Development of a Robust Quantitative Analysis Procedure for PIGE Spectra

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Introduction

Per- and polyfluoroalkyl substances (PFAS) are man-made chemicals that have become a major environmental concern[1]. They can be found in a broad range of products including food packaging, stain- and water-repellent fabrics, nonstick products, makeup, fire-fighting foams, and electronics. PFAS pose a significant risk to the public due to their adverse health effects[2,3]. In addition to this, they are persistent, bioaccumulate, and do not break down in the environment. We aim to employ proton induced gamma ray emission (PIGE) to screen for these hazardous chemicals within our samples. By using PIGE, we are able to clearly see the fluorine peaks, a key identifier of PFAS, within our spectra. Furthermore, PIGE is a powerful technique that is quick and efficient as well as non-destructive. While this analysis method has been developed at other research institutes across the country[2], it is our goal to develop it at Union College so we can begin screening potential hazardous sources of PFAS.

PIGE

Proton induced gamma-ray emission works by bombarding a sample with a beam of protons produced in an accelerator[4]. As the protons penetrate the sample, there are instances where the protons inelastically collide with a nucleus leaving it an excited state. When the nucleus de-excites it releases a gamma-ray which can be detected. The energy of the gamma ray identifies the element and the intensity of gamma-rays at a particular energy can be used to determine the concentration of the element. The PIGE process is illustrated in Figure 1. In UCIBAL, the samples are bombarded in air using our external beam facility and the gamma rays are detected with a high-purity Germanium detector. This experimental setup is shown in Figure 2.

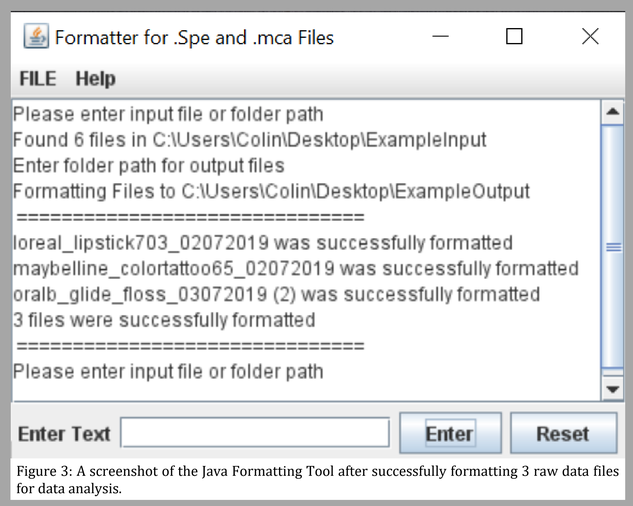

Figure 3: A screenshot of the Java Formatting Tool after successfully formatting 3 raw data files for data analysis.

Analysis Method

Goal: To develop an effective and efficient method to quickly format and fit PIGE spectra to determine gamma-ray yields

1. Format: Employ a code to quickly format raw data files to be easily read into fitting and graphing software.
2. Fit: Use fitting software to fit Gaussian functions to critical peaks in order to determine gamma-ray yields.
3. Analyze: Compare gamma-ray yields to well known standards to determine concentration range or use Emitted Radiation Yield Analysis[5] to achieve precise results.

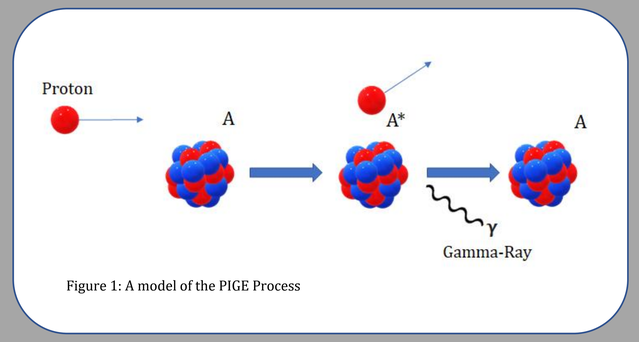

Figure 1: A model of the PIGE Process

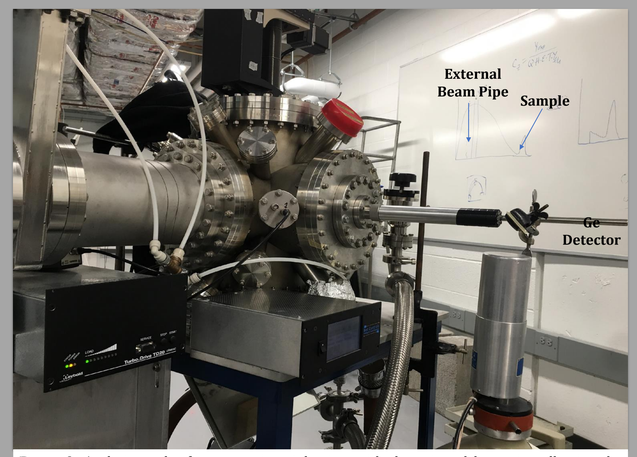

Figure 2: A photograph of our experimental setup with the external beampipe allowing the protons to collide with the target in the air. Also pictured is the Ge detector used to detect the Gamma Rays.

