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PROTON INDUCED X-RAY EMISSION (PIXE) ANALYSIS ON THICK SAMPLES AT HUS 5SDH-2 TANDEM ACCELERATOR SYSTEM

LE HONG KHIEM
Institute of Physics, Vietnam Academy of Science and Technology
NGUYEN THE NGHIA, VI HO PHONG, AND BUI VAN LOAT
Department of Nuclear Physics, Faculty of Physics, Hanoi University of Science, Vietnam National University, Hanoi, Vietnam

E-mail: lhkiem@iop.vast.ac.vn

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Abstract. *The main purpose of this work is to establish a method of elemental analysis by Proton-Induced X-ray Emission (PIXE) technique on thick samples. Our study has been carried out at Hanoi University of Science (HUS) using a 5SDH-2 Tandem accelerator. The X-ray spectra were measured by a Si(Li) detector (FWHM = 139 eV at 5.9 keV) and analyzed off-line using GUPIX software. The validity of the proposed method has been checked through its application to NIST standard samples. The concentrations of the elements have been determined in the standard samples are in agreement with the certified values within the error limits. Our method is now used for the analysis of environmental samples at our laboratory.*

Keywords: PIXE, Pelletron.

I. INTRODUCTION

Among other analytical techniques, PIXE is a highly sensitive, multi-elemental analytical technique which is already proved in all prospective areas such as thin films, water, air, archaeological and biological samples etc. Nowadays, PIXE has been widely and successfully used in many areas. At Hanoi university of Science, a 5SDH-2 tandem accelerator system was installed in 2011. This is the first accelerator in Vietnam can be used for the elemental concentration analysis using charged particles, including the PIXE. The system consists of two ion sources, a 1.7 MV tandem accelerator. PIXE elemental analysis is one among many applications can be done using this accelerator.

PIXE analysis is based on the excitation of characteristic X-rays by MeV proton beam. An energy spectrum of emitted X-ray is recorded by Si(Li) detector. The elements in the sample are identified from the energies of the characteristic peaks in the x-ray emission spectrum. The quantity of a particular element in the sample is determined from the intensity of its characteristic x-ray emission spectrum.

In this report, we attempt to demonstrate the ability of our system for quantitative elemental analysis using thick target proton induced X-ray emission (TTPIXE) technique. The configuration of the system used for this technique is described. For quality assurance and step by step improvement of the accuracy of the method, a procedure was applied for a series of NIST standard samples that are available in our laboratory. This procedure has been successfully applied to some environmental samples that will be presented in this report.

PIXE analysis of thick target is often more complicated than that of thin target. It involves matrix effects when impinged protons lose their energy in the sample and the X-ray emissions at a certain point of the beam path are attenuated. The formula of X-ray intensity of K shell case for PIXE thick target can be described as [2]:

$$I(Z) = \frac{N_{av}\omega_z b_z \Omega\varepsilon_z^i t_z N_p C_z}{A_Z} \times \int_{E_0}^{0} \frac{\sigma_Z(E)\exp\left\{-\left(\frac{\mu}{\rho}\right)\frac{\cos\alpha}{\sin\theta_{TO}}\int_{E_0}^{0}\frac{dE}{S(E)}\right\}}{S(E)} \tag{1}$$

where $I(Z)$ is the intensity of a particular K X-ray line, $\sigma_Z(E)$ is the ionization cross-section for the K shell, and N_p is the number of protons of energy E_0 incident at angle α to the normal of sample; ω_Z is the corresponding fluorescence yield, and b_Z is the fraction of K X-rays in the selected line; N_{av} is Avogadro's number; $S(E)$ is the proton stopping power; A_Z is the atomic mass of element Z; θ_{TO} is the X-ray take-off angle; $\Omega\varepsilon_z^i$ is the absolute efficiency of detection, which involves both X-ray detector solid angle and intrinsic efficiency of the silicon detector; t_z is the attenuation of the X-rays in any absorber placed between sample and detector; $\frac{\mu}{\rho}$ is the attenuation coefficient within the sample matrix for the X-ray line of interest.

Determination of concentration is quite straightforward when the concentrations of major elements in the sample are known. However, in case of unknown matrix composition, some procedures have to be applied to determine the matrix composition such as the use of a PIXE analysis tuned for determination of major elements or the use of "interactive solution" approach as described in [3]. It should be noted that the matrix effect can be neglected with the use of internal standards.

