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CITATION:

TOMITA, Michio ...[et al]. An External Beam Method for Multi-Elemental Analysis of Heavy Metals in Stream Water. *Memoirs of the Faculty of Engineering, Kyoto University* 1990, 52(3): 245-251

ISSUE DATE:

1990-07-31

URL:

<http://hdl.handle.net/2433/281421>

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# An External Beam Method for Multi-Elemental Analysis of Heavy Metals in Stream Water

by

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(Received March 30, 1990)

## Abstract

An improvement has been made on a liquid target preparation for an external proton beam **PIXE** which is regarded as an excellent technique for multi-elemental analysis. A 2 MeV proton beam taken out to the atmosphere through an exit Kapton foil bombards an acidic solution target directly. Such direct bombardment enables the direct comparison of X-ray yields of a liquid sample with those of the standard solution so that one can determine the elemental concentration in a liquid sample more precisely and easily. An example is given for the analysis of heavy metals in stream water.

## 1. Introduction

In the field of trace element analysis, there are many methods such as Atomic Absorption Spectrophotometry, X-Ray Fluorescence, Rutherford Back Scattering, Instrumental Neutron Activation Analysis etc. Among them, **PIXE** (Particle Induced X-ray Emission) is one of the useful tools for its multi-elemental capacity and high sensitivity<sup>1)</sup>. For analysis of trace elements in a liquid sample, however, the target preparation of **PIXE** measurements has some problems. A **PIXE** measurement is usually carried out in a high vacuum, so a liquid target is hardly used. Thus, a filter method has often been used to analyze heavy metals in stream water. This is because the filtration can catch almost all of the suspended matter which is the main carrier of heavy metals<sup>2)</sup>. In general, suspended matter consists of fine fragments of creature and mineral so that its compound and size would change seasonally. The seasonal change of filter residues causes ambiguity in evaluation of concentration. In such a

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method, therefore, it is very important and difficult to prepare the appropriate standard samples which are used for determining the element contents of the filter residues.

If one can make use of a liquid sample for the **PIXE** measurement, many advantages are expected in the field of trace element analysis. Williams<sup>3)</sup> gave a review paper on the application of the external beam **PIXE**, where were seen only a few experiments on liquid target although he emphasized that the advantages of direct analysis of liquids were obvious.

In this paper are described an external beam method for a liquid target and a new technique of target preparation. The suspended matter was dissolved with acid and the solution was self-sustained by surface tension in a cylindrical container placed horizontally. A direct bombardment on liquid samples enabled the determination of element concentration to be more precise and easier, because the X-ray yields of the liquid sample could be compared with those of the standard solution without any correction.

## 2. Experimental procedures

### 2. 1. Arrangement of apparatus

An analyzed 2 MeV proton beam from the 4 MV Van de Graaff accelerator of Kyoto University was collimated and taken out from the beam transport duct to the atmospheric specimen chamber through a 7.5  $\mu\text{m}$  exit-foil of Kapton. The beam diameter was 1.5 mm or less at the entrance of the specimen chamber. The beam duct was evacuated by a triple differential-pumping to protect the accelerator vacuum against the breakdown of the exit foil. In addition, we adopted a quick valve which was triggered to close when the vacuum at the end of the beam duct exceeded 2.7 Pa. An exit foil was affixed to an end of an aluminum tube of 7 mm in the inner diameter and 10 mm in the outer one. In our preliminary experiment a breakdown of exit foil occurred several times at 0.8 to 1.0 mC of a 2 MeV proton dose under 10 to 20 nA in intensity. The exit foil was, therefore, renewed by a dose of 0.7 mC. The experimental arrangement of the present external beam system is shown schematically in Fig 1.

