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Implementing PIXE and PIGE at the Texas A&M University Cyclotron Institute

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Abstract. Accelerator-based Ion Beam Analysis (IBA) has been actively used at the Cyclotron Institute (CI) at Texas A&M University (TAMU) to support the undergraduate research program. PIXE (Particle Induced X-ray Emission) and PIGE (Particle Induced Gamma-ray Emission) are examples of traditional ion beam techniques for elemental analysis. In the past year, our laboratory has assembled PIXE and PIGE experiments with the intention of collaborating with other departments and universities in the study of contaminants' pathways to the environment and characterization of materials and, in addition, contribute didactically to undergraduates involved in the project. The implementation of routine PIXE and PIGE analysis at the CI allows students to perform elemental composition studies nondestructively, for a large number of samples in a variety of matrices (environmental or biological) with minimal time and sample preparation. The experiments were performed at the TAMU CI, using the K150 cyclotron. Each matrix was bombarded with a proton beam that ranged from 3.6 - 6.3 MeV, with an intensity between 5 - 9 nA and a beam spot size of 5 - 10 mm. The resulting x- and gamma-rays were measured with SiPIN, SDD and CdTe high-performance x- and gamma-ray detectors, located at 45^0 and 135^0 with respect to the beam direction. We will discuss our recent projects in detail and the impact they have on the research program and on undergraduate education.

INTRODUCTION

Ion beam analysis (IBA) is a set of analytical techniques using ion beams for studying structure and composition of samples. The K150 cyclotron at TAMU accelerates ion beams, which include protons, deuterons, helium, and other heavier ions [1]. PIXE (Particle Induced X-ray Emission) and PIGE (Particle Induced Gamma-ray Emission) are traditional ion beam techniques for elemental analysis [2]. The individual IBA techniques and detection system used are determined by which exit channel results from an interaction between an ion beam and the sample.

PIXE, for example, is used for determination of minor content of elements from aluminum to uranium. Each sample is bombarded with protons (or alpha particles), inducing x-rays characteristic for each element [3,4]. The technique is widely used for quantification of heavy metals in environmental and biological samples as well as studying vintage paints' composition.

PIGE is based on nuclear reactions induced by MeV protons producing prompt nuclear gamma-rays [5]. The energy of the gamma-ray is characteristic according to the identity of the isotope and its intensity gives a measure of the concentration of the isotope present in the sample. Gamma-rays are more energetic than x-rays, so the method allows the analysis of light elements in environmental and biological samples [6,7], resulting in PIGE being considered a complementary technique to PIXE in characterizing materials.

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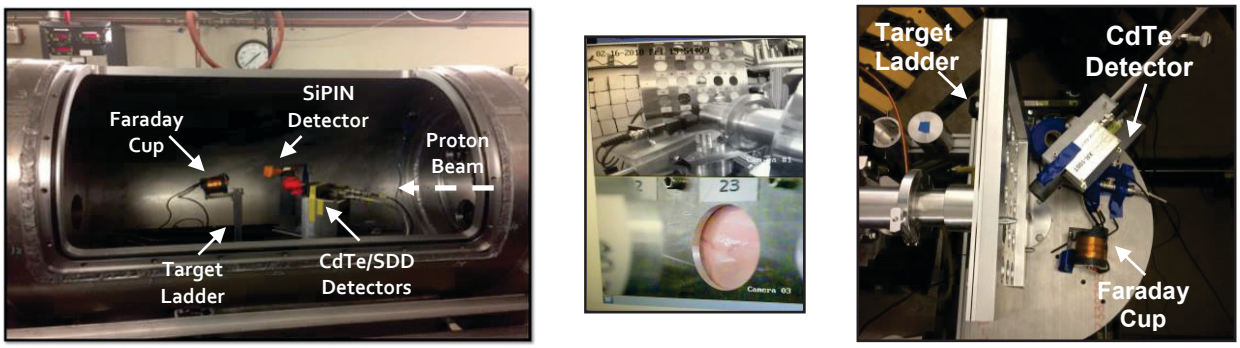
Both techniques allow multi-elemental, quantitative/semi-quantitative and quick analysis of the sample, with high sensitivity, non-destructive and minimal sample preparation. In addition, both use relatively easy instrumentation and analysis, hence, are appropriate for undergraduate students starting research using particle accelerators. The goal of this work is to implement a theoretical and experimental methodology to use PIXE and PIGE at the CI. In particular, we are focused on determining and optimizing the conditions of operation of the cyclotron, the instrumentation required to run these experiments and familiarizing students with the nuclear instrumentation and the computational interphase for quantification of elements and their concentration on samples.

