

Guest Forum

Lecture by a Jury Member for the 2006 Masao Horiba Awards

High-Sensitivity Small-Size X-Ray Fluorescence Spectrometers



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Using a small X-ray tube, X-ray fluorescence analysis can achieve a high sensitivity through such means as appropriate geometrical arrangement, pretreatment and total reflection. This article outlines relevant X-ray element technologies, with a focus on high-sensitivity small-size X-ray fluorescence analysis that is being developed by a researchers' team including the author. This method permits an analysis accuracy of 0.1 ppm Cr using a pyroelectric crystal X-ray source. And it has achieved a minimum determination limit of 3×10^{13} (in terms of the absolute number of atoms) through the use of a 1.5 W air-cooled miniature X-ray tube for total reflection X-ray fluorescence.

Introduction

X-ray fluorescence analysis is an analysis method involving the irradiation of a sample with X-rays (or primary X-rays) and the measurement of excited X-rays (fluorescent or secondary X-rays). This method is used for the qualitative as well as quantitative analysis of elements: it identifies an element from the energy (wavelength) of characteristic X-rays, and the quantity of the element from the intensity of the X-rays. Though its principle is simple, the method could not have been put into practice without the efforts of pioneers to solve many problems^[1]. Fifty years ago, it was believed that the method could not possibly be used for process control analysis in the manufacturing industry. This was because of the matrix effect, which refers to the fact that, at high concentrations of a coexistent element, the intensity of characteristic X-rays is not proportional to the concentration of the element. Thanks to the synergism of steady basic studies and research in practical settings, the accuracy of the method has improved so much that it can now be used for control analysis in steel production. A spectrometer for process control is usually a full-automatic large apparatus designed for a particular purpose. Such an apparatus is as

big as a large refrigerator for business use.

Meanwhile, many desktop X-ray fluorescence spectrometers have also been developed. These spectrometers have begun to be used as general-purpose applications that do not require an accuracy as high as that for industrial process control, but that involves the handling of samples of various shapes. Such applications include the analysis of toxic elements in soil, water, plastics or electric parts; and samples for biological and archaeological studies. A desktop spectrometer is easy to use, and has a sensitivity and an accuracy sufficiently high for ordinary purposes of analysis, though its determination accuracy is not as high as in process control analysis (and as a matter of fact, the reason for this lies in how a sample is pretreated). Furthermore, many desktop spectrometers with spatial resolutions in an order of 10 μm have been introduced to the market, and begun to be used as analyzers that can meet a comprehensive range of demands. A spectrometer with a high spatial resolution is also available with an elemental imaging. The size of a desktop analyzer can be best pictured as that of a small refrigerator in a business hotel room. Also, small handy analyzers have come to be used

recently. Though their sensitivity, at about 10 ppm, is not very high, they offer the great advantage of operation with only one hand. This kind of analyzer is as small as a hair drier or an iron. Intended for outdoor use, these analyzers are designed strong enough to prevent damage even when handled carelessly. Some handy analyzers allow users not expertized in analysis to perform qualitative and quantitative analysis of an element, by displaying the elements and their concentration in real-time on a liquid crystal screen, or showing the name of an alloy directly on the screen.

The extreme opposite to these three kinds of X-ray fluorescence spectrometers is X-ray fluorescence analysis at a synchrotron radiation facility. This method is used for a highly important analysis task that justifies a great expense. It is also suitable for cases in which record-setting accuracy in analysis is required.

My research team is developing a new X-ray analysis method using synchrotron radiation light. But we are also trying to analyze samples at the lowest-ever concentration of an element, using dry electric batteries as our power source. This attempt is a challenge, in our manner, to synchrotron radiation analysis. Our goal is to prove that a passable analysis can be conducted even with dry batteries; such a feat will point to the possibility of lowering the minimum detection limit further not only for synchrotron radiation, but also for ordinary spectrometers. Our effort may be likened to those of athletes trying to demonstrate how fast a human can run a 100 m course in an Olympic game.

