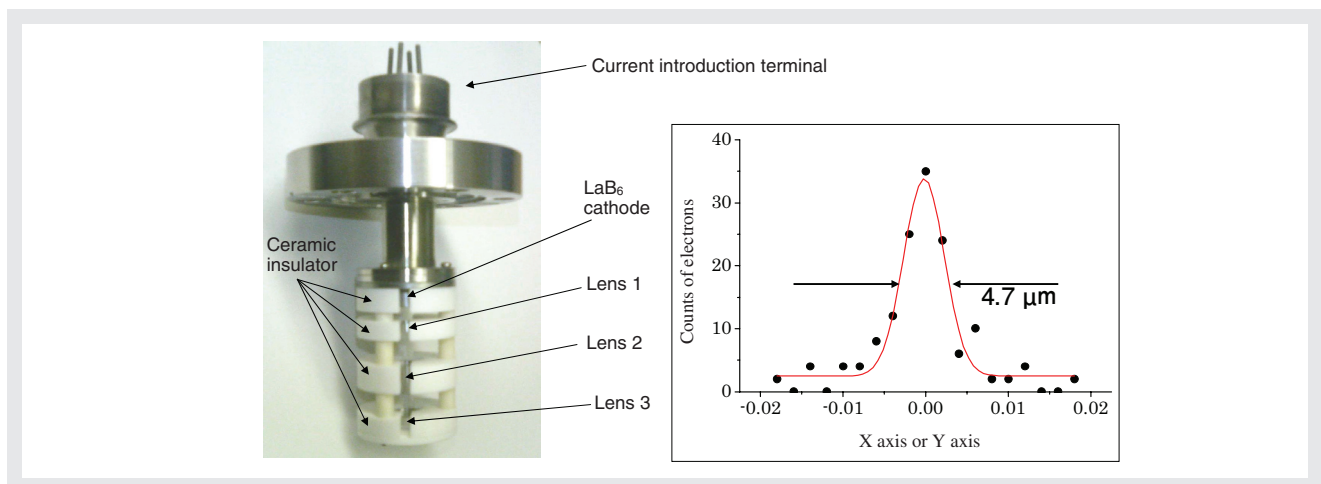


Figure 8 Microfocus electron gun

A conventional 50-something W X-ray tube can only handle focal sizes as small as about 50 μm . But by combining simple electronic lenses, the X-ray tube can focus on 4.7 μm . Though you might say that the improvement is only a digit, from 50 μm to 4.7 μm , this enhancement is equal to two-digit improvement in luminance and it is effective in use of measurement of microscopic parts.

Doubly Curved Crystal (DCC)

In order to focus X-ray while dispersing, we developed a device that dispersed light at the part inside a cylindrical crystal. Moreover, to further enhance the intensity, we developed a device that dispersed light with the entire surface of the crystal. It is a dispersing device using a doubly curved crystal (DCC) and looks like a Johan crystal wrapped around a cylinder. Figure 9 shows the

producing equipment and a doubly curved crystal. This crystal is made of about 15 μm thick silicon crystal pressed to become curved and bonded, however, we can only focus into 30 to 40 μm because of the limit of adhesive bond for accuracy. One of the solutions we are trying now is anodic bonding of Si on SiO_2 glass. As the result of this solution, divergent X-rays emitted from a tube are focused and in monochrome and we recognized the peak intensity was raised to 2400 times greater than with the original crystal (Figure 10).

X-ray Detector

We initiated the work of producing a detector with a large area jointly with KETEK, Germany. The target detector is one with an effective area of 100 mm^2 and a diameter of about 22 mm and of a size slightly larger than a cigarette pack (Figure 11). At present, the detector has an energy

