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External Scanning Proton Microprobe –A New Method for In-Air Elemental Analysis–

T. Sakai,* M. Oikawa, and T. Sato

Advanced Radiation Technology Center, Japan Atomic Energy Research Institute (JAERI), 1233 Watanuki, Takasaki, Gunma 370-1292, Japan

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A novel external scanning proton microprobe system has been developed at JAERI Takasaki. The system enables multi-elemental mapping of samples in-air environment with spatial resolution of 1 μm. The elemental analysis is based on Particle Induced X-ray Emission (PIXE) and Particle Induced Gamma-ray Emission (PIGE) techniques. Sodium and heavier elements can be analyzed by the former method while light elements such as fluorine and boron can be detected by the latter. This system has already been targeted for a wide variety of applications in fields such as biomedical research, dental study, environmental science, and geology.

1. Introduction

The scanning nuclear microprobe is regarded as a powerful technique for two dimensional elemental analysis because it can be employed for almost all ion beam analytical methods, such as Particle Induced X-ray Emission (PIXE), Particle Induced Gamma ray Emission (PIGE), Rutherford Backscattering Spectrometry (RBS) and so on.[1] The PIXE technique exhibits a superior sensitivity compared with analogue electron micro-analysis. Minimum detection limits for PIXE are at the level of ppm for most elements. However, conventional PIXE setups have no sensitivity for elements lighter than neon due to low energy X-ray attenuation in the energy dispersive X-ray detector window. On the other hand, the PIGE technique is widely used for detection of light elements such as lithium, beryllium, boron, and fluorine. The RBS method is sometimes used for carbon, nitrogen, and oxygen analysis in biological specimens. These analytical techniques compensate for and complement each other.

In the TIARA facility, JAERI Takasaki, a novel external scanning proton microprobe system with spatial resolution of 1 μm was developed.[2] The external beam, which enables in-air proton irradiation of the samples, has many advantages: it requires no special sample preparations against a vacuum environment, makes for easier handling and observation of the samples, and reduces damage caused by heating and charging. The system is already being applied to elemental analysis in many research fields.[3] This paper outlines an experimental setup of the in-air micro-PIXE and -PIGE system. Several new applications and related techniques are also introduced.

2. Instruments

External scanning microprobe. A proton beam accelerated by a TIARA 3 MV single-ended machine was extracted to a light-ion focusing system.[4] The typical beam spot size is 1 μm with a beam current of a few hundred pA. The maximum scan area is 1 mm^2 for 3 MeV proton beams.

A beam exit window, which separates samples from the high vacuum beam line, is essentially required for the external scanning microprobe. A thin organic film is an ideal material for this purpose, because it is composed of lightweight elements and has good physical properties. Four μm-thick Mylar and/or 5 μm-thick polycarbonate foils were mainly used for the window. The foils also play the role of sample backing to minimize the distance between the window and the samples. A window is attached on each sample holder, which is an annular disk made by acrylic resin; the tapered hole has a 1.2 mm diameter on the atmospheric side. Samples are set on holders; up to six holders can be mounted on the revolving stage. The final resolution of the extracted proton beam can be kept at 1 μm.[2, 5]

X-ray detectors for PIXE. Two conventional X-ray detectors and a unique backward X-ray detector were operated simultaneously for PIXE analysis. Figure 1 shows a schematic diagram of the configuration of these three X-ray detectors, and Table 1 indicates the properties of the detectors.

The hp-Ge X-ray detector has moderate energy resolution and poor detection efficiency below 2 keV because of its Ge L-absorption edge and backscattering proton absorber (60 μm-thick polypropylene). The Si(Li) X-ray detector was set at a symmetrical position with the hp-Ge X-ray detector with respect to the beam axis. The energy resolution of the Si(Li) detector is excellent, and this higher energy resolution results in a better signal-to-background ratio and smaller peak overlapping, especially in the low-energy regions. The detector window was 8 μm-thick Be and attached with an annular type absorber (100 μm-thick Mylar), which has a center hole 3 mm in diameter, so that the detection efficiency below 2 keV is

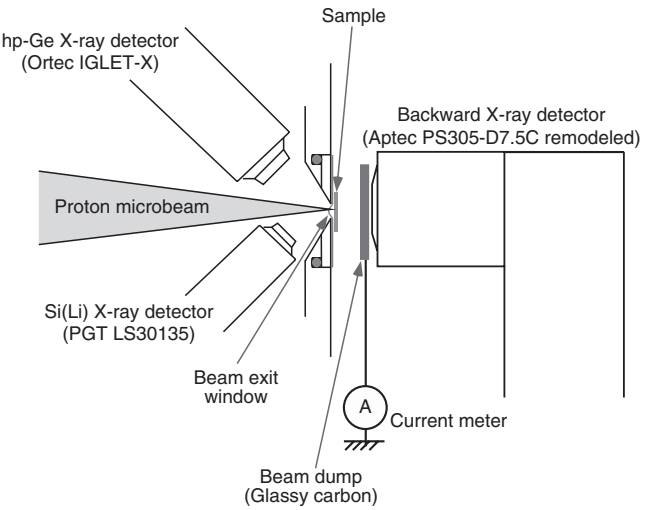

Figure 1. Schematic diagram of the three X-ray detectors and the sample cooling system arrangement with a sample.

