

II. 3. Determination of Heavy-Metal Concentrations in Water by PIXE Analysis Using Zirconium as an Internal Standard

*Yamazaki H., Tanaka M., Tsutsumi K., Ishii K., Matsuyama S., Inoue J.,
Murozono K., Iwasaki S., and Orihara H.**

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

Introduction

Owing to great awareness of a pollution problem in natural environment, composition of rain and surface water has been often analyzed for many years by atomic absorption spectrophotometry (AAS). Particle-induced X-ray emission (PIXE) has been used extensively for analyzing aerosol samples and offered higher sensitivity (nano-gram level) than AAS measurements¹⁻⁵⁾. However, little work has been reported on the PIXE analysis of water samples due to problems of sample preparation⁶⁻⁷⁾. Since PIXE is conveniently used for analysis of thin uniform samples, metals in aqueous samples should be concentrated into a thin solid-target of uniform composition, *i.e.*, some chemical treatment is required for the target preparation in PIXE measurements.

In a preceding paper⁸⁾, a combination of chelation by dibenzylthiocarbamate (DBDTC) ions with subsequent condensation into dibenzylidene-*D*-sorbitol (DBS) gels has been developed for preconcentration of heavy metals (Fe^{3+} , Co^{2+} , Hg^{2+}) in conjunction with rapid preparation of thin uniform targets for PIXE analysis. The DBS gels containing the metals in solutions are then collected on a nucleopore filter for direct irradiation by 3 MeV protons in a system of vertical beam type in-air PIXE at 4.5-MV Dynamitron laboratory of Tohoku University. Details of the system was described in Reference 9. At present, proportionality of the beam current *vs.* X-ray yields was confirmed to be good, but the absolute value of the impinging beam current has remained uncertain. In order to maintain high quality of the PIXE analysis, it is necessary not only to procure the accurate value of impinging beam current but also to calibrate the detection efficiency of the analytical system at regular intervals. Use of an internal standard in the PIXE analysis enables determination of the absolute concentrations of metals from the elemental X-ray yields without exact knowledge both of the surface density of incident protons and of the measuring arrangement. However, we can find few reports on a metal-preconcentration procedure using an internal standard for the PIXE analysis. This is probably ascribed to the difficulty in preparing thin target specimens containing homogeneously an internal standard element.

In this study, elemental reactions in the preconcentration step (the metal-DBDTC complex formation and condensation into DBS gels) are optimized to contain the internal standard of zirconium in target specimens. The modified preconcentration procedure is applied to preparation of targets obtained from solutions containing seven heavy metals (Fe, Co, Ni, Cu, Cd, Hg, Pb) in different amounts, and the accuracy in determination of the metal-concentrations in the 5-100 ppb range is examined on the present in-air PIXE setup of our laboratory.

Preparation of targets with Zr internal standard

In the preceding paper⁸⁾, the following procedure was recommended for preconcentration of metals in the ppb-ppm range: Into 25 ml of a solution containing a heavy metal ($4 < \text{pH} < 5$), 3.5 moles of DBDTC (1.25 ml of 0.1% (w/v) DBDTC in methanol) were pipetted, and the solution was kept stirred for 4 minutes. After pH of the solution was adjusted to around 5.2 with 1M acetate buffer solution, 0.4 mg of DBS (10 μl of 4%(w/v) DBS in dimethylsulfoxide) was added and immediately set to gelation. The metal-DBDTC complexes condensed into the DBS gels were collected under a reduced pressure (~ 250 mm Hg) on a nucleopore filter (0.2 μm pore) for direct irradiation by proton beams. On the other hand, the filtration was carried out under a reduced pressure of ~ 400 mm Hg through a nucleopore filter of 0.4 μm pores (10 μm thick and 1×10^8 pore density) in the present study; the filtration time was shortened to < 3 minutes, and no loss of metals was detected in the filtrates. A thin layer of the gels on the filter (13 mm diameter) was washed with 10 ml of deionized and distilled water and then dried over silica-gel. The filter was mounted on a Mylar holder, which was screwed on a steel slide frame for the direct irradiation.

