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A Comparative Study of GUPIX and GeoPIXE Software in the Analysis of PIXE Spectra of Aerosol Samples

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A Comparative Study of GUPIX and
GeoPIXE Software in the Analysis of
PIXE Spectra of Aerosol Samples

By

Sean Collison

Submitted in partial fulfillment
of the requirements for
Honors in the Department of Physics

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ABSTRACT

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ADVISOR: Mike Vineyard

Proton-induced X-ray emission (PIXE) spectroscopy is a powerful tool used in the Union College Ion-Beam Analysis Laboratory for the elemental analysis of environmental pollution. Samples are bombarded with proton beams from the 1.1-MV Pelletron accelerator and characteristic X-rays emitted from the samples are detected, resulting in X-ray energy spectra. These spectra are analyzed using software packages that fit the data and calculate the concentrations of elements in the samples. I have performed a comparative study of two of the most popular software packages, GUPIX and GeoPIXE, in the analysis of atmospheric aerosol samples to assess the strengths and weaknesses of each and determine which is the best package to use in our analysis. While GeoPIXE has transparency in the way it deals with its fit of the background, GUPIX is the far more trustworthy and consistent of the two software packages.

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1. Motivation

Acid rain in the Adirondacks has been a consistent issue that can cause adverse health effects to those living in the area as well as the environment. Acid rain results when sulfur dioxide (SO_2), nitrogen oxides (NO_x) and ammonia (NH_3) combine with moisture to produce sulfuric and nitric acid. Major sources of these chemicals are coal-fired power plants, vehicles and factories. In addition to these nearby factors, wind blows pollutants from the Midwest heavy industries to the Adirondacks.

Once the pollution arrives, it destroys the balanced chemistry of the lakes. The lakes, as a result, have declining fish populations. In addition, as surface water becomes acidic, mercury continues to be deposited in the lakes. This makes consuming fish caught in the Adirondack lakes unsafe to eat, especially in women and children. Unfortunately the Adirondacks do not have limestone deposits or soils to neutralize the acid, thus they have a low buffering capacity. According to the Department of Environmental Conservation, 26% of lakes cannot lower their acidity to a tolerable level, and 70% have the potential to become too acidic at certain times of the year. Also, 16 of 48 surveyed lakes showed aluminum levels too high. Since 1990 when Congress revised the Clean Air Act to require controls on sulfur dioxide and nitrogen oxide emissions, the levels have declined. However, they have not decreased to the point of which they are not a problem [1]. The Environmental Protection Agency predicted that “If acidic deposition levels were to remain constant over the next 50 years (the time frame used for projection models), the

acidification rate of lakes in the Adirondack Mountains that are larger than 10 acres would rise by 50 percent or more” [2].

The pollution is not solely detrimental to humans in that it has adverse effects to geology, plants, and wildlife in the area. According to the Adirondack Museum “Hundreds of lakes and ponds once teeming with trout and tadpoles, frogs and salamanders, are now clear and empty of such life. Also gone from these lakes and ponds are creatures higher on the food chain, such as otters, osprey, and loons” [3]. Clearly this is a problem important not just to people in the area, but to the future of the wildlife in the Adirondacks.

Getting accurate and consistent results for the elemental composition and concentrations of aerosol samples is vital when investigating air pollution. To determine these concentrations, we will use a technique called Proton Induced X-ray Emission Spectroscopy. Broadly, PIXE allows us to measure characteristic X-rays in order to gain information about our samples. Our goal is to draw conclusions about the ability of two software packages, GUPIX and GeoPIXE, to fit our spectra well and also agree with each other. In addition, we will examine GUPIX and GeoPIXE more generally to determine other strengths and weaknesses they might have.

2. Theory

In order to determine elemental composition, we use Proton Induced X-Ray Emission (PIXE) Spectroscopy. It is an ion-beam analysis technique that is used to discover not only what elements are in an unknown target, but the concentration of

those elements. PIXE is a very useful and non-destructive technique most commonly used by geologists, archaeologists, and others. Henry Moseley was the first to recognize this effect in 1913, but PIXE was really used as an analysis technique beginning in the mid 1970s. PIXE, however, only provides information on elements between Sodium ($Z=11$) and Uranium ($Z=92$). Figure 1 shows x-ray energy spectra obtained with PIXE vs. a similar technique called EDS (energy dispersive spectroscopy) and it is clear that PIXE produces much more defined peaks [4].

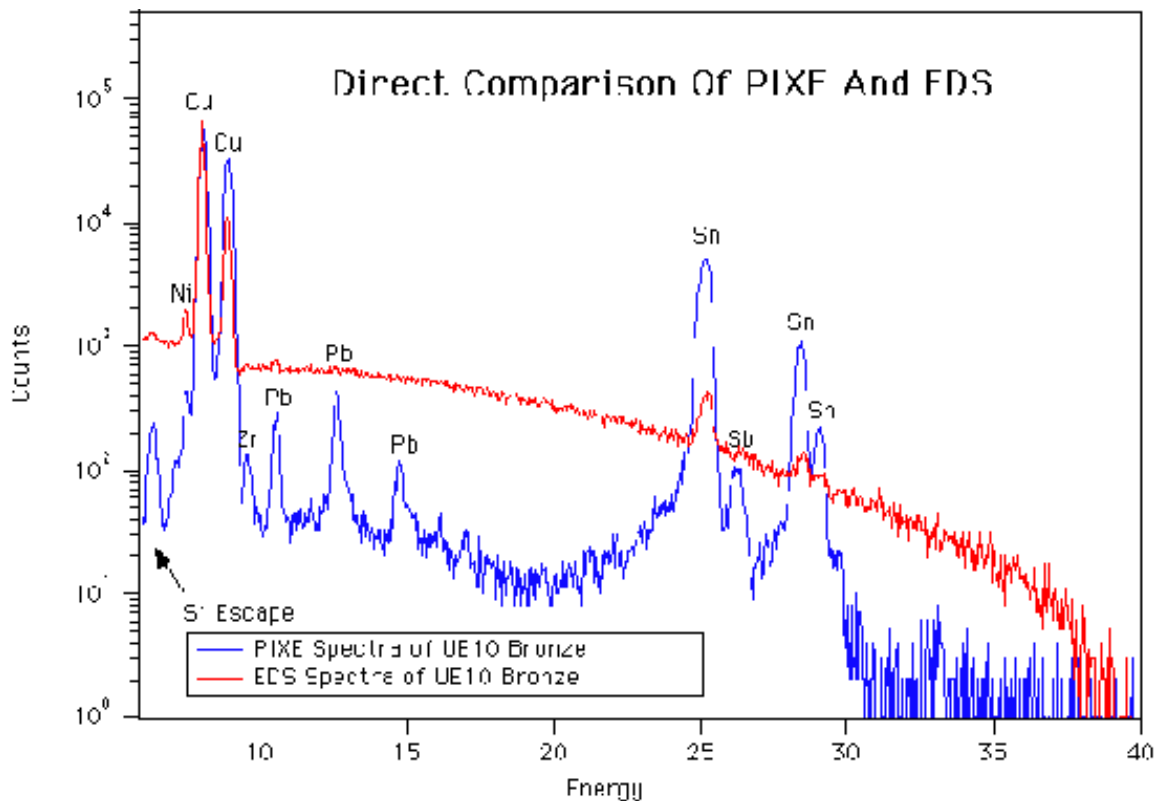


Figure 1: A comparison of x-ray energy spectra obtained with PIXE (blue) and EDS (red) [4].

We use an accelerator to produce proton beams with energies of a few MeV and bombard the targets with these protons. Occasionally a proton knocks out an electron from the inner shell of a given atom. With an empty spot in the inner shell,

the atom is no longer in its lowest energy state. Therefore, an electron moves from an outer shell to fill the void. When this happens, a characteristic x-ray is emitted. Because the energy of this x-ray is unique to each atom, if we can measure the energy we can determine the atom. In this particular experiment, we will only be looking at K and L transitions for our elements. K transitions involve an electron transitioning from any higher n -level to the $n=1$ state. The L transitions involve an electron transitioning from any level higher than $n=2$, to the $n=2$ state. Shown in Figure 2 is an atomic energy level diagram illustrating these transitions.

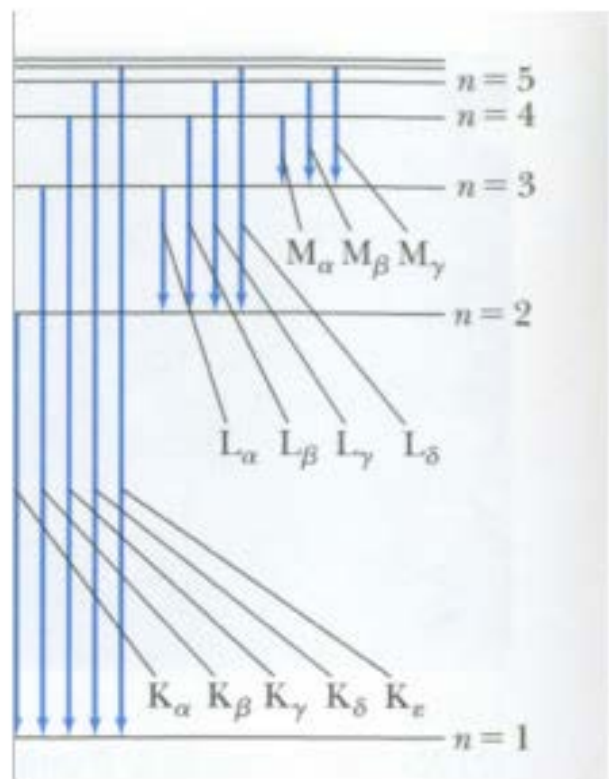


Figure 2: An atomic energy level diagram showing the K, L, and M transitions.

Knowing these discrete energy levels we can determine what elements are present in the sample, but this is only a part of the information we are looking for.

Not only do we want to find what elements are present, but we want to find how much of those elements there are. In order to do that, our software uses Equation 1.

$$C_z = \frac{Y_z}{Y_t \epsilon QTH} \quad (1)$$

Here C_z is the desired concentration in mass per unit area, the Y_z is the sample x-ray intensity, Q is the charge collected, ϵ is the efficiency of the detector, T is the coefficient of transmission for X-rays through any absorbers between the target and the detector, and H is the solid angle of the detector. The values in the denominator are calculated or determined during the experiment; therefore finding the sample x-ray intensity allows the software to determine the concentration.

3. Experimental Procedure

3.1 Sample Collection

The aerosol samples were collected using a PIXE International, nine-stage cascade impactor. A schematic diagram of the impactor is shown in Figure 3. Here you can see the 9 different stages as well as their cutoff in microns. Their cutoff is basically an indication of the size of particles one can expect to see at each stage. Since the particles are filtered using aerodynamics, it is clear that at the top we have the larger particles followed by subsequently smaller and smaller particles until the bottom where we have all of the leftover “after filter” particles. They are separated into different Particulate Matter (PM) sizes shown on the far left of Figure 3.