EXPERIMENTAL SETUP AND MEASUREMENT

The pilot PIGE (PIXE) experiment was performed at the TAMU CI, using the K150 cyclotron over the course of a six (three) day run. Each sample was bombarded with a proton beam of 3.6 MeV, with an intensity of 5 - 9 (0.5 - 3) nA and a beam spot size of 5 - 10 mm. The resulting gamma (x) -rays were measured with a XR-100T-CdTe (XR-100/CR SiPIN) high-performance gamma-ray (x-ray) detector, located at 45º (135º) with respect to beam direction [8]. The gamma-ray detector consists of a 1 mm CdTe diode located behind a 4mil Be window, excellent for high detection efficiency applications, at energies up to 100 keV. For x-ray detection, a fully depleted 500 μm SiPIN photodiode with 0.5mil Be window is used and is 100% efficient up to 10 keV [9]. Figure 1 shows the experimental setups for PIXE (panel (a)) and PIGE (panels (b) and (c)).



(a) (b) (c)

FIGURE 1. Panel (a) shows the setup for the PIXE experiment. This includes the SiPIN and CdTe detectors, the Faraday cup and the five-position target ladder. The white dashed line indicates the beam path through the vacuum chamber. Panels (b) and (c) show the PIGE setup. In panel (b), a frontal view of the twenty-five position target ladder for holding samples is shown (upper part of the figure). The bottom part of the figure displays a toothpaste sample. Panel (c) shows a top view of the PIGE experimental set up. The beam is coming from left to right in the figure, which also displays the target ladder, the CdTe detector and the Faraday cup used in the experiment. (color online)

In the case of the PIXE pilot run, the experimental set up included a SiPIN, CdTe and Silicon Drift (SDD) detectors, a Faraday cup, and a target ladder mechanism, all placed in a vacuum chamber, as shown in Fig. 1(a). The CdTe and SDD detectors were used to corroborate the results from the SiPIN. The five-position target ladder mechanism was connected to a rod that allowed samples to be changed within the chamber without breaking vacuum. The target ladder had to be changed out frequently to test different samples and standards. After each target ladder change, an electron-suppressed Faraday cup was used to measure the beam intensity. Each run was approximately fifteen minutes long, whereas the beam intensity measurements lasted around two minutes.

For the PIGE pilot run the experiment was run in air and included a CdTe detector, a Faraday cup, and a twenty-five-position target ladder mechanism, as shown in Figs. 1(b) and 1(c). Each run was approximately ten to twenty minutes long. The beam current was measured for thirty seconds at the beginning and at the end of each day of measurements. Two characteristic gamma-rays from the decay of the ^{19}F nucleus were integrated (110 keV and 197 keV [10,11]), without interferences for total fluorine determination. The efficiency of the XR-100T-CdTe detector is about 40% at 100 keV and about 12% at 200 keV. The total number of counts in the two peaks, integrated per beam

current in target and per time of beam delivered, is proportional to the total fluorine concentration. The peaks are integrated above a linear background, which is determined by selecting manually four points about each peak and subtracting from the integrated peak counts.

RESULTS

PIXE

The main goal for the PIXE pilot run was to characterize the elemental composition and concentration of fourteen thin films of poly(diallyldimethylammonium chloride) (PDAC) and poly(styrenesulfonate) (PSS), supplied by the TAMU Chemical Engineering Department. The samples were treated with KBr, NaCl and other unknown salts.

We utilized the user-friendly Guelph PIXE Software Package (GUPIX) [12] to analyze the peaks. GUPIX fits spectra from layered matrices, based on a theoretical spectrum compared to filtered data. The fitting procedure is based on information on the detector and matrix inputs, windows, filters, bombarding ion type, incident energy and intensity of particles striking the target. Those parameters are tuned to obtain concentration values for the samples, using standards. The SiPIN detector was calibrated using standards (CsBr, InS, KCl, and NaCl) that provided a wide range of x-ray energies. Figure 2 shows the spectrum from a CsBr standard which included other noticeable elements such as Al, Ca, Fe, Cu, and Br. The x-ray emission lines (K_α, K_β, L_α, and L_β) were extracted from [13].

