Standardization of proton-induced x-ray emission technique for analysis of thick samples

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This paper describes the standardization of the proton-induced x-ray emission (PIXE) technique for finding the elemental composition of thick samples. For the standardization, three different samples of standard reference materials (SRMs) were analyzed using this technique and the data were compared with the already known data of these certified SRMs. These samples were selected in order to cover the maximum range of elements in the periodic table. Each sample was irradiated for three different values of collected beam charges at three different times. A proton beam of 2.57 MeV obtained using 5UDH-II Pelletron accelerator was used for excitation of x-rays from the sample. The acquired experimental data were analyzed using the GUPIXWIN software. The results show that the SRM data and the data obtained using the PIXE technique are in good agreement.

Keywords: standardization, thick samples, PIXE analysis

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1. Introduction

The proton induced x-ray emission (PIXE) technique was first proposed by Johnson of Lund University in 1970.[1] PIXE has a wide range of applications in biology, medicine, atmospheric aerosol analysis, earth science, and archeology.[2] In the last few decades, the invention and development of mega volts particle accelerators have increased the scope of PIXE analysis. The PIXE technique is attractive due to its ability of multi-elemental, non-destructive, high sensitivity, trace element analyses and identification of high atomic number elements as compared to the other analytical techniques.[3,4] The PIXE provides minimum beam attenuation in the sample, greater cross-section, and minimum emission of the background radiation.

We report the standardization of the PIXE measurement setup for thick samples. In thick samples, the incident projectile loses a significant portion of its initial energy and/or the emitted gamma rays or x-rays are largely attenuated.[5,6] The PIXE analysis is very useful for trace element detection in thick samples. The Rutherford back-scattering is efficient for the matrix element analysis but not suitable for the trace element analysis due to its poor resolution. The electron beam analytical technique is good for the analysis of thick samples but not suitable for the trace element analysis due to the high background radiations. The x-ray fluorescence technique is good for the trace element analysis but cannot be combined with the micro-beam analytical technique, while PIXE can be combined with the micro-beam analytical technique to obtain a higher resolution. The standardization of the PIXE analysis is very important for obtaining accurate results.[2,7]

The PIXE is based on a two-step process, i.e., creation of electron vacancies in the innermost shell and filling of these vacancies by outer shell electrons, as shown in Fig. 1. In addition to the emitted x-rays, the Auger effect (electron emission due to the emitted x-rays) and Coster–Kronig transition (non radiative transitions between sub-energy levels) also occur, as shown in Figs. 2(a) and 2(b), respectively.[8] All these phenomena result in the loss of the fluorescence yield of PIXE.

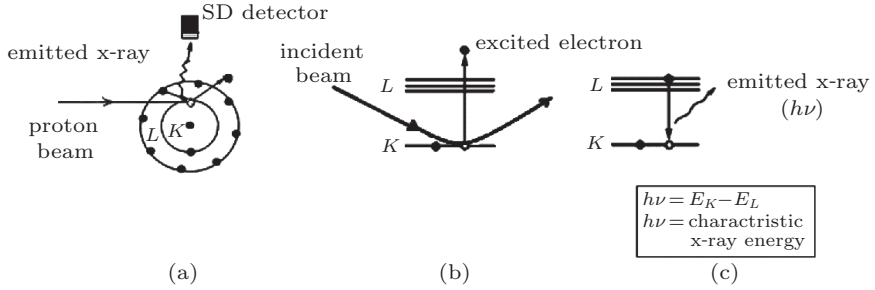


Fig. 1. (a): Excitation of an atom using a proton beam, (b) ionization of the atom, (c) x-ray emission from the atom.