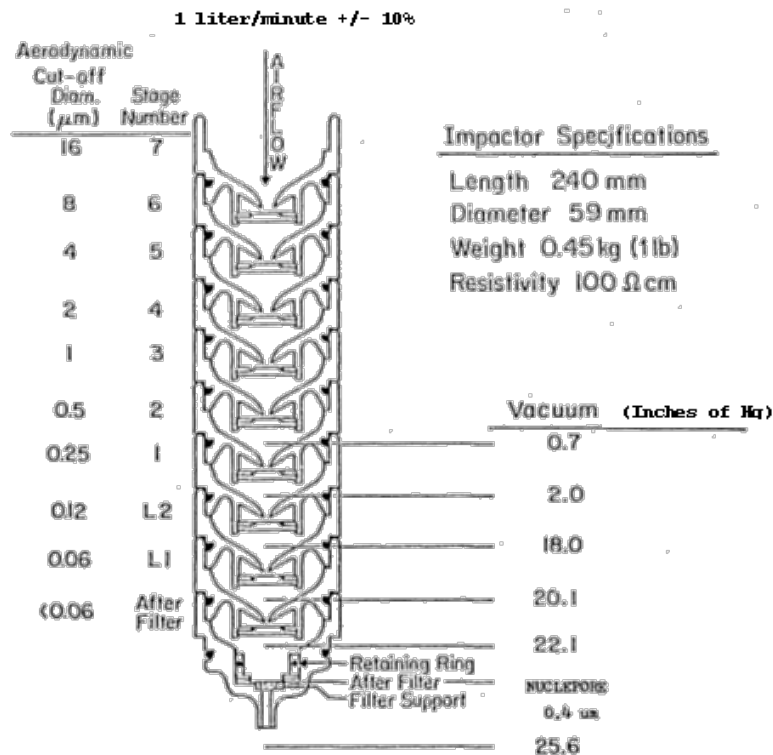


Figure 3: A Schematic Diagram of the cross section of the International Cascade Impactor.

Setting up the impactor was a fairly straightforward process. First, we needed to clean it by removing each of the stages and applying methanol to them. Then we needed to replace each one of the previously used Kapton foils with new ones. Once we did this, we put the stages back on in the correct order and our impactor was ready for testing.

Our samples were taken at Piseco Lake in the Adirondack Mountains in July of 2012. Setting up the impactor there required a pump and a power source for that pump. Figure 4 shows the impactor mounted in the Adirondacks.



Figure 4: A picture of the impactor setup in the Adirondack Mountains.

Once the pump was plugged in, we simply mounted the impactor, connected the pump to a power source and to the impactor, and let it run. The samples were collected for approximately 48 hours at a flow rate of 1 liter/minute.

3.2 PIXE Experiments

The impactor allowed us to get aerosol samples to be analyzed at the Union College Ion-Beam Analysis Laboratory. The experiments were performed using the 1.1-MV Pelletron accelerator pictured in Figure 5.

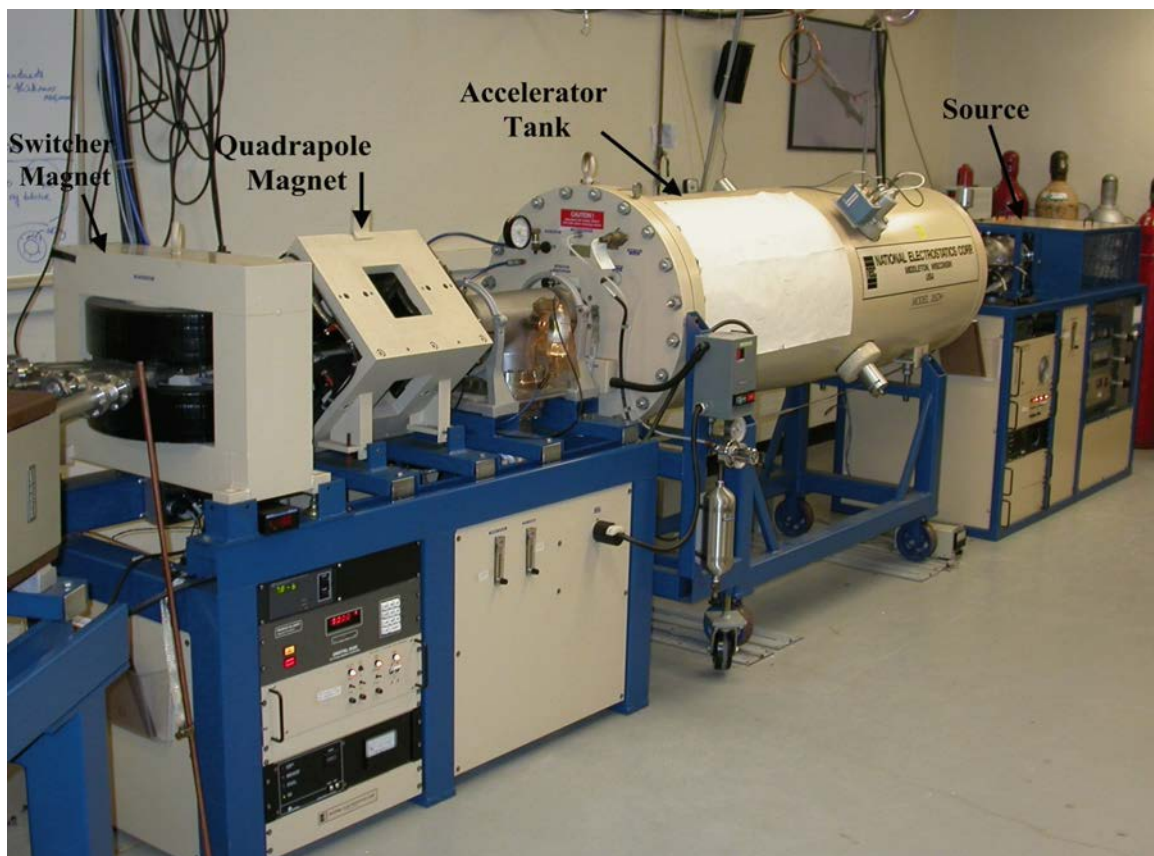


Figure 5: A photo of the Union College 1.1-MV Pelletron accelerator.

The accelerator produced proton beams with energies of 2.2 MeV, diameters of 1-2 micrometers, and currents of 8-12 nA. The samples were positioned at the center of a scattering chamber, pictured in Figures 6 and 7 (inside and outside view, respectively).

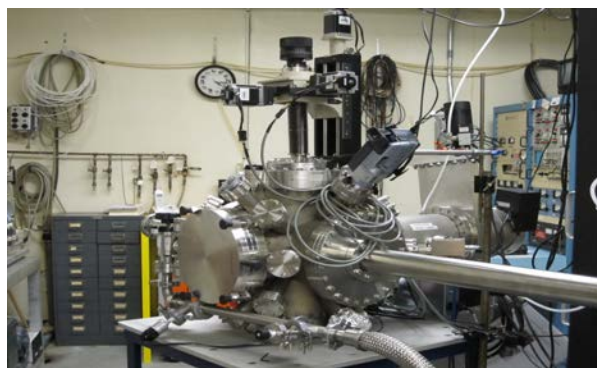


Figure 6: An outside view of the chamber where the samples were bombarded.

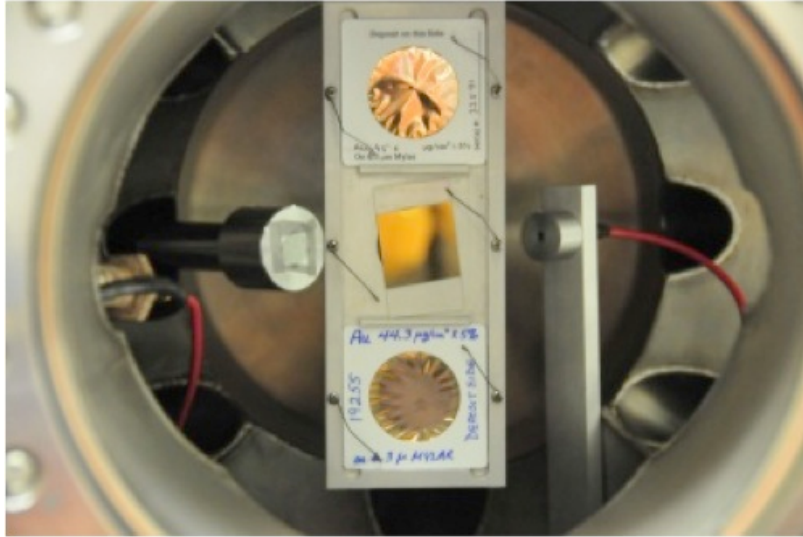


Figure 7: An inside view of the aerosol samples within the chamber.

PIXE spectra were collected on each aerosol sample and a set of MicroMatter standards [5]. A beam charge of 30 microCoulombs was accumulated on each sample and 1 microCoulomb on each standard. The emitted X-rays were detected using an Amptek silicon-drift detector.

4. Analysis

4.1 GUPIX

When working with both GUPIX and GeoPIXE, we must first make sure that we have the right file format otherwise GUPIX will not be able to read our spectrum. The file written by the data acquisition software writes a “.mca” file that has header and footer information that must be removed. All we need is “1024 0” in the first line to indicate to GUPIX that we have 1024 channels, and the file is ready for GUPIX (ideally separating GUPIX and GeoPIXE files into different folders will help distinguish between the two). Once the file is properly formatted, we saved it as a

“.dat” file. When we load the spectrum in for the first time, the window looks as shown in Figure 8.

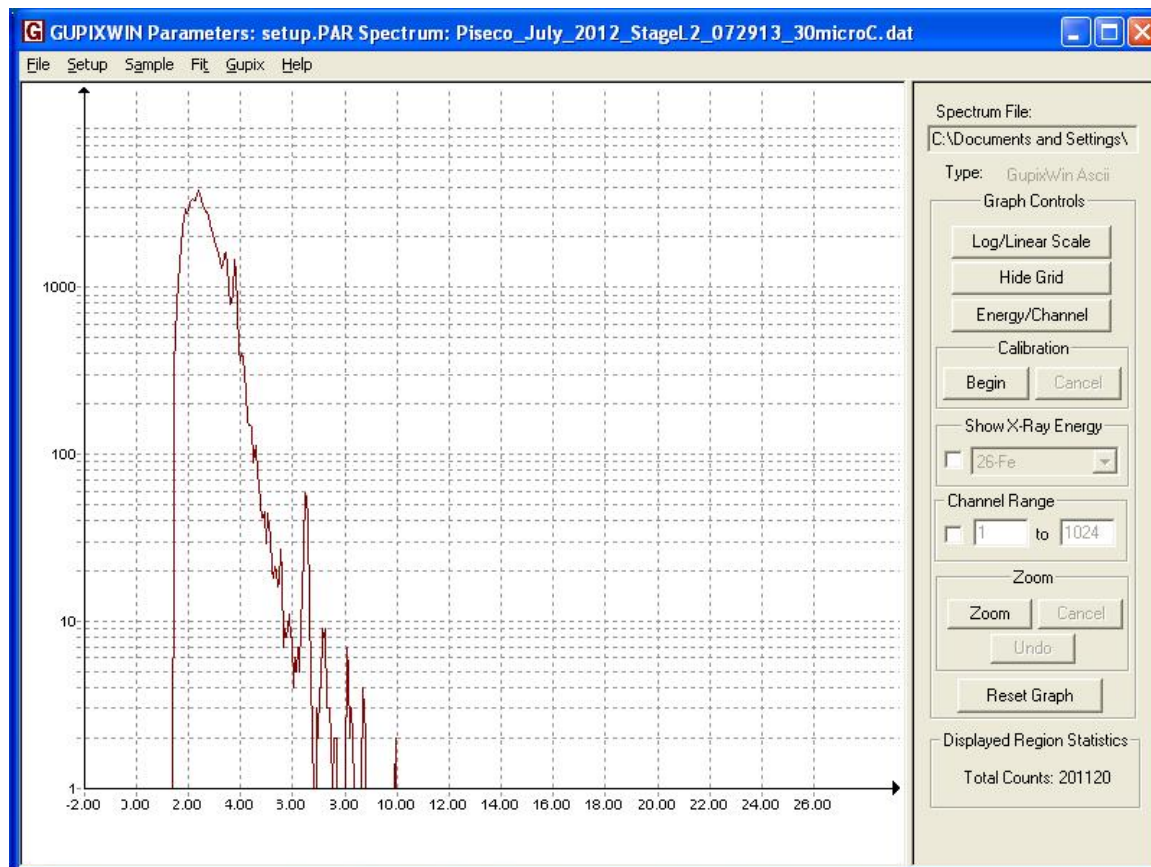


Figure 8: The initial spectrum window before any fitting.