This lecture presents two types of ultrasmall low-power X-ray fluorescence analyzers of a high sensitivity, both developed by our laboratory.

Ultrasmall Pyroelectric Crystal X-Ray Fluorescence Analyzer Using Dry Batteries

A small X-ray source, like the one shown in Figure 1, is commercially available in the U.S. A pyroelectric crystal is contained in a small vessel resembling the package of an operational amplifier. X-rays are emitted when dry batteries (3 V) are connected, as shown in Figure 2. The batteries are used to increase or decrease the temperature by running a current through a Peltier device. A voltage of about 30 kV can be generated by changing the temperature of the pyroelectric crystal, of a thickness of several millimeters, from room temperature to 100 °C

and vice versa. According to Brownridge, a researcher in the State University of New York, who invented this X-ray emitter, he tried to measure the low temperature properties of the ferroelectrics of cesium compounds in the 1980s, but he failed at every attempt due to the occurrence of an electric noise. This experience led to the discovery of a mechanism causing the generation of the above-mentioned voltage. To the best of my knowledge, three or more groups of researchers independently discovered the method of accelerating electron beams or generating X-rays by changing the temperature of a ferroelectric substance (a pyroelectric crystal is this kind of substance) and thereby generating a high voltage^[2-4]. This X-ray source generates weak X-rays whose intensity changes periodically, in synchronization with periods of heating and cooling. Saddled with these double problems, namely the low level and periodical changes of intensity, the source was supposed to be of no use for element analysis. In fact, it was thought to be useful only as a toy. Prior to the commercial introduction of the X-ray source shown in Figure 1, my colleagues and I had started a research into the mechanism involved in the generation of X-rays as a result of the electrification of an insulator^[5, 6]. As these circumstances allowed us to recognize the importance of a pyroelectric crystal ahead of others, we tried to apply the crystal to X-ray fluorescence analysis.



Figure 1 A pyroelectric crystal-type X-ray emitter manufactured by Amptek Inc.

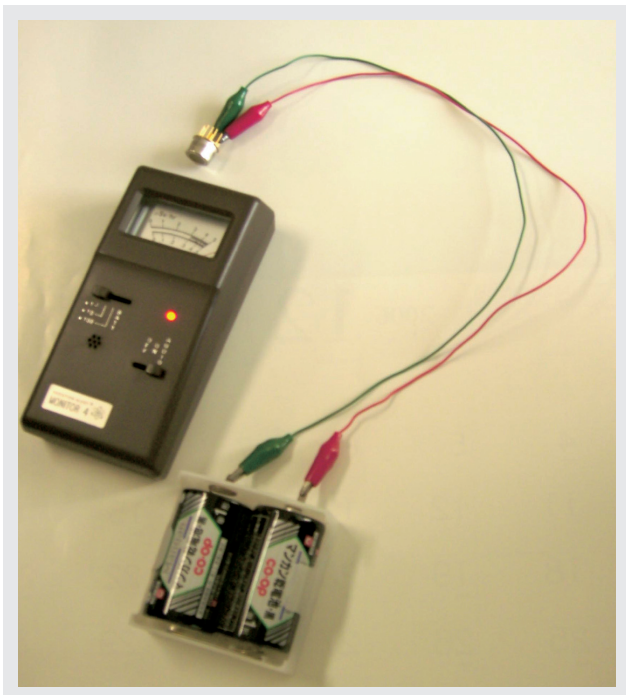


Figure 2 X-rays are being generated by applying a voltage of 3 V to the X-ray generator (Figure 1)

D-size batteries are used. The LED of the survey meter is turned ON, indicating that X-rays are being counted. The meter's pointer has swung to the limit. An animation showing the crocodile clip being connected or detached can be viewed on our website (<http://www.process.mtl.kyoto-u.ac.jp/>). Even an X-ray source as simple as this one permits the measurement of a Cr solution to a detection limit of 0.1 ppm.

