

## Long Term Accuracy and Precision of PIXE and PIGE measurements for Thin and Thick Sample Analyses.

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### Abstract

This paper describes PIXE/ PIGE measurements on thin Micromatter Standard ( $\pm 5\%$ ) foils run over a period of 10 years. The selected foils were typically  $50 \mu\text{g}/\text{cm}^2$  thick and covered the commonly used PIXE X-ray energy range 1.4 keV to 20 keV and the light elements F and Na for PIGE studies. For the thousands of thick obsidian and pottery samples analysed over a 6 year period, the Ohio Red Clay (ORC) standard has been used for both PIXE and PIGE calibration of a range of elements from Li to Rb. For PIXE the long term accuracy could be as low as  $\pm 1.6\%$  for major elements with precision ranging from  $\pm 5\%$  to  $\pm 10\%$  depending on the elemental concentration. For PIGE accuracies were around  $\pm 5\%$  with precision ranging from  $\pm 5\%$  in thick samples to  $\pm 15\%$  in thin samples or for low yield  $\gamma$  ray production.

### Introduction

The accelerator based methods of PIXE and PIGE for multi-elemental characterisation of a broad range of thin and thick samples have become routine [1-7]. At ANSTO we perform these analysis techniques on a 36 year old 3 MV Van de Graaff accelerator which still operates 10 hours a day five days a week. We now have several data bases of thousands of analyses from regular customers. These span many years of work on both thick and thin samples. Typically we have used 2.6 MeV protons, with beam currents of 10 to 200 nA measured in a Faraday cup and beam diameters from 3 to 10 mm.

Where ever possible we have supply absolute elemental concentrations. These can be provided through an accurate knowledge of cross sections, input parameters and experimental conditions or through normalisation to known reference standards for each run [8-11]. Here we describe the accuracy and precision of PIXE and PIGE techniques from 10 years of analyses on thin Micromatter Standards and 6 years on a thick Ohio Red Clay (ORC) Standard. These standards were not fully certified reference standards.

### Thick Target Standards

Thick targets are defined as those for which the incoming ion loses significant fraction of its initial energy and/ or the outgoing X-ray or gamma ray are significantly attenuated. For thick target PIXE typically 80% of the yield originates from the first 30% of the ion range [11]. The range of 3 MeV protons in carbon is around  $75 \mu\text{m}$ , so even if the beam diameter is several millimetres, the actual sampled volume in PIXE is very small. It is important that this small sample volume is representative of the bulk of the sample itself. Furthermore, for small concentrations of trace elements particle size becomes important as to how many individual particles may be

present in the sampled volume. For example, for 3 MeV protons in carbon, ten  $5 \mu\text{m}$  diameter FeO particles corresponds to about  $8 \mu\text{g}/\text{g}$  of Fe. Whereas you need only one  $50 \mu\text{m}$  diameter particle to have about  $800 \mu\text{g}/\text{g}$  of Fe in the sampled volume. This implies sub  $10 \mu\text{m}$  particle diameters and trace element concentrations above  $200 \mu\text{g}/\text{g}$  if homogeneities due to particle size effects are to be unimportant in thick sample reference standards.

During the past 6 years obsidian and clay pottery thick sample have been analysed for over 20 different elements for sourcing and provenancing studies [12]. Fig. 1 shows a typical PIXE spectrum and PIXAN fit to the data obtained for  $50 \mu\text{C}$  of 2.6 MeV protons on ORC standard using a pinhole filter [9,11]. These fits provide the peak areas, fitting errors and minimum detectable limits (MDL) for each element present.

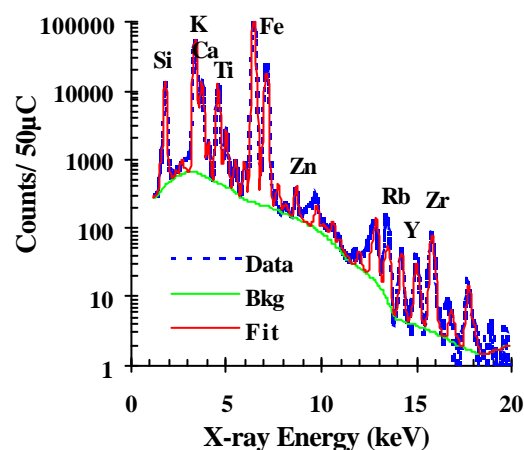


Fig. 1. Typical PIXE spectrum, using a pinhole filter, and PIXAN fit to the data [9,11] obtained for  $50 \mu\text{C}$  of 2.6 MeV protons on ORC red clay standard.