Zirconium can serve as a suitable internal standard, because it is a rare element in natural water and its characteristic X-rays do not interfere with determination of elements of interest to measure water pollution by PIXE. However, the PIXE analysis shows low sensitivity to zirconium due to the small inner-shell ionization by protons of 2-3 MeV. As compared with the reported concentrations of heavy metals in surface water samples, a large amount of Zr (25 μg) must be used from the standpoint of statistical errors of the Zr-peaks in the PIXE spectrum; under the present condition of the PIXE analysis (3 MeV proton beams of 3-mm diameter and 2 nA of apparent currents), the X-ray yield of Zr atoms in target specimens is around 2000 counts in its K_{α} peak for 2 μC of accumulated charges. On the other hand, Zr ions are easily hydrolyzed even in strongly acidic solutions¹⁰⁾. The principal species, which is formed by reversible hydrolysis at concentrations of acid greater than several tenths molar, is a polynuclear $\text{Zr}_4(\text{OH})_8^{8+}$. At lower acidity, a slow irreversible hydrolysis occurs, accompanied by an increase in polymerization. Therefore, a standard solution containing 1000 ppm zirconium in 1 M HNO_3 is used, and it is assumed that Zr ions might act as the "yl" ion, ZrO^{2+} , in the chemical reaction with DBDTC ions.

Zr-recovery in the preconcentration step was investigated as a function of the amounts of DBDTC ions; a desired amount of DBDTC ions was added into 25 ml of 1 ppm Co^{2+} solution of pH around 4 and then 25 μl of the standard solution of zirconium in 1000 ppm was pipetted while stirring. The concentrations of Zr and Co ions in the filtrates were determined by spectrophotometry using arsenazoIII as coloring reagent¹¹⁾ and by atomic absorption spectrophotometry, respectively. The Co-concentrations in filtrates were lower than the detection limit (0.01 ppm), indicating the quantitative recovery. On the other hand, Table 1 reveals constant but incomplete recoveries of Zr ions (94~96 %), even though a large excess amount of DBDTC ions exists in terms of the stoichiometric DBDTC-complexation of ZrO^{2+} and Co^{2+} ions totally in 0.7 μmole . The Zr-recovery also was examined in sample solutions free from Co ions, but there appeared no improvement of the recovery. These facts suggest a decrease in chemical reactivity of polymerized zirconium species such as $\text{Zr}_4(\text{OH})_8^{8+}$.

Figure 1 shows the effect of pH on the recovery of 25 μg Zr in preconcentration step of 1 ppm Co solution (25 ml) at 1 pH 5 by the use of 8.5 μmole of DBDTC and 0.4 mg of DBS. The recovery obviously depends on the pH values in sample solutions; the largest recovery (95 ± 1 %) can be obtained only when DBDTC ions are initially added to samples at pH=4 and then Zr-DBDTC complexes are formed at pH around 3. The succeeding changes of pH value to both lower and higher sides ($2 \leq \text{pH} \leq 5$) have no effect on the Zr-recovery. There appeared milky turbidity when the DBDTC-solution was added to samples at pH 3, indicating precipitation of carbamic acid due to the small dissociation constants ($2.95 \leq \text{pK}_a \leq 5.19$)¹²⁾, *i.e.*, an undesirable side reaction of DBDTC ions added to sample solutions. The Zr-recovery slightly decreases in a solution buffered at pH 5. This might be ascribed to slow irreversible hydrolysis of Zr ions accompanied by increase in polymerization to less reactive species.

Based on the results shown in Table 1 and Fig. 1, the following procedure was derived for target preparation: 2.5 ml of 0.1% (w/v) DBDTC solution was added into 25 ml of a sample solution, which is initially neutralized (4 pH 5) and then 25 μl of 1000 ppm Zr in 1M HNO_3 was pipetted as the internal standard. This solution was processed by the same manner as before. The thin layer of DBS gels containing metals and Zr-standard on a nuclepore filter was mounted on a sample holder and ready to be exposed to proton beams.

Table 2 shows the results of the PIXE analysis of four targets independently prepared under the same condition. The counts in Co- and Zr- K_α peaks were normalized to $2\mu\text{C}$ of accumulated charges. A little bit larger fluctuation appears in the counts of the K_α photons (3.3~4% of standard variation) than in the ratios of Co- to Zr-counts (2.4 % of standard variation). The ratio remains unchanged within the statistical errors of the peak counts for different location of impinging beam spots on the identical target. These facts indicate the

reliability of the PIXE analysis using an internal standard and the reproducibility of preparing the target specimens of uniform composition.

