

Application of PIXE Analysis to Elemental Study of Drinking Water Supply

著者	Yamazaki H., Ishii K., Amartaivan Ts., Matsuyama S., Takahashi Y., Satoh T., Orihara H.
journal or publication title	CYRIC annual report
volume	2001
page range	71-78
year	2001
URL	http://hdl.handle.net/10097/30120

I, 14. Application of PIXE Analysis to Elemental Study of Drinking Water Supply

*Yamazaki H., Ishii K., Amartaivan Ts., Matsuyama S., Takahashi Y., Satoh T. and Orihara, H.**

*Department of Quantum Science and Energy Engineering, Graduate School of Engineering,
Tohoku University
Cyclotron and Radioisotope Center, Tohoku University**

INTRODUCTION

The toxic effects of various species of heavy metals in the biosphere have been pointed out in many studies^{1,2)}. Since drinking water is one of the most essential pathways to uptake harmful heavy metals by people, the quality control is particularly important in water supply. A wide variety of analytical techniques are currently available for monitoring water quality and many new techniques are still emerging³⁻⁶⁾. PIXE offers the advantages of a truly multi-elemental nature, high sensitivity and high speed analysis with a small amount of samples. In addition, PIXE measurement allows direct determination of both soluble and insoluble species of elements in water samples due to versatility in the form of specimens to be analyzed.

In this study, we examined the capability of PIXE in monitoring quality of drinking water supply in our city, especially the incidence of metal contamination. In our city of around the 1 million populations, five water treatment plants are located, and each plant supplies drinking water after physicochemical treatment of raw water from different sources. We carried out PIXE analysis for both raw water and clear water at the five plants as well as tap water at several houses located in each supply region. This test should recognize in a simple and fast way trace level concentrations of heavy metals in water samples. In this context, we used a simple and rapid procedure for preparing thin uniform targets of inorganic components in both soluble and insoluble fractions of aqueous samples in combination with pre-concentration of trace heavy metals⁷⁻⁹⁾.

EXPERIMENTAL

PIXE target preparation

We collected 1dm³-volume of both raw and purified waters at the five treatment plants on January 21 and 23, 2002. These water treatment plants take in raw water from three different rivers flowing through Sendai city or from three multi-purpose dams upstream each river, as shown in Table 1. On January 22 and 24, we also collected domestic tap water samples at 7 houses located in each water-supply region.

Water samples were stored in Nalgene-linear polyethylene containers and processed into PIXE-targets within 24 hours. Three kinds of PIXE targets were prepared from raw water samples collected at each water treatment plant using the three-step method developed previously; that is, the Nuclepore filter target for insoluble constituents (FILT), the pre-concentration target for heavy metal ions (PRECON), and the deposit target for soluble major constituents (DEP)⁷⁻⁹.

The residue on Nuclepore filter of 0.4- μ m pores in filtration was classified into an insoluble fraction and the filtrate was regarded as a soluble one. This classification is a rather rough way, and it is more proper to consider that the FILT target contains only a coarse fraction of insoluble components and the DEP target also includes a fine fraction of insoluble ones. In the case of clear water and tap water, residue on the filter was not detected in an appreciable amount, and hence these samples were processed into two kinds of PIXE targets such as DEP and PRECON.

PIXE analysis

The targets of water samples were irradiated for 3 to 10 minutes in a vacuum chamber by 3 MeV protons (beam currents, 10-70 nA; beam diameter, 4 mm). X-rays from targets were measured with two Si(Li) detectors; No.1 detector having 500- μ m Mylar absorber and high geometric efficiency allows the detection of X-rays > 4 keV, and No.2 detector with a low geometric efficiency is well suited for the detection of elements of the atomic number $Z \leq 20$ ¹⁰. For PIXE-spectrum analysis, we used a least-squares fitting computer program, which has been developed in our laboratory based on the pattern analysis method¹¹. The lower detection limit was obtained based on the statistics 3σ error of the background counts integrated over the width of detector resolution (FWHM) at the position of the X-ray energy characteristic to the element of interest in PIXE spectrum for a sample.