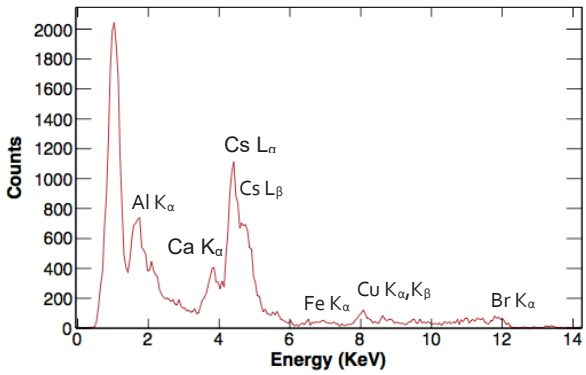
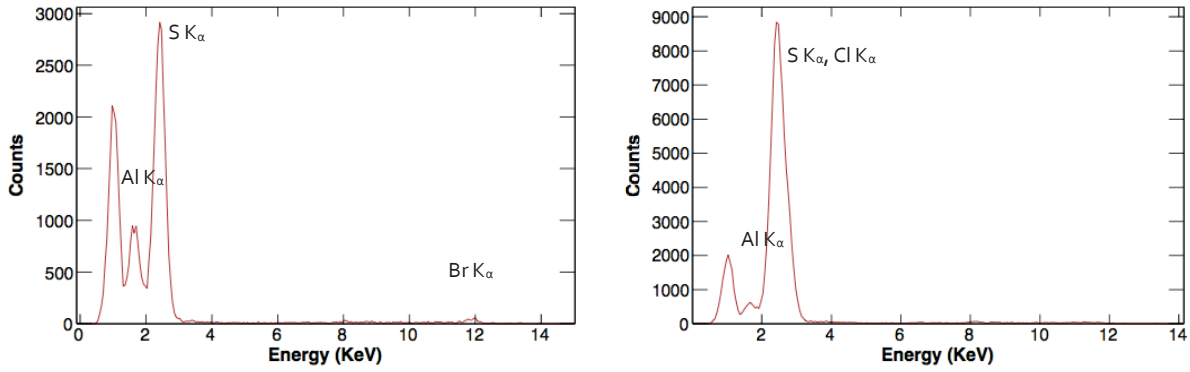


FIGURE 2. Spectrum measured with the SiPIN detector of the CsBr standard. Other noticeable elements in the spectrum included Al, Fe and Cu from the target ladder material.



(a) (b)

FIGURE 3. "KBr" and "NaCl" samples in panels (a) and (b) respectively. The "KBr" and the "NaCl" samples consistently showed high concentrations of S.

Figure 3 shows the spectra from one of the "KBr" and "NaCl" treated polymers, in panels (a) and (b), respectively. Additional elements found in the analysis included S, Ca, Al, Cu, and Fe, the first two were from residuals of PDAC and PSS, and the last three were from the target ladder.

To find the concentration of the elements in the samples, the GUPIX parameters of the standards were computed and then applied to the samples. We found very low concentration of K, while considerable amounts of Br and Cl and high concentration of S. We were not able to report the concentration of Na because the low energy of the Na x-ray made it indistinguishable from the electronic noise. The results are shown in Figs. 4(a) and 4(b) for the "KBr" and "NaCl" samples, respectively. The 10% error accounts for the uncertainty in the beam current estimation, the fitting procedure and the statistical uncertainty in the peak areas. The results are consistent, within uncertainties, with the information on the samples provided by the Chemical Engineering Department, demonstrating the utility of using PIXE for elemental composition studies.