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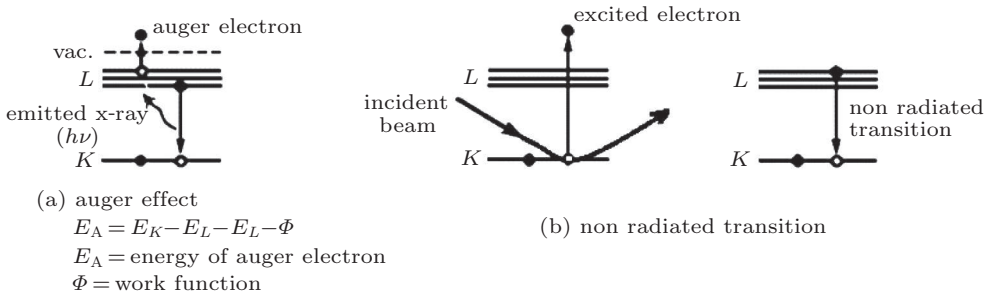


Fig. 2. Schematic diagrams showing (a) Auger effect, (b) electron emission due to incident proton and non-radiated transition.

2. Experimental setup

The standardization of PIXE for thick samples is carried out in two steps. The first step is to identify the atomic composition of the target.[8] The second step is to obtain a PIXE spectrum for each SRM using a proton beam of 2.57 MeV obtained from a 5UDH-II Pelletron accelerator and a 100 μm thick protective Mylar foil with no holes which also absorbs x-rays of low atomic number elements. The emitted x-rays pass through a thin Mylar or beryllium window and enter the silicon drift lithium detector (SDD). As shown in Fig. 3, this SDD (resolution of 138 eV at 11 keV) is placed at an angle of 45° to the incident beam. The advantage of the 45° orientation is the reduction of electron bremsstrahlung or background radiations. The lowest energy x-rays that can be detected with this detector are about 1 keV and the elements of $11 < Z < 92$ can be detected. Light elements ($11 < Z < 50$) are detected from their K x-rays and heavy elements ($Z > 50$) are detected from their L x-rays.[9] The PIXE technique has its maximum sensitivity or minimum detection limit in two regions of the periodic table, i.e., $20 < Z < 40$ and $75 < Z < 85$.[2] The sensor converts the x-rays' energy into a proportional amount of charge by the process of ionization. By applying a bias to the chip of the SDD and exposing it to x-rays, x-rays are converted to an electron cloud. These electrons rise to the conduction band and act as charge carriers.

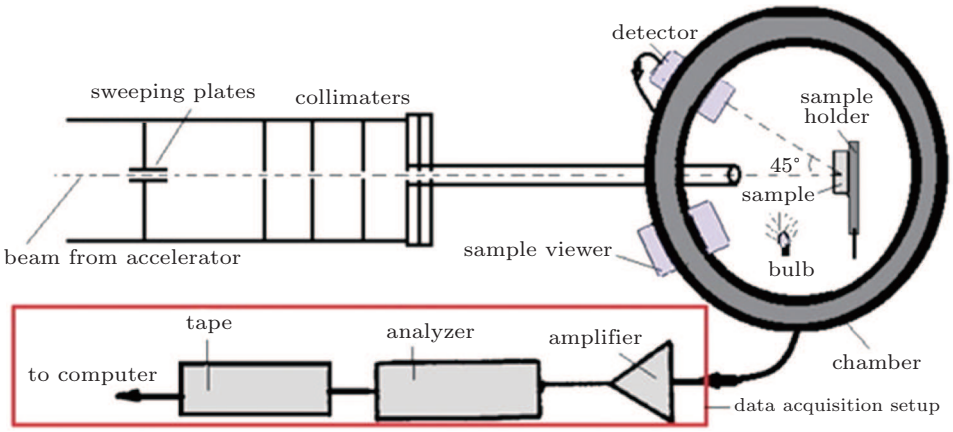


Fig. 3. (color online) Schematic diagram of experimental setup for PIXE.

The field effect transistor (FET) is directly connected to the sensor. The FET optimizes the detector output and acts as an analogue to digital converter (ADC). These digital signals are fed to the computer automated measurement and control (CAMAC) with Kmax interface software to obtain the x-ray spectrum by the multi-channel analyzer (MCA) terminal, which provides the bases for quantitative analysis of the sample by GUPIXWIN.

Using the GUPIXWIN software with suitable experimental setup parameters, sampling, and fitting yields the analysis of the PIXE spectrum. A combined K and L H value vs. energy document (HED) files are developed for three samples (stainless steel SRM1155, TiV alloy SRM6IA-4V, and cadmium). With these HED files, the measured concentrations for each sample are compared with the corresponding SRM concentrations.