II. EXPERIMENT

II.1. Experiment setup

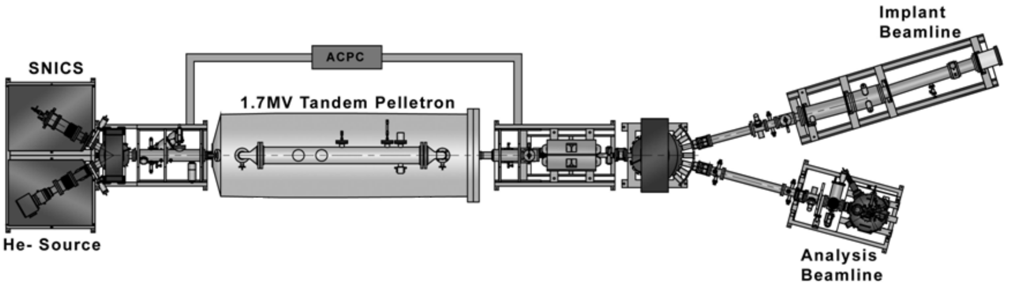

Fig. 1. The schematic of the Pelletron accelerator 1.7 MV model 5SDH-2

A proton beam, accelerated by the 5SDH-2 tandem accelerator at HUS was used for the present study. The schematic of the system is presented in Fig. 1. Proton beam is produced by a standard radio frequency ion source. After passing through the tandem accelerator tank, maximum proton energy of 3.4 MeV can be obtained. PIXE analysis was performed using analysis beam line and a standard chamber which is located at the end of the beam line. The vacuum inside the chamber is about 10^{-6} torr during analysis. The sample holder is at zero degree to the beam direction. Multiple samples can be inserted into an analytical chamber via load lock and oriented with respect to the beam with a five axis manipulator. A Silicon Drift Detector (SDD) with a resolution of 139 eV at 5.9 keV, which is connected to a multi-channel analyzer through a conventional electronic chain, was placed at 32.8° to the beam direction. In Fig. 2, the schematic diagram of the analytical chamber and its associated electronics for X-ray spectroscopy are shown.

In our study for each sample, two proton beams were used. The first beam has energy of 831 keV and the second beam has energy of 2618 keV. In both cases, the intensity of the beams was 6 nA. For 831 keV proton beam, a thin 12.8 μm Kapton absorber foil was put in front of the detector. For 2618 keV proton beam, a 100 μm Mylar absorber foil was used. These foils were used to reduce the high intensity low-energy X-rays in the spectra due to light elements as well as to stop the back-scattered protons and thus to improve the analytical sensitivity.

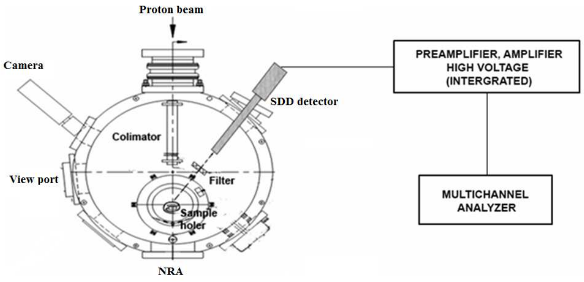

Fig. 2. An overview of the analytical chamber and its set-up for PIXE analysis.

For PIXE quantitative analysis, the exact value of the total charge that arrived at the sample is essential. According to the original design of the chamber, the entire of analytical chamber is electrically isolated and the integrated charge on the samples was collected using a current integrator. This gives us an absolute beam current value. However, currently we are not using this method due to some technical difficulties. To obtain the absolute value of beam intensity, we did a calibration by using standard samples.

II.2. Sample preparation

In order to check the PIXE analysis method using the thick sample, two standard samples named NIST-611 and NIST-613 were prepared. The standard samples were putted into the glass support, which has a nominal composition of 72 % of SiO2, 14% of Na_2O, 12% of CaO, and 2% of Al_2O_3 in mass fractions. This composition is similar to the matrix composition of most of geological and environmental samples. The samples are thick enough so that they can fully stop the incoming proton beam. The analyzed samples of soil obtained from Faculty of Environmental Science of HUS were also prepared for analysis in the same way as the standard ones.

