EIGHTEENTH AND NINETEENTH CENTURY PRINT INK ANALYSIS USING THE PIXE METHOD

by

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ABSTRACT

The purpose of the project was to develop a method for studying trace elements in eighteenth and nineteenth century printed materials. The elemental content in the ink will be used to distinguish ink of one source from ink of another. External PIXE (Particle Induced X-ray Emission) was the method used in this experiment to determine the elements in the inks. This paper discusses the steps of setting up an experiment of this nature as well as possible ways to make the results more effective. The only element that proved to be distinguishable in the ink was lead; however, lead was not present in most of the samples that were analyzed.

INTRODUCTION AND BACKGROUND

The composition of ink is important to many different areas of study. Analyzing the ink composition will help identify the authenticity of historic documents. One common method of fraud is to alter or improve older documents in an attempt to increase the value. PIXE analysis will allow suspect spots to be analyzed to determine if they were written by the same ink as the rest of the document. The analysis will also be useful because it will allow time frames and locations to be determined for a specific document based on the content of its ink. The content of the inks will be different based on recipes used in different parts of the world and in different eras. The major advantage to this method over other chemical analyzing methods is that it can be preformed with virtually no damage to the document of interest.

The way PIXE avoids destruction is by only affecting the electron states in the material studied. To do PIXE analysis, we use a 2.7 MeV proton beam produced by a Van de Graaff accelerator. The beam travels out of the accelerator at roughly 5% of the speed of light and is then bent by a bending magnet. The intensity of the magnetic field and the energy of the protons work together to provide a constant beam energy at the desired angle. After the bending, the proton beam travels through two collimators that narrow it down to a smaller diameter. Following the collimators, the beam leaves the evacuated beam-line into the atmosphere through a Kapton foil. The Kapton foil absorbs some of the beam's energy. The beam also travels through air or helium until it hits the target. The air and helium dissipate some of the beam's energy as well.

When the beam hits the target, protons from the beam interact with electrons in the target, ionizing the target atoms. Electrons form higher energy levels drop back to

fill the vacancies and give off an X ray in the process. A germanium detector absorbs those X rays and sends out a signal proportional to the energy of each X ray. The data are then read by a program called Genie. The detector and program can detect x-ray energies from 1.4 KeV to 25 KeV. For elements with Z from 13 (Al) to 50 (Sn) those energies correspond to K-α and K-β X rays that are given off (only K-α for Al). Those energies also correspond to L-α and L-β X rays for elements with $Z \geq 37$ and M X rays for $Z \geq 69$. The received data are then analyzed with a program called "Gupix." The PIXE analysis in this setup can determine elemental concentrations at a level of about 1ppm.

One study has already been done using PIXE on ballpoint and fountain pen inks. This study used a low beam current in order to prevent damage. It also showed an ability to distinguish many different inks' ingredients using PIXE. This study was done in air and found a 5% error in the accuracy. [1] The experiment in this paper was conducted in an enclosed balloon with Helium in order to decrease error due to air. Older inks should also be more distinguishable than ball-point pen inks because they will most likely contain more metals. The study did find some inks that it was unable to distinguish because it was limited to only two or three metals of interest.[1]

Another study used PIXE to analyze iron-gall ink. It mentioned sixteen metals of interest (Na, Mg, Al, Si, P, S, Cl, K, Ca, Ti, Cr, Mn, Fe, Ni, Cu, and Zn) found in iron-gall inks from the seventeenth century. In this study, the researchers used a 2.8MeV beam with only 300pA current over a .3mm diameter beam. The study ran each sample for about 150 seconds and was successful in distinguishing paper from ink, but it did not try to determine one ink from another. Rather, it focused on a water treatment and the absorption of the elements of the ink into the paper upon treatment.[2]

The only information found regarding the production of printer ink was a comment, "The ink used by the ancients…was fine powdered charcoal; mixed with some mucilaginous or adhesive fluid; it was consequently…somewhat more [like] printer's ink."[3] This causes some concern that detectable levels of chemicals may not be present in a more pure batch of ink because carbon, the primary chemical in charcoal is not detectable in PIXE analysis.