Absolute concentrations, from the elemental peak areas, were obtained in the standard way [11] after the current, solid angle and detection efficiency had been calibrated against the NBS278 Reference Standard. Fig. 2 shows a typical calibration curve for elements 11 elements, Si, Cl, K, Ca, Ti, Mn, Fe, Zn, Rb, Sr and Zr, spanning the X-ray region of interest, 2 keV to 16 keV. Adjustment of experimental parameters provided a good flat response with a mean [Measured/ Nominal] ratio of unity and a minimum standard deviation about the mean of  $\pm 3\%$ .

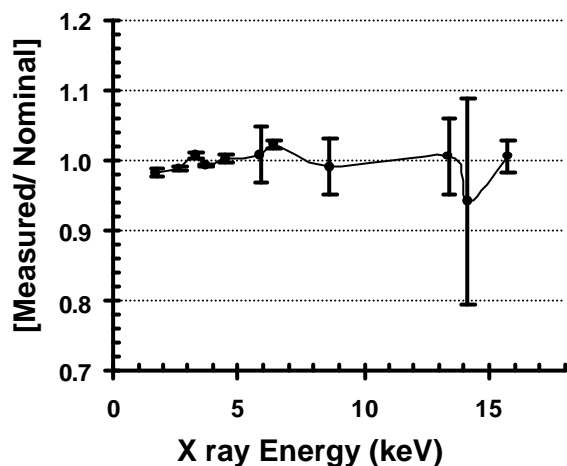


Fig. 2. Typical calibration curve for PIXE system using the NBS278 Reference Standard, 25  $\mu\text{C}$  of 2.6 MeV protons.

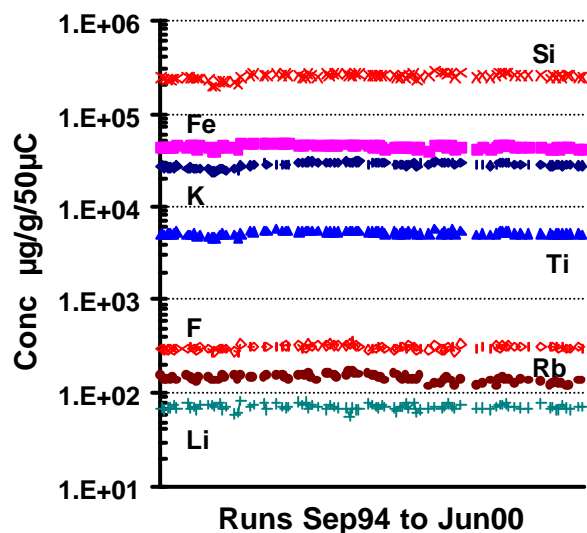


Fig.3. Concentration versus time for 7 key elements measured by PIXE/ PIGE on ORC standard for thick pottery and obsidians samples.

In order to better understand the long term accuracy and precision of our PIXE/ PIGE system 87 separate ORC red clay thick target spectra, obtained over the 6 year period (September 1994 to June 2000) were analysed under identical conditions. Fig. 3 shows the concentration

versus time plots for 7 key elements, Li, F, Si, K, Ti, Fe and Rb, present in the ORC standard. Elemental concentrations range from 25% for Si to 71  $\mu\text{g/g}$  for Li and are relatively flat with time. These concentrations are absolute with no scaling or normalisation, using the same single set of detector parameters for all runs.

The precision of the results is reflected by the spread about the mean or standard deviation of the mean and the accuracy is obtained by comparison with the recommended ORC values taking into account the quoted errors. Table 1 shows the nominal and measured concentrations, the percentage standard deviation of the means, the minimum detectable limits (MDLs) and the error on the measurements for the ORC sample. It is based on all of the 87 different ORC runs over the 6 year period. The measurement error used here included three components, the fitting/ counting error, the experimental system error ( $\pm 5\%$ ) and the reference standard concentration error ( $\pm 3\%$ ), all added in quadrature.

Elt	Nominal Conc $\mu\text{g/g}$	Measured Conc $\mu\text{g/g}$	SD %	MDL $\mu\text{g/g}$	Error %
F	310	310	$\pm 5$	18	6
Na	1,165	1,165	$\pm 5$	48	6
Li	71	71	$\pm 6$	7	8
Mg	7,032	7,032	$\pm 15$	2,515	19
Al	79,100	79,100	$\pm 4$	451	6
Si	246,300	250,877	$\pm 7$	1,574	6
K	29,420	28,216	$\pm 6$	49	6
Ca	3,385	3,268	$\pm 7$	75	6
Ti	5,343	5,269	$\pm 5$	24	6
Fe	44,220	44,027	$\pm 5$	14	6
Zn	82	83	$\pm 10$	7	8
Rb	151	143	$\pm 9$	9	7

Table 1 PIXE/ PIGE elemental concentrations, standard deviations, minimum detectable limits and analysis errors for thick ORC standard samples using 50  $\mu\text{C}$  runs and 2.6 MeV protons.