In order to correctly setup the fit parameters, we must move from left to right through the menus. Therefore, we began with the “Setup” menu. We wanted “Solution Type” to be a “Fixed Matrix solution”. Also, under the option “Setup” we needed to make some changes to fit our specific experiment.

For the samples analyzed here, our beams entered the chamber with a beam normal of 0 and the X-ray normal was 45 degrees. Next, for Beam Parameters, we had a proton beam with an energy of 2.2 MeV (2200 keV). The charge collected is 30 microCoulombs. The cross-section is “Theoretical”. We changed the detector to the

Union SDD, and used the Efficiency from Formula option. Finally, the Energy Dependence was constant with an H-Value of .00074 sr, which was determined by analyzing standards. The window is shown in Figure 9.

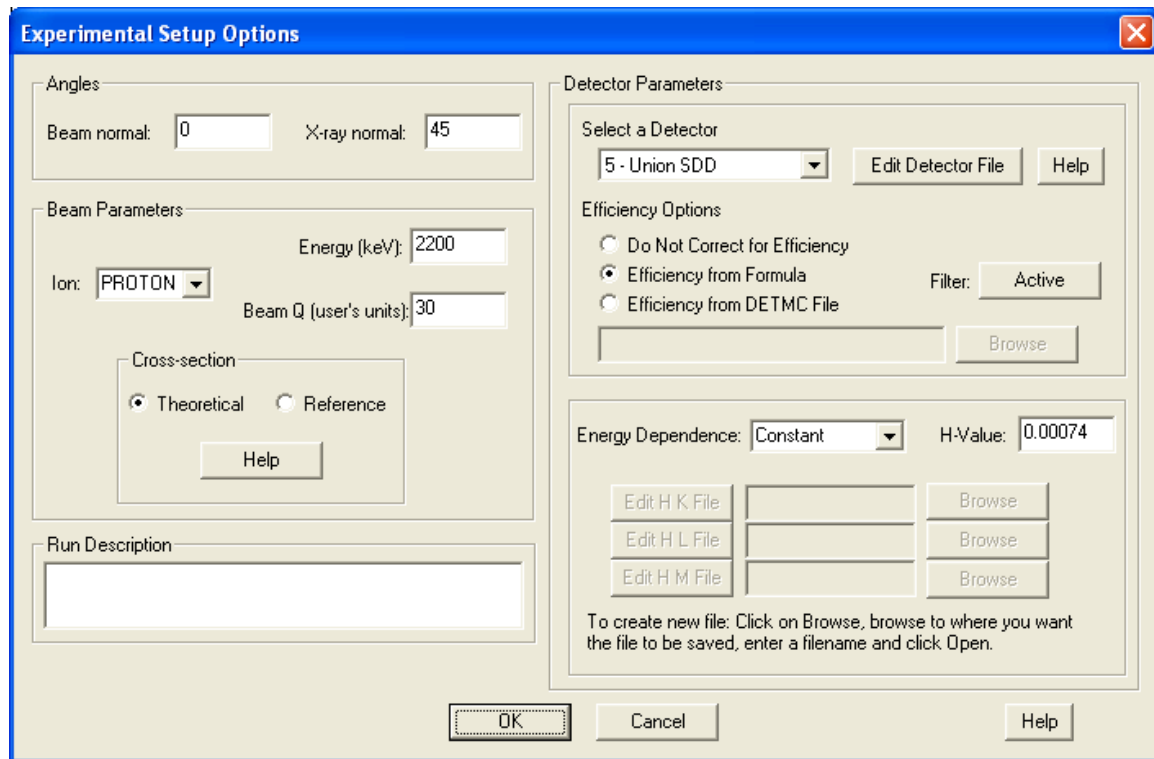


Figure 9: The Experimental Setup Window.

Within this menu we must also select “Filter: Active” which brings up a new menu looking for the specifications of our filter. For this experiment, we were using a Beryllium filter with a thickness of 76.2 microns.

Under the “Sample” menu is where we find the option to select the elements we want to look for in the sample. If we look under “Fixed Matrix Solution” then “Define Fit Elements” then “Add Elements” we can get a look at a Periodic Table to select the elements of interest. Clicking on them adds them to the list, and GUPIX

automatically decides what transition to look for (K, L etc.). At any point if we want to eliminate some elements we can select “Remove Elements” and take them off the list. Figure 10 demonstrates what a final list of elements might look like.

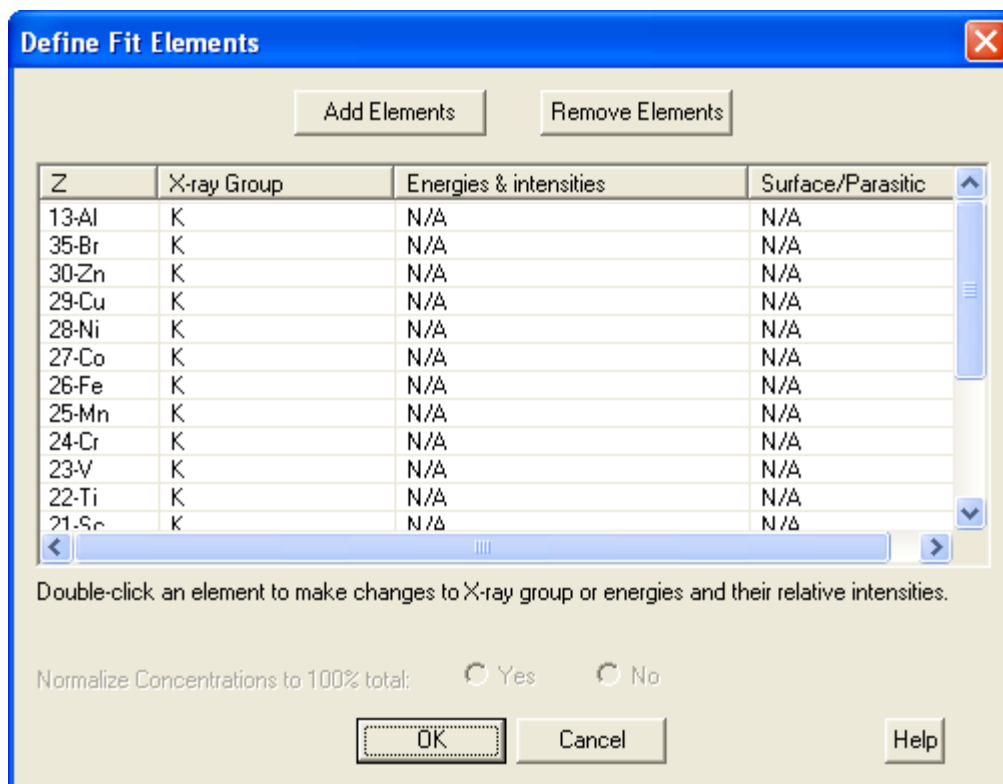


Figure 10: The Define Fit Elements Window where one defines the elements to look for in the sample.

Next we needed to set up the “Spectrum Details” window. The most important part of this window is the Calibration Parameters section in the top right. Here is where the parameters are specified for converting energy into channel number. By entering 0 for A3 we have chosen to ignore the quadratic term of the equation as we have determined that it is a linear function to convert energy to channel number. The values for A4 and A5 have to do with the width of the peaks we fit and are determined by GUPIX by selecting “Input A5”. The rest of the window

has valuable information, but not information we need to change, so the end result looks as shown in Figure 11.

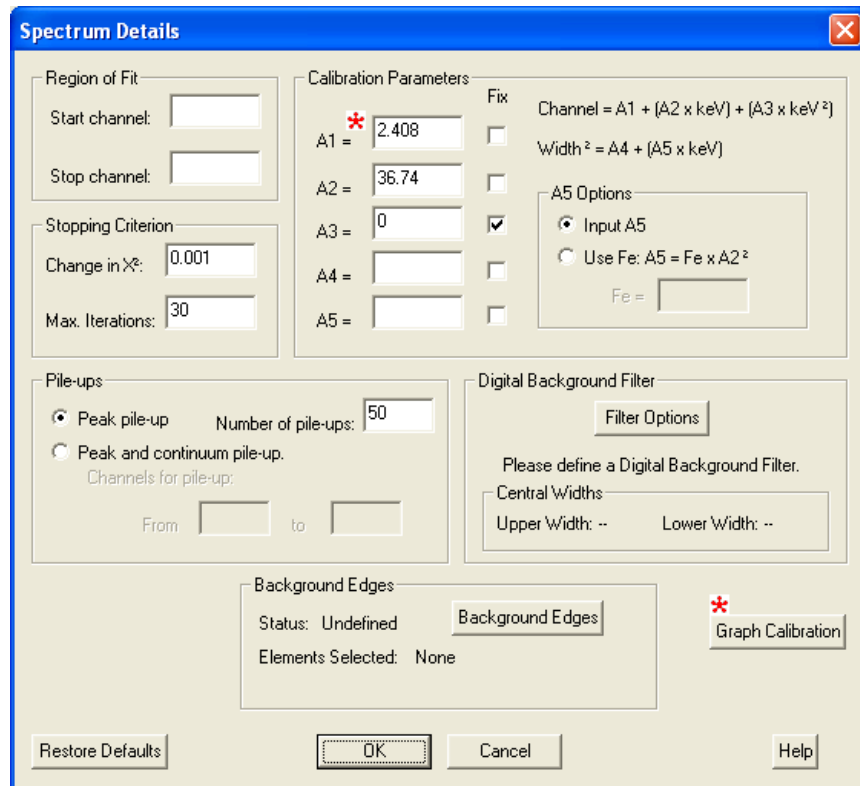


Figure 11: The Spectrum Details Window where the initial fit parameters can be defined.

Once all of the setup is done, we select “GUIX” then “RUN” in order to get the fit for the spectrum. Figure 12 shows the Data&Fit with the Residuals below. We can see that on the right of the window, we have the option to view other graphs such as Data-Fit. Also, we can compare all these graphs on the same screen, or enlarge them to examine them on their own.