II.3. Data analysis

GUPIX software was used for the quantitative analysis of the X-ray spectra. The software analyzes PIXE spectra by an algorithm of non-linear least-squares fitting. The concentrations of the elements in the samples are quantitatively calculated from the X-ray characteristic peak areas using the fundamental parameter method. Spectral interferences by escape and summing effects in the X-ray spectra could be automatically resolved by GUPIX. Experimental geometry, information of Si(Li) detector, absorber thickness, energy of the incident particle and the net charge collected are instrumental parameters required by the program. The formula used by GUPIX for determination of elemental concentrations is as bellow:

$$C_z = \frac{Y(Z,M)}{Y_{lt}(Z,M).H.Q.\varepsilon_z.t_z} \tag{2}$$

where Y_{1t} is the theoretical intensity or yield per μC of charge per steradian per unit of concentration, Q is the measured beam charge, ε_Z is the intrinsic efficiency of the SDD detector and t_z is the transmission of the respective X-rays through any absorber placed between the detector and the target. H is the instrumental constant that takes into account the correction of beam charge, solid angle, intrinsic efficiency of the detector and the other systematic errors. In general, this parameter can be determined by using the reference samples. In our work, the H value was assumed to be independent of the X-ray energy (i.e. intrinsic efficiency of the detector calculated by GUPIX is acceptable).

For data analysis, we have mainly followed the H value method described in [2, 5]. The PIXE spectra of samples obtained from the first run with 831 keV proton beam was analyzed under the “Iterated matrix solution” option of GUPIX software to determine the major element concentration of the sample. The nominal concentration of an internal standard was used as reference to provide normalization factor for the H value. The second run with 2618 keV proton beam, which is designed for determining the trace elements of the sample, would use the information of major element concentration as an input for the “Fixed matrix solution” option. An internal standard can also be used to adjust the H value. In our study, this procedure was generally applied for all the samples. However, since they are irradiated under the similar experimental conditions (charge collection, the detector and geometry), the H value obtained in previous measurement can be used for the next one.

III. RESULTS AND DISCUSSION

The NIST 611 standard sample was measured first. The PIXE X-ray spectra for low and high energy proton beam are shown in Fig. 3. The spectra contain many overlapping X-ray peaks emitted from more than 50 elements according to the certificate sheet of NIST-611 standard. For the run with 831 keV proton beam, the certified value of concentration of calcium was used to adjust the H value. For the run with 2618 keV proton beam, the certified concentration value of copper content in the sample was used for the same purpose. The spectrum is then analyzed by GUPIX software.

It is clearly seen from the Table 1 that a good agreement was found for most of elements except some elements such as Na, Al, Ag, Cd. This can be explained by overlapping of very strong peak of Ca that locates in the region contained L peaks of Ag and Cd. For Na and Al, an absorption effect of their characteristic X-ray also plays an important role in increasing the error