Calibration with using matrices of known compositions

In order to evaluate reliability of the quantitative PIXE analysis through the present system, calibration curves were measured for a multielemental sample of 25 ml containing 25 μg of Zr as an internal standard, which was prepared by adding known and different amounts of seven metals (obtained from atomic absorption spectrophotometry standard solutions) to deionized and distilled water. The seven heavy metals, viz, Fe^{3+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Cd^{2+} , Hg^{2+} and Pb^{2+} , were used from the standpoint of an analysis of water quality. The measurement covered the concentration range from 5 to 100 ppb of the seven metals.

Typical PIXE spectra of the targets with and without the metals are shown in Fig. 2. The X-rays emitted from excited heavy atoms are superimposed onto a continuum of bremsstrahlungs and γ -ray Compton tails. The continuous components come from the air gap over the targets (0.6 cm), the sample sediments ($<10\ \mu\text{m}$ thick) and the nuclepore filter ($10\ \mu\text{m}$ thick). The spectrum of the blank, which does not contain the seven metals, reveals no detectable impurities under the experimental condition; no other X-ray peak except K X-rays of S in DBDTC, Ar in air and Zr standard was observed in the blank spectrum. The computer program, named SAPIX,¹³⁾ was used in order to separate peaks in the PIXE spectra. In this program, a combination of a polynomial curve and two exponential ones is fitted to the continuous components in the spectrum by the least-squares method. The polynomial curve describes the lower energy side of the bremsstrahlungs, while the two exponential curves express the higher energy side of the bremsstrahlungs and the γ -ray Compton tails. Succeedingly, the peak area of X-rays characteristic to each element is determined by the Gaussian-peak fitting. When the K_β peak of an element Z overlaps with the K_α peak of element Z+1, the counts in K_α peak of the element Z+1 are obtained by subtracting the product of the K_α peak counts and the intensity ratio ($\text{K}_\beta/\text{K}_\alpha$) of the element Z¹⁴⁾ from the total counts in the overlapping peak. In this way, the yield of K_α X-ray characteristic to each element can be determined for the irradiated target specimens.

Figure 3 shows calibration curves for the PIXE analyses of the seven heavy metals. The ratio of peak counts of the metals to those of Zr-standard is plotted against the nominal metal concentration in ppb; the counts in K_α X-ray peak are used except for Hg and Pb, where the L_α X-ray yields are used for the analysis. A good linear relationship is obtained between the concentrations and the X-ray yields for all the metals, indicating a good quantitative analysis of these metals in the concentration range of 5-100 ppb by means of the PIXE setup of our laboratory. The use of Zr internal standard can eliminate systematic errors in charge integration of impinging beams and in determination of the geometrical parameters of the analytical arrangement (the distance between target and detector, the solid angle subtended by a beam spot on target at the detector, etc.).

The absolute concentrations of the metals in sample solutions were calculated from the experimental results in order to evaluate the accuracy of the PIXE analyzing system in our laboratory. Since chelation of DBDTC can be exerted in the same way to almost all of monomeric transition metals¹²⁾, the recovery of the seven metals in target preparation is taken as 100 % except for Zr-standard, for which the constant recovery (95 ± 1 %) is obtained as shown in Table 1 and Fig. 1. Based on the mass attenuation coefficients of X-rays in the energy range from 5 to 20 keV¹⁵⁾, the authors can estimate almost flat efficiency curve for a 5 mm-thick Si(Li) detector of 25 μ m-thick beryllium window, along with attenuation less than 4 % due to 0.85 cm of the air gap between the targets and the detector and a 12 μ m-thick Kapton film on the beam exit assembly with a built-in detector. Detection efficiency of the analytical system can clearly be assumed to be constant over the X-ray energy region from 5 to 20 keV. Under these conditions, we use the formula

$$C_M = \frac{N_M}{N_{Zr} \cdot \alpha} \times \frac{\sigma_{Zr} \cdot \gamma_{Zr}}{\sigma_M \cdot \gamma_M} \times \frac{A_M}{A_{Zr}} \times C_{Zr} , \quad (1)$$

where C represents the metal concentration in sample solutions [ppb], N is the number of photons in K - or L -peak per 2 μ C of accumulated charges, A is the atomic weight of metal, α is total K- or L-shell X-ray production cross-sections for 3 MeV protons [10^{-24} cm²], α is the correction for the Zr-recovery in preconcentration [1.05 ± 0.01], γ is the correction for the relative intensities of multiplets in PIXE spectrum, and the subscripts of Zr and M are used to designate the zirconium internal standard and the metal of interest, respectively. The values of the physical parameters used in quantification (Table 3) were obtained from the text book by Johansson and Campbell¹⁴⁾.