Figure 2 shows the detailed arrangement of the specimen chamber and the X-ray detector, respectively. The chamber and the cylinder shaped specimen holder were made of acrylicite and coated with a thin film of highly purified carbon to make themselves electrically conductive. The size of the holder was 0.8 cm in diameter and 1.2 cm in depth. Being filled with a liquid sample, the specimen holder was set horizontally. The sample surface was, however, well

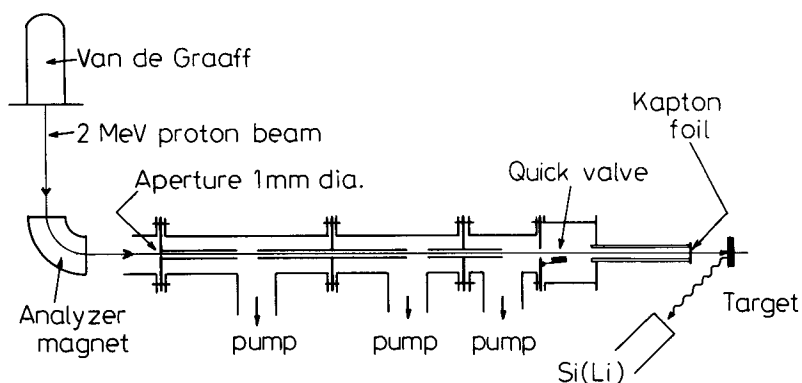


Fig. 1 Schematic drawing of experimental setup for external beam

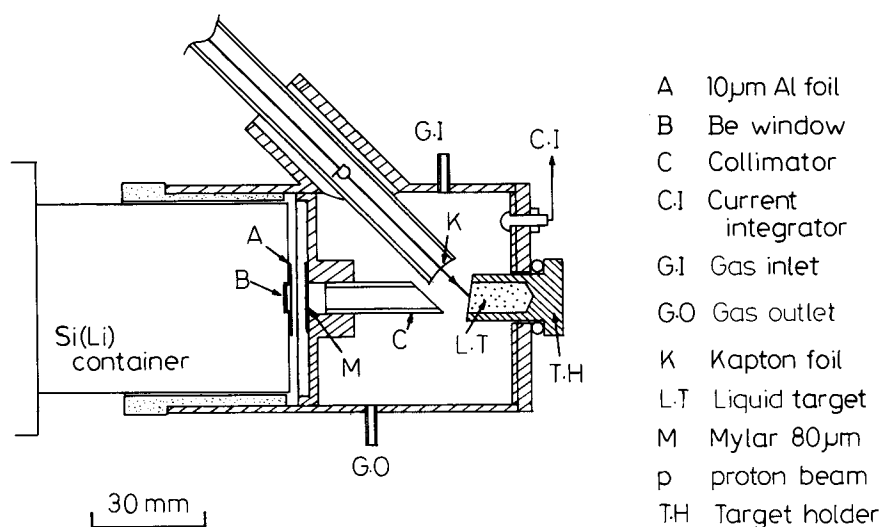


Fig. 2 Details of arrangement (top view) of specimen chamber and Si(Li) detector for external beam **PIXE**. The hatched is acrylite

held perpendicular with only a slight inclination by the surface tension. Therefore the external beam traveling horizontally could bombard the liquid surface directly. In order to exclude the intense X-rays of argon contained in air, the specimen chamber was filled with helium gas that flowed at a constant rate during irradiation. The evaporation rate of the sample increases due to the work of  $3.7 \times 10^{-2} \text{ J} \cdot \text{s}^{-1}$  given by 20 nA of 2 MeV protons. In practice the sample surface receded about 1 mm or less after the beam bombardment for 2000 seconds, so that the sample was renewed for further irradiation. A Mylar foil of

80  $\mu\text{m}$  in thickness, affixed to the Si(Li)-side end of the X-ray collimator, prevented the beryllium window of the Si(Li) detector from being damaged by the acidic liquid samples. This foil also excluded the effect of scattered protons from the X-ray spectrum.

## 2. 2. Sample preparation

A 500 ml sampling-bottle made of polyethylene was previously washed with a 40° C 10% -solution of nitric acid for 40 minutes and with distilled water afterward. Being sampled at the undersurface of flow in the middle of the stream, the water's pH value was lowered to  $\sim 1$  by adding the reagent of nitric acid that was specially prepared not to contain heavy metals more than 1 ppb except Cr < 2 ppb. Reagents used for dissolution afterward were all specially prepared ones. In order to condense the stream water, 200 ml of the sample was dried by evaporation at 80° C in the electric drier. The residue was dissolved by the mixture of two kinds of acidic reagents, *i. e.*, 0.5 ml nitric acid(60%) and 1.5 ml hydrochloric acid(80%). The solution was heated and finally, diluted with the filtered distilled-water to 2 ml, the heavy metals contained in the residue were transferred to the solution. The X-ray yields of this solution could directly be referred to those of the standard ones.