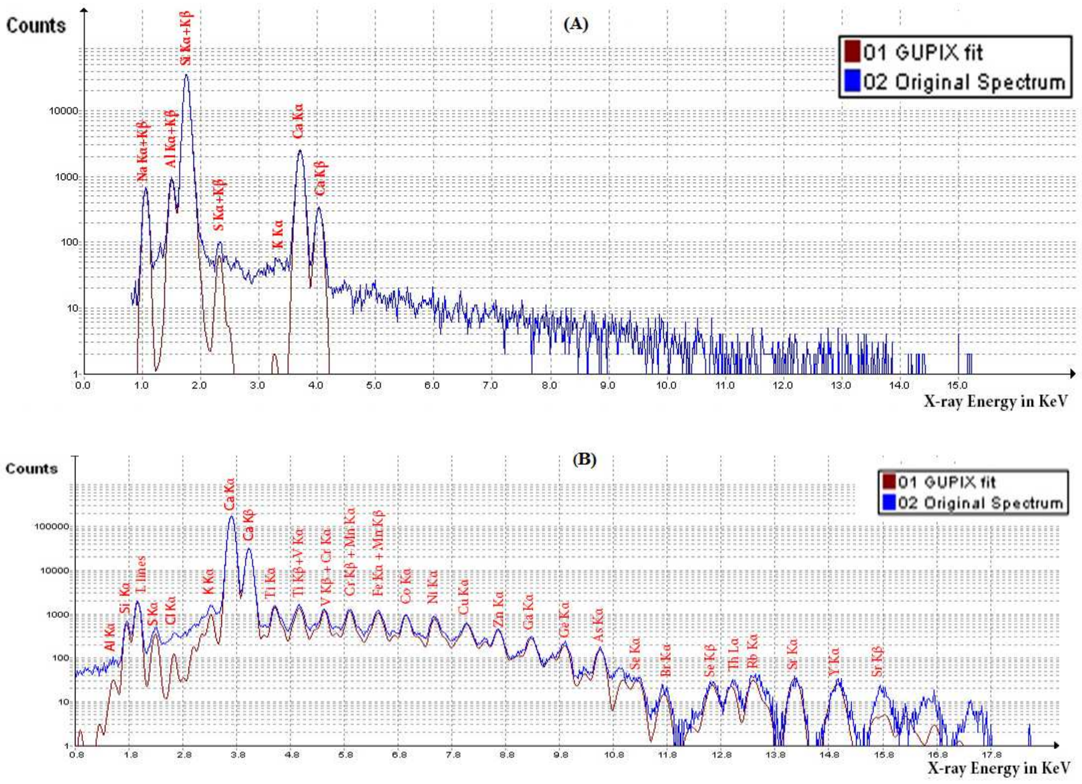

Fig. 3. PIXE spectrum of NIST-611 standard. The sample was irradiated by low energy proton beam (A) and high energy proton beam (B).

of the analysis results due to their low energies. In addition, there are small differences between the obtained values and the certificated ones for Pb, Th and U. These differences might due to small yield of L_α peaks emitted from these elements. The effect of pile-up occurred from intense X-ray lines of major elements also plays a role in these discrepancies. Furthermore, the results obtained by two options of data analysis differ less than 6.2%. Therefore, it is concluded that the exact matrix information do not play an important role in the results obtained by GUPIX software.

For the NIST-613 standard sample, the experiment conditions were not changed so that the same H value, which has been found, can be used. The similar procedure with NIST 611 has been applied and the results are also presented in Table.1. The good agreement between calculated and certificated values has been found, whereas some discrepancies in Ag, Cd, Pb, Th, U also observed. The influence of matrix information was introduced to be less than 9.2 %.

We applied the same PIXE analysis to a soil sample. The previous H value obtained from NIST-611 standard sample was used for each run. The matrix composition that was obtained from the run with low energy proton beam is given to GUPIX for the run with higher energy proton beam. The obtained concentrations as well as other information given by GUPIX are presented in Table 2.

Table 1. Elemental concentrations determined by TTPIXE in standard samples, compared with nominal values