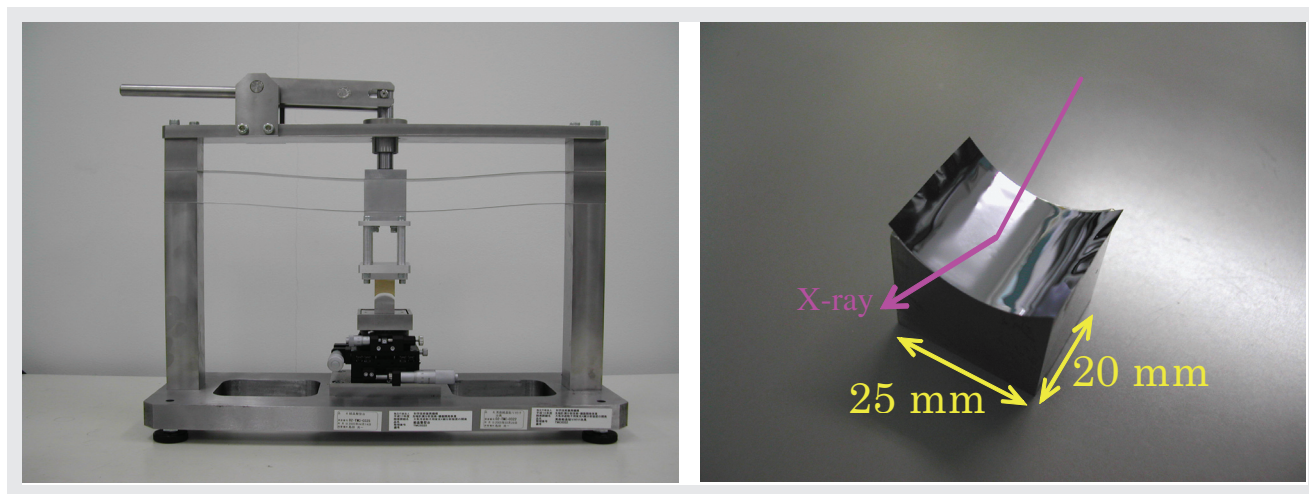


Figure 9 Crystal pressing device and the doubly curved crystal produced

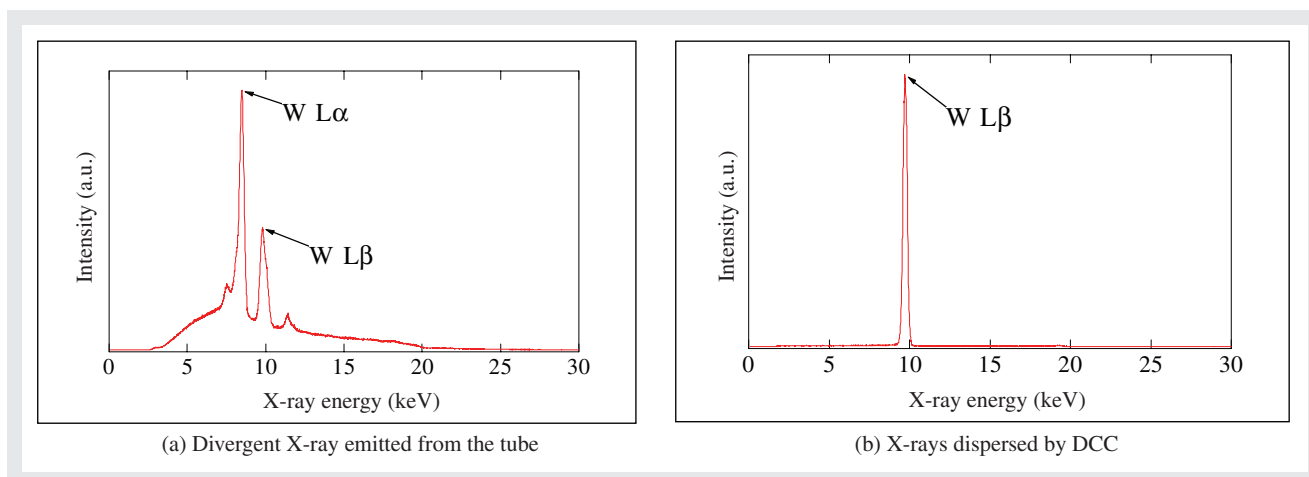


Figure 10 Dispersing and focusing by DCC

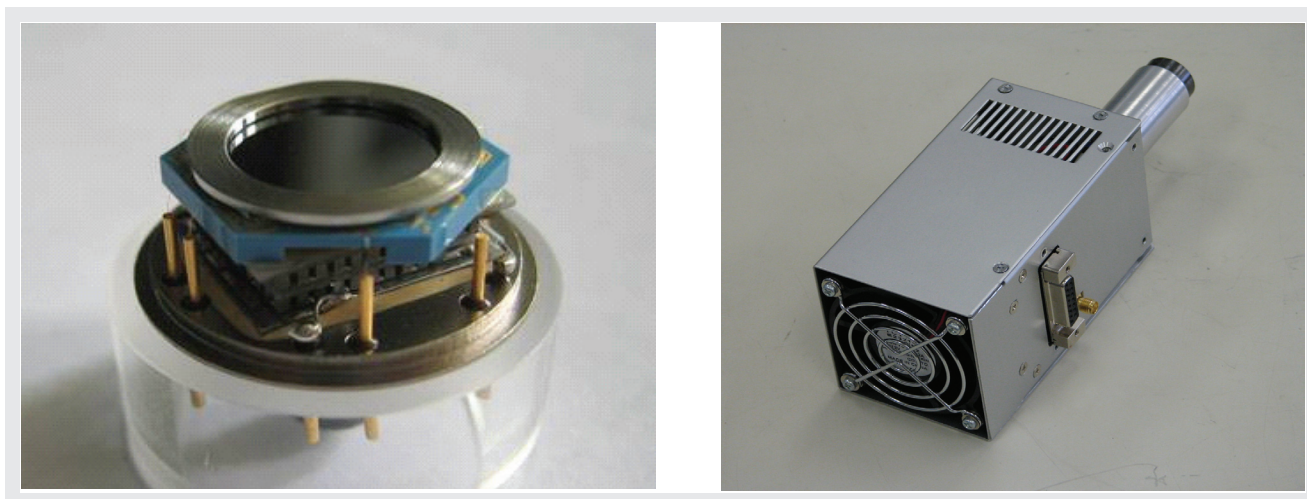


Figure 11 Silicon drift detector (SDD)

resolution of 131 eV (FWHM at Mn K α 5.898 keV peak) and it is better than the energy resolution of large Si (Li) detector. Besides, more important characteristic than resolution is the height (background) of the tail from the peak position to the low energy side, and our detector achieved over 7000 in peak height/background ratio (PB ratio). It is a Peltier-cooled detector using no liquid nitrogen. This is the present state of development we have achieved so far for the X-ray detector.

The maximum energy resolution of a typical silicon-based detector is 130 eV, and we are developing ultimate detectors, or superconducting transition edge micro calorimeter (TES) and a series-connected superconducting tunnel junction detector.

Microcalorimeter (TES)

When we irradiate X-ray to a material cooled down to a temperature at the superconducting transition edge where electric resistance suddenly changes, the temperature changes and the electric resistance also greatly changes as X-rays are converted to thermal energy. The calorimeter is an X-ray detector using this phenomenon (Figure 12). SII is engaged in development of the device and system. In energy resolution of 6.6 eV, we recognize separation of Mn K α 1 and Mn K α 2 (Figure 13).