## 3. Results and Discussion

Sensitivity to the X-rays of ten elements, *i. e.*, Ti, Cr, Mn, Fe, Co, Ni, Cu, Zn, As and Sr, has been determined by using the acidic standard solutions that contained 25 ppm of each element, respectively. For lowering the counting rate of Cl's K X-rays due to the hydrochloric acid added to the samples, measurements of sensitivity were performed by putting an Al foil of 10  $\mu\text{m}$  in thickness in front of the Si(Li) window. Sensitivity,  $E(K_{\alpha})$  (counts  $\cdot \mu\text{C}^{-1} \cdot \text{ppm}^{-1}$ ), for  $K_{\alpha}$  lines obtained are given in Table 1 and plotted in Fig. 3 as a function of the atomic number. The maximum of sensitivity appeared at  $Z=24$  and this was attributed to the effect of the thick absorbers in front of the Si(Li) window.

Table 1 Sensitivities to  $K_{\alpha}$  X-rays of ten elements.

Element Atomic number	Ti 22	Cr 24	Mn 25	Fe 26	Co 27	Ni 28	Cu 29	Zn 30	As 33	Sr 38
Sensitivities $E(K_{\alpha})$ (counts $\cdot \mu\text{C}^{-1} \cdot \text{ppm}^{-1}$ )	4.65	4.96	4.62	3.80	3.06	2.79	1.82	1.55	0.736	0.176
Standard deviation	0.15	0.11	0.10	0.10	0.14	0.07	0.07	0.06	0.038	0.039

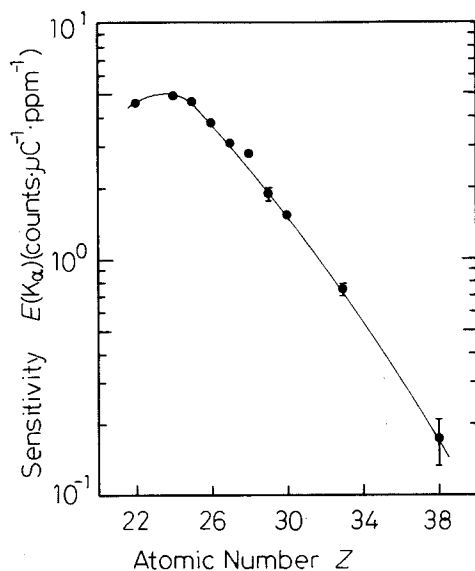


Fig. 3 Sensitivity to  $K_\alpha$  X-rays of present experiment. Full circles represent the experimental values and solid line is drawn for manifesting their tendency

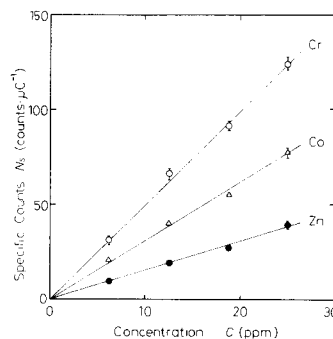


Fig. 4 Linear relation between specific counts and element concentration

The sensitivities for ten elements varied smoothly except that only Ni( $Z=28$ ) had a rather large value in comparison with the other elements. The deviation of the Ni value was ascribed to the error of concentration of the standard solution (nominal 100 ppm) because the repeated measurements for solutions with a different degree of dilution reproduced the same trend.