Table 4 shows the metal concentrations along with the precision from counting statistics under the present arrangement of in-air PIXE system; the impinging beam spot (2 nA of 3 MeV protons) on targets has around 3 mm diameter, and the 5 mm-thick Si(Li) detector of 30 mm² area is placed at 135° position and a distance of 30 mm from the target surface. Although there appears rather poor precision in determination of Cd-concentrations due to the low X-ray yield, the concentrations of other metals can be determined with a small statistical deviation (less than ± 7 %). The differences between the nominal and the analyzed concentrations seldom exceed ± 14 % in the concentration range from 5 to 100 ppb. Good accuracy in the PIXE analysis reveals applicability of the X-ray production cross-sections cited in the literature¹⁴⁾. Moreover, it is clear that the PIXE measurement of targets containing Zr-internal standard enables the quantitative analysis of elements producing X-rays of 5-20

keV without exact knowledge of the beam current and the analytical arrangement of the PIXE setup used.

PIXE analysis of drinking water

As just described, many kinds of heavy metals together with Zr internal standard can be simultaneously concentrated into thin uniform target specimens, and the peak areas in PIXE spectra can be correctly translated into the absolute concentrations in terms of the reported data pertinent to inner shell ionization and subsequent X-ray emission¹⁴⁾. Hence, the methodology is applied to monitor time variation of heavy metal-concentrations in drinking water.

A sample of drinking water (30 ml) was collected from a faucet in our laboratory at four hour intervals and was chemically treated in the same manner as before. The targets were irradiated by 2 nA of 3 MeV proton beams in the PIXE system, and the spectrum was analyzed by the SAPIX program. The absolute concentrations of detected elements in drinking water were determined in accordance with the equation (1); the values of parameters relevant to the X-ray productions of detected elements were also obtained from the reference (14).

Figure 4 shows the time variation of elemental concentrations in drinking water over 20 hours. The analytical errors based on counting statistics are less than $\pm 16\%$ for all elements except As, Br and Pb, for which much larger errors (from $\pm 38\%$ to $\pm 97\%$) appear due to overlapping of small peak of As- K_{α} with that of Pb- L_{α} X-rays and of As- K_{β} with the peak of Br- K_{α} X-rays. Many kinds of elements were detected in the samples of pH 6.8, but the concentrations were within the limit of quality of water to drink; [Mn] < 50 ppb, [Fe] < 300 ppb, [Ni] < 10 ppb, [Cu] and [Zn] < 1000 ppb, [As] < 10 ppb, and [Pb] < 50 ppb¹⁶⁾. High sensitivity of the PIXE analysis makes it possible to clearly distinguish the change in elemental concentrations in the samples; the concentrations of Mn, Cu and Pb appreciably increase in the second sample (4 hours elapsed) and then decrease slowly, but the other elements have slowly decreasing or rather constant concentrations over the time span. The widespread elemental concentrations in the samples can be detected by PIXE; the concentrations of Zn and Fe are ten to hundred times higher than those of other elements in all samples. Since As and Br exist as anionic species in neutral solutions, these elements can be coprecipitated with metal-DBDTC complexes in the preconcentration step due to low solubility of arsenate or bromate of major transition metals in water.

Conclusion

In this study, the metal-preconcentration procedure was established to prepare a thin uniform target containing Zr as an internal standard for the PIXE analysis. The target preparation and the PIXE measurement are not time-consuming; the target preparation requires less than 10 min, and the peak areas with good statistical precision can be obtained

within 20-min irradiation (2 nA of 3 MeV proton beams) through the present PIXE system of our laboratory. The use of Zr internal standard permits simultaneous determination of seven heavy metals in ppb-concentrations by the PIXE setup without exact knowledge of the integrated charges of impinging beams and the analytical arrangement (the distance between targets and the detector, the solid angle, etc.). The data pertinent to inner shell ionization and subsequent X-ray emission, compiled by Johansson and Campbell¹⁴⁾, are quite useful to translate the elemental X-ray yields in PIXE spectrum into the absolute concentrations in sample solutions. The difference between the PIXE results and the nominal concentrations is found to be less than $\pm 14\%$. No appreciable correction for the detection efficiency and the attenuation of X-rays are needed to obtain absolute values of the concentration of elements producing X-rays of medium energy (5 to 20 keV). However, these corrections are important in analyzing the yields of X-rays having lower (<5 keV) or higher (>20 keV) energy. Moreover, overlapping of peak areas in PIXE spectra makes it uncertain to identify responsible elements. Therefore, it would be preferable to develop a new methodology for the spectrum analysis in order to promote the PIXE analysis to a truly effective means of dealing with many samples of complexity as in monitoring water pollution. Development of a new analyzing method for PIXE spectrum is currently in progress in our laboratory.