RESULTS AND DISCUSSION

The *K* and *L* X-ray lines were observed for 19 elements in PIXE spectra obtained from three kinds of water samples collected from different sources. The ionic fraction of heavy metals in trace concentration (< 10 ppb) were clearly detected in spectrum for target-PRECON. On the other hand, the spectrum on target-DEP allowed us to determine concentrations of major elements excluded in the preconcentration step, *e.g.*, alkali metals, alkaline earth metals and anionic species of P, S and Cl along with the fine particulate fraction of hydrolysable elements like Al, Si and some heavy metals in water with neutral pH, which pass through Nuclepore filter of 0.4- μm pores. An important result is that the PIXE analysis for the three kinds of target reveals elemental distribution in the widespread concentration range between the soluble and insoluble fractions of water samples.

Figure 1 shows elemental concentrations in raw water and clear water samples collected two times at five water treatment plants. The detection limits of the PIXE analysis were on the order of several tenths of ppb for elements producing X-rays > 5 keV, while the large continuum background of backings in PIXE spectra incurred an inferior limit, that is, several tens of ppb for elements of atomic number $Z < 20$. In the plant F which takes raw water mainly from river, concentrations of Al and Si, element derived from soil, largely increased immediately after a heavy rainfall on Jan. 21. Since the plant N gets raw water at a river water intake just downstream a dam, such a carrying-in of soil components to the river seems difficult to appear immediately after rainfall. In the other plants with raw water intake from a dam, similar time lag in the concentration change was observed. In either case, the increase in concentration of Mn, Fe, Cu, Zn and Pb corresponds to that of soil components like Al and Si. On the other hand, the concentration fluctuation by the heavy rainfall was not remarkable for major components such as K, Ca and the anionic species of P, Cl and S in raw water.

In the case of clear water at the five plants, concentrations of elements except trace level Cu and Zn did not vary largely among the samples with physicochemical treatment of raw waters for which the concentrations of soil components and heavy metals largely differed. Samples of clear water did not include coarse particles of the major and minor constituents to be removed by Nuclepore filter of 0.4- μm pores. By the elimination of the coarse particulate fraction, concentrations of hydrolysable components such as Al and Si in clear water decreased to 50-85% in raw water, and then concentrations of heavy metals adsorbed in hydroxide colloids of Al and Si were also reduced to several tens of ppb or less

irrespective of the composition of raw water. In addition, the result in Fig.1 shows little difference in water quality among five water supply systems in our city.

PIXE results for alkali metals, alkaline earth metals and heavy metals in both raw and clear waters were compared with the concentration range of these elements determined using colorimetry, AAS and ICP-AES techniques at each water treatment plant during last year. PIXE showed the concentrations close to the results of other analytical techniques for both major and minor components except Al; the concentration of Al was two or three times higher by PIXE than by AAS analysis. Apart from nonconformity of analysis of Al, we confirmed the applicability of PIXE method in monitoring the incidence of heavy metal contamination of water supply in our city.

For the F and M plants with different time lag for the concentration change by rainfall, the fraction of dissolved states for each element is tabulated in Table 2. Silicon is a major constituent as colloids in river water with neutral pH¹²⁾. The PIXE analysis of raw water samples at the water treatment plants showed the result of agreeing with this preview, and it is confirmed that above mentioned heavy metals were mainly adsorbed to the coarse and fine particles of a soil component which rain brought in river. Therefore, the rainfall greatly influences the grade of raw water at each water treatment plant. As shown in Table 2, the quite small portion of a major element such as Ca was included in particulates of soil component like Si. In addition, it was revealed that concentrations of these major elements were almost constant in raw waters from different sources, as shown in Fig. 1. The ionic fraction of the heavy metals dissolved in clear water greatly increased compared with the results of raw water. In clear water, therefore, the coarse particulates of major components and the heavy metals adsorbed on them seem to be efficiently removed by the flocculation and the filtration with polyaluminum chloride at water treatment plants.