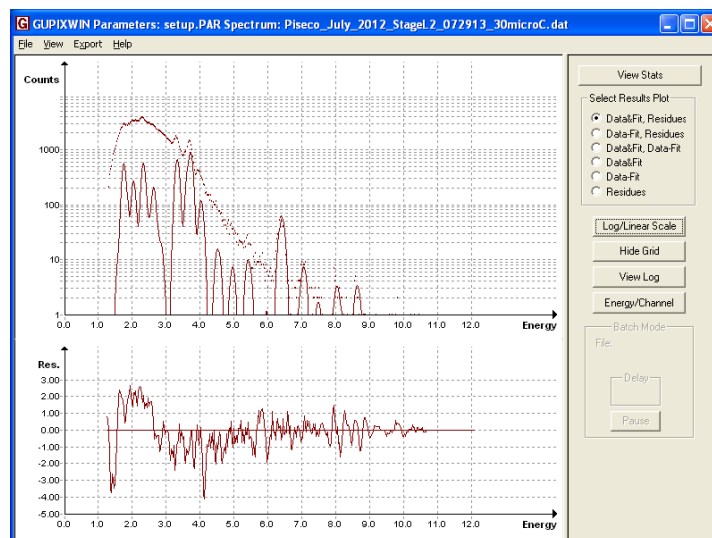


Figure 12: The fit results window.

Selecting “View Stats” in the top-right corner allows us to look at various statistical measures for our fit. At the top of the window are the specifications of the fit. Some numbers that were always considered were the “Chi**2” and “RMS sys err” values as these were an indication of how well we fit the data. The rest of the given information can be seen in Figure 13.

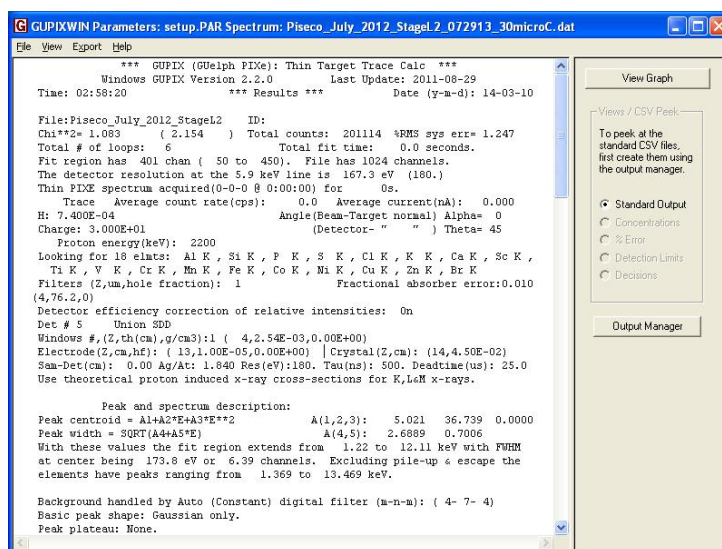


Figure 13: The fit specifications portion of the View Stats window

Below the specifications section is the portion where GUPIX indicates whether or not the elements are present, their concentrations, and the associated errors. This is perhaps more important than seeing the fit itself. It was beneficial to be able to see how well our fit mirrored the raw data and draw conclusions from the residuals, but in reality our goal was to see the concentrations and the presence of elements in our aerosol sample. This window is shown in Figure 14.

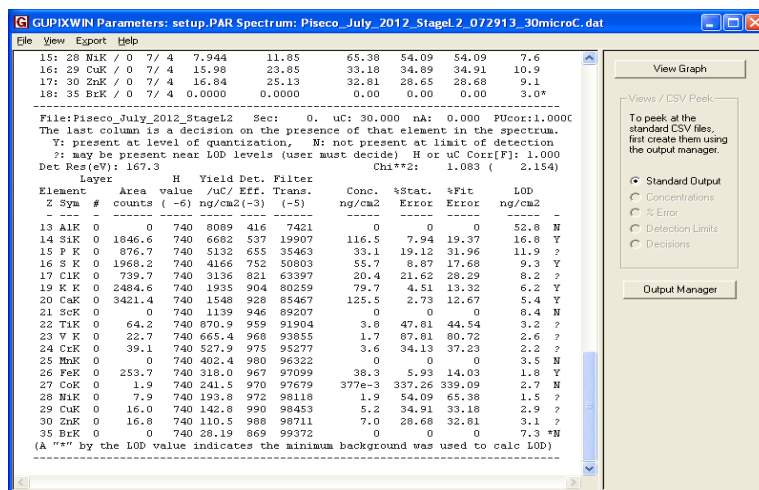


Figure 14: The fit statistics window.

There is a lot of data in this Figure but the crucial pieces are the Conc. (ng/cm²) and the final column that lists “Y”, “N”, or “?” values (obviously the name of the element on the left side is also important). The latter is an indication of whether or not GUPIX thinks that the element is present in the sample, with the “?” indicating GUPIX is not sure. The concentration column lists the calculated concentration for each element. In this particular example, we can see that Calcium has the highest concentration in the sample of about 125 ng/cm². This chart has the most valuable information, and was used for each stage to determine final concentrations and compare them with GeoPIXE.

4.2 GeoPIXE

In order to perform PIXE analysis using GeoPIXE, we first imported the spectrum that we were looking to fit. We only had to make a minor adjustment in the file we used for GUPIX so that the “.dat” file will be ready for GeoPIXE. We simply deleted the first line of the file that says “1024 0” as GeoPIXE does not need to be told how many channels there are.

To import the file, we selected “File” then “Import” then “Spectra”. This brought up a menu of formats of the data, in which our data was classified as “Generic data and native GeoPIXE”. This brought up another menu to select file type and we selected “ASCII spectrum (Data only)”. Selecting the file from the following menu gave us our spectrum.

The first step, once we had our spectrum, was to calibrate the energy scale. When the spectrum is loaded, the y-axis is in counts while the x-axis is in channels. We selected the “Window” dropdown option, and then clicked on “Calibrate Energy”. To convert channel number to energy, we entered values of $A=0.0272199$ and $B=-0.0655352$. These values are merely the slope and intercept, respectively, of a linear function that converts channel number to keV, obtained from a fit to an X-ray spectrum of an Americium-241 source. It is the inverse function of the one used in GUPIX to convert keV to channel. We selected the “keV” button to change the units, and then we applied it to “One” and it converted the spectrum from counts vs. channel to counts vs. energy in keV.

As the scale of keV is far smaller than that of channel number, we used the “Expand” button in the Spectrum Display window to get a better look at the spectrum since it had been calibrated. In the leftmost dropdown menu, we selected “View 0,1” and moved the red vertical lines to the boundaries of the spectrum. These red lines are essentially our way of determining the region in which we want GeoPIXE to fit the spectrum. The end result looks as shown in Figure 15.

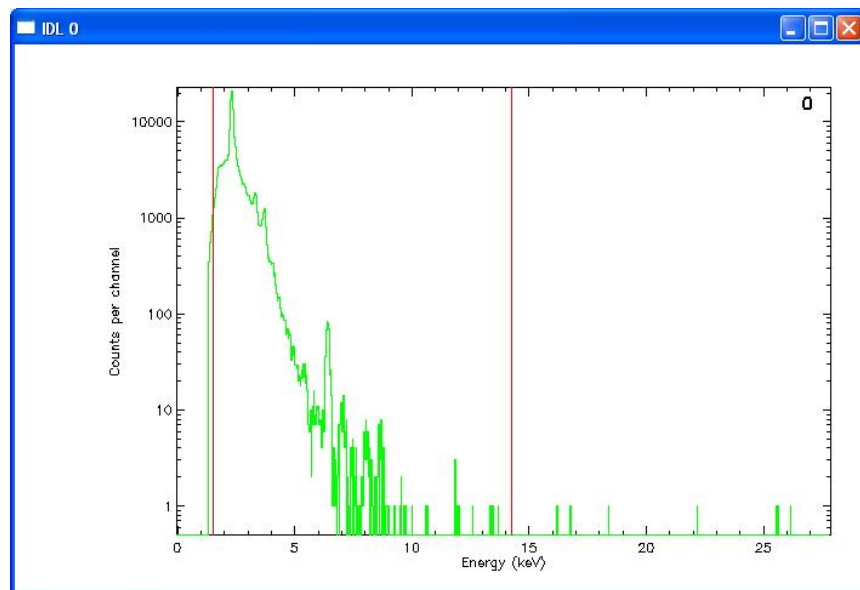


Figure 15: A window showing a calibrated spectrum in GeoPIXE.

The reason that the left red line cuts off a fraction of the spectrum is that we get a far better fit of the data when we start near the top of the initial peak. Also, we can still fit all the elements we are looking for, so no information is lost by eliminating that portion. The same is true for the small peaks to the right of the other red line. We know with counts that low that the likelihood of those peaks being anything other than noise is slim. Therefore, we got the best fits by using the region shown above.

Next, we went to “Window” then “X-ray Spectrum Fit” to fit our data. The first time performing a fit, we needed to determine the Yields section, and to do so we selected the “New” option. Under the “Beam Particle” section, we set Energy to 2.2 as this is the energy, in MeV, of our proton beam. The charge for every spectrum was 30 microCoulombs. The detector angle, “Theta”, was -135 (although we found there was no difference between -135 and 135).

The bottom “Layer” section is in reference to the impactor and the composition of the different layers. The “Yield Calculation” window is shown in Figure 16. In order to correctly input these layers, we needed to set the “# Layers” section to 2, the “Unknown” section to 1, and the “Define Layer” section merely indicates which layer is shown and able to be edited. The first layer we set to Iron, with a thickness of .0548 mg/cm². The density can be left as an unknown to be calculated by GeoPIXE. The formula entered is the formula for the current layer, or Fe in this case.

PIXE/SXRF Yield Calculation

Set-up: Load Save

Title:

Beam Particle Proton +1 Z: 1 A: 1 Energy: 2.2 Charge: 30.000		Energy Range E min: 2.00000 E max: 48.0000
Detector Theta: 135.000 Phi: 0.000000 ? <input type="checkbox"/> Array		Target Alpha: 0.000000 Beta: 0.000000

Target Layer Selection

Layers: 2 Define Layer: 1 Unknown: 1

Target Layer Details

Thick: One .0548 mg/cm² Density: 0.00

Formula Mode: Type in formula Atomic Fraction

Formula: Fe

Output:

Calculate Yields Plot Yields Export Close

Enter target, beam and detector details and "calculate yields" to a "YIELD" output file. Remember to save settings in an LCM file using "Save" at the top.

Figure 16: The yields setup window.

Changing the "Define Layer" value to 2 will move to the next blank layer where we will fill in the values for the Kapton layer. The thickness for the Kapton layer is 7.5 microns (note that in the above setup the unit was not microns for the thickness). The density, which is known, is 1.43 g/cm³, and the formula is C₂₂H₁₀N₂O₅ entered without subscripts. The Kapton setup is shown in Figure 17.

Target Layer Selection

Layers: 2 Define Layer: 2 Unknown: 1

Target Layer Details

Thick: One 7.5 microns Density: 1.43

Formula Mode: Type in formula Atomic Fraction

Formula: C22H10N2O5

Figure 17: The second layer setup window in which the Kapton foil is described.

Once the yields are calculated, we returned to the X-ray Spectrum Fit window to finish fitting the data. We selected “Use View” to use our selected range as the Energy Range for GeoPIXE to fit. The detector we have at Union is the Union SDD detector, and the dropdown menu was specified to that. Also, our filter is a 76.2 micron Beryllium filter and the appropriate dropdown menu was set to that. The “Boost” option was always selected as it gave a closer fit than without it.