Study into the paper source in the late seventeenth – early eighteenth centuries showed that "the best paper is made from used linen and cotton rags."[4] Another paper from 1814 stated that paper mills are equipped with a rag house where rags are stored for making paper.[5] Paper made from recycled rags will most likely contain a variety of contaminants. These contaminants may cause some concern if they are present in higher rates than the contaminants of the ink. The presence of these contaminants in high levels may drown out any small level contaminants in the ink.

SETUP AND METHODS

In order to establish a series of elements of interest, the first step in setup was to run three small samples cut from a book of interest in the internal beam line which was already calibrated. Each sample was approximately 2cm x 1cm and was mounted to a standard aluminum slide. These samples were run in an evacuated beam-line with a beam current of about 5nA for 30, 20, and 15 minutes. The samples gave a high background believed to be from charge buildup in the paper from the proton beam. The theory was that proton buildup would then induce an arc of electrons to jump from nearby metal. That arc would release X rays over the entire spectrum. The process was

repeated with a larger piece of paper (4cm x 2cm) that was attached directly to the mount and not on a slide. The background was significantly increased on the fourth sample. This is consistent with the theory of the background being from charge buildup. The reason is believed to be that the slides provided a near by source of electrons. By removing this electron source, the charge build-up increased and caused greater arcing and thus greater background. By running the samples in air the charge would be somewhat dissipated by the air and the background decreased.

The samples run in the above test were also observed to have a slight bleaching where the beam hit the paper. In hopes to explain the bleaching damage, a piece of similar, but cheaper paper, was placed in front of the external beam. The beam was run at a low current (~5nA) for about 30 min. to see if the same effect would happen in air. The paper was mounted to an aluminum block. The block covered the entire back surface of the paper and greatly reduced charging. The process was repeated in a helium balloon for 60min. Both in air and in helium, the paper was bleached like it was in the internal beam. The paper was damaged less in air than the vacuum and less in helium less than in air, but they all allowed at least a little damage. More pieces of the cheaper paper were placed near a soldering gun at various distances for 30 min to determine if heat was the source of the discoloration. The paper nearest the gun (approximately 5 mm from the tip) experienced the same discoloration as the papers that had been run in the proton beam. This discoloration from the proton beam clearly matched the discoloration due to the heat of the soldering gun. In order to avoid damage to the valuable books, a smaller beam intensity would have to be used. The samples should also be run in helium for the best protection.

The next step was to optimize the detector. This was done by placing an Fe^{55} source over the detector opening. The amplifier gain, ADC gain, time step, and output source were then adjusted. The signal was evaluated based on the peak channel location and FWHM of the peak from Mn X rays given off from the Fe^{55}. At first the optimal setting appeared to be the maximum setting on the ADC and minimum on the amplifier that would give the right channel number for the peak. This proved to be a disillusion because the maximum setting on the ADC constricted the channels as much as it could, making only the peak of the Mn in the right spot and all other peaks too close together. In the end, the ADC gain needs to be set to 2K in order to spread the energies that can be detected over the maximum numbers of channels. The amplitude is then adjusted to set the Mn peak in the right channel. The best time step is 4μs.

After we determined the optimum detector settings, we needed to measure the beam intensity. For this, a scintillator was placed in the path of the beam. The beam was set to 5nA and allowed to darken a spot on the scintillator the spot had an area of $50.3mm^2$ giving a beam intensity of $9.49nA/cm^2$.

The initial beam signal showed a high background while the accelerator was running. In order to cut down on this background, lead was put in various places to block radiation from the accelerator and anything it may contact in the beam path. The beam was allowed to travel the normal distance in air to the target. In this case the target was a copper cent. Three regions of interest were established and the counts in each were due entirely to background because they had no peaks in them. The data showed that a large amount of the radiation was coming from the floor side of the detector. Shielding was also needed on both sides and above the detector.

Following shielding came filtering. The above scenario was repeated with constant shielding and a beryllium, Teflon, thick Teflon (3 layers), and a combination Teflon with beryllium foil. Each was run for a set amount of time and three areas of interest were recorded: Cu K-α, K-β, and background. The results showed the filters made little to no difference in the resolution of the peaks of interest. No filters were used in the final process.

