Implementation of PIGE analysis in the Texas A&M Cyclotron Institute

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Introduction

Ion beam analysis (IBA) is a set of analytical techniques using ion beams for studying structure and composition of samples. PIXE (Particle Induced X-ray Emission) and PIGE (Particle Induced Gamma-ray emission) are examples of traditional ion beam techniques for elemental analysis [1]. The individual IBA techniques are distinguishable by the different exit's channels following after each interaction between the ion beam and the solid target. Particles emitted after the reaction suggest, therefore, the use of a specific type of detection system.

For example, PIXE is used for determination of minor content of elements from Aluminum to Uranium. Each sample is bombarded with protons (or alphas), inducing x-rays that are characteristic for each element. The technique is widely used for quantification of heavy metals in environmental and biological samples as well as studying vintage paints' composition [2].

PIGE, on the other hand, is based on nuclear reactions induced by MeV protons (mainly), where prompt nuclear gamma rays are produced and detected [3]. Considering gamma rays are more energetic than x-rays, the method allows the analysis of light elements in environmental and health related samples [4,5], resulting in PIGE being considered a complementary technique for PIXE in characterizing materials. PIGE is also of interest for energy calibration procedures in accelerators [6], among other applications, and without a doubt, is the most common application of nuclear analysis, both for fundamental physics and analytical applied projects.

PIGE analysis is based on the detection of the prompt gamma rays emitted from the excited nuclei following the nuclear reactions (p, γ), (p, p' γ), (p, α γ), and (p, n γ) induced by protons. The energy of the gamma-ray indicates the identity of the isotope and its intensity gives a measure of the concentration of the isotope present in the sample. PIGE is a multi-elemental method, with high sensitivity and has the advantage of being isotopic in nature with virtually no interference.

In the past year, our laboratory has assembled PIXE and PIGE experiments with the intention of systematically partake with other departments and universities in the study of contaminants' pathways to the environment and characterization of materials and, in addition, contribute didactically to students involved in the project.

Recently, one of our collaborators has been working on an interesting research regarding the study of fluorinated chemical substances [7]. The authors highlight that per and polyfluoroalkyl substances (PFASs) have been detected in a wide range of household products but also food contact materials (FCMs). The latter particularly, may contribute to raise awareness in entities making health policies regarding the fact that this substances can migrate into food, indoor air, dust, etc, contributing to human exposure. Already, epidemiological and toxicological studies in humans and animals, respectively, have found bounds between exposures to some PFASs and different types of cancer, thyroid disease, pregnancy induced hypertension and immune-toxicity in children, among other health effects [8-

10]. Moreover, the exposure to PFASs from fast food packaging must be worse in children according to [7], mainly because in the USA, 1/3 of the children are high consumers (daily) of fast food, and all in all, because in general children are more susceptible than adults to the adverse health effects associated. Nevertheless, PFASs are still globally produced in a wide range of products.

Traditionally, the main screening methods to detect fluorinated chemicals have been HPLC (chromatography) and MS (mass spectroscopy) [11], but PIGE allows to determine total fluorine quickly, no matter the origin of the matrices [12,13].

The implementation of PIGE serves to analyze, non-destructively, a large number of samples and variety of matrices (i.e. environmental or biological), with minimum time frame and requirements for sample's preparation and analysis, and without interferences for determination of total fluorine.

Experimental setup and measurement

The experiment was performed at Texas A&M University Cyclotron Institute, using the K150 cyclotron. Each standard/sample 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 gamma-rays were measured with a XR-100T-CdTe high performance x-ray and gamma-ray detector, located at 45º and 135º with respect to beam direction [14]. The detector consists of a 1mm of CdTe diode thickness located behind a 4mil (100μm) Be window and it is excellent for high detection efficiency applications, at energies up to 100 keV, due to its high stopping power. The specifications about the detector were taken from [15]. Fig. 1 shows the experimental set up.