Next we selected our elements. The periodic table on the X-ray Spectrum Fit window allowed us to select the elements and the transition levels to look for. For our purposes, we only needed to look at the K transitions for the elements we looked for. If we wanted to check for, say, Gold in the sample, we would click the appropriate amount of times to match the color with the “L” transition color (key is at the top). The final X-ray Spectrum Fit window is shown in Figure 18.

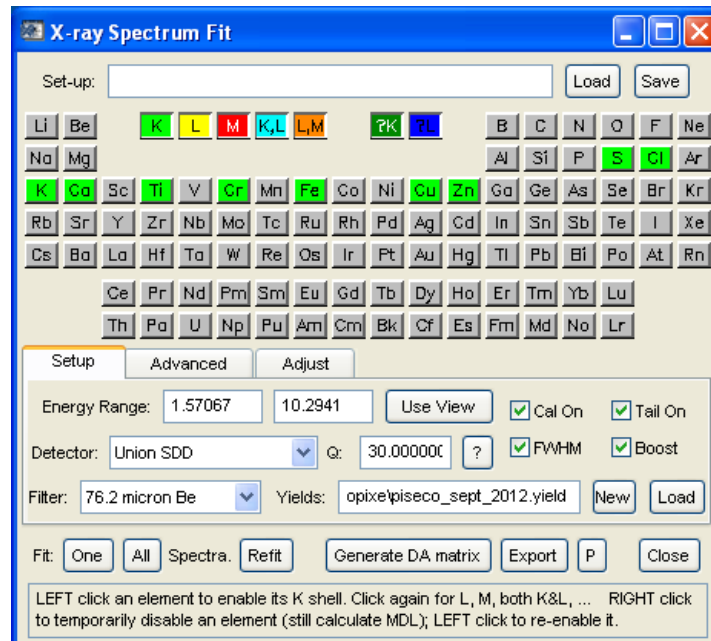


Figure 18: The X-ray Spectrum Fit Window.

Then we were able to select the “One” option next to “Fit:” in order to fit the spectrum we had. When done correctly, our spectrum and fit looked as shown in Figure 19.

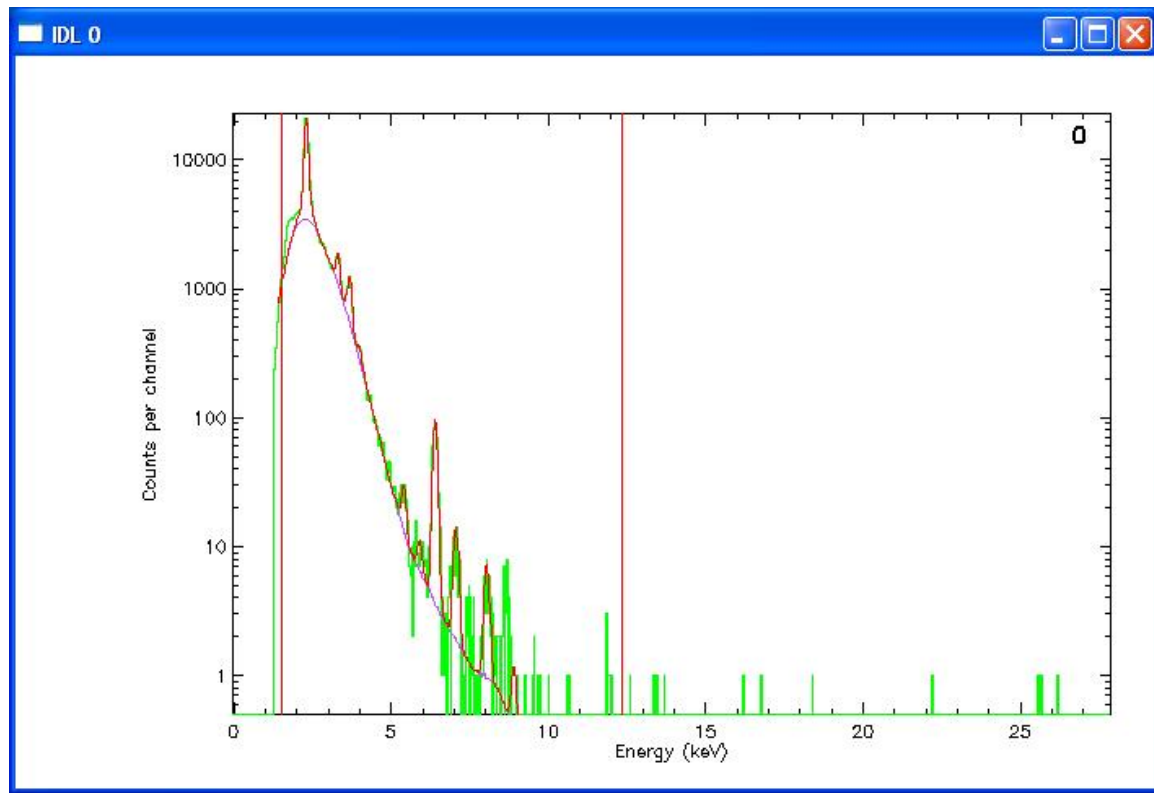


Figure 19: An example of a fitted spectrum in GeoPIXE.

In this spectrum, the red line covering the peaks is our fit while the purple is the baseline of the background. As we will discuss later, there can sometimes be issues at this step, so seeing that the fit looks correct means we can have some confidence in our results.

To further examine the fit and the resulting concentrations, we selected “Window” then “Fit Results”. When we did that, we got a dialogue box that had the various concentrations for all the elements. To see these concentrations, we first

selected “ng/cm²” in the drop-down menu second from the right. An example of the Fit Results window is shown in Figure 20.

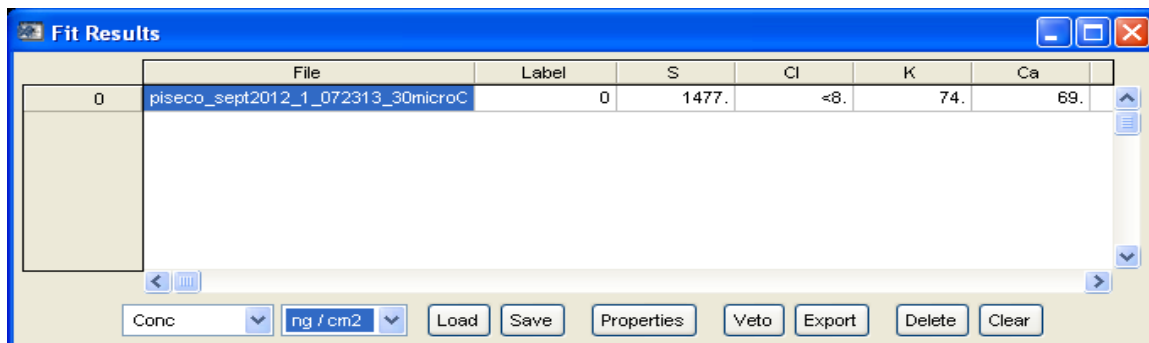


Figure 20: The Fit Results window.

In addition to concentrations, we can see error values and other important information by looking in the “Conc” drop down menu (left most). This gave us our fit and our concentrations, as well as our uncertainties and yield amounts.

4.3 GUPIX vs. GeoPIXE

Both GeoPIXE and GUPIX are very complex pieces of software that come with many advantages and disadvantages. The spectra gained from PIXE were analyzed using both pieces of software for two purposes: to gain experience with the two in order to determine the pros and cons of each, and to validate the results we obtain for the concentrations found. Essentially, our goal is to compare GUPIX and GeoPIXE and we can do that by analyzing lots of spectra.

The most immediate difference between GeoPIXE and GUPIX refers to the concentration equation given by Equation 1. As described before, all of the values with the exception of H, are known. They can be determined by us, given by the

manufacturer, or calculated from theory. GUPIX and GeoPIXE handle the H value, or the solid angle of the detector, in two distinct ways.

GUPIX helps us determine the solid angle through experimentation. In order to do this, we ran PIXE on various samples of which the concentrations are known [5]. Instead of entering a correct value for H, we let H=1. GUPIX now runs and determines a concentration for, say, Aluminum in our Aluminum standard sample. Then we take the ratio of our measured concentration to the actual concentration to obtain an experimental value for H. The results are shown in Table I.

Table I: The H values obtained from the standards.

Standard	Z	Rep. Conc. (ng/cm ²)	Meas. Conc. (ng/cm ²)	H (sr)
Aluminum	13	48100	32.2	0.00067
Titanium	22	55000	39.6	0.00072
Iron	26	54800	39.7	0.00072
Copper	29	60500	44.4	0.00073
Germanium	32	49000	35.9	0.00073
Gold	79	45600	35.8	0.00078
Lead	82	52800	40.9	0.00077
			Average	0.00074
			Stand. Dev.	0.00004

Then we plotted H value versus Z to see, ideally, a straight line as the solid angle of the detector should have no dependence on Z. The results are shown Figure 21. We do see a slight Z dependence in that higher Z values tended to have a higher

H value, but the slope was so small that it can be neglected. Therefore, we can average our H values to obtain our experimental number to enter into GUPIX.

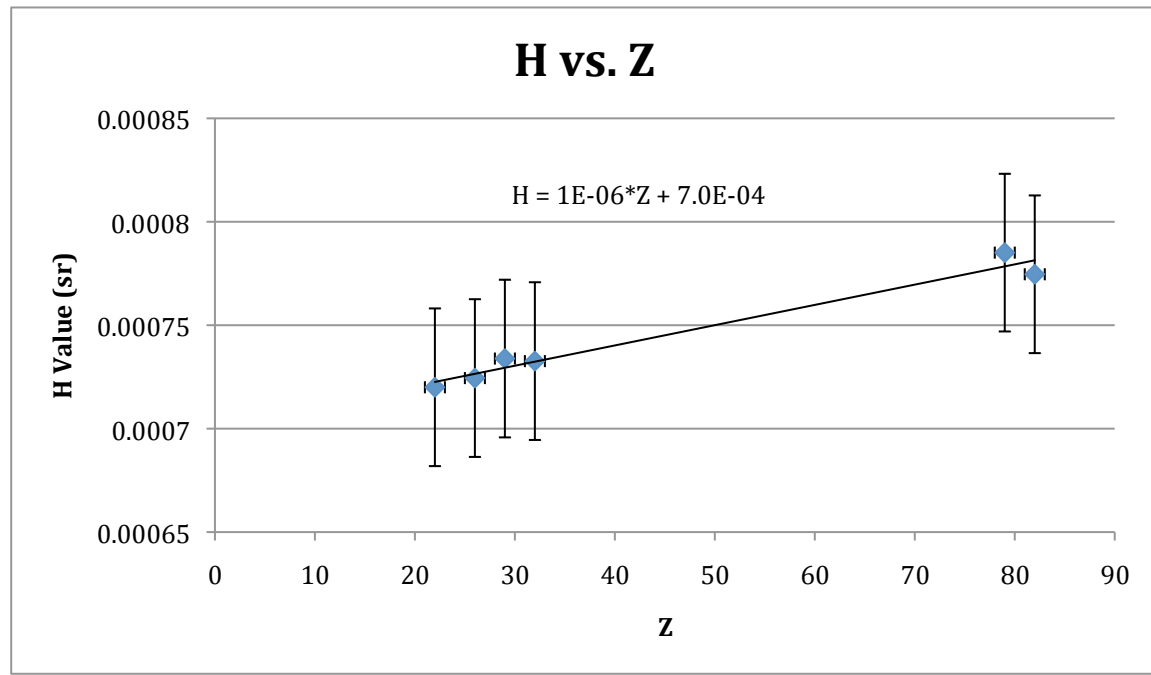


Figure 21: A plot to examine Z dependence in our H value measurements.