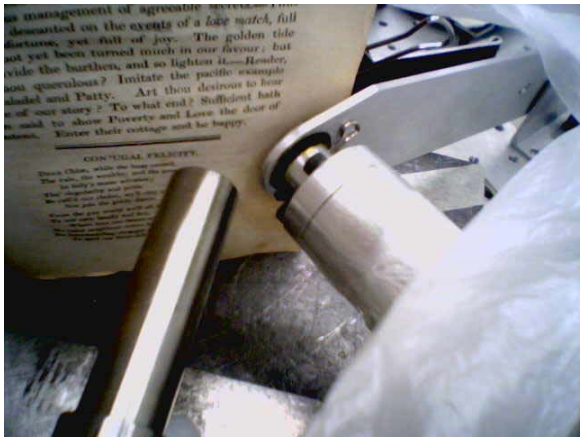
The final step in establishing the setup was aiming. To accomplish this, a collimator was used to specifically pinpoint the location of the beam. The collimator was placed directly against the page of interest with the ink spot visible to both the beam source and the detector. The collimator was made from highly pure carbon so it would not be detectable. The paper was removed and the collimator was run in the beam line at 5-15nA to check for impurities. Large amounts of lead were detected in the carbon of the collimator. The collimator was then moved back up against the Kapton (within 1mm) so the carbon would stop the lead x-rays on the front surface. The lead X rays were heavy enough to penetrate the carbon, and lead was still detected. Finally, a lead sheet about 3mm thick with a hole larger than the collimator hole was glued to the back of the collimator to catch the lead X rays (fighting fire with fire). This final method with the collimator against the Kapton foil was able to stop the lead X rays from being detected.

Since the collimator could not be placed against the paper, a new method of aiming needed to be created. For this, the collimator and the sample were attached to a movable stand. We slid the stand away from the Kapton foil on a track parallel to the beam-line. Then we placed a laser between the beam-line, shining through the collimator to the target. To test this system, graphing paper was used as the target for the laser and the

point was marked. The laser was then removed and the table moved back into place. The beam was run at high intensity (30nA) for 30 minutes to burn a spot on the paper. The difference in the center of the laser and the center of the proton beamed were measured and the process was repeated three times. The vertical alignment of the laser was off by 0.23mm ±0.03 to the left of where the proton beam actually hit, and the horizontal alignment was off by 0.4mm ±0.2. The error margin of the horizontal alignment was too great to be useful unless the target was a horizontal line in which case it would not affect the significant factor of aiming. Aiming would have to be done visually with a scintillator.

The final factor of the setup was refiguring the beam intensity. First the area of the burning on the graphing paper used above was measured. This bad measurement led to the use of a low beam current because the paper was only burnt in the middle of the beam area. For a more accurate area, the area darkened on a scintillator that was left in the beam path at the location of the target was measured. The current on the collimator was measured and compared to the current on an aluminum piece placed where the target would normally sit. The ratio of current on the aluminum to current on the collimator was 1:5. Current measurements could be taken on the collimator and simply converted by the factor of 5. The final intensity used was 1nA on an area of 50mm^2 which give and intensity of 1.99nA/cm^2; two orders of magnitude lower than the intensity in other ink experiments.[1, 2]

The paper runs were taken with the final configuration as follows: The collimator was set within 1mm of the Kapton. The target was 2.5cm from the Kapton and 3.5cm from the detector. The detector was surrounded in lead above and below.



The sides were not completely shielded. The normal to the target paper was between the detector and the beam-line at 25˚ to each. Each sample was set up in a helium balloon. The current was set at 1nA on target. The current was measured on the collimator (5nA). Each sample was run for 30min. Two pages in each book were tested: one towards the front and one towards the back. Three runs were taken on a specified line of ink and one on nearby paper for each page. The bending magnet was set to 4730 gauss.

The ink spots chosen on each page had to be decorative marks so that the beam area did not exceed the ink area. An aluminum oxide scintillator was used to aim the proton beam. The scintillator was placed next to the point of interest so the edge of the beam area would touch the scintillator. Once the correct beam aim was established, the scintillator was removed.