At first, we applied it to the determination of the main constituents of stainless steel and other substances, and obtained encouraging results indicating that such elements as Fe, Ni and Cr could be analyzed correctly. Subsequently, the method began to develop further when Ida at the Forensic Science Laboratory, Kyoto Pref. Police H. Q., showed that it could be applied to the identification of similar articles for daily life^[7-9].

For example, it was shown that an imprint could be analyzed regarding its Hg, Pb and other contents, to identify the red ink used (Figure 3^[7]). Also, it was shown that as the amount of iron contained in an aluminum foil for cooking varies according to the foil type, the type of a given foil could be easily identified through analysis (Figure 4^[7]). For instance, the iron content in an aluminum foil, accounting for a weight ratio of 0.1 %, can be easily identified through analysis.

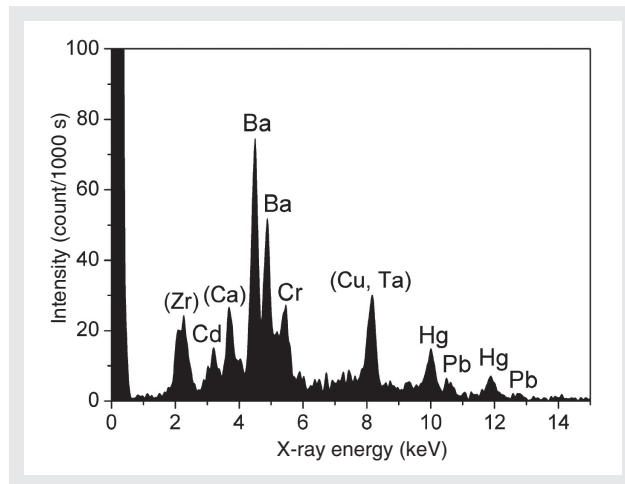


Figure 3 Results of the analysis of an imprint on paper (regarding the type of ink used) using a pyroelectric crystal X-ray emitter (reproduced from Reference [7] by permission)

As mentioned before, a pyroelectric crystal generates a high voltage by going through cycles of heating and cooling. As the polarity for heating is reverse to that for cooling, the intensity of X-rays fluctuates periodically. Accordingly, it was believed that the crystal was of no use for quantitative analysis, given such an unstable intensity of X-rays. However, contrary to the general opinion, Ida and others disproved this by obtaining a linear analytical curve for the constituent elements of steel^[10]. Of course, this result was achieved by optimizing the angles and distances for X-ray irradiation and detection, as well as the geometrical arrangement of a secondary target, etc., through a number of trials^[11, 12]. Also, Ishii and others showed that the crystal could be applied to the analysis of elements contained in soil or rice^[13, 14].

Significantly, a minimum determination limit of 0.1 ppm was achieved for a Cr solution, by applying preliminary concentration and other pretreatment methods to the solution sample^[15].

It has also become possible to measure the X-ray absorption spectrum, though a high level of noise still forbids the practical use of this measurement method^[16, 17]. These researches were reported as guidances in Reference^[18-20].

More surprisingly, it was recently reported that a pyroelectric crystal could be used for a palm-size low-temperature nuclear fusion device. It is a well-known fact that nuclear fusion takes place when deuterium ions are accelerated under a voltage of approximately 100 kV.

According to the report, neutrons were generated by colliding accelerated D^+ ions with a rare earth target that had absorbed D_2 [21, 22]. To accelerate D^+ ions, an electric field was generated by cooling a pyroelectric crystal to the temperature of liquid nitrogen, then heating it to a room temperature. This means that a palm-size neutron source that does not require any power source has now been developed.