*Corresponding author. E-mail: tsakai@taka.jaeri.go.jp. FAX: +81-273-346-9690.

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TABLE 1: Characteristic Properties of Three X-ray Detectors for PIXE Analysis

	hp-Ge X-ray detector	Si(Li) X-ray detector	Backward X-ray detector
Manufacturer, model no.	Ortec IGLET-X	PGT LS30135	Aptec PS305-D7.5C remodeled
Active area	100 mm^2	30 mm^2	260 mm^2
Solid angle	~0.2 sr	~0.13 sr	~π sr
Energy resolution at 5.9 keV X-ray	160 eV	135 eV	260 eV
Absorber	60 μm-thick polypropylene	annular 100 μm-thick Mylar	500 μm-thick glassy carbon
Detectable Elements	≧Si	≧Na	≧Mn

fairly good. On the other hand, the backward detector can be used to improve the detection efficiency X-rays above 6 keV. The detector (Aptec PS305-D7.5C remodeled) has a 260 mm^2 active area with 260 eV energy resolution. The endcap of the detector was converted to an L-shape to set the detector crystal just behind the sample. Although the configuration provides a very large solid angle, a proton beam dumper must be attached in front of the detector window. This 500 μm-thick high purity glassy carbon (Tokai Carbon co. ltd.) attached as the beam dump also plays the role of low-energy X-ray absorber. The backward detector has five to ten times higher efficiency than other detectors for X-rays above 6 keV.[6]

Nuclear reactions and gamma-ray detectors for PIGE. A nuclear reaction $^{19}F(p, \alpha\gamma)^{16}O$ was used for fluorine analysis. This reaction emits gamma-rays of 6.13 MeV, 6.92 MeV, and 7.18 MeV.[7] The energy is much higher than the background gamma-ray energy in the experimental room; therefore this technique has a good signal-to-background ratio. The gamma-rays of the reaction are detected by a 4" NaI scintillation detector (Bicron, 4x4H4/3.5A), which is located just behind the sample instead of the backward X-ray detector.[5]

Boron has two stable isotopes, ^{10}B and ^{11}B. The most intense gamma-ray from the proton-bombardment of boron has an energy of 2.12 MeV resulting from the first excitation level of ^{11}B.[8] However, the sensitivity is not good when the proton energy employed is below 3 MeV. Another possible reaction is $^{10}B(p, \alpha\gamma)^{7}Be$, which emits 428 keV gamma-rays. The cross-section has a wide resonance at the proton energy of 1.54 MeV[9]; thus, the latter reaction was adopted for boron analysis. The peak of 428 keV is Doppler broadened and subject to interference with the 440 keV gamma-rays of ^{23}Na. This is important for biological applications, because many biological specimens contain sodium. Since higher energy resolution is required to distinguish these elements, we have remodeled a coaxial hp-Ge gamma-ray detector (Ortec 1601-1231- S-2) which has 100 cm^3 crystal volume, similar to the backward X-ray detector.[10] The energy resolution of the detector is 1.7 keV at 1.33 MeV gamma-rays from a standard ^{60}Co source. Figure 2 shows an example of the gamma-ray spectrum from ^{10}B containing a biological sample. The sample was prepared for the study of BNCT (Boron Neutron Capture Therapy) at Tsukuba University. Two peaks are barely distinguished at 428 keV (^{10}B) and 440 keV (^{23}Na).

Data acquisition system. In prior experiments, a PC-based multi-parameter data acquisition (DAQ) system was used for the micro-PIXE and -PIGE measurements.[5, 11] The DAQ software has been updated and the PC upgraded to be the latest one capable of simultaneously processing the signals from these multiple detectors. The improved DAQ system can manage up to four independent detectors with a total count rate of 30 kHz. Collected data are saved to the hard drive as binary files without disturbing the data acquisition. The DAQ-PC is connected to the local area network (LAN) via an Ethernet link, so that the data file can be accessed from other PCs. The file can also be copied to the FTP server automatically for a preset time period, so that the data can be retrieved easily over the Internet.[11, 12]