References

- 1) Akselsson K. R., *Nucl. Instr. and Meth.*, **B3**, 425 (1984).
- 2) Cahill T. A., *Nucl. Instr. and Meth.* **B49**, 345 (1990).
- 3) Kasahara M., Yoshida K. and Takahashi K., *Nucl. Instr. and Meth.*, **B75**, 240 (1993).
- 4) Kasahara M., J. H. Park and Yamamoto K., *Nucl. Instr. and Meth.*, B109/110, 471 (1996).
- 5) Horvath H., Kasahara M. and P. Pesava, *J. Aerosol Sci.*, **27**, 417 (1996).
- 6) Aprilesi G., et al., *Nucl. Instr. and Meth.*, **B3**, 172 (1984).
- 7) Tanaka S., Durzi M. and J. W. Winchester, *Environ. Sci. Technol.*, **15**, 354 (1981).
- 8) Yamazaki H., et al., *I. J. PIXE.*, **6(3 & 4)**, 483 (1996).
- 9) Iwasaki S. et al., *I. J. PIXE.*, **6(3 & 4)**, 441 (1996).
- 10) Baes C. F. Jr. and Mesmer R. E., John Wiley and Sons, Inc. New York (1976), 152.
- 11) Onishi H., *Jpn. Analyst*, **12**, 1153 (1963).
- 12) Hulanicki A., *Talanta*, **14**, 1371 (1967).
- 13) Private communication from Dr. Sera K. (Cyclotron Research Center, Iwate Medical University, Takizawa 020-01, Jpn.)
- 14) Johansson S. A. E. and Campbell J. L., "*PIXE. A Novel Technique for Elemental Analysis*," John Wiley & Sons, New York (1988), p.313-329.
- 15) Leroux J. and Thinh, T. P., "*Revised Tables of X-ray Mass Attenuation Coefficients*," Corporation Scientifique Claisse Inc., Quebec (1988).
- 16) "Water Analysis," The Japan Society for Analytical Chemistry, Hokkaido Branch (1994), p.16-24.

Table1. Effect of DBDTC amounts on the Zr-recovery

DBDTC (μmole)	Equivalent ratio (DBDTC / Metals)	Zr-recovery (%)
5.7	4.1	91~ 93
6.8	4.9	93~ 95
8.5	6.2	94~ 96
10.2	7.4	95~ 97
13.6	9.9	94~ 96

Table2. Reproducibility of the PIXE analysis using Zr-internal standard

Counts in Co K_{α} peak		Counts in Zr K_{α} peak		Ratio in counts Co / Zr	
39760		1846		21.5	
42944	$\pm 1715^{1)}$	2131	$\pm 68^{1)}$	20.2	$\pm 0.5^{1)}$
42080	(4.0%)	2039	(3.3%)	20.6	(2.4%)
47907		2138		22.4	

Sample: 25cm³ of 0.9 ppm Co solution (0.38 $\mu\text{mole Co}^{2+}$, pH4), 25 μg of Zr-standard (0.27 $\mu\text{mole ZrO}^{2+}$). 1): standard variation.