Formatting Tool

The formatting tool is a java program written specifically for use in the Union College Ion Beam Analysis Laboratory. The purpose of the tool is to quickly format raw data files for data analysis. This is done by reading and writing the relevant data to a new data file with the inclusion of a calibrated energy column generated by using the specified energy fit of the germanium detector. An example format is shown in Figure 3.

Fitting

Fitting the peaks are vital in order to determine the amount of gamma rays emitted at each specific energy. For our purposes, we are purely focusing on the yield of the peaks associated with the energy values of Fluorine (110 and 197 keV). To fit the necessary peaks, we employed the use of the software Fityk; a program designed for data processing and nonlinear fitting[6]. In this program, we were able to manually remove the background using a spline function before fitting the appropriate peaks to a gaussian function. This then produced the yield counts by calculating the area under the created function. An example of this fit is displayed in Figure 4: a fitted spectra of data taken on Oral-B Glide Floss. The statistical analysis of the fit is shown in Figure 5 to illustrate the goodness of the fit and the validity of the fit method.

Quantitative Analysis

The final part of the analysis process is taking the fitted yield counts and determining quantitative concentration values. This can be done in two different ways:

1. The yield values can be compared with known standards to determine a range of possible concentration values. By comparing element yield values to yield values of a known amount of the same element, concentration values can be resolved within a certain range of values. However, this method does not allow for precise concentration values as the actual values will most likely fall in between two standards. An example of an initial standard is shown in Figure 6.
2. The other option is to use ERYA to simulate the possible concentration values based off of the generated yield values. This program provides a comprehensive way to generate concentration values but requires a vast understanding of our experimental setup values and detector specifications.

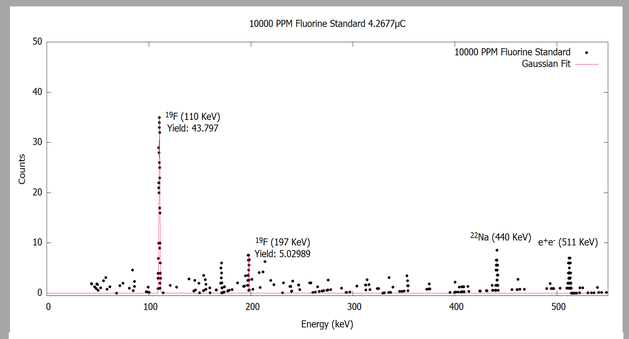

Figure 6: Fitted PIGE spectra for 10000 ppm Fluorine standard taken over 5 minutes with recorded charge collection of 4.2677 Micro Coulombs.

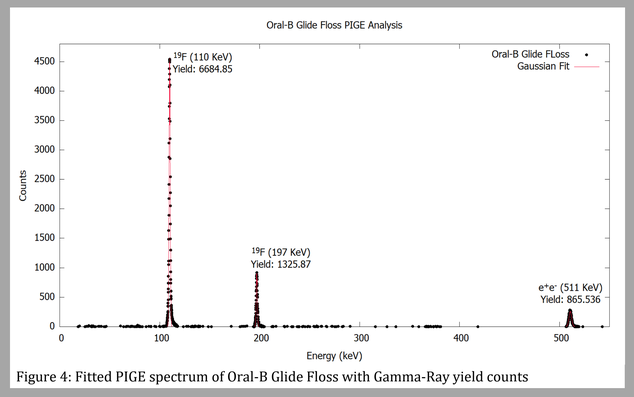

Figure 4: Fitted PIGE spectrum of Oral-B Glide Floss with Gamma-Ray yield counts

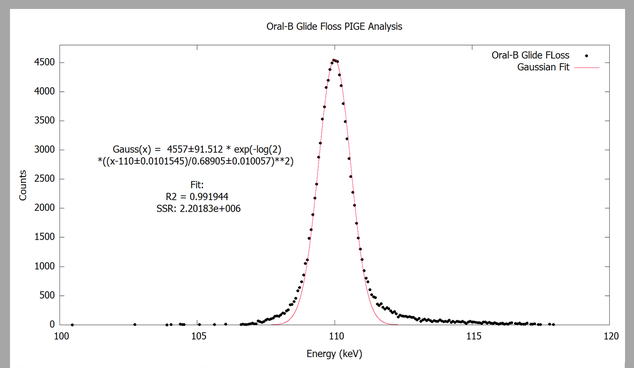

Figure 5: Zoomed in graph of Figure 4 to show goodness of fit along with statistical residuals.

Future Work

In the future we will continue work on developing precise standards for numerous concentration values. These will provide us a comprehensive method for quickly determining concentration range values for any potential PFAS contaminated sample. Along with these standards, we will continue to work on employing ERYA by learning the software and making any necessary experimental setup modifications. With the completion of this quantitative analysis procedure, we will be able to screen a wide variety of materials for hazardous levels of PFAS.

References

[1] See for example: Turkewitz, Julie. Toxic 'Forever Chemicals' in Drinking Water Leave Military Families Reeling. The New York Times, 2019

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[3] Basic Information on PFAS, EPA.gov, 2019

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