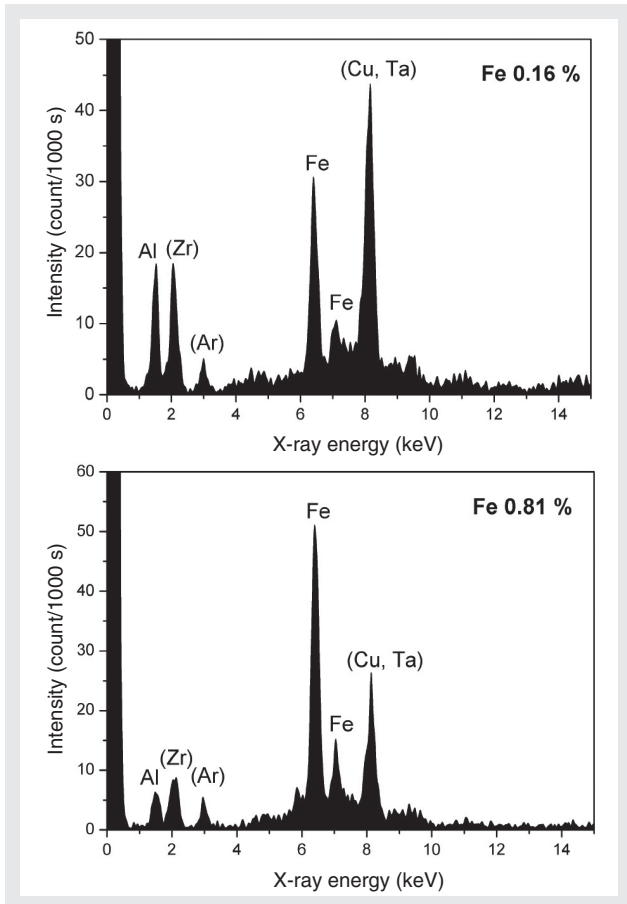


Figure 4 Results for the analysis of two types of cooking aluminum foil, using a pyroelectric crystal X-ray emitter (reproduced from Reference [7] by permission)

Handy Ultra-high Sensitivity Total Reflection X-Ray Fluorescence Spectrometer (with a Total Weight of 3 kg)

A small X-ray fluorescence analyzer, such as the sulfur analyzer for heavy oil, uses a miniature X-ray tube. The history of the development of miniature X-ray tubes is described in Reference [23]. Recently, various types of miniature X-ray tubes have begun to be introduced [24].

Kunimura and others assembled a total reflection X-ray fluorescence spectrometer using a miniature X-ray tube [25]. This analyzer consists of a small X-ray tube, its controller, an X-ray waveguide, a quartz optical flat, a Si-

PIN detector, and a digital signal processor; these components are housed in an acrylic box as large as an attache case of A4-format documents size (Figure 5). The acrylic slab of 0.3 mm-thick equivalent lead is used to prevent the leak of X-rays.

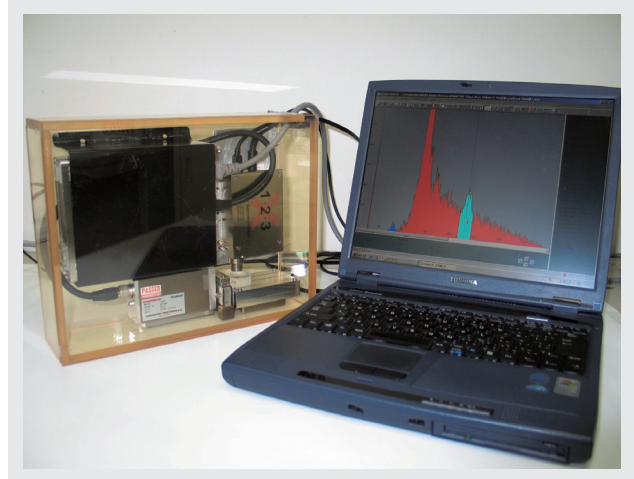


Figure 5 Portable total reflection X-ray fluorescence spectrometer
This spectrometer consists only of a box with a lead-reinforced acrylic cover shown at the left, and a notebook PC shown at the right. The detector in the acrylic box at the left is connected with the PC via a USB cable.