For detector calibrations each sample was mounted to an aluminum mount and run until the error in the known chemical peak was below 5%. The samples were run in air for convenience. The normal to the sample was again at 25˚ to the detector and to the beam-line. The beam current was set to 15nA on the aluminum mount. Twenty samples

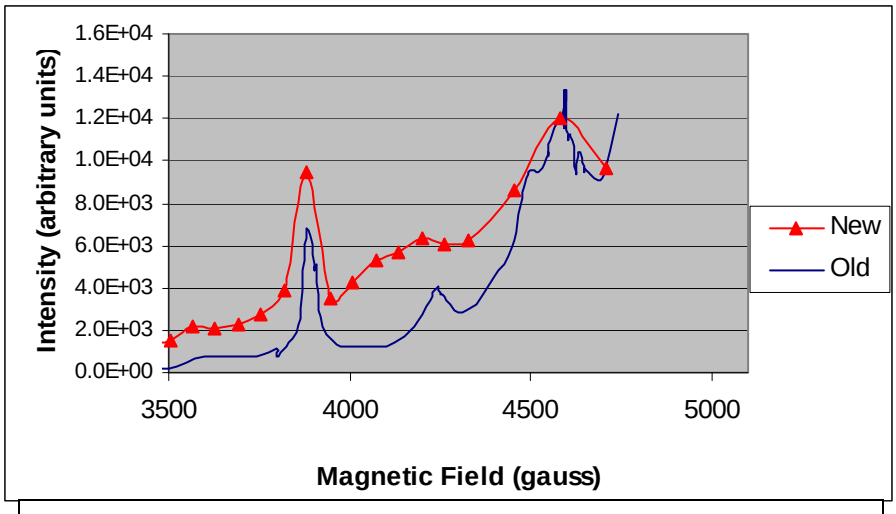
of various chemicals and known concentrations were run. The bending magnet was again set to 4730 gauss.

For energy calibrations, a fluorine target was placed in front of the beam with a gamma detector set at 90˚ to the beam-line. The gamma detector was set on the opposite side from the x-ray detector for convenience of placement. The target was mounted on an aluminum slide with its normal at 45˚ to the detector and beam-line. The target was run in a helium balloon. Counts were taken on the Genie system in three areas of interest and evaluated according to their total area.

RESULTS

Through this experiment, I was able to derive three sets of results. I found the energy calibrations for the proton beam based on the magnetic field settings; I found the adjustment factor for the computation of precise quantitative results; and I found that the setup I used was mostly ineffective at identifying the elemental concentrations of Ink from the early 19th century.

To calculate the energy of the proton beam, I ran the proton beam with various magnetic field settings a fluorine target. The bending magnet at each setting would bend a different energy of beam down the beam-line through the collimators to the target. The fluorine at specific energies gives off high intensity of gamma rays.



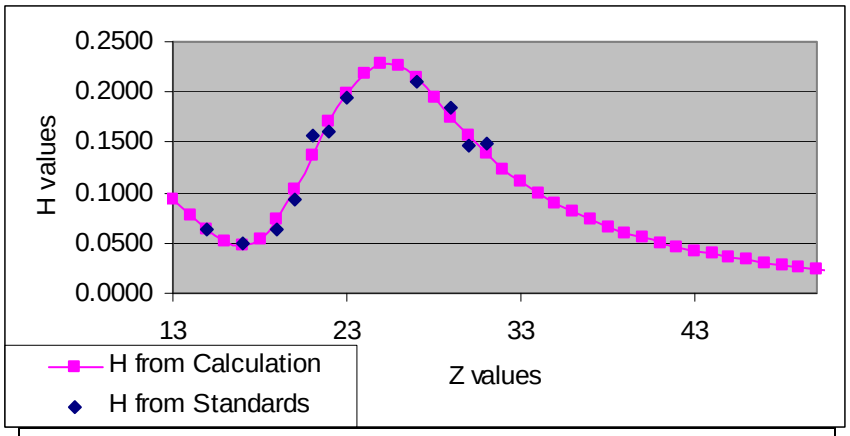
Graph 1: Energy comparisons

These points of high intensity correspond to the peaks (see graph 1). The plot of this magnetic field verses the gamma ray intensity was then compared to a similar plot where the energies of the peaks was known (graph 1). By comparing these two graphs, the energy that corresponds to each magnetic field setting was found. The important value for these experiments is that the magnetic field setting of 4730 gauss. This setting corresponds to 1.83MeV in the helium balloon and 1.22MeV in the normal room air. arbitrary units

