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A Study on PIXE Spectrum Analysis for the Determination of Elemental Contents

Jong-Seok OH, Jun-Gyo Bak and Hae-iLL Bak
Department of Nuclear Engineering, Seoul National University

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원소별 함량결정을 위한 PIXE 스펙트럼 분석에 관한 연구

오종석 · 배영덕 · 박혜일
서울대학교 원자핵공학과

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Abstract

The PIXE (Proton Induced X-ray Emission) method is applied to the quantitative analysis of trace elements in tap water, red wine, urine and old black powder samples. Sample irradiations are performed with a 1.202 MeV proton beam from the SNU 1.5-MV Tandem Van de Graaff accelerator, and measurements of X-ray spectra are made by the Si(Li) spectrometer To increase the sensitivity of analysis tap water is preconcentrated by evaporation method. As an internal standard, Ni powder is mixed with black powder sample and yttrium solution is added to the other samples. The analyses of the PIXE spectra are carried out by using the AXIL (Analytical X-ray Analysis by Iterative Least-squares) computer code, in which the routine for least-squares method is based on the Marquardt algorithm. The elements such as Mg, Al, Si, Ti, Fe and Zn are analyzed at sub-ppm levels in the tap water sample. In the red wine sample prepared without preconcentration, the element Ti is detected in the amount of 3 ppm. In conclusion, the PIXE method is proved to be appropriate for the analysis of liquid samples by relative measurements using the internal standard, and is expected to be improved by the use of evaluated X-ray production cross-sections and the development of sample preparation techniques.

요 약

PIXE(Proton Induced X-ray Emission)법을 수도물, 적포도주, 소변 및 흑분시료의 미량원소분석에 적용하여 보았다. SNU 1.5-MV 탄뎀 반데 그라프 가속기에서 얻은 1.202 MeV 양성자빔을 시료에 조사시켰으며 X-선 스펙트럼은 Si(Li) 스펙트로미터로 측정하였다. 분석의 감도를 높이기 위해 수도물은 증발법을 사용하여 농축하였다. 표준시료로서 흑분에는 Ni가루를 섞었고 다른 시료에는 yttrium용액을 첨가하였다. PIXE 스펙트럼은 AXIL(Analytical X-ray Analysis by Iterative Least-squares) 컴퓨터 프로그램을 사용하여 분석하였는데, 최소자승법은 Marquardt알고리즘에 기초하고 있다. 수도물에서는 Mg, Al, Si, Ti, Fe, Zn 등과 같은 원소들이 ppm 이하의 함량으로 분석되었다. 농축을 하지 않은 적포도주 시료에서는 Ti 원소가 3 ppm의 함량으로 검출되었다. 결론적으로

표준시료를 쓴 상대측정법에 의한 수용액시료분석에 PIXE법이 적합함을 입증할 수 있었으며, 정확한 X-선 발생단면적을 사용하고 시료준비기술을 개발하면 이 분석법을 향상시킬 수 있으리라 기대한다.

I. Introduction

A heavy ion beam in passing through a thin sample removes inner shell electrons with extremely high probability and creates vacancies. The filling of these vacancies by outer shell electrons produces X-rays with energies which are characteristic of the element present in the sample, and the intensities are proportional to the amount of each element. Since the yield of X-rays per atom is a smoothly varying function of atomic number, and since modern X-ray detectors are capable of resolving K X-rays from elements adjacent in the periodic table, many elements can be detected simultaneously.

The analytical application of particle accelerators in producing ion-induced characteristic X-rays from test samples has been extensively developed in recent years.[1,2] This method has been applied to a wide variety of specimens in the areas of pollution control, metal analysis, surface analysis, elemental analysis of biological materials, etc.[3,4,5,6] From the consideration of sensitivity the best choice of excitation projectile appears to be 1~2 MeV proton.[2,7]

At the present work, the limiting factors in PIXE analysis arise from problems associated with the purity of the backing materials, the resolution and the efficiency of the detectors, and the background radiation associated with X-ray production.

Because of the complex nature of the PIXE spectrum, the most critical step in PIXE method is the data analysis procedure. A computer-based spectrum analysis is strongly required not only to save time but also to improve the accuracy and sensitivity of the analysis.

The PIXE experiments have been performed to establish the routine procedures for trace element analyses. The present report describes the technical experience of particular sample preparations and shows the final results deduced from the computer-based spectrum analyses.