GeoPIXE handles this value in a far more direct way in that it merely assumes that we already know the solid angle of the detector. Clearly, we needed to find this value for GUPIX so we did not “know” it like GeoPIXE traditionally wants. As a result, we used our experimental value found using GUPIX to be our “known” value in GeoPIXE. Despite these being drastically different processes, for our purposes there ended up being no difference.

An issue we found while performing the analysis was that GeoPIXE has issues getting consistent concentrations for elements with low Z values, near where the spectrum falls off due to the effect of the 76.2 μm Beryllium absorber. GUPIX seems to be robust to this issue, which gives us more confidence in the results of those

concentrations given by GUPIX. For GeoPIXE, the resulting concentration depends greatly on which elements are selected to be searched for by the software. In other words, telling GeoPIXE to search for Phosphorus and Sulfur will give drastically different results than if we tell GeoPIXE to search for just Sulfur. We see that the Sulfur value will change immensely, with of course only one of these values agreeing with the value obtained in GUPIX. The reason for this discrepancy is most likely the lesser ability of GeoPIXE to fit the low-energy fall-off of the spectrum.

Sometimes this issue is abundantly clear when we run GeoPIXE and obtain a fit that is clearly not fitting the peaks well. A good example of this is in Figure 22. Clearly we can see towards the left side of the spectrum that the fit (red line) does not fit the peaks well but rather encompasses multiple peaks, giving us over and underestimated values for certain elemental concentrations. What is perhaps even more troublesome about these results, is that the fit for the iron peak (~ 6 keV) is far off as well. It would seem that the issue GeoPIXE has towards the left side of the spectrum can ruin the entire fit, giving concentrations for all elements that are incorrect. This is why it is always important to examine the fit before opening the fit results window. If the results from this particular fit were used to say, for example, that there are dangerous levels of Iron in the atmosphere then this would be a conclusion based on a poorly fitted spectrum.

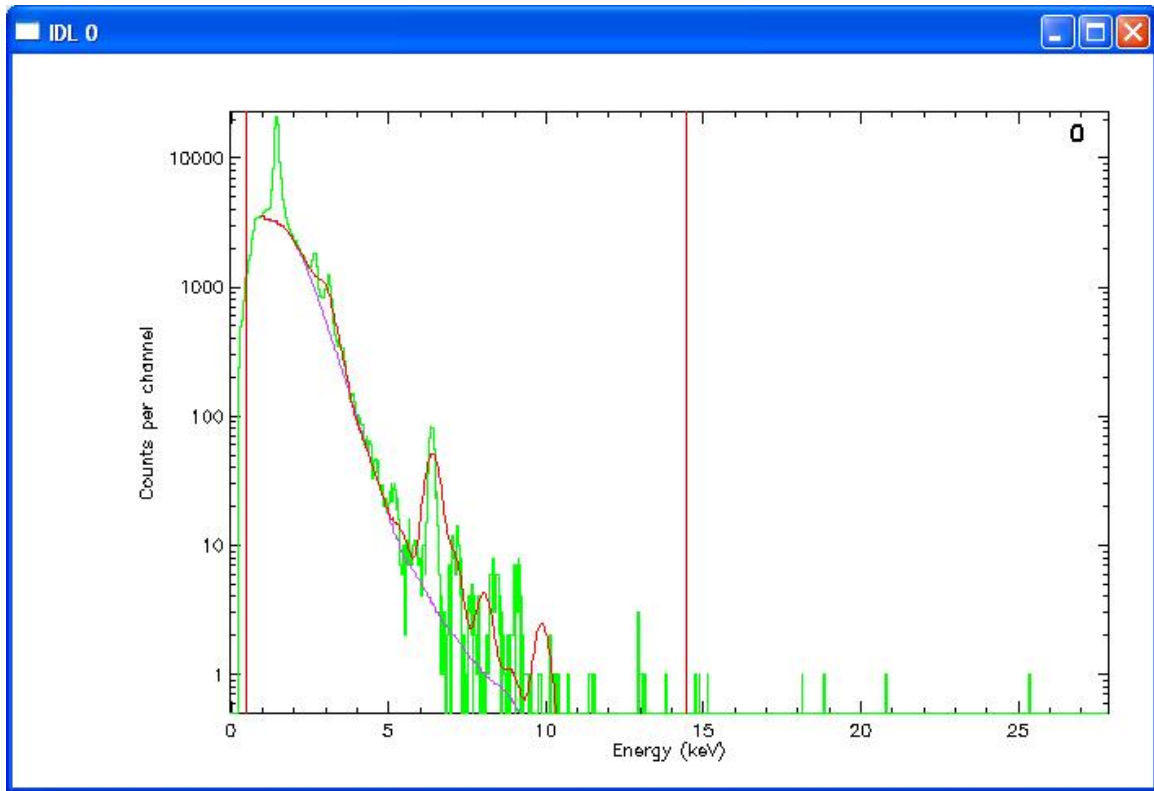


Figure 22: An example of a poorly fit spectrum in GeoPIXE.

One way this problem seems to be remedied is by taking advantage of another useful GUPIX feature. When fitting a spectrum, the results are displayed in table form, but GUPIX includes a column far on the right that indicates whether or not an element was discovered in the sample. The possible values are “Y”, “N”, or “?”. Clearly, “Y” and “N” indicate “Yes the element is present” and “No the element is not present”, respectively. The “?” indicates that GUPIX is not confident enough to say it is present, but also not confident enough to definitely say it is not there. This determination is made using the concentration value paired with the error. In other words, if a concentration was calculated to be significant but had a substantial fit error, the element would typically be a “?” or “N”.

In order to get consistent results, we first recognized that GeoPIXE would not give accurate concentrations if asked to look both for Phosphorus and Sulfur, so we decided to eliminate Phosphorus in the list of elements to search for (the benefit being that our fit results would more closely match that of GUPIX). Then, the elements included in the list for GeoPIXE were based off of elements GUPIX determined were definitely in the sample (received “Y” values). Using this, we were able to find concentrations that generally agreed between the two pieces of software, but it is clear from Figures 23-28 that occasionally some results did not agree.

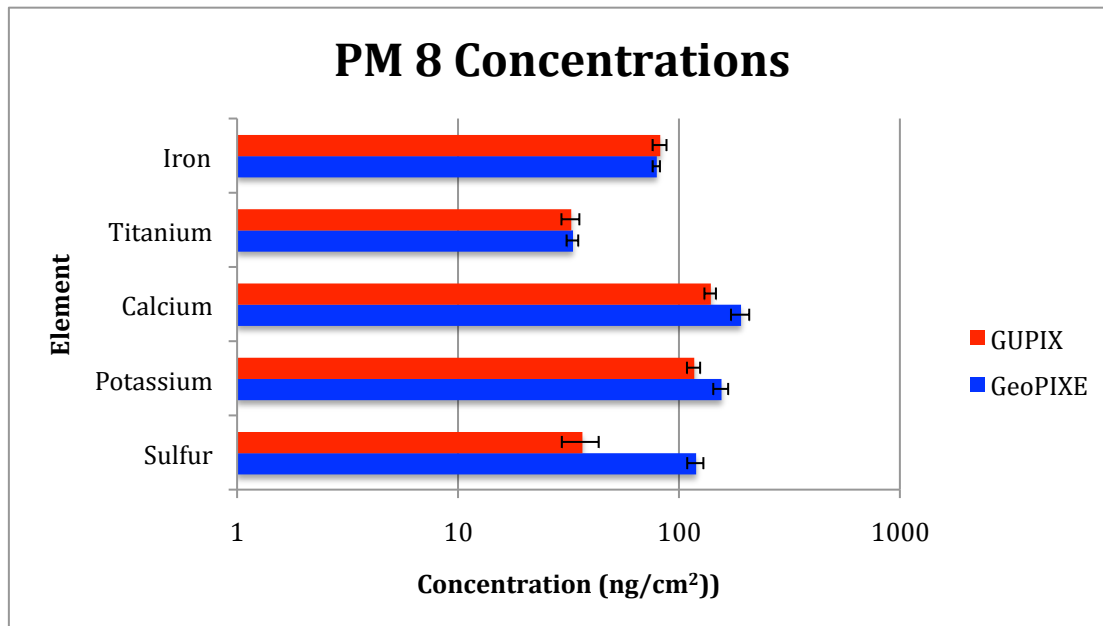


Figure 23: A comparison of concentrations determined with GUPIX and GeoPIXE for elements in the PM 8 sample.

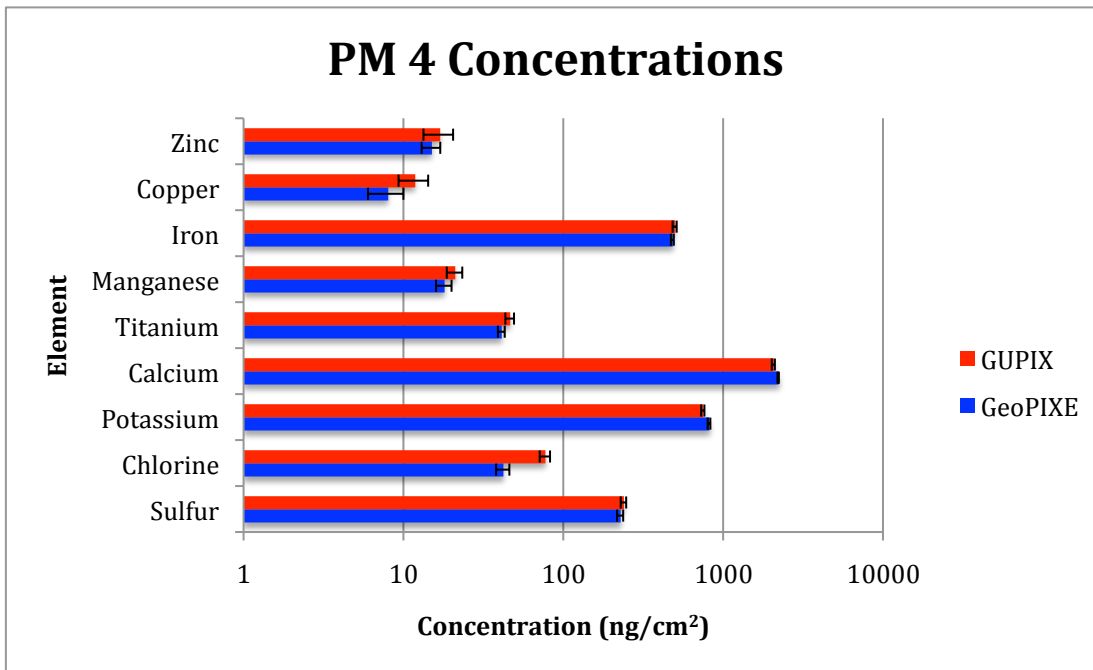


Figure 24: A comparison of concentrations determined with GUPIX and GeoPIXE for elements in the PM 4 sample.