Figure 2 shows the comparison of elemental concentrations in drinking water in each service area of five water treatment plants. As shown in Table 1, samples were collected at 2 places in the water supply district of the K and M treatment plants. We compared the mean value of concentrations including both particle and ionic fractions in two samples taken on January 22 and 24, 2002, because the elemental concentrations did not largely fluctuate. The concentrations of major components like Al, S, Si, K and Ca were similar in all supply systems and close to the concentrations in clear water samples at the five plants. In the domestic sampling points of *T*, *K2* and *F* which belong to the different supply system, however, concentrations of heavy metals like Fe, Cu or Zn were much

higher than those in other tap water, and this concentration largely increased compared with the concentrations in clear water supplied from either plants. Most of these heavy metals were present as a soluble component in the range of concentration from 0.016 to 0.12 ppm. Lead, which was not detected in clear water from the plants, existed as ionic species of the resolved state in all domestic tap water samples in the concentration range of 0.4 to 1.7 ppb, and a rather high concentration of Pb, 1.0-1.7 ppb, was detected in tap water samples in which concentrations of other heavy metals were relatively high. Drinking water distribution systems are primarily composed of iron and steel pipes that are subject to corrosion. The apparent rise in concentrations of some heavy metals compared to the clear water samples indicates the possibility of corrosion of the piping at these domestic sampling points. Besides this, the elemental concentrations in the drinking water samples are much lower than the quality standards of drinking water in Japan; [Na] and [Cl] \leq 200 ppm, [Mg] and [Ca] \leq 300 ppm, [Cu] and [Zn] \leq 1 ppm, [Fe] \leq 300 ppb, [Pb] and [Mn] \leq 50 ppb, [Ni] and [As] \leq 10 ppb.

CONCLUSION

In this study, the techniques developed for PIXE target preparation can be successfully applied to examine quality of water supply in our city. The target preparation and the PIXE measurement are not time-consuming; the pre-concentration step requires less than 10 minutes, and the samples are analyzed by PIXE in which targets are irradiated with 3-MeV proton beams for 3 to 10 minutes. Many kinds of elements can be detected simultaneously in the widespread concentrations from several tenths of ppb to a few tens of ppm due to the multielemental nature and wide dynamic range of detection of the PIXE analysis. PIXE analysis for three kinds of targets, which are prepared from a small volume of water such as 30 ml, reveals the increase of insoluble component of some heavy metals in raw water taken from rivers on a day with heavy rainfall and elution of Cu, Zn and Pb in drinking water by corrosion of the piping on some of water distribution systems. Hence, the methodology developed in this study promotes the PIXE analysis to a truly effective means for monitoring the incidence of heavy metal contamination in a distribution system of drinking water.

References

- 1) Gruiz K., *et al.*, *Wat. Sci. Tech.*, **37**, 273-281 (1998).
- 2) Wilken R. D., *Fresenius J. Anal. Chem.*, **342**, 795-801.
- 3) Goulden P. D. and Anthony D. H. J., *Anal. Chem.*, **54**, 1678-1683 (1982).

- 4) Barreiros M. A., *et al.*, X-ray Spectrometry, **26**, 165-171 (1997).
- 5) Romberg B. and H. Müller, *Anal. Chem. Acta*, **353**, 165-172 (1997).
- 6) Bobeldijk I., *et al.*, *J. Chromatogr. A*, **929**, 63-74 (2001).
- 7) Yamazaki H., *et al.*, *Int. J. PIXE*, **7**, 31-40 (1997).
- 8) Yamazaki H., *et al.*, *Int. J. PIXE*, **7**, 101-107 (1997).
- 9) Yamazaki H., *et al.*, *Int. J. PIXE*, **9**, 83-102 (1999).
- 10) Sera K., *et al.*, *Int. J. PIXE*, **2**, 325-330 (1992).
- 11) Murozono K., *et al.*, *Nucl. Instrum. Meth. B150*, 76-82 (1999).
- 12) Base C. F. and Mesmer R. E., John Wiley & Sons, New York (1976), 112-123; 215-219; 336-342; 365-370.

Table 1. Raw water intake at five water treatment plants and sampling of domestic tap water.