Table 3. Physical parameters used in the quantitative analysis¹⁴⁾

X-ray	σ (10^{-24} cm^2)	K_{α} / K_{β}	γ L_{β} / L_{α}	L_{γ} / L_{α}	A
Fe- K_{α}	173	0.136	-	-	55.49
Co- K_{α}	142	0.137	-	-	58.93
Ni- K_{α}	117	0.138	-	-	58.69
Cu- K_{α}	96.2	0.139	-	-	63.55
Cd- K_{α}	1.99	0.216	-	-	112.4
Hg- L_{α}	64.8	-	0.595	0.0894	200.6
Pb- L_{α}	54.1	-	0.595	0.0894	207.2
Zr- K_{α}	9.69	0.191	-	-	91.22

Table 4. Accuracy of the PIXE analysis using Zr as an internal standard

Nominal concn. [ppb] ¹⁾	Fe	Co	Ni	Cu	Hg	Pb	Cd
100	100±2.6*	99.8±2.6	104±2.8	107±3.0	98.3±5.0	109±6.0	103±18
75	72.9±1.9	72.2±2.0	73.9±2.1	76.8±2.3	71.1±4.2	75.1±4.8	72±15
40	42.6±1.2	39.4±1.2	45.6±1.9	37.7±1.6	39.7±2.6	45.1±3.5	45±12
20	20.2±0.6	19.7±0.6	21.6±0.6	21.6±0.7	17.6±1.1	17.9±0.8	21.9±4.3
5	5.0±0.1	4.9±0.1	5.1±0.1	5.7±0.1	5.3±0.3	5.8±0.4	6.0±0.6

Targets were prepared from 25 ml of solutions containing seven metals and Zr-internal standard. Irradiation condition: 2 nA of 3 MeV proton beams and 2 μ C of accumulated charges. 1): ± 1.6 % error due to dilution of stocked solutions of the metals. *: the precision based on the statistical deviation of the characteristic X-ray yields.

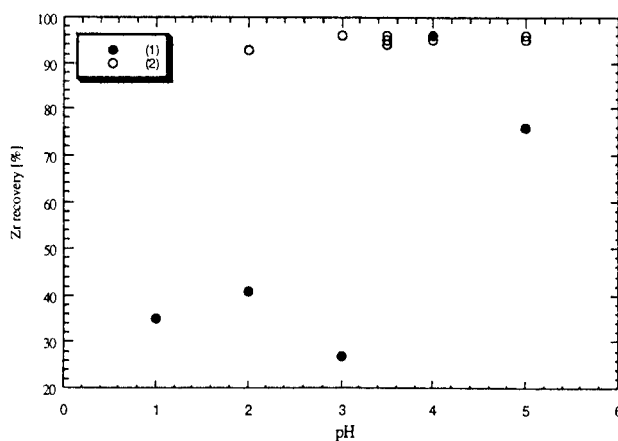


Fig. 1. Effect of pH on the Zr-recovery in the preconcentration step. (1): The pH of solutions remained at the specified value ($1 \leq \text{pH} \leq 5$) throughout the reaction. (2): First, DBDTC- and Zr-solutions were added to sample solutions of pH 4 and then, after 4-min stirring, the pH in the solutions was adjusted to the specified value by using HNO_3 or acetate buffer solutions.

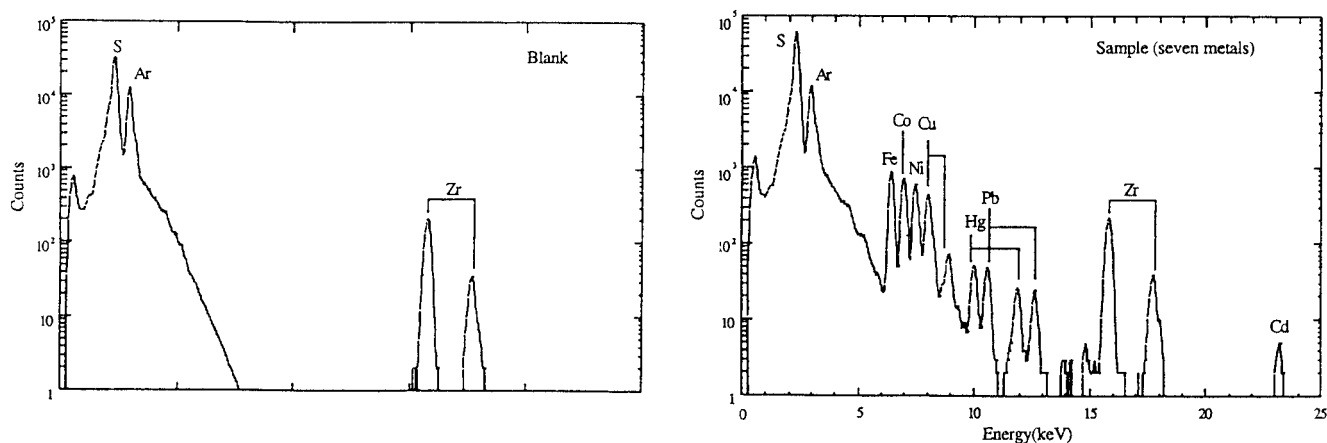


Fig. 2. Typical spectra of the in-air PIXE analyses. Targets were prepared from 25 ml of solutions containing seven metals and Zr-internal standard. Irradiation condition: 2 nA of 3 MeV proton beams and 2 μ C of accumulated charges.