3. Results and discussion

Three different samples are analyzed with the GUPIXWIN software and the measured values along with the standard reference material (SRM) concentration data are presented in the next sections. The respective plots of dis-

persion for the three samples, i.e., stainless steel, cadmium, and TiV alloy, measured at different dates are presented and compared.

3.1. HED files

The most important files which we have created in the parameter file (PAR file) are the H value vs. energy document files. Using these HED files in the PAR-file, we can determine the composition of the sample.

Our analysis is mainly based on the instrumental constant H value determination.[10] The HED file is simply consisting of the H value related to different energy of the emitted x-ray, as H is dependent on the energy. The x-ray energy is the characteristic of the emitted photon. Physically, the H value is equal to the geometrical solid angle Ω made by the x-ray at the detector[11] and is defined as

$$\Omega = H = \frac{A}{d^2},$$

where A is the area of the detector and d is the distance of the detector from the sample. For the first iteration of the available setup in our laboratory, we use $A = 30$ mm and $d = 14$ cm, the H value obtained is 0.00153. The K and L HED files created for the samples are given in Tables 1 and 2, respectively. These HED files are also called combined HED files because each of them is the sum of individual K and L x-ray HED files for each individual sample. These HED files are used for the analyses of our samples and the data of all samples are presented in the following section.

Table 1. K x-ray HED file.

x-ray energy/eV	H value
1.4867	3.2976
1.740	0.855
4.478	0.00154
4.510	0.002793
4.9318	0.000915
4.952	0.002263
5.4147	0.000921
6.403	0.003037
6.39	0.00093
7.478	0.00093

Table 2. L x-ray HED file.

L x-ray energy/eV	H value
2.293	0.0011
3.313	0.0036764
3.604	0.001091

3.2. Analysis of stainless steel sample

The experimental data obtained from the stainless steel sample are processed using the GUPIXWIN software, the PAR-file spectrum obtained is shown in Fig. 4. A PAR file is created for this spectrum which contains all details of the experimental setup like beam energy, current, and tentative composition of the sample in the GUPIXWIN software. After analysis by the GUPIXWIN software, the plot shown in Fig. 4 is obtained. In this figure, the relative height of peak for each element is proportional to its concentration in the sample.

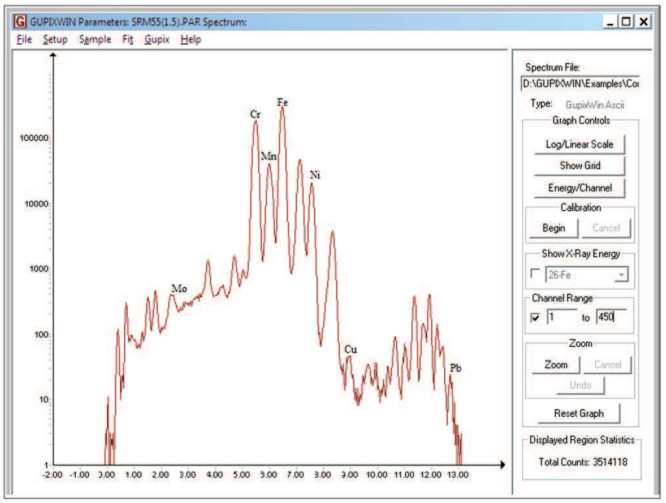


Fig. 4. (color online) PAR-file spectrum of the stainless steel sample obtained from the measured data after processing using GUPIXWIN software.

The major elements in the stainless steel sample are iron (Fe), chromium (Cr), nickel (Ni), and molybdenum (Mo). The differences between actual (already known) and measured data, i.e., actual SRM concentration – measured concentration, for trace and matrix elements are calculated and shown in Table 3.

Table 3. Comparison of actual (already known) and measured elemental composition of stainless steel sample.