	NIST SRM 611			NIST SRM 613		
Element	Measured (with exact matrix)	Mesured (matrix calculated from first run)	Certified concentration	Measured (with exact matrix)	Mesured (matrix calculated from first run)	Certified concentration
Na*	136692.0 ± 4100.76	136692.0 ± 4100.76	103848.3692	134817.0 ± 4300.66	134817.0 ± 4300.66	103848.4 ± 0.00
Al*	13805.0 ± 310.61	13805.0 ± 310.61	10585.00685	13774.0 ± 336.09	13774.0 ± 336.09	10585.0 ± 0.00
Si*	385613.0 ± 1966.63	385613.0 ± 1966.63	336553.1428	365895.0 ± 3256.47	365895.0 ± 3256.47	336553.1 ± 0.00
K	< 41.9	< 45.4	64	420.0 ± 34.48	444.0 ± 36.45	461.0 ± 0.00
Ca**	85728.0 ± 600.10	85728.0 ± 600.10	85762.892	85730.0 ± 934.46	85730.0 ± 934.46	85762.9 ± 0.00
Ti	31.0 ± 6.29	32.5 ± 6.60	50.1 ± 0.80	448.1 ± 14.12	463.1 ± 14.59	437.0 ± 0.00
Cr	26.7 ± 5.02	27.6 ± 5.20	29.9 ± 4.20	407.9 ± 14.52	416.9 ± 14.88	415.0 ± 29.00
Mn	37.1 ± 5.07	38.2 ± 5.15	37.7 ± 3.80	420.1 ± 14.87	427.6 ± 15.14	457.0 ± 55.00
Fe	51.5 ± 3.89	52.5 ± 3.97	51.0 ± 2.00	469.2 ± 11.03	475.6 ± 11.18	458.0 ± 9.00
Co	38.0 ± 6.90	38.9 ± 7.00	35.5 ± 1.20	367.1 ± 20.15	371.5 ± 20.32	390.0 ± 0.00
Ni	49.0 ± 6.80	49.7 ± 6.87	38.8 ± 0.20	392.6 ± 17.04	394.3 ± 17.15	458.7 ± 4.00
Cu**	26.0 ± 5.14	26.3 ± 5.18	37.7 ± 0.90	444.0 ± 17.54	445.3 ± 17.63	444.0 ± 4.00
Zn	43.4 ± 7.06	43.7 ± 7.08		419.2 ± 19.74	420.3 ± 19.75	433.0 ± 0.00
As	29.0 ± 7.17	29.0 ± 7.11	37.4 ± 0.00	236.4 ± 17.66	235.7 ± 17.58	340.0 ± 20.00
Se	14.0 ± 4.99	13.9 ± 4.98	16.1 ± 1.60	88.0 ± 15.49	87.7 ± 15.44	115.2 ± 2.20
Rb	12.0 ± 9.68	11.9 ± 9.61	31.4 ± 0.40	364.8 ± 35.02	362.8 ± 34.90	425.7 ± 0.80
Sr	73.7 ± 16.62	73.3 ± 16.52	78.4 ± 0.20	482.6 ± 38.70	479.4 ± 38.45	515.5 ± 0.50
Ag	211.1 ± 88.07	229.4 ± 95.61	22.0 ± 0.30	620.1 ± 108.77	657.6 ± 115.21	268.0 ± 29.00
Cd	212.4 ± 77.23	229.6 ± 83.69	29.9 ± 4.20	485.1 ± 103.81	513.4 ± 109.82	244.0 ± 22.00
Tl	< 21.1	< 21.2	15.7 ± .30	25.7 ± 22.10	25.4 ± 22.01	61.8 ± 2.50
Pb	11.1 ± 17.54	11.2 ± 17.50	38.6 ± .20	332.6 ± 41.11	331.0 ± 40.88	426.0 ± 1.00
Th	26.6 ± 20.22	26.5 ± 20.07	37.8 ± .08	571.2 ± 61.06	568.0 ± 60.72	457.2 ± 1.20
U	< 40.6	< 40.5	37.4 ± .08	361.5 ± 62.94	359.4 ± 62.75	461.5 ± 1.10

All values are given in ppm (mg/kg).

* Calculated value obtained from the first run using low energy proton beam.

** These elements were used as reference to obtain H value

Table 2. Elemental concentrations determined by TTPIXE in the soil sample.

Element +Principal line	Peak area	Filter transmission (%)	Concentration (ppm)	Error (%)	Detection limit (ppm)
NaK	535.3	1.03	5747.1	6.92	618
MgK	8956	6.441	14177.6	1.03	129
AlK	62237.9	18.291	39552.5	0.36	62.3
SiK	436657	33.794	182272	0.13	45.9
S K	11054.5	62.032	4973.6	0.89	30.3
ClK	2604.2	72.069	1352.9	2.21	33.4
K K	21258.5	84.962	17194.7	0.61	40.9
CaK	195059	88.893	221836.2	0.2	174.5
TiK	21774.3	52.592	2781.8	0.63	8.6
CrK	558.3	69.15	62	7.79	8.2
MnK	4082.8	75.268	474.4	1.63	7.5
FeK	181152	80.177	22293.7	0.2	12.7
CoK	273.7	84.062	38.5	117.8	75.5
NiK	222.4	87.147	35.9	25.77	17.2
CuK	105.4	89.592	20.8	18.35	6.7
ZnK	269.7	91.53	63.9	7.16	4.4
GeK	21.7	94.303	8.3	82.85	10.7
AsK	39.8	95.29	19.5	31.88	12.3
RbK	58	97.681	88.5	17.13	22.1
SrK	333.4	98.032	691.4	6.24	41.9
PbLA	38.2	95.301	36.5	45.55	35.8

IV. CONCLUSION

PIXE technique proved to be a reliable multi-elemental and high sensitive analytical tool. Thin-target PIXE offers the possibility to determine elemental concentrations without corrections for X-ray self-absorption and proton stopping in target as for the case of thick-target PIXE. However, sample preparation is rather difficult in comparison with the thick sample method. In this work, PIXE analysis on thick samples at HUS tandem accelerator was established and applied successfully in analysis of the environmental samples. The method has been checked by analyzing the elemental concentrations in NIST standard samples. The consistency between our results with the certified values confirms the validity of the established PIXE analytical technique.

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