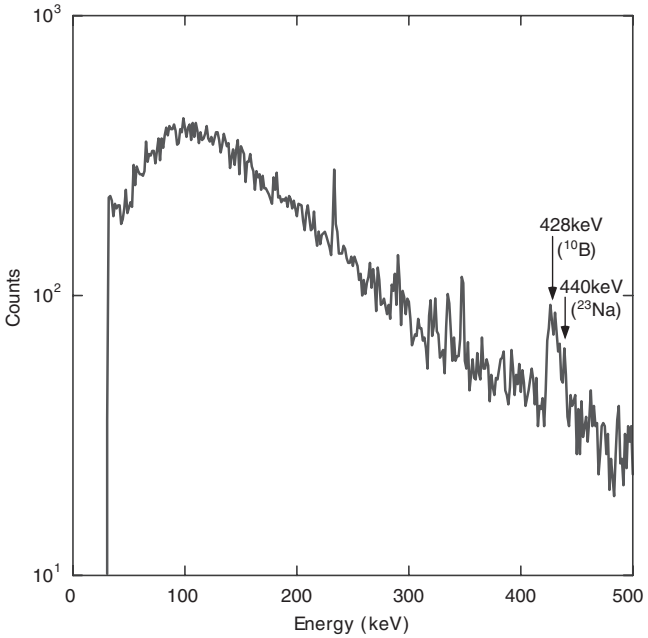

Figure 2. A sample gamma-ray spectrum from ^{10}B containing a biological sample in PIGE analysis.

3. Applications

Biomedical applications. One of the major applications in TIARA micro-PIXE is the analysis of biological specimens. The observation of pharmaceutical compounds diffusing within the cells is a key technique to reveal the agent uptake mechanism at a cellular level. The measurement of elemental distributions within the tissues is also important for physiology and pathology. Many biomedical research programs have adopted TIARA micro-PIXE[6, 13, 14] because of the superior capability of its multi-elemental analysis with good spatial resolution.

Most raw biological samples are very vulnerable to ion beam bombardment because they are subject to heat damage. Sample cooling is considered to be an effective technique to reduce this damage. A CryoJet® (Oxford instruments) sample cooling system has recently been installed. In this system, a flow of evaporated gas from liquid nitrogen is blown onto the sample to keep the frozen state of the raw biological samples. The flow temperature can be set down to 90 K within the stability of ±0.1 K. The combination of this technique with the external scanning microprobe enables the elemental mapping of frozen raw biological specimens.[6]

Dental study. Fluorine uptake and distribution in teeth are noteworthy subjects in the dental research field, because the fluoride ion exhibits cariostatic properties on the teeth's hydroxyapatite.[15] However, the small atomic number of the fluorine and its strong chemical reactiveness prevent non-destructive quantitative chemical analysis except by ion beam analysis. The combination of micro-PIXE and -PIGE techniques is an excellent tool for measuring the microstructures of fluoride distribution in teeth because the teeth's shape can be measured by PIXE while fluorine maps can be taken by PIGE, simultaneously. This combined technique has discovered different uptake process from several fluorine-releasing dental materials.[16]

The total charge of the proton beam is indispensable for quantitative analysis. However, in the case of thick and non-conductive targets like teeth, direct measurement of the beam current is not possible. An indirect periodic beam chopping method has been developed and used for beam current moni-

toring for quantitative analysis.[17]

Environmental science. A large number of studies on aerosol analysis using ion beam techniques have been reported, but only a few studies on single particle analysis have been reported.[18] The analysis of a single raindrop or single aerosol particle is expected to give new and interesting information about air pollution, and various airborne particles, such as single raindrops, individual fog droplets, snow crystals, and Kosa (yellow sand) dusts have been analyzed.[18–20] These results have revealed chemical and physical properties of individual particles and have given detailed information on multiple scavenging processes in the atmosphere.

Intense efforts have been made to clarify the migration behaviors of toxic heavy metals in soil, such as cadmium, lead and arsenic, for the conservation of the living environment. Clay and apatite are promising candidates as sorbents for heavy metals to decontaminate soils and water.[21] Uptake processes of heavy metals in those sorbents are being studied using the micro-PIXE technique.[22] The external beam has another advantage for analysis of thick non-conducting targets such mineral specimens: No conductive material coating on the sample surface is needed. Ambient gas provides a path for the charge leak away from the insulating samples, so that the problem of charge build-up on samples is eliminated.[8]

4. Summary

The TIARA external scanning proton microprobe system and related techniques were developed. This novel system has been applied to various research programs and has proved to be a useful tool. Several excellent results have been discovered.

Recently, two unique apparatuses have been installed in the system. The multiple X-ray detection system succeeded in drastically improving X-ray detection efficiency. This system is used in usual operation of micro-PIXE analysis. Another improvement is a sample cooling system that blows cryogenic gas onto the sample. The sample cooling technique is very attractive method for biological applications, because it enables elemental mapping of a frozen raw biological specimen without serious irradiation damage.

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