Q/μC	Element	Actual	Measured	Difference
1.5	Fe	64.31%	64.561%	–0.251%
	Cr	18.37%	18.4266%	–0.0566%
	Mn	1.619%	0.8006%	0.8184%
	Ni	12.35%	12.41%	–0.06%
	Mo	2.26%	2.0742%	0.186%
	Cu	0.175%	0.0656%	0.1094%
	Si	0.5093%	0.1953%	0.314%
	Pb	0.001%	0.1864%	–0.1854%
1	Fe	same as above	64.389%	–0.079%
	Cr		18.3957%	–0.0257%
	Mn		0.7841%	0.8349%
	Ni		12.34%	0.01%
	Mo		2.2563%	0.0037%
	Cu		0.0766%	0.0984%
	Si		0.1943%	0.315%
	Pb		0.2004%	–0.1994%
0.5	Fe	same as above	64.389%	–0.079%
	Cr		18.3957%	–0.0257%
	Mn		0.7841%	0.8349%
	Ni		12.34%	0.01%
	Mo		2.2563%	0.0037%
	Cu		0.0766%	0.0984%
	Si		0.1943%	0.315%
	Pb		0.2004%	–0.1994%

In each PAR-file spectrum, the peak height of the characteristic curve shows the concentration of the element and the background continuity shows the bremsstrahlung radiation. The data presented in Table 3 are obtained for three different charges (1.5 μC, 1 μC, and 0.5 μC) collected. For the stainless steel sample, we only obtained one date, therefore the dispersion in the obtained data cannot be calculated.

From Table 3, it is clear that the measured data are in good agreement with the already known concentrations of elements present in the sample. The collected charge vs. difference of the actual and analyzed data for different collection charges is plotted in Fig. 5. From the plot, it is evident that the actual and the measured data are in very good agreement with each other, thus proving the strength of our measurement technique.

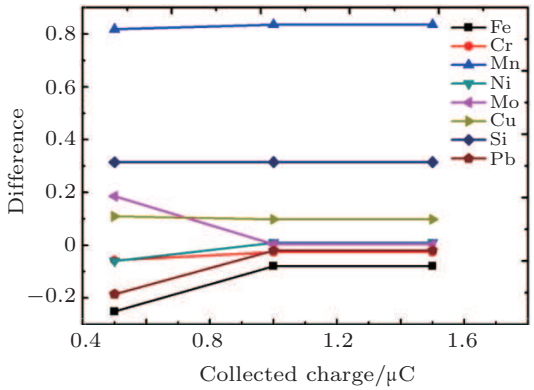


Fig. 5. (color online) Collected charge vs. difference of measured and actual elemental composition for stainless steel SRM 1155.

3.3. Analysis of titanium vanadium sample

The PAR file obtained for the titanium vanadium alloy sample using our experimental setup is shown in Fig. 6. In the figure, the relative height of peak for each element is proportional to the concentration of the element present in the sample. For this sample, using the HED file and satisfying the fit requirements, the concentration of each element is obtained by analyzing the data using the GUPIXWIN software. After analysis by the GUPIXWIN software, the plot shown in Fig. 6 is obtained. As shown in the figure, the major elements in the titanium vanadium sample are aluminum (Al), titanium (Ti), vanadium (V), iron (Fe), chromium (Cr), and copper (Cu).

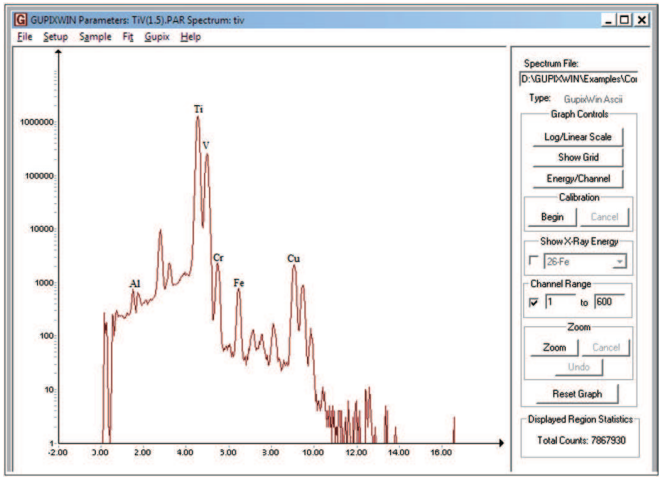


Fig. 6. (color online) PAR-file spectrum of the titanium vanadium sample obtained from the measured data after processing using the GUPIXWIN software.