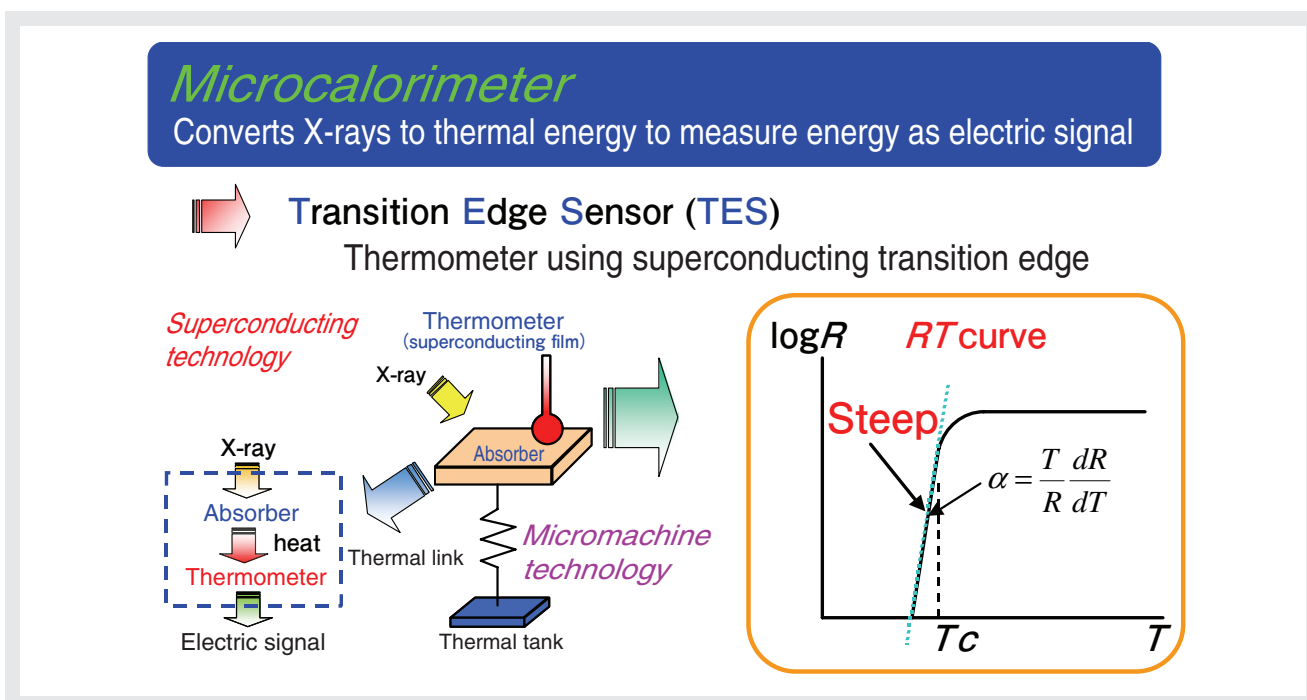


Figure 12 Principle of microcalorimeter

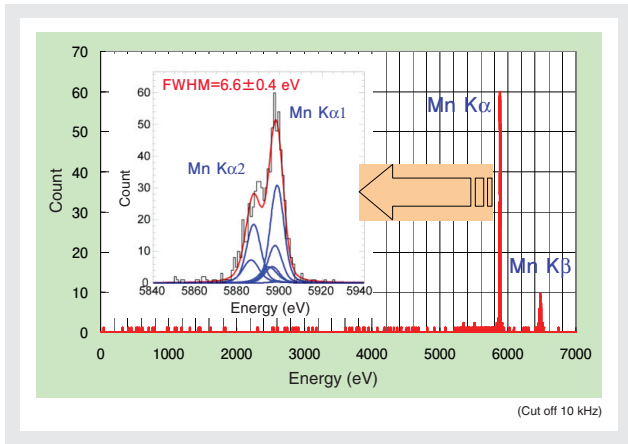


Figure 13 Evaluation of TES

Series-connected Superconducting Tunnel Junction (STJ) Detector

Containing an about 1 nm thick insulated film sandwiched by two superconducting films, the superconducting tunnel junction detector takes out excited electrons by X-rays in the superconductor as signal current using the tunnel effect.

This single-junction detector has a thin film and its detecting efficiency of high-energy X-rays is low and the area is small. Because of these imperfections, the series-connected type is currently under development by Prof. Kurakado, as the main player, which has many superconducting tunnel junctions connected in series on the substrate and uses phonons emitted as the substrate absorbs X-rays.

As shown in Figure 14, the current data; the resolution from ⁵⁵Fe to Mn K α is 258 eV; is not good with the sapphire substrate 0.4 mm in thickness. However, there is

big room for improvement of the resolution and the sapphire substrate can be much thicker. Therefore, we expect that they will be able to make a good detector that can efficiently detect X-rays up to 100 keV.

X-ray Fluorescence Analysis of Airborne Suspended Particles

Microparticle Measurement — Antarctic Continent Observation Plan

A project is under way that tries to elucidate the causes of the climatic changes in the past (glacial age and interglacial age) by excavating the ice sheets of the Antarctic and measuring microparticles and space dust in the atmosphere of the ancient Antarctic. As we dig down to 3000 m, we can get ice up to one million years in the past. Ice confines snow dust that came from the space, and dust generated by climatic changes of the ancient Earth in it. Analysis of ice sheets unravels the history of the Earth and the history of space. Figure 15 shows a part of the ice sheet core coming from a period in which black belts exist. Those black areas correspond to the periods when almost no sunlight reached the ground for decades. From the analysis of the microparticles in black areas, we clarify whether the glacial age emerged as the result from volcanic eruption or the strike of meteorites. And component analysis of the ice sheet core helps elucidation on whether the cause of the past meteorological changes is related to the sea, volcano or meteorite. Those pieces of information will enable us to predict future meteorological changes (Figure 15).