The  $K_\alpha$  X-ray counts,  $N(K_\alpha)$ , obtained from a liquid sample of stream water would immediately give the concentration,  $C$ (ppm), of respective elements according to the equation

$$C = N(\bar{K}_\alpha) / E(\bar{K}_\alpha) \cdot D, \quad (1)$$

where  $D(\mu C)$  is the integrated beam current fed to the sample. The linearity of specific counts,  $N_s$  (counts· $\mu C^{-1}$ ), against the concentration was measured for Cr, Cu and Zn, respectively and shown in Fig. 4. The relative errors of the gradients were 0.9%, 2.9% and 1.3% for Cr, Cu and Zn, respectively. In the present measurement the liquid target is one hundred times as condensed as the 200 ml stream water. The sensitivity in Table 1, therefore, can give the concentration of  $\sim 10$  ppb with an accuracy comparable to that in the linearity relation,

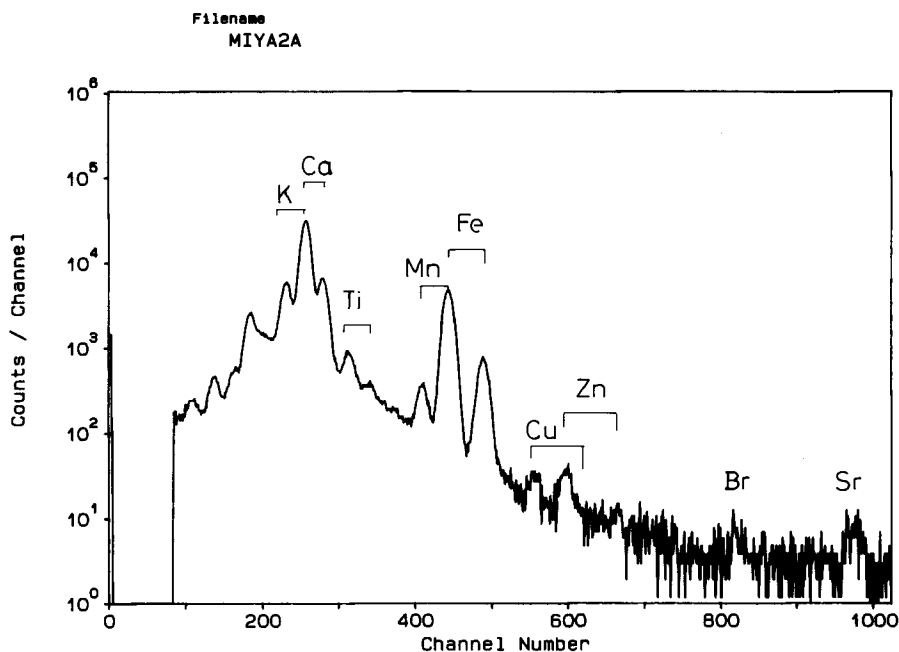


Fig. 5 Typical X-ray spectrum of liquid target sampled in February in 1990 at Miyamae-bashi bridge over the Katsura River in Kyoto

whereas the 25 ppm standard solutions were used to determine the sensitivities. It should, however, be noted that at present uncertainty is still left in the fraction of dissolution of heavy metals in suspended matter.

In Fig. 5 is shown a typical X-ray spectrum of the condensed matter that was sampled in February in 1990 at Miyamae-bashi bridge over the Katsura River in Kyoto. The X-ray lines of several elements are seen. With the aid of a gaussian fit program the net counts of the respective  $K_{\alpha}$ -lines were computed. According to Eq. 1, the concentrations of Ti, Mn, Fe, Cu, Zn and Sr in the sample were successfully determined. They are  $0.18 \pm 0.01$ ,  $0.097 \pm 0.007$ ,  $2.35 \pm 0.06$ ,  $0.020 \pm 0.007$ ,  $0.025 \pm 0.007$  and  $0.05 \pm 0.03$  in units of ppm, respectively. Emphasis should be put on the fact that a considerable amount of these elements were included in the suspended matter.

Element contents in stream water generally differ from river to river. It is considered fundamental and significant for environmental science to recognize seasonal and positional variations in contents of heavy metals in stream water along a river. It has been indicated that the liquid target by the present method is useful for observing more precisely such variations.

We are indebted to Professor emeritus M. Sakisaka for his suggestions on this subject. Valuable discussions with Professor N. Imanishi are gratefully acknowledged.

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