For accurate results, the experimental data are measured at two different dates and then compared with the already known data (actual data). The standard deviation σ for each element is calculated.

The dispersion of the measured data is plotted versus the collected charge for all the elements present in the sample. The comparison of standard deviation σ of the experimentally measured data and the actual SRM concentration (which is already known) clearly shows the accuracy and strength of our measurement technique. For comparison, the actual and the measured data for different collection charges and dates are also presented in Table 4.

Table 4. Comparison of the measured and actual compositions of TiV sample for different collection charges measured at different dates.

Q/μC	Element	Actual	Measured at 29-01-2013	Measured at 11-02-2013	Average of measurement	Difference	σ
1.5	Al	6.34%	6.39%	6.0865%	6.23%	0.11%	0.354%
	Ti	88.97%	89.01%	88.7234%	88.8667%	0.1033%	0.1433%
	V	4.31%	4.308%	4.3688%	4.3384%	–0.00092%	0.0369%
	Fe	0.23%	0.2298%	0.7548%	0.75375%	–0.52375%	0.00105%
	Cr	0.025%	0.1520%	0.3894%	0.02707%	–0.40145%	0.1601%
	Cu	0.004%	0.0275%	0.059%	0.0591%	–0.52375%	0.0791%
1	Al	same as above	7.23%	7.1%	7.165%	–0.825%	0.065%
	Ti		85.8079%	85.56%	85.6839%	3.28605%	0.124%
	V		4.1%	4.1691%	4.13455%	0.17545%	0.03455%
	Fe		0.7019%	0.7047%	0.7033%	–0.4733%	0.0014%
	Cr		0.4081%	0.3780%	0.39305%	–0.36805%	0.01505%
	Cu		0.0823%	0.08455%	0.08343%	–0.07943%	0.001125%
0.5	Al	same as above	6.8064%	7.1378%	6.9721%	–0.6321%	0.1657%
	Ti		88.571%	85.4603%	87.0157%	1.95435%	1.5556%
	V		4.187%	3.8847%	4.03585%	0.27415%	0.15115%
	Fe		0.6925%	0.6590%	0.67575%	–0.44575%	0.01675%
	Cr		0.4054%	0.459%	0.4322%	–0.4072%	0.0268%
	Cu		0.0797%	0.07%	0.07485%	0.07085%	0.024624%

The highest dispersion for titanium (indicated by red color graph) at 1.5 μC collection charge is most probably due to some experimental errors. The deviation in the data for all the constituent elements of the sample is much less than 1%, which shows that the PIXE technique is a very powerful tool for multi-elemental analysis.

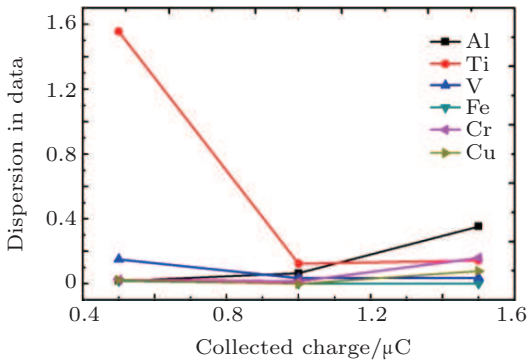


Fig. 7. (color online) Dispersion vs. collected charge plot for the titanium vanadium sample.

3.4. Analysis of cadmium sample

The PAR file obtained for the cadmium sample from the data acquisition setup is shown in Fig. 8. The major elements are cadmium (Cd), calcium (Ca), iron (Fe), and copper (Cu). In the figure, the relative height of peak for each element is proportional to the concentration of the element present in the sample. The analysis is made by using the HED file and completing the fit requirements (e.g. setup, sample, fit, and run) of the GUPIXWIN software. Similarly, after analysis by the GUPIXWIN software the final data obtained are recorded and the dispersion in the measured data for the matrix elements is shown in Table 5 and plotted in Fig. 9. Figure 9 shows the deviation σ in the actual and the measured data for all the matrix and trace elements at different collection charges. It is clear from the plot that the measured and the actual data (which is already known) are in very good agreement.