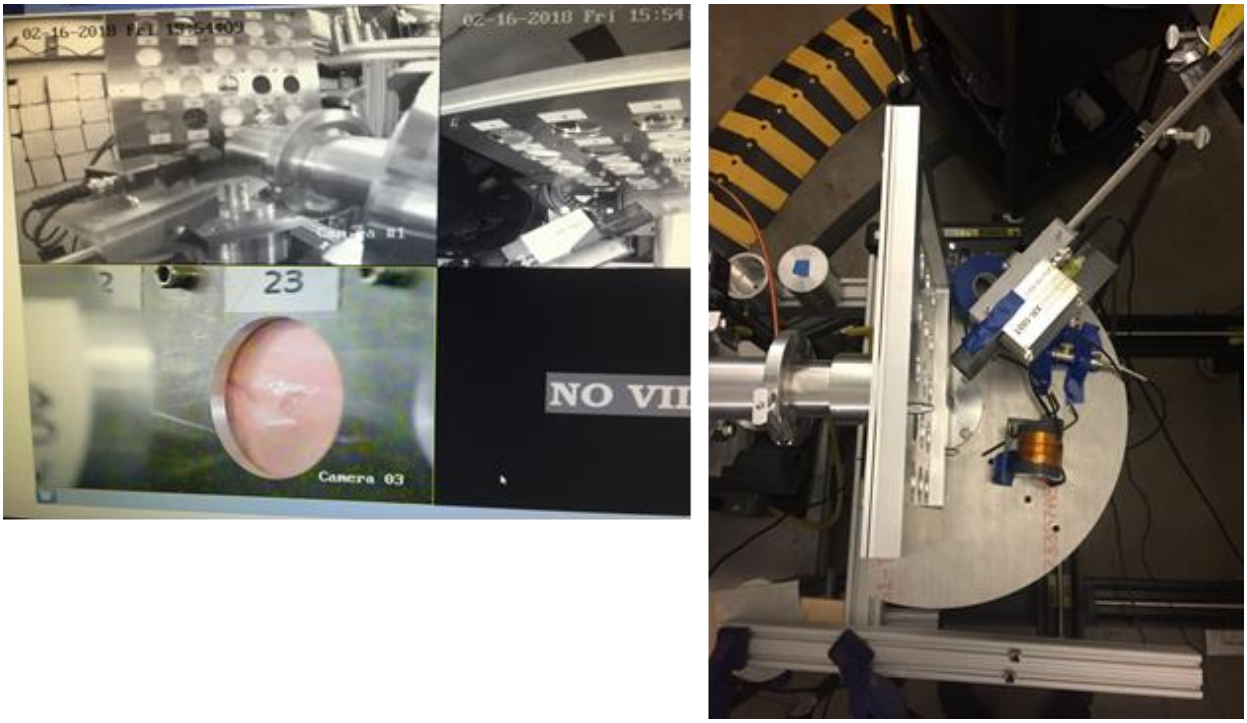

FIG. 1. Left panel shows the target ladder with 25 standards and samples. On display, the toothpaste sample. The right panel shows a top view of our experimental set up. Beam is coming from left to right in the figure, which also displays the target ladder, the CdTe detector and faraday cup.

The analysis of these results are currently in progress. The beam current was measured for 30s at the beginning and at the end of each day of measurements. A linear regression is used to estimate the delivered beam current. Two characteristic gamma rays from the decay of the ^{19}F nucleus will be integrated (110 keV and 197 keV [13]). 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, per beam current in target, per time of beam delivered, is proportional to the total fluorine concentration. The peaks are integrated above a linear background built by selecting manually four points about each peak and subtracting from the integrated peak counts.

Results

The measurements were taken in 30 consumer product samples (paper and textiles), all considered "thin samples" for the purpose of this analysis (i.e. thickness ranges from 0.20 mm to 0.65 mm, as in [7]). The standards used were provided by Dr. Graham Peaslee from University of Notre Dame. We performed measurements in 6 paper standards and 4 inorganic standards. Fig. 2 shows a typical gamma-ray spectrum from a PIGE measurement of a fluorinated compound treated paper (from a