Total reflection X-ray fluorescence analysis, one kind of X-ray fluorescence analysis, involves the irradiation of an optical flat for sample stand with narrowly focused X-rays entering close to the surface, to occur total reflection. A solution sample is dripped and dried on the optical flat beforehand, for the qualitative and quantitative analysis of elements in the solution, mainly metallic ones. Since scattered incident X-rays do not enter the detector, the background is deliberately low. This results in a remarkable improvement of the minimum determination limit, compared to conventional X-ray fluorescence analysis. Figure 6 shows a total reflection X-ray fluorescence spectrum obtained using a portable total reflection X-ray fluorescence spectrometer (Figure 5).

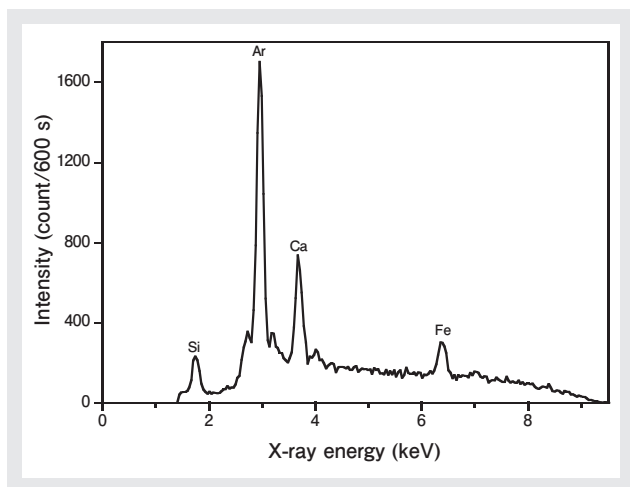


Figure 6 Example of total reflection X-ray fluorescence spectrum measured by a portable total reflection X-ray fluorescence spectrometer (Figure 5)

With the total reflection, the Si X-ray fluorescence peak from the quartz optical flat becomes weak, as shown in this figure. The figure shows the peak for Ar, which accounts for 0.9 volume percentage of air.

Compared to atomic absorption analysis and ICP emission analysis, total reflection X-ray fluorescence analysis requires a smaller amount of sample, while attaining a higher sensitivity and permitting the simultaneous analysis of multiple elements. Since the total reflection X-ray fluorescence analysis has developed as an international standard analysis method for Si wafers, there has been a preconception that the method has limited applications. However, it is highly likely that this method will replace the ICP-MS method in the analysis of environmental water, etc. As shown in Figure 5, the spectrometer based on this method is small and weighs only 3.5 kg. With an air-cooled 1.5 W X-ray tube, the spectrometer can determine the amount of down to 3 ng (in terms of absolute volume) of Cr. This amount of Cr corresponds to the residue obtained by dropping 10 μL of water with a 0.3ppm Cr content on the optical flat. Also, the amount corresponds to 3×10^{13} atoms.

Conclusion

In this way, the portable X-ray fluorescence analyzer, being operable with only dry cell batteries or a power source of about 1 W, has achieved a sensitivity exceeding that attainable by PIXE (particle induced X-ray emission) analysis using a high energy particle accelerator; and is getting higher sensitivity close to the synchrotron radiation X-ray fluorescence analysis. The ease of

operability in analysis overwhelms the conventional spectrometers, which are heavy and require high amount of electric powers. For example, graphite furnace atomic absorption analysis consumes a huge amount of power; and the ICP (inductively coupled plasma) emission analyzer requires argon gas, a high-frequency power supply and exhaust equipment. Though it may still take some time to introduce the portable analyzer commercially, a self-manufactured portable analyzer, designed for laboratory use, is superior to conventional analyzers in many aspects, including costs of analysis. These facts point to a great potential of the portable analyzer in terms of future development.

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(Publication member have responsibility for the translation)

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