In this sample, Cd is the major element (whose concentration is 99% or above) and all other elements are minor (1% or less). The deviation in the data for all the elements is less than 1%, which shows the ability of the PIXE technique for multi-elements composition study in a sample.

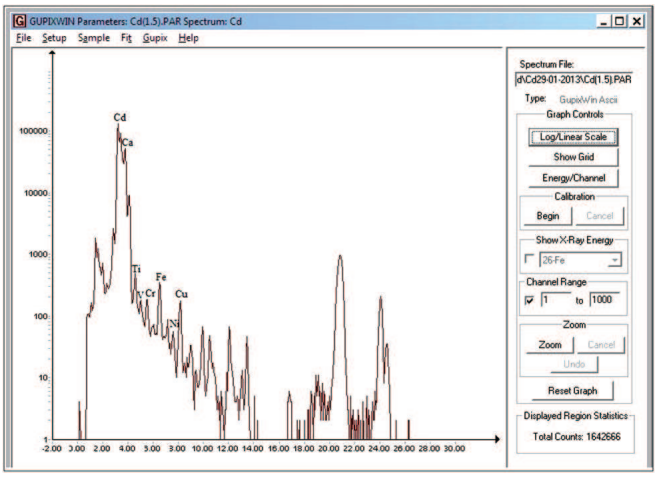


Fig. 8. (color online) PAR-file spectrum of the cadmium sample obtained from the measured data after processing using the GUPIXWIN software.

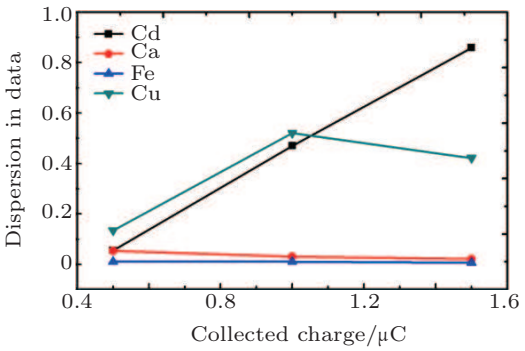


Fig. 9. (color online) Dispersion vs. collected charge plot for the cadmium sample.

Table 5. Comparison of the measured and the actual composition of cadmium sample for different collection charges measured at different dates.

Q/μC	Element	Meausred at 29-01-2013	Meausred at 11-02-2013	Average of measurement	Difference	σ
1.5	Cd	99.151%	98.4%	97.3267%	1.4584%	±0.8591%
	Ca	0.0933%	0.0481%	0.07843%	–	±0.02146%
	Fe	0.1365%	0.1473%	0.1393%	–	±0.00647%
	Cu	0.0734%	0.0874%	0.07717%	–	±0.4217%
1	Cd	98.842%	99.991%	99.601%	0.399%	±0.47%
	Ca	0.092%	0.0497%	0.089%	–	±0.03093%
	Fe	0.13%	0.1537%	0.1396%	–	±0.01062%
	Cu	0.0725%	923.1%	0.10046%	–	±0.5208%
0.5	Cd	99.067%	99.1857%	99.1071%	0.8929%	±0.056%
	Ca	0.0942%	0.0497%	0.11707%	–	±0.053144%
	Fe	0.1284%	0.1537%	0.14147%	–	±0.010345%
	Cu	0.0689%	0.1050%	0.1063%	–	– ±0.13455%

4. Conclusion

The PIXE analysis was calibrated for finding the elemental composition of thick samples. Two NIST samples and one local sample of known composition were analyzed using the PIXE technique and the GUPIXWIN software. Using the PIXE technique, the data from the samples were acquired at two different times for three different collection charges. The experimentally measured elemental compositions of all the samples was in good agreement with the already known concentrations of the samples. In the stainless steel sample, only the difference between known and measured data was calculated. In the TiV sample, the deviation of the matrix element concentration was calculated. The standard deviation is 0.1657% for Al, 0.15115% for V, and 1.5556% for Ti. Similarly for the Cd sample, the maximum standard deviation for the Cd element is 0.8591%. All other standard deviations are much less than 1% in both samples. This shows the reliability and feasibility of the PIXE measurement setup for multi-elemental analysis of thick samples.

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