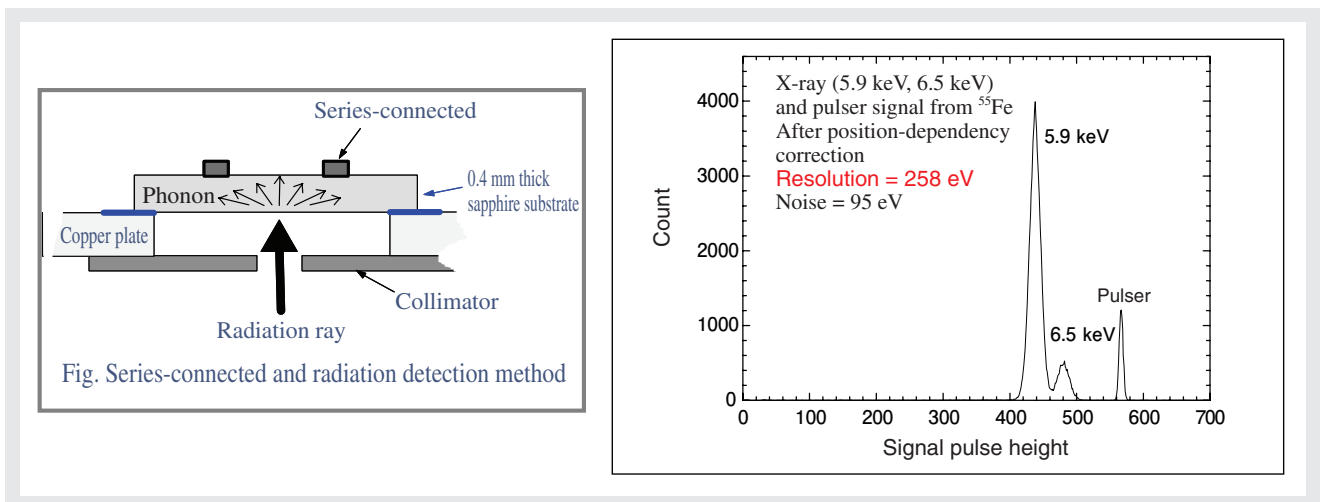


Figure 14 Spectra measured by series-connected STJ

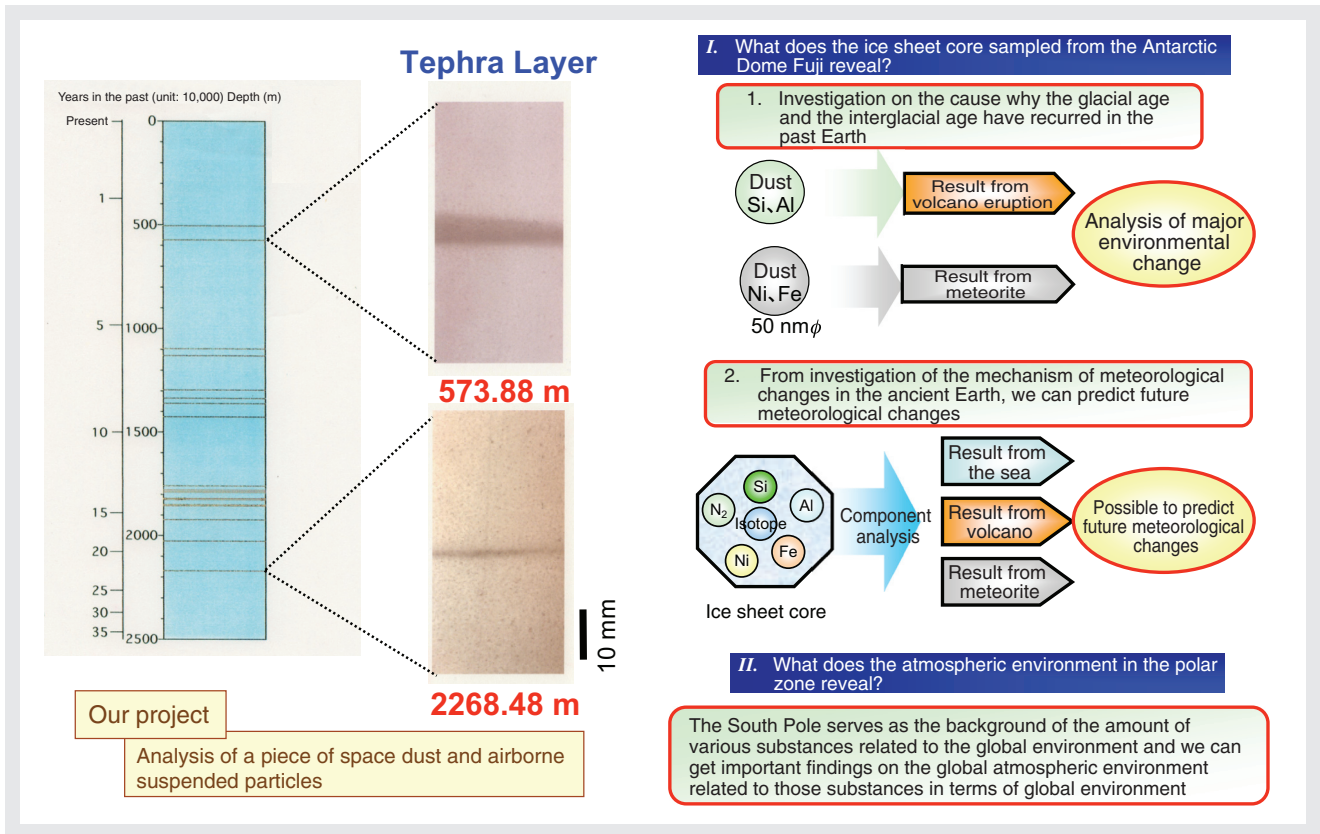


Figure 15 Quantitative and qualitative analysis of airborne suspended particles in the Antarctic

Development of X-ray Fluorescence Analyzer for Airborne Suspended Particles

Invisible space dust exists in large quantities in very small spaces. For the purpose of analyzing every one of those dust particles, we are developing a super-sensitive

X-ray fluorescence analyzer for airborne suspended particles that can measure particles as small as 50 nm in diameter and carry out quantitative analysis of fg (10^{-15} g) in the microparticles (Figure 16).

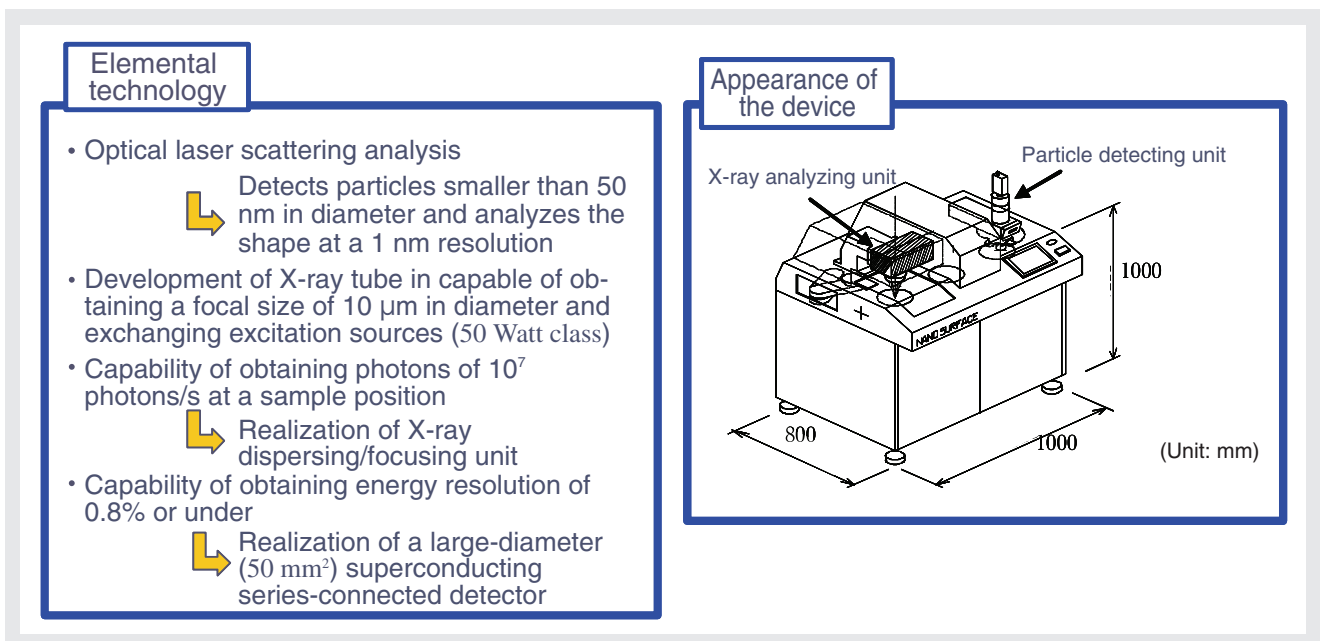


Figure 16 Super-sensitive X-ray fluorescence analyzer for airborne suspended particles

Conclusion

A variety of X-ray analyzers have been developed and applied in various ways together with the development of elemental technologies for X-ray measurement. This report outlines the equipment centering on X-ray fluorescence analyzers, their applications, and the equipment under development and its applications. I am going to continue my research and do my best to contribute to the development of advanced scientific measurement.

<Excerpt from the Lecture in the Lecture Meeting by a Jury Member for the 2006 Masao Horiba Awards (On May 30, 2007)>

(Publication members have responsibility for the translation)