For thick target PIXE the long term absolute accuracy was  $\pm 1.6\%$  for major elements from Si to Rb well within the 6-9% measurement error. The corresponding precision ranged from  $\pm 5\%$  to  $\pm 10\%$  for all elements above their MDL and was typically lower than the measurement error. PIXE zinc measurements had the largest standard deviation about the mean, and hence the lowest precision, because it had one of the lowest elemental concentrations and may have been affected by particle size inhomogeneities as discussed above.

For the PIGE results there was no systematic variation with atomic number like there was for PIXE hence it was not possible to produce an equivalent plot to that shown in Fig. 2. Consequently, the mean of the 87 measured PIGE values was forced to be identical to the ORC nominal standard value. However the standard deviation

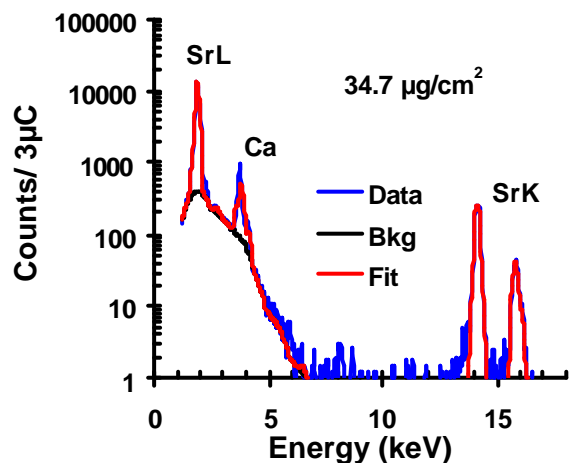
of the mean still provided an estimate of the precision of the measurements. For Al, Na, F and Li the standard deviation of the mean, or the precision, was less than or equal to  $\pm 6\%$ . Mg had a larger spread ( $\pm 15\%$ ) due to the exceedingly low ( $p,\gamma$ ) yields (relative to the other PIGE yields). This also explains the higher MDL for this element.

### Thin Target Standards

For PIXE and PIGE analysis samples thinner than a few hundred  $\mu\text{g}/\text{cm}^2$  are usually considered as thin targets since the proton energy loss in them is small.

Calibration standards were selected to span the energy range and elements of interest for each of the detection systems. Thin Micromatter standards of about  $50 \mu\text{g}/\text{cm}^2$  of Al, Si, NaCl,  $\text{CaF}_2$ , Fe and  $\text{SrF}_2$  samples evaporated onto thin Mylar backings were ideal for both the PIXE and PIGE systems used here.

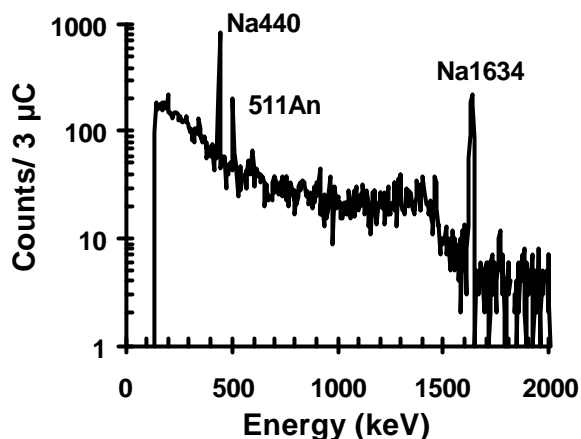
Typical PIXE and PIGE spectra obtained for a strontium fluoride and sodium chloride Micromatter Reference Standard are given in Figs. 4 and 5 respectively.



**Fig. 4.** Typical PIXE spectrum for  $50 \mu\text{g}/\text{cm}^2$   $\text{SrF}_2$  Micromatter Reference Standard

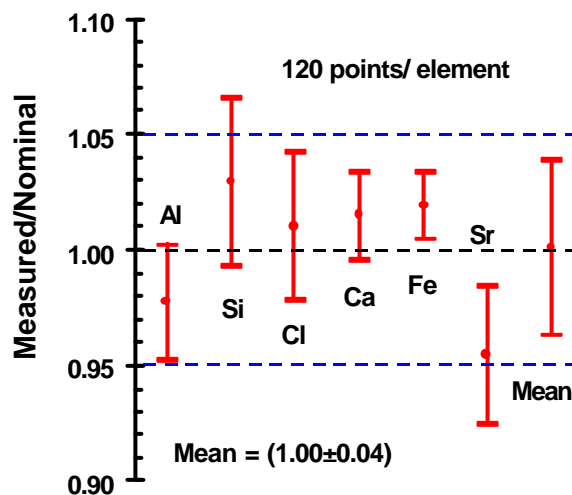
The PIXE spectrum is relatively clean except for some calcium contamination and the PIGE spectrum clearly shows the 440 keV and the 1634 keV lines from Na. We use the 440 keV line throughout this work for Na determinations as it had a higher yield.