II. Quantitative Analysis

The basic formula used to calculate the amount of a certain element in a sample from the corresponding peak in the X-ray spectrum is

$$dN_{PZ}=N_Z(s)n(s)\,\sigma_Z\,k\Omega\epsilon_Z\,dS, \quad (1)$$

where $N_Z(s)$ is the number of atoms in a surface element dS of the sample, dN_{PZ} the number of peak counts due to these atoms, n(s) the total number of protons per cm^2 passing through the same surface element, σ_Z the X-ray production cross-section for the corresponding shell, k the relative transition probability for the particular X-ray transition used in the measurement, Ω the solid angle subtended by the detector, and ϵ_Z the detection efficiency including the transmission through the window of the target chamber and the self-absorption in the sample.[8,9,10]

To obtain the total number of counts in a peak, Eq.(1) has to be integrated over the entire surface of the sample :

$$N_{PZ}=\sigma_Z k\Omega\epsilon_Z \int N_Z(s)n(s)dS. \quad (2)$$

If the density distribution of the beam is homogeneous, Eq.(2) becomes

$$N_{PZ}=\sigma_Z k\Omega\epsilon_Z\, nN_Z, \quad (3)$$

where N_Z denotes the total number of atoms in the sample of the particular element. From N_Z of Eq.(3), elemental concentration C_Z is then calculated as

$$C_Z=\frac{N_Z M_Z}{mN_A}=\frac{N_{PZ}M_Z}{mN_A}[\sigma_Z k\Omega\epsilon_Z]^{-1}, \quad (4)$$

where M_Z is the atomic mass, m the sample mass and N_A the Avogadro's number. In the internal standard method, C_Z is obtained as follows :

$$C_Z=\frac{m}{m-m_S}\frac{[N_{PZ}M_Z]}{[N_{PZ}M_Z]_S}\frac{[\sigma_Z k\varepsilon_Z]_S}{[\sigma_Z k\varepsilon_Z]}, \quad (5)$$

where subscript s denotes the standard mixed in the sample.

III. Experimental Setup

The PIXE analysis system consists of three major components which are the accelerator to produce the proton beam, the target chamber as shown in Fig.1, and the detection system with a Si(Li) detector. Sample irradiations were performed with a 1.202-MeV proton beam obtained from the SNU 1.5-MV Tandem Van de Graaff accelerator. The beam energy was stabilized by means of regulated corona discharge. Samples were mounted on slide-type sample changer which were placed at 45° with respect to the incident proton beam. The electron gun was installed close to the sample to eliminate charge accumulation arising in the case of poor conducting materials. The sample-to-detector distance was 7.35 cm and the detector was set at 135° with respect to beam direction in order to minimize the background.[11] A Canberra Si(Li) detector with an effective area of 80 mm^2 and 1 mil thick Be window was used for the X-ray measurements. The overall resolution of the system was 175 eV(FWHM) for the 5.9 keV Kα line from Fe-55. X-ray spectra recorded in 1024-channel multichannel analyzer were transferred to Micro-VAX II for subsequent analysis with the program AXIL.

IV. Target Preparation

For many types of samples, a backing substrate is often necessary. Backing materials should have the characteristics such as high mechanical strength, good electrical and thermal conductivity, high purity, and inertness to chemical solution containing samples. Materials suitable for use as a backing support are carbon, collodion, formvar, kapton, mylar, kimfol and polystyrene, etc.[12] In these experiments, 6 μm mylar film was used as a backing material.

The black powder solution was obtained by dissolving the mixture of black powder and Ni powder as an internal standard in nitric acid mixed with fluoric acid. Tap water was preconcentrated by evaporating 2 l in a beaker and dissolving the residue in nitric acid, then doped with standard

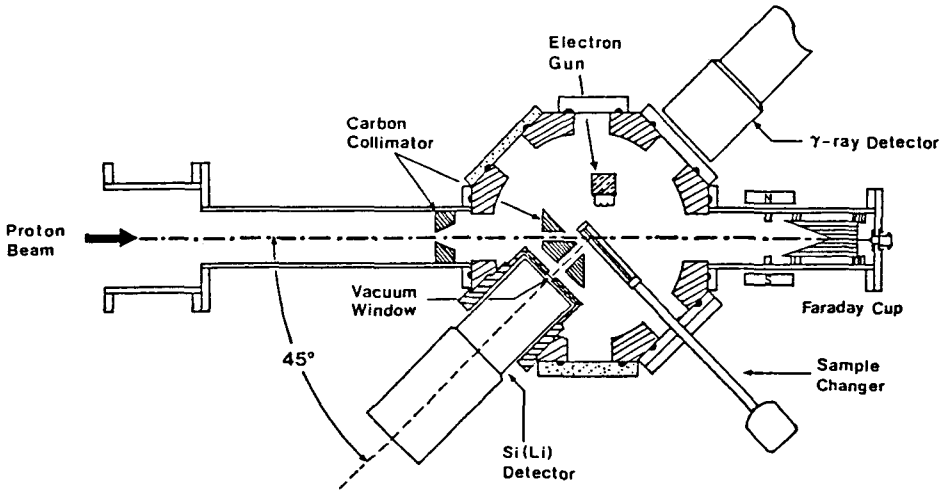

Fig. 1. Target Chamber for PIXE Analysis.