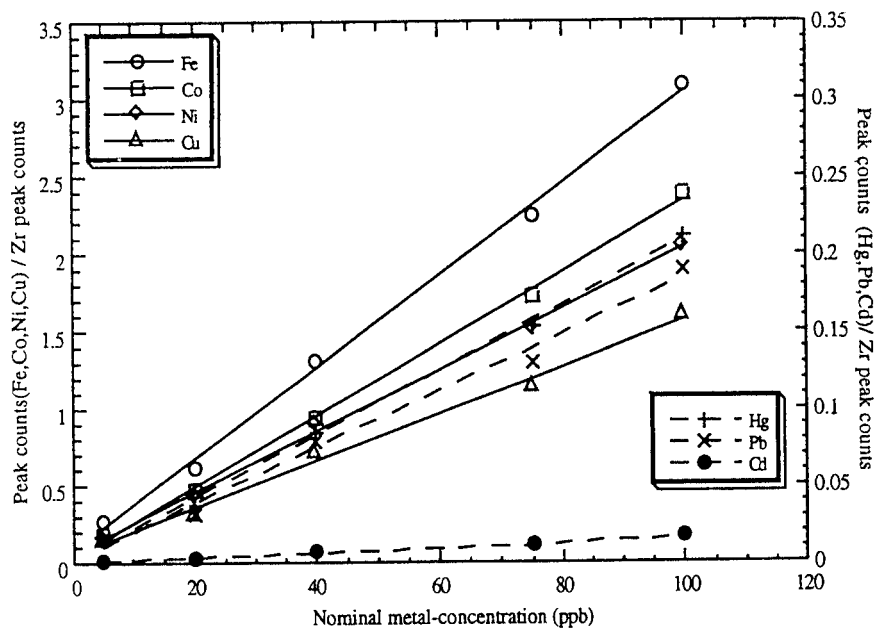


Fig. 3. Calibration curves for the PIXE analysis of heavy metals.

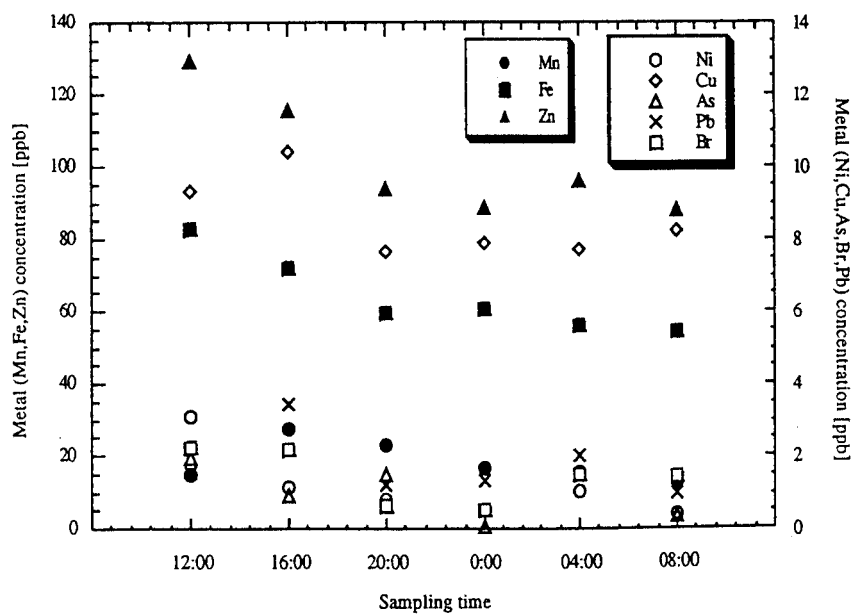


Fig. 4. Time variation of elemental concentrations in drinking water. Targets: 30ml of drinking water (pH 6.8) was chemically treated in the same manner as described in the text. Irradiation condition: 2 nA of 3 MeV proton beams and 2 μ C of accumulated charges.