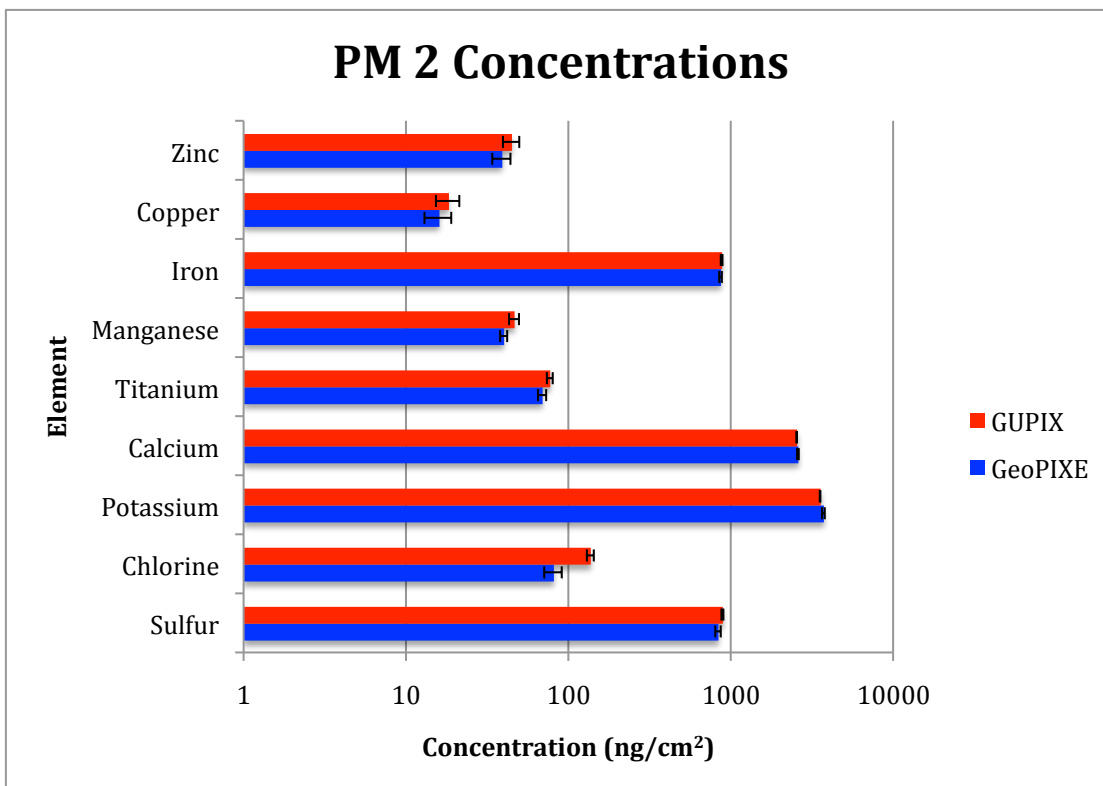


Figure 25: A comparison of concentrations determined with GUPIX and GeoPIXE for elements in the PM 2 sample.

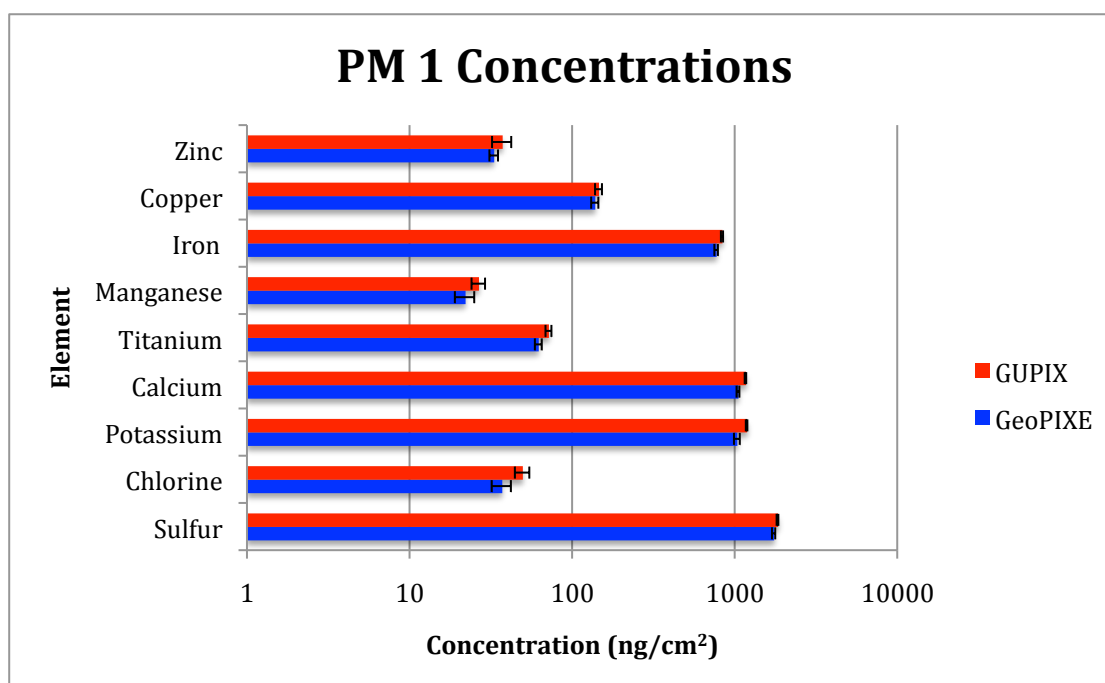


Figure 26: A comparison of concentrations determined with GUPIX and GeoPIXE for elements in the PM 1 sample.

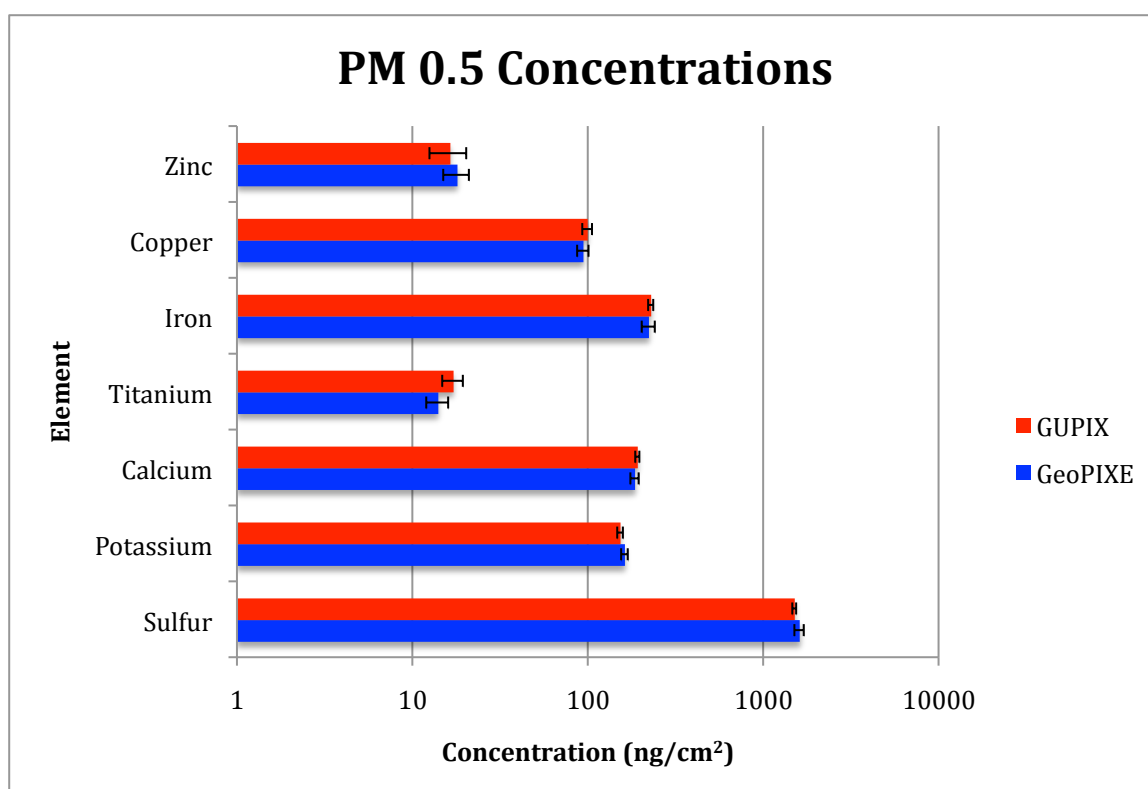


Figure 27: A comparison of concentrations determined with GUPIX and GeoPIXE for elements in the PM 0.5 sample.

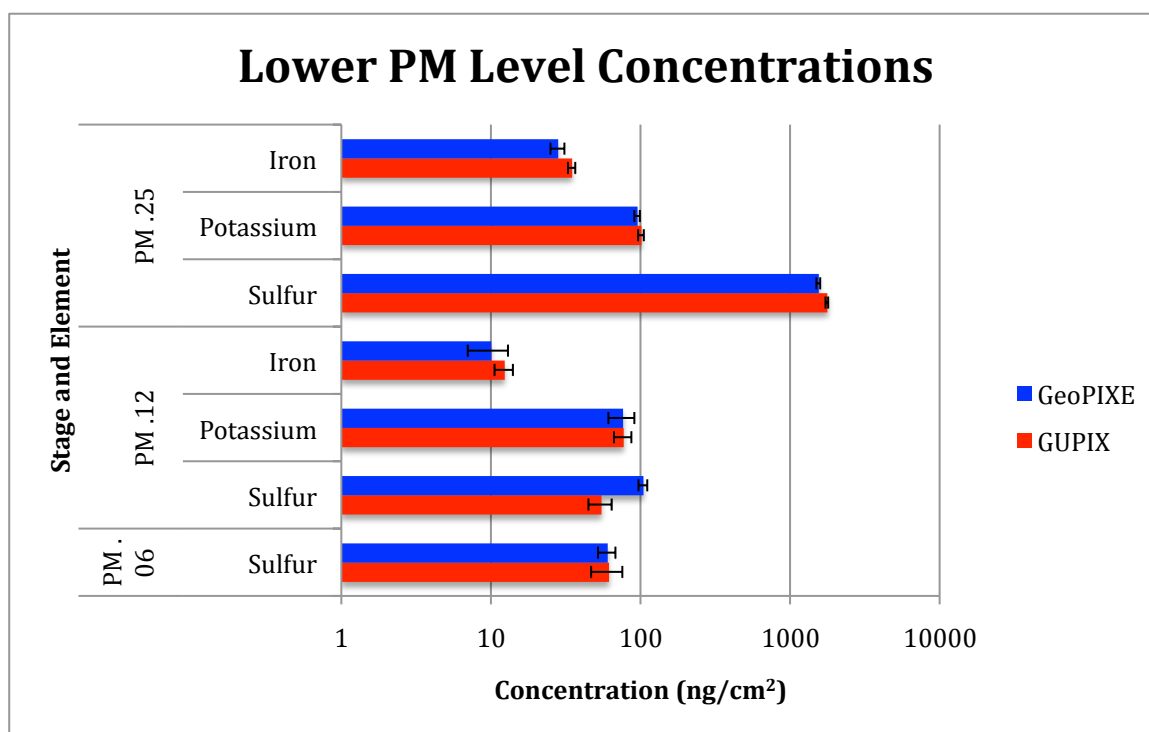


Figure 28: A comparison of concentrations determined with GUPIX and GeoPIXE for elements in the Lower PM samples.