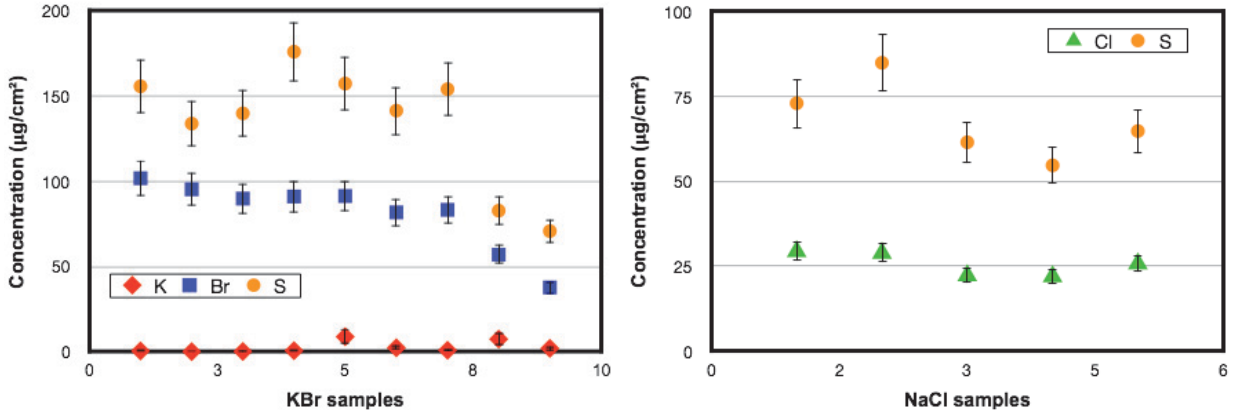


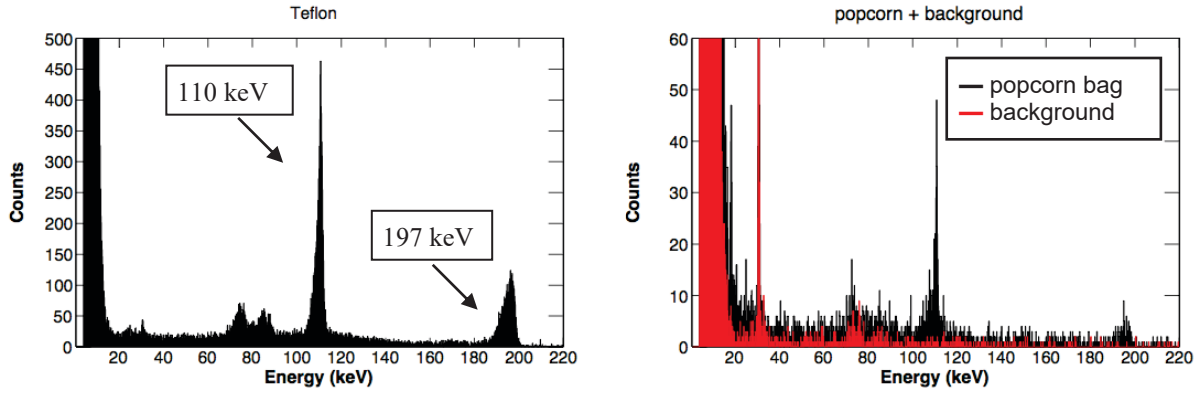
FIGURE 4. KBr and NaCl samples' concentrations, in panels (a) and (b), respectively, using GUPIX. High concentration of S was also found in the samples. (color online)

PIGE

The PIGE measurements were made on thirty consumer product samples (paper and textiles), that were all considered "thin samples" (thickness ranges from 0.20 mm to 0.65 mm, relative to the penetration depth of the protons used), hence, there is no self-absorption of emitted radiation inside the sample. For the textile samples, this is an approximation. Future campaigns will include thickness correction studies as in [14]. The samples studied for contamination from fluorinated compounds included paper wrappers from several fast food chains, carpets (including dog- and kid-proof carpets) and curtains. The unknown elemental concentrations are deduced by comparing the gamma-ray yields with those of an elemental standard. We used five paper standards and two inorganic standards. Choosing the beam energy was crucial since the gamma-ray emission cross sections must be constant over the beam energy loss in the sample. Figure 5 shows a typical gamma-ray spectrum from a PIGE measurement of a paper treated with a fluorinated compound: Teflon in panel (a), which has 50% F, and a typical spectra for a microwave popcorn bag (in black) and background (in red) in panel (b). Both panels show the distinctive ^{19}F peaks. Gamma-rays of known energies from ^{133}Ba, ^{241}Am and ^{57}Co sources were used for the detector calibration.

Figure 6 shows, in red and blue circles, the standards' concentration for the 110 keV and the 197 keV peaks, respectively, in addition to the samples' concentration in green stars. The y-axis is the measured yield normalized per integrated beam current and time while the x-axis is the concentration in units of particles per million. The black lines are linear fits to the fluorinated standards. The y- values of the samples (green stars) are the measured yields normalized per integrated beam current and time. The concentration value of the samples (x-axis) is determined from the fits to the fluorinated standards. Panel (a) shows our results for the papers and panel (b) for the textiles. We found fluorinated compounds in samples of McDonalds' paper bags and packages, microwave popcorn bags (from ACT II), pet-proof carpets and outside turf carpets (from Home Depot). The main error sources for elemental