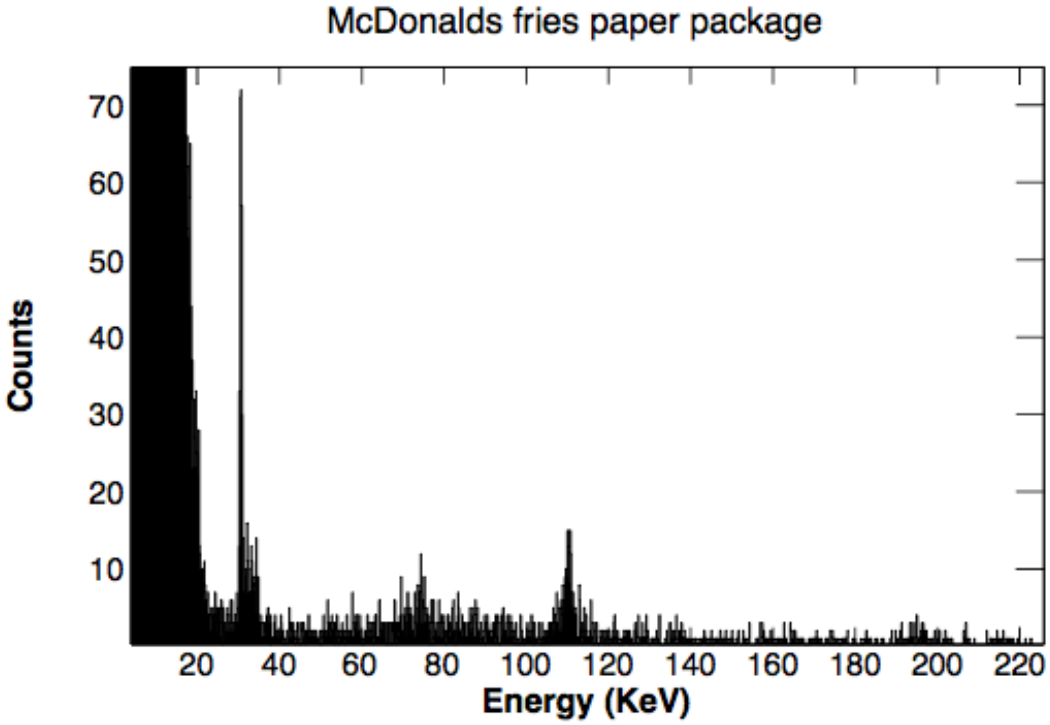

FIG. 2. Typical gamma-ray spectrum from a PIGE measurement of a fluorinated compound treated paper, from a McDonald's fries bag.

McDonald's paper fries bag). The sources of errors for each PIGE measurement come typically from the errors associated with the background subtracted peak and the uncertainty in the integrated beam current measurement. The total uncertainty is estimated to be around 10%. Fig. 3 shows our paper standards measurements, to be used as calibration to estimate our samples' concentration of fluorine. Based on the calibration curve, the concentration of the samples where fluorinated compounds were found were

calculated and are shown in Table I. The table also shows the concentration values reported in [7] for the same type of samples. Both results seem consistent.

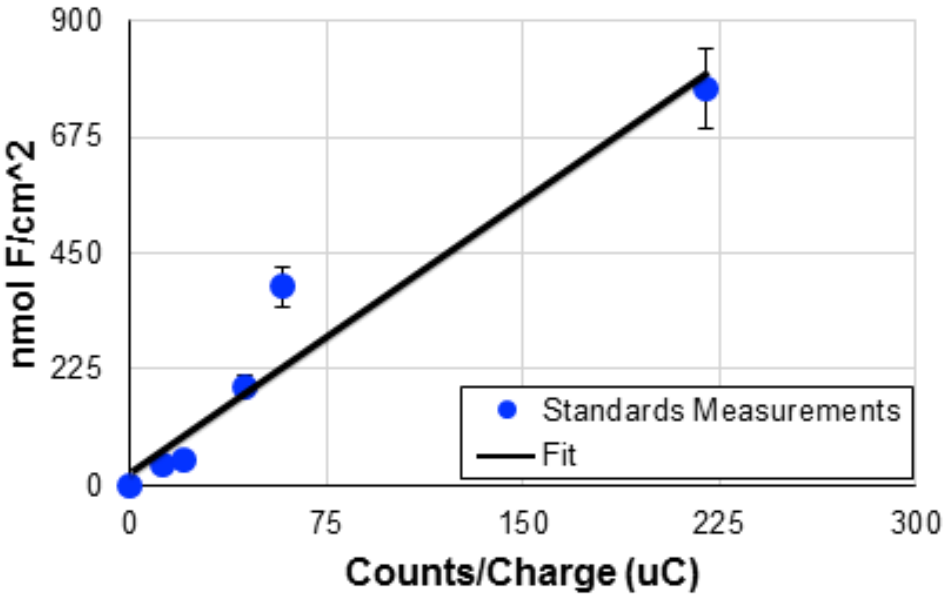

FIG. 3. Paper standards' concentration in nmol F/cm^2 as a function of the counts per charge.

Table I. Concentration of samples compared with literature.

Samples	**Concentration (nmol F/cm^2)**	**Literature** [7] **(nmol F/cm^2)**
McDonald Fries	335 ± 35	161-445
Happy Meal Box	572 ± 57	161-445
Popcorn	733 ± 73	161-445
Pet Proof Carpet	161 ± 16	78-113
Outside Turf	90 ± 9	78-113

The work is still in progress but already the results from the data show the utility of using PIGE techniques for rapid screening for the presence of total fluorinated compounds on consumer products. In addition to that, considering is a non-destructive method, 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 studies and human exposure studies.

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