We can see that for the most part, the results agree within uncertainties with only a few exceptions. However, in some cases the uncertainties are large and it's not surprising or impressive to have results agree with large uncertainties. In order to examine the results closer, we plotted the absolute difference versus the Z value, to see if there was some relationship between the element and the differing predictions. The results are shown in Figure 29.

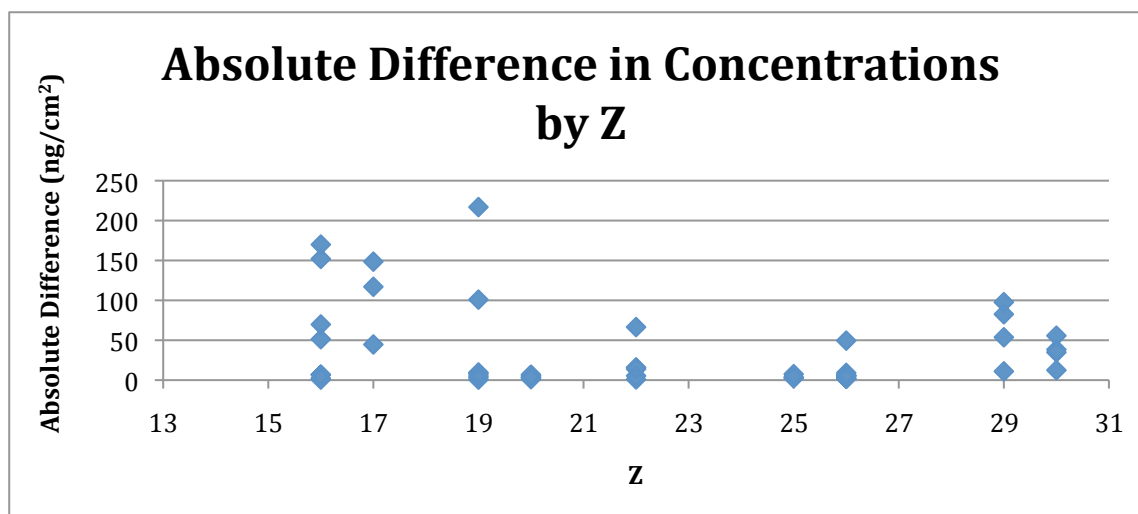


Figure 29: A plot of absolute difference in concentrations determined with GUPIX and GeoPIXE, vs. Z.

Here we can see a small trend towards the lower Z values (Sulfur, Calcium etc.) in that it looks like the error is higher for smaller Z elements. Alone, however, this plot is not the whole story. While the smaller Z values can have higher absolute differences, they also have much higher concentrations. Two elements can have the same absolute difference, for example 5 ng/cm², but the first element may have a concentration of 10, while the second could have a concentration of 1000. Clearly, that difference is far more significant in the first element and thus more of a cause for concern. To further examine this issue, we made a plot of the percent difference (using GUPIX as the baseline), shown in Figure 30.

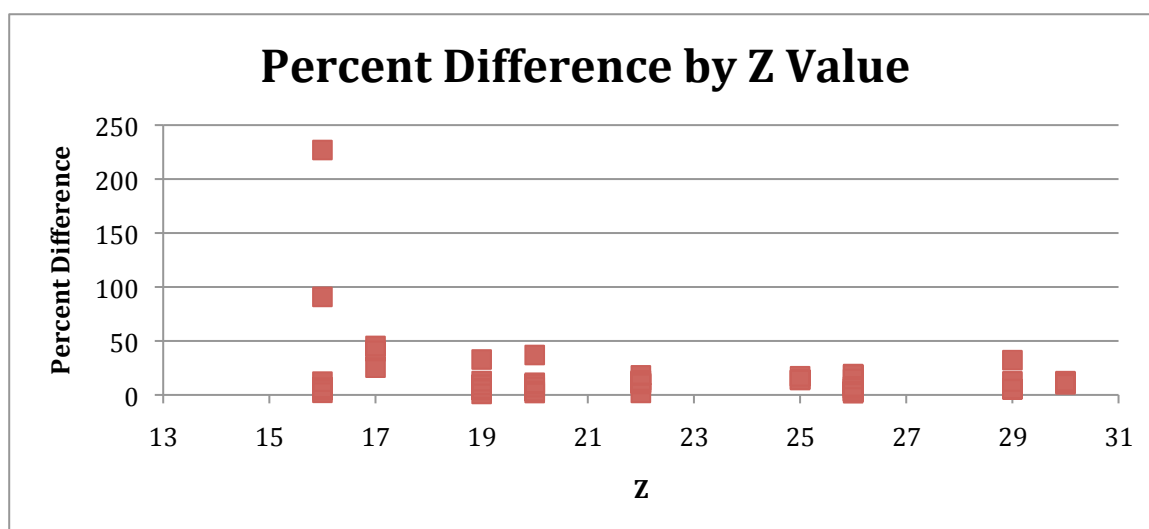


Figure 30: A plot of percent difference in concentrations determined with GUPIX and GeoPIXE, vs. Z.

There are a few points towards the smaller Z values that are of note in that GUPIX and GeoPIXE completely missed each other, but otherwise there does not seem to be much of a trend in the error between the software packages. Also, we can see that GUPIX and GeoPIXE consistently agree on certain elements such as Iron, where the absolute and percent difference is always low.

There is no question that GUPIX and GeoPIXE will sometimes disagree on concentrations, so the important question to then ask is “Why do they miss”? One logical avenue to explore is to look at the final yields for each element in each spectrum and see how those compare. If the yields are consistently different, then the difference lies in the fit. If the yields are similar, then the difference is most likely from how the software calculates the concentrations. Chances are it is not one or the other but a combination of the two, but we can get a good idea of which has the more dominant effect.

Figure 31 tells us that the yields are significantly different which could absolutely be the reason behind the difference we see in simulations. However, the yields being this different from each other lends to the idea of a discrepancy in both the yield total and the calculation of concentrations, as our results for concentrations were not quite as different as this plot would indicate.

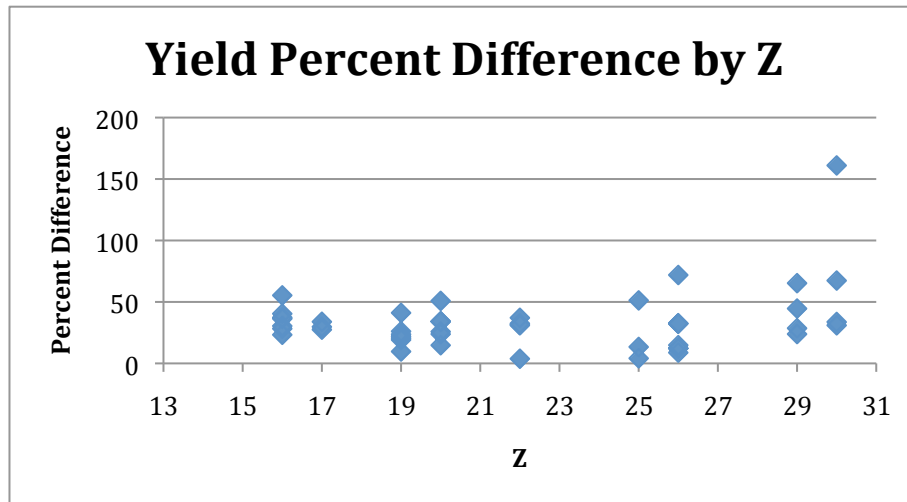


Figure 31: A plot of percent difference in yields determined with GUPIX and GeoPIXE, vs. Z.

Another important distinction between GUPIX and GeoPIXE is the way that each software package deals with background in the spectra. One of the stronger aspects of GeoPIXE is its transparency in how it deals with modeling background. We can see, from Figure 19, that the purple curve is the background while the red curve is the fit. This was helpful when deciding to add the “Boost” quality as it clearly fit the background better so that we would accurately measure the peaks. In addition, it was beneficial to identify the instances in which GeoPIXE failed to accurately fit the data. Because it was so clear what the fit was, immediately we

were able to troubleshoot and fix our setup to make sure we had an accurate estimate for the concentrations.

GUPIX is less transparent about its background calculations and the fit. While it gives plots of the residuals, it is not as clear to determine whether or not GUPIX has given us the right fit. However, GUPIX excels in that the results are easily reproducible. By this we mean that, for example, the number of elements selected will have little effect on the resulting concentrations. Consistency is really important when making these fits because it gives us confidence in our results.

5. Conclusion

GUPIX and GeoPIXE are two software packages designed to analyze PIXE spectra. PIXE is a way to determine the presence of an element in a sample as well as the concentration. In many instances it is vital to be able to get consistent and accurate results for elemental concentrations.

GUPIX is the far more consistent of the two software packages. With GUPIX, the number of selected elements has little effect on the ability to get accurate and consistent results. If we are interested in the concentration of one single element, we can search for just that one element. Conversely, we can search for a wide range of elements in the case we do not know what is present in a sample, and get consistent results for those. GUPIX then will present the results, as well as other information regarding fits, in a data table while also clearly indicating whether or not an element is present. In addition to that information, GUPIX will also present a

graph of the peaks as well as the residuals and Chi-squared value to help us come to the conclusion that we have a good fit. Where GUPIX is weak is the lack of transparency in the handling of the background. It is not very apparent how the background is fit, and while we can see the peaks we cannot tell if those are accurate visually.

GeoPIXE is the less consistent of the two software packages. Element selection is a big issue, at least for the spectra we were analyzing. In many cases the fits and resulting concentrations varied greatly depending solely on the number of elements selected to search for. It seemed that GeoPIXE really wanted us to know which elements were in the sample, and search for exactly those in order to obtain a good fit (although that was not even the case with Phosphorus). While that is a workable option when using both GUPIX and GeoPIXE (because GUPIX tells us what is in the sample), using GeoPIXE alone to find out the composition of a sample would be risky. However, the biggest benefit of GeoPIXE is that it is completely transparent in its fit in that we can see immediately whether or not we like the results. It shows the sum of the peaks and background fit to the data. When we got a bad fit, we knew right away and discarded those results and fixed the issue.

As for the actual elemental concentrations in the air, we found a range of elements from Silicon to Zinc. Sulfur, in particular, had high concentrations at low PM sizes. The problem with smaller Sulfur particles is that their size allows them to remain in the air longer. Those particles can travel long distances and continue contributing to the acid rain problem if the Sulfur is in the form of an oxide. The distribution of the other elements seemed to indicate that those concentrations

were coming from the soil. In other words, the particles found that contained many of the later elements were found at the larger PM sizes, indicating that the origin of those elements is from the local soil and not the industrial Midwest.

While GUPIX and GeoPIXE are two software packages that have benefits in various areas, GeoPIXE should be used to complement GUPIX. Consistency is the most important quality as consistency helps to confirm accuracy, and GUPIX excels in that area above the capabilities of GeoPIXE.

6. References

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