Plant	Raw Water Intake Ratio		Water Supply in Sendai city	Sampling Point of domestic Tap Water
	River Water	Dam Water		
F	0.85 the Nanakita River ¹⁾	0.15 Nanakita Dam ²⁾	Northern region	<i>F</i>
K	-	1.0 Ohkura Dam ³⁾	Northeast region	<i>K1, K2</i>
N	1.0 the Ohkura River ⁴⁾	-	Western region	<i>N</i>
M	-	1.0 Kamafusa Dam ⁵⁾	Eastern region	<i>M1, M2</i>
T	0.2 the Natori River ⁶⁾	0.8 Kamafusa Dam ⁵⁾	Southern region	<i>T</i>

1): the first class river which flows through the northern region in Sendai city, 2): the multiple purpose dam upstream the Nanakita River in northern hill zone of the city, 3): the multiple purpose dam upstream the Hirose river which flows through the central part of the city, 4): the tributary of the Hirose river, flowing in the mid west hill zone of the city, 5): the multiple purpose dam upstream the Natori River in southwest hill zone of the city, 6): the first class river which flows through the southern region in the city.

Table 2. The fraction of dissolved states for typical elements in three kinds of water samples.

Element		Plant F / Domestic <i>F</i>					Plant M / Domestic <i>M1</i>								
		Raw		Clear		Tap Water	Raw		Clear		Tap Water				
		Coarse	Fine	Ion	Fine	Ion	Fine	Ion	Coarse	Fine	Ion	Fine	Ion		
Si	A	0.33	0.67	-	1.0	-	1.0	-	0.08	0.92	-	1.0	-	1.0	-
	B	0.10	0.90	-	1.0	-	1.0	-	0.35	0.65	-	1.0	-	1.0	-
Ca	A	0.03	0.97	-	-	1.0	-	1.0	0.01	0.99	-	-	1.0	-	1.0
	B	0.01	0.99	-	-	1.0	-	1.0	0.03	0.97	-	-	1.0	-	1.0
Mn	A	0.84	0.09	0.07	0.91	0.09	0.85	0.15	0.59	0.28	0.13	0.87	0.13	0.88	0.12
	B	0.69	0.27	0.03	0.73	0.27	0.78	0.22	0.71	0.10	0.19	0.92	0.08	0.79	0.21
Fe	A	0.97	0.01	0.02	0.67	0.33	0.01	0.99	0.87	0.01	0.12	0.63	0.37	0.25	0.75
	B	0.92	0.01	0.07	0.41	0.59	0.03	0.97	0.95	0.02	0.03	0.52	0.48	0.19	0.81
Zn	A	0.54	0.14	0.32	0.32	0.68	0.22	0.78	0.16	0.05	0.79	0.20	0.80	0.03	0.97
	B	0.18	0.41	0.41	0.18	0.82	0.16	0.84	0.40	0.14	0.46	0.33	0.67	0.11	0.89

Alphabetical symbols of plants are the same as those in Table 1. A: the samples collected on Jan. 21st, 2002 with intense rainfall, B: the samples collected 2 days later on Jan. 23rd, 2002, besides domestic tap water was collected one day after sampling at the plants.