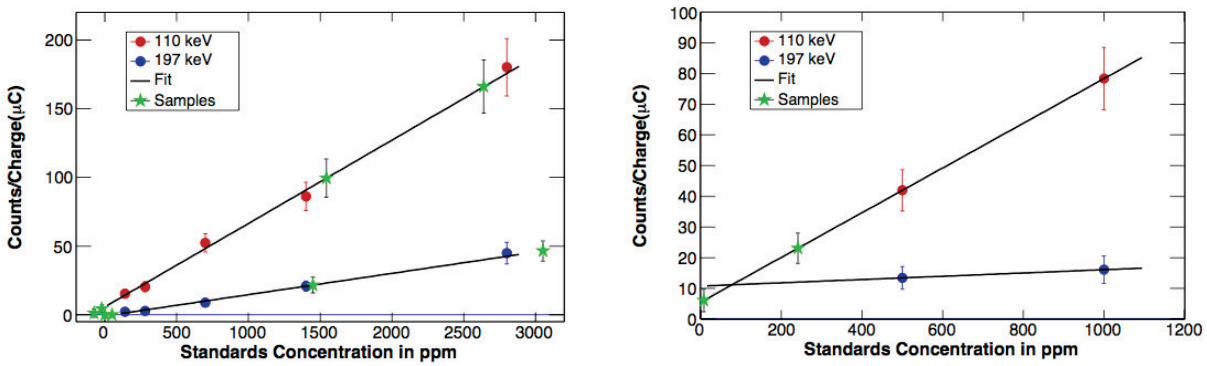
concentrations from PIGE typically come from the sum of independent uncertainties associated with the determination of the peak areas (*i.e.* gamma-rays counting statistics



(a) (b)

FIGURE 5. Typical gamma-ray spectra from PIGE measurements of fluorinated compound treated papers, from Teflon in panel (a) and a sample of a microwave popcorn bag (black) and background measurement (red) in panel (b). (color online)

and fitting uncertainties on background subtraction, depending on the limits of detection), and the integrated beam current measurement. Our relative error was about 10-20%. The limits of detection were 20-30 ppm for the 110 keV peak and about 150 ppm for the 197 keV peak.



(a) (b)

FIGURE 6. Fluorine concentrations for standards (in red and blue circles for the 110 keV and the 197 keV peaks respectively) and samples (in green stars) where fluorinated compounds were found. Panel (a) corresponds to the papers and panel (b) to the textiles. (color online)

Figure 7 shows the paper and textile standards measurements in units of nmol F/cm^2, integrating both the 110 keV and the 197 keV peaks, to be used as calibration to estimate our samples' concentration of fluorine and to be compared with literature. Based on the calibration curve, the concentrations of fluorinated compounds found in the samples were calculated and shown in Table 1 (middle column). The table also shows the concentration values reported in [14] (right column) for similar samples. The results are consistent.

The results show the utility of PIGE techniques for screening rapidly the presence of total fluorinated compounds in consumer products. Since the technique is non-destructive, after rapidly determining if a sample is fluorinated, a more elaborated method could be used to specifically identify the fluorinated compound in the product. The applications include environmental and human exposure studies.

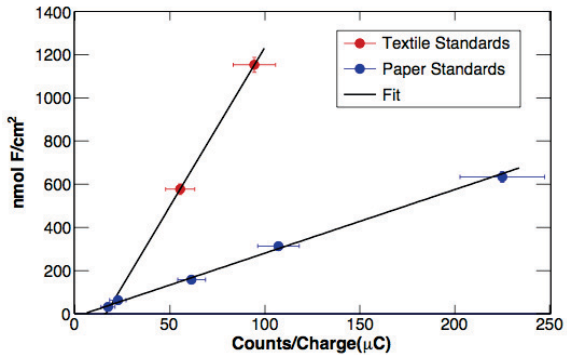


FIGURE 7. Concentration of the paper and textile standards in units of nmol F/cm^2, integrating the 110 keV and 197 keV peaks. (color online)

TABLE 1. Concentration of samples where fluorinated compounds were found in our pilot PIGE run (middle column) compared to literature [14] (right column).

Samples	Concentration (nmol F/cm^2)	Literature (nmol F/cm^2)
McDonalds' fries paper bag	340 ± 59	161-445
Popcorn bag	602 ± 90	161-445
Pet Proof Carpet	280 ± 84	78-113
Outside Turf	79 ± 43	78-113

SUMMARY AND OUTLOOK

In summary, the PIXE and PIGE pilot runs with the K150 cyclotron proton-beam were successful. Not only were samples' composition determined non-destructively and with minimal requirements for samples' preparation, but also the concentrations were calculated. Applications, in addition to basic research, can include lead and fluorine contamination studies, which have been linked to numerous potentially deadly health effects [15-17], and archeologic studies. In addition, these kinds of experiments have an enormous impact on educational programs demonstrating that (nuclear) applied physics can be part of the bridge connecting basic physics with the "real world". Finally, developing these projects and running the associated experiments, granted us participation in the REU (Research Experiences for Undergraduates) Cyclotron Institute program for two consecutive years.

Our future plans include involving in this project students from multidisciplinary backgrounds (*i.e.* Chemistry, Chemical Engineering, Physics, Public Health, Archeology, etc.) expanding the impact of PIXE and PIGE studies to different departments in the university, but also other universities and laboratories. In particular, we want to develop future projects with potential social impact linked to health and environmental applications.

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