solution consisting of 1000 mg/ *l* of yttrium. Red wine and urine samples were not treated but doped with yttrium standard solution. All prepared samples were deposited as a drop from micro-pipette onto the thin mylar backing material mounted on aluminum frames and then allowed to dry.

V. Results and Discussion

The yields of X-rays for each element were determined by the computer program AXIL which fits the full energy peaks with the Gaussian distributions and the background with a polynomial. The least-squares routine is based on the Marquardt algorithm but parameters are confined within physically significant intervals predetermined by experiments.[13,14]

The PIXE spectrum of black powder is shown in Fig.2 with the fitted result, and the results of analysis for peak areas of each element are shown in Table 1 with calculated values.[15] The peak located on the left hand of Ca Kα line seems to be a single K Kα peak. But from the results of AXIL, it was found that it consists of K Kα(3.313 keV) and Sn Lα(3.144 keV) peaks. Note that Ni peaks are due to Ni powder mixed as an internal standard.

The PIXE spectrum of preconcentrated tap water sample is shown in Fig. 3 with the fitted result. PIXE data and the results of analysis are shown in Table 2. Sum peaks such as Ca Kα+Ca Kα, Ca Kα+Ca Kβ are due to the large amount of Ca element existing in the tap water sample. Also, Fig.3 shows the peaks of yttrium used as an internal standard. Several elements such as Mg, Al, Si,

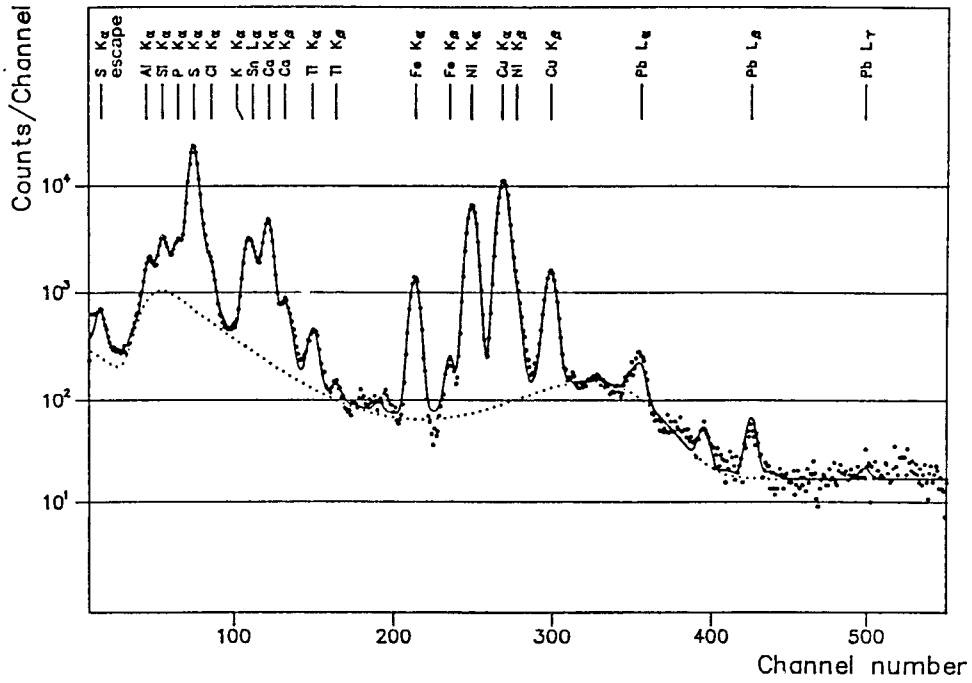

Fig. 2. PIXE Spectrum of Black Powder Bombarded with 1.202 MeV Proton Beam (Fitted by Use of AXIL Code).

Table 1. Comparison of Peak Areas Fitted by AXIL with Calculated Values* for PIXE Spectrum of Black Powder.

Element	k	N_{iv}(AXIL)	N_{iv}^{*}
Al	1.0	6,714	3,192
K	0.887	16,886	22,341
Sn	0.553	9,364	0
Ca	0.880	25,383	25,021
Ti	0.879	2,456	1,808
Fe	0.879	8,911	9,826
Ni	0.877	48,792	47,253
Cu	0.880	83,755	83,383
Pb	0.315	501	239

Table 2. PIXE Data and the Results of Analysis of Condensed Tap Water Sample.