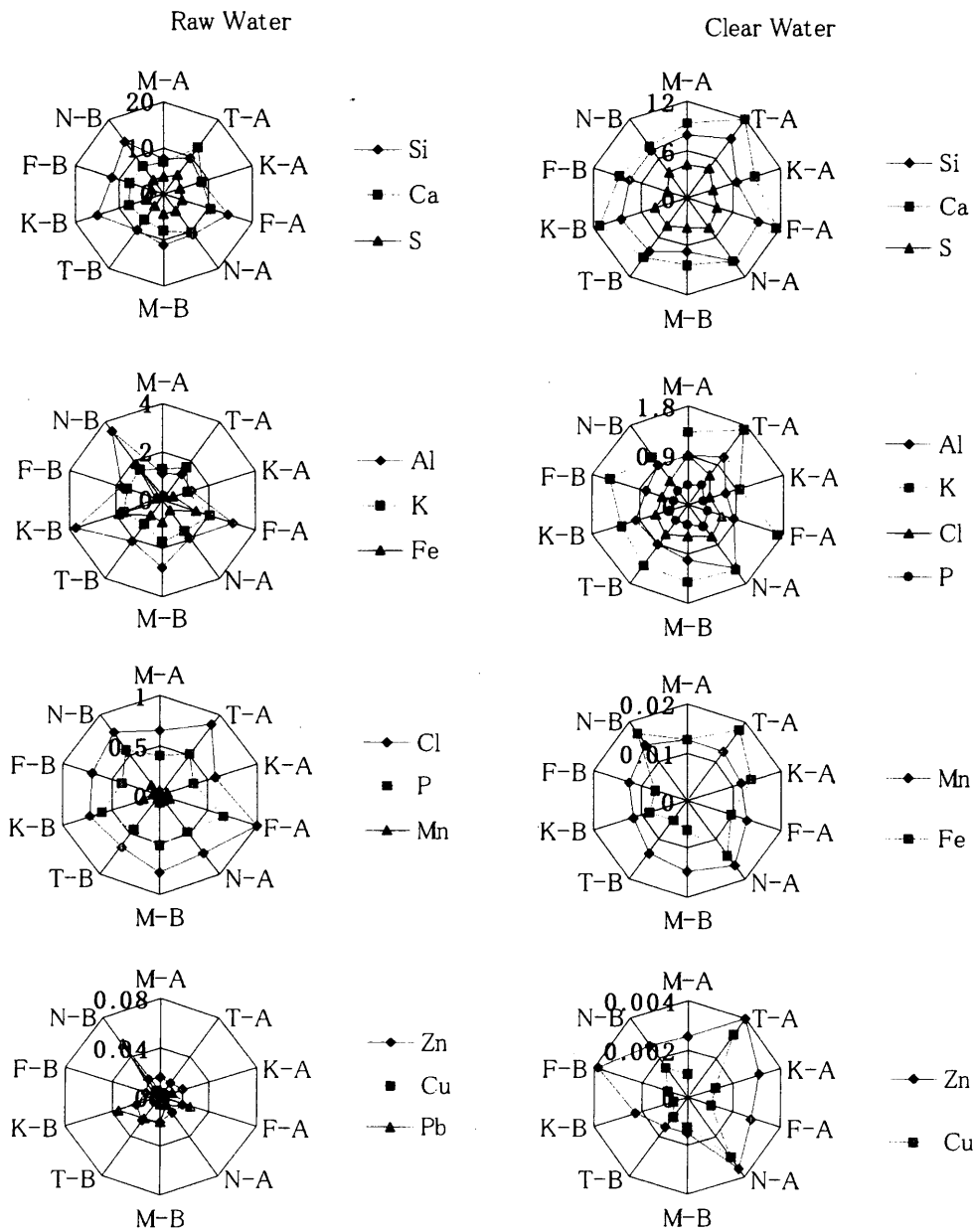


Fig. 1. Concentrations in ppm for components in raw water and clear water at five water treatment plants. Alphabetical symbols are the same as those in Table 1. A: the analysis value of samples collected on Jan. 21st, 2002 (heavy rainy day), B: the analysis value of samples collected on Jan. 23rd, 2002 (cleared up day).

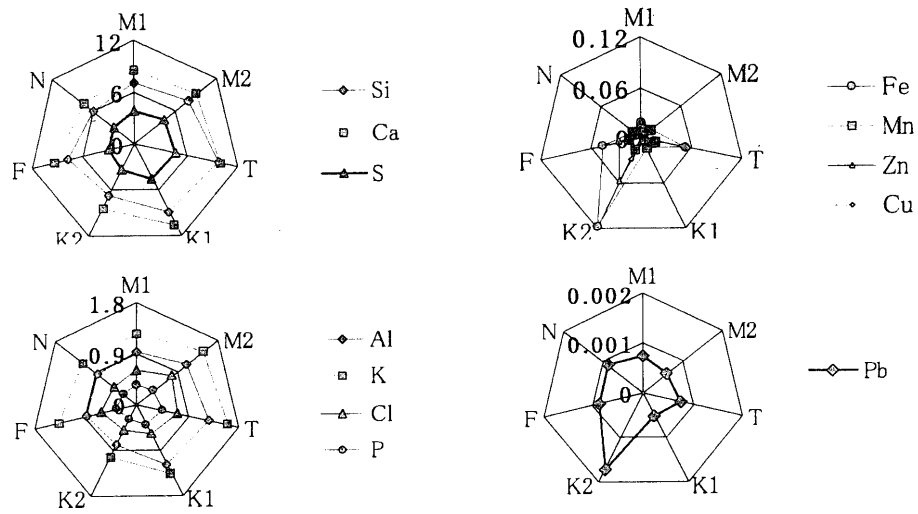


Fig. 2. Concentrations in ppm for typical elements in drinking water (average value of 2 samples).