The X-ray yields for elements from Si to Sr were larger than the  $\gamma$ -ray yields for elements F to Al reflecting the atomic rather than nuclear processes related to their origins. Hence for thin samples, when thin X-ray filters are also used, Al is generally estimated by the PIXE method rather than the less sensitive PIGE technique.



**Fig. 5.** Typical PIGE spectrum for  $47 \mu\text{g}/\text{cm}^2$  NaCl Micromatter Reference Standard

Fig. 6 is a comparison of the measured to nominal ratios for the 6 common Micromatter Reference Standards used in the thin target PIXE calibrations. Each point represents the mean and standard deviation of 120 different monthly measurements taken over ten years. The thin Micromatter Reference foils were quoted absolutely to  $\pm 5\%$ . The precision, defined as the long term standard deviation of the mean, as measured across all 6 Reference Standards using PIXE was  $\pm 3.8\%$ . The accuracy of the individual PIXE measurements can be seen in Fig. 6 with each element lying within the  $\pm 5\%$  quoted by the suppliers. However, Al (0.98) and Sr (0.95) were consistently lower than the quoted reference values and Si (1.03) was generally higher. This may have been due the PIXAN fitting routine procedures used. Gaussian peaks without tails were used for all peak area determinations [9,11].



**Fig. 6.** Measured to nominal ratios for 6 Micromatter Reference Standard foils used in PIXE calibrations from 1991 to 2001.

The X-ray detection efficiency was always significantly lower for Al than Si. Also background determination was

difficult at the few percent level required here for Al and Si peaks on the peak of the secondary electron bremsstrahlung background.

The Measured/ Nominal ratio for 120 independent Na and F measurements by PIGE is shown in Fig. 7. The  $\gamma$ -ray yields for thin targets are significantly reduced from their thick target counterparts and the larger standard deviations about the mean mainly reflect the poorer counting statistics.

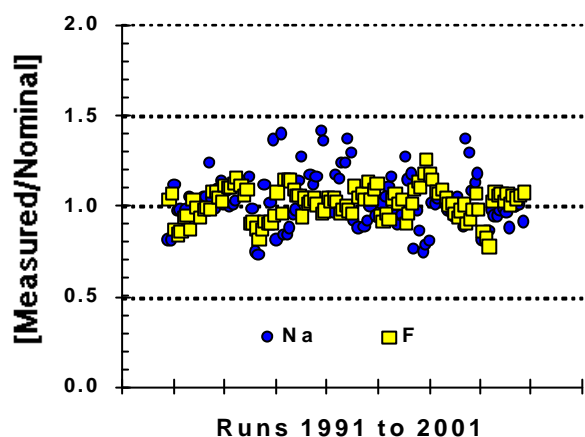


Fig. 7. Measured/ Nominal concentrations of Na and F for 120 different runs from 1991 to 2001.

The long term precision of the PIGE determinations was obtained from the standard deviation of the mean and found to be  $\pm 15\%$  for Na and  $\pm 9\%$  for F.

### Conclusion

In summary, accelerator based ion beam analysis (IBA) techniques, such as PIXE and PIGE, provided a very powerful, routine, multi-elemental analysis method for both thin and thick sample studies. They provided elemental information on a broad range of elements including, Li, F, Na, Mg, Al, Si, P, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Cu, Ni, Zn, As, Sr, Y, Zr, Br and Pb. However care should be taken for elemental concentrations below a couple of hundred  $\mu\text{g/g}$  that particle size effects do not affect the assumed homogeneity of the sample.

With careful calibration, setup and attention to detail long term accuracy and precision for both PIXE and PIGE techniques over many years are possible. PIGE being a nuclear and not atomic process generally has lower production cross sections and is more affected by variations due to low counting statistics. Thin samples were generally measured with slightly higher accuracy and precision than thick samples. For PIXE the long term accuracy could be as low as  $\pm 1.6\%$  for major elements with precision ranging from  $\pm 5\%$  to  $\pm 10\%$  depending on the elemental concentration. For PIGE accuracies were generally around  $\pm 5\%$  with precision ranging from  $\pm 5\%$

in thick samples to  $\pm 15\%$  in thin samples or for low yield  $\gamma$  ray production.

The ability to provide elemental concentration information on a broad range of elements across the Periodic Table means that statistical techniques such as principal component analysis and chemical mass balance programs can be applied to the large databases generated. This in turn provides further information for source fingerprinting and provenancing studies [4-7,12]. PIXE and PIGE techniques methods are truly well suited to quantitative, accurate and precise analysis of thin and thick samples.

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