Element	N_{iv}	σ_i(barns)	k	ε	C_i(ppb)
Mg	10,178	978.4	1.0	0.0097	434
Al	10,812	781.1	1.0	0.058	106
Si	114,594	616.7	1.0	0.164	529
S	478,118	375.5	0.927	0.384	1,906
K	209,176	172.1	0.887	0.698	1,275
Ca	1,785,094	132.0	0.880	0.763	13,394
Ti	2,225	77.34	0.879	0.857	30
Fe	798	26.36	0.879	0.945	34
Zn	3,792	9,073	0.580	0.975	803

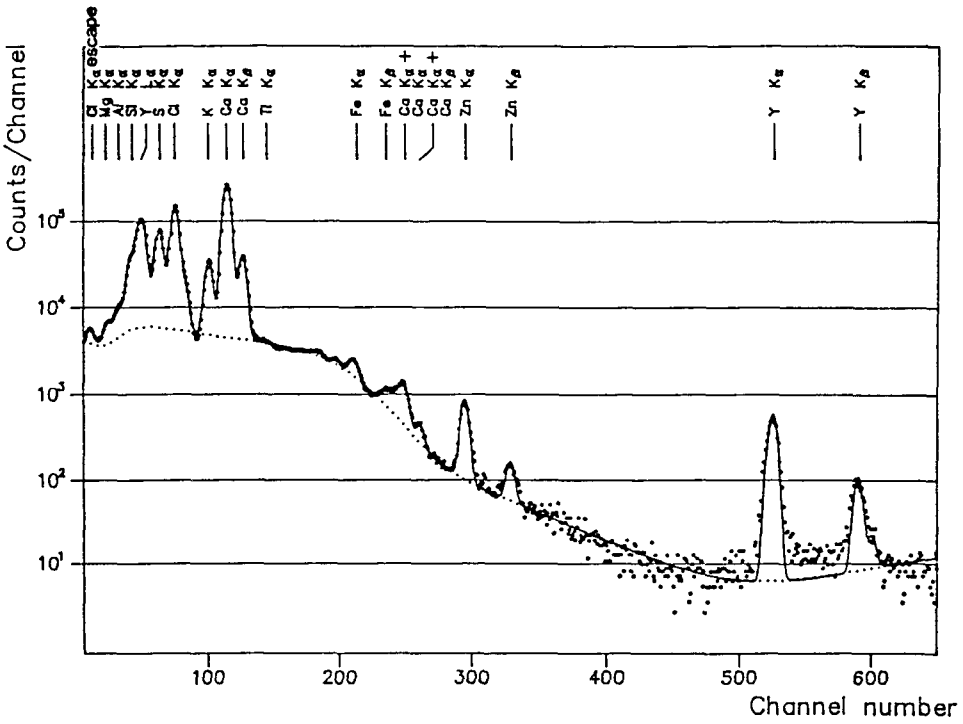

Fig. 3. PIXE Spectrum of Condensed Tap Water Sample Bombarded with 1.202 MeV Proton Beam (Fitted by Use of AXIL Code).

Ti, Fe, Zn are analyzed at sub-ppm levels.

The PIXE spectra of red wine and urine are shown in Figs. 4 and 5, respectively. The results of analyses for these samples are shown in Tables 3 and 4. In the red wine sample prepared without preconcentration, the element Ti was detected in the amount of 3 ppm.

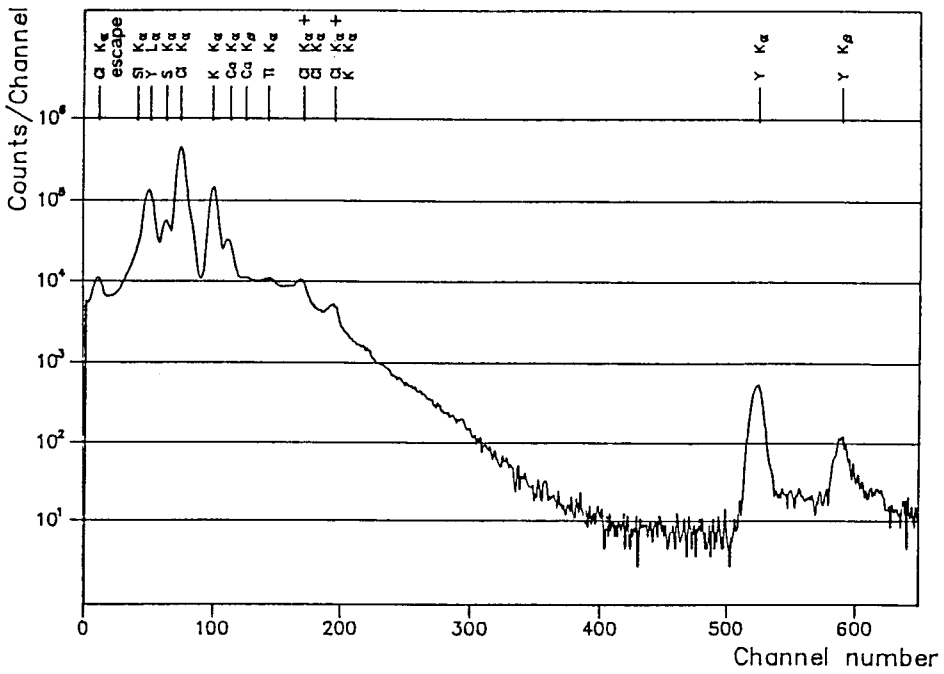

Fig. 4. PIXE Spectrum of Red Wine Sample Bombarded with 1.202 MeV Proton Beam.

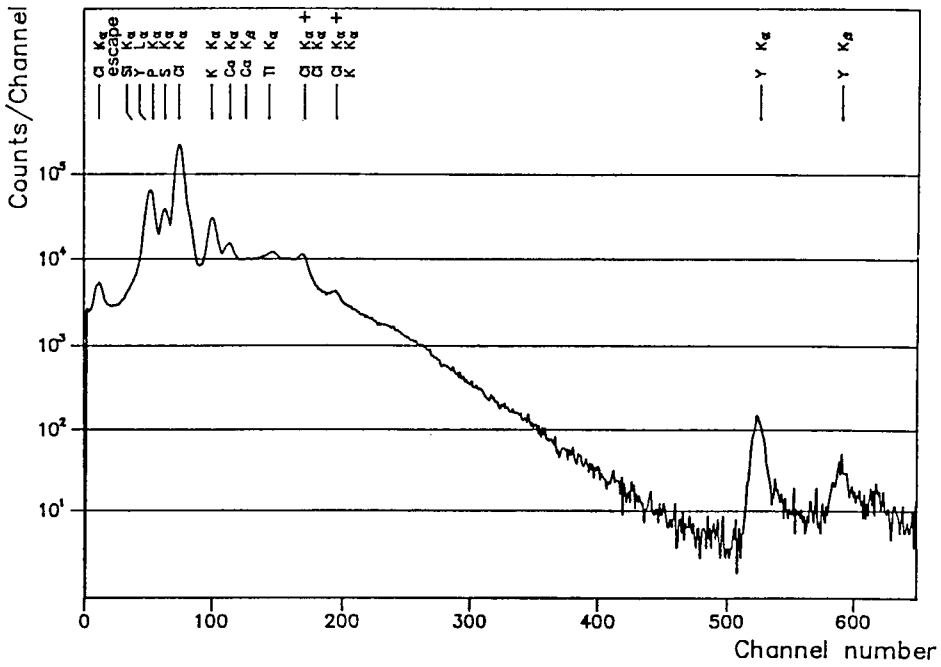

Fig. 5. PIXE Spectrum of Urine Sample Bombarded with 1.202 MeV Proton Beam.

Table 3. PIXE Data and the Results of Analysis of Red Wine Sample.

Element	N_{pz}	σ_z(barns)	k	ε	C_z(ppm)
S	279,655	375.5	0.927	0.384	97
K	931,013	172.1	0.887	0.698	491
Ca	49,124	132.0	0.880	0.763	32
Ti	2,431	77.34	0.879	0.857	3

Table 4. PIXE Data and the Results of Analysis of Urine Sample.

Element	N_{pz}	σ_z(barns)	k	ε	C_z(ppm)
P	271,119	482.9	1.0	0.275	389
S	217,152	375.5	0.927	0.384	321
K	154,586	172.1	0.887	0.698	349
Ca	24,065	132.0	0.880	0.763	67
Ti	7,316	77.34	0.879	0.857	37

VI. Conclusion

The routine procedures for trace element analyses by PIXE method were fully established and applied to several liquid samples. The results of the analysis of condensed tap water sample show that the present PIXE analysis system is capable of detecting trace elements at sub-ppm levels by the preconcentration techniques. Experimental results indicate PIXE method is a useful technique for the liquid sample analysis because of the ease of sample preparation and the simultaneous determination of a large number of elements. This method is expected to be improved by the use of evaluated X-ray production cross-sections and the development of sample preparation techniques.

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