Once the energies were known, the detector was calibrated to give quantitative values in parts per million (ppm). The elemental calibration involved running each standard with known concentrations and analyzing the results with Gupix. A correction factor for each element, called the H value, was set to 1, and Gupix calculated the $\mu g/cm^2$ it thought was present in each standard. The values were then compared to the known $\mu g/cm^2$ and an H value was calculated for each element. The H value can now be multiplied by the Gupix output to give an exact quantity of each element in any sample.

The problem that came up was the H values are supposed to be somewhat consistent and form a smooth line when plotted against the Z for each element. The initial H values did not form a smooth line. To calculate consistent H values, the values with an error greater than 3% (all of which were also greater than 9.5%) were thrown out and the remaining H values were averaged, each point with the point before and after it. The averages were plotted and compared to previous graphs of H values. Though this plot differed from other H value plots for different setups, the thing all graphs had in common was that they matched the background plots taken when the accelerator was running but the beam was stopped before reaching the target area. The elements in the standards that were tested corresponded to Z's between 13 and 34. The background plot for this

detector was then used to extrapolate H values for elements with Z's below 13 and elements with Z's above 34. Graph 2 shows the comparison of the average H values from the standard runs to the final calculated H values for this detector. The final H values fit the curve established by the standards and match the background from the accelerator.

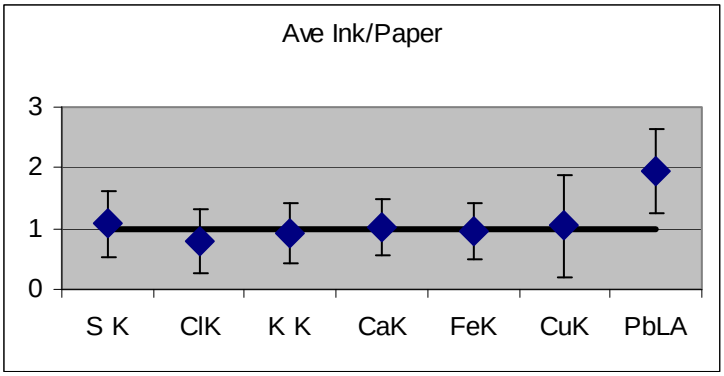


Graph 2: H values for external detector.

The data for the run on ink and paper were analyzed using the Gupix program. The energies and H values from the above sections were used in the analysis. Seven elements (S, Cl, K, Ca, Fe, Cu, and Pb) were analyzed. Because some elements could be from paper and some from the ink, each run on ink was divided by the run on the paper (I/P) for that same page. The ratios of I/P for each element were then averaged and a standard deviation taken. A ratio less than one for an element could be caused by the ink shielding the element from the paper, and a ratio greater than one would be from an element that is found more predominantly in the ink.

The standard deviation was plotted with the average for each element. Graph 3 clearly shows for each element the standard deviation overlaps the line at one. The exception is lead which is only found in one book (book 1). All six runs resulted in I/P>1. In other words, all the runs on the ink found more lead than the corresponding runs on only the paper. Unfortunately, lead is not a common element found in paper, but for the pages

with lead, it did prove to be a distinguishable factor. However, due to the small number of runs, it is possible that this result is not statistically significant. The I/P statistical errors for lead range from 24%-69%. The reassuring factor from the experiment is that none of the other elements have I/P values that are consistently above or below I/P=1 for any book, and all the I/P values are above I/P=1 for the lead in book one.



Graph 3: Ink to paper ratios with standard deviations

CONCLUSIONS

From this research, it is clear that this method of analyzing printer inks from the 18th and 19th centuries did not work. The runs taken were not sufficiently accurate to be able to distinguish ink from paper on any element other than lead, and lead alone is not a good element for distinguishing inks because it was only present in one of the four books tested.

There are several different ways in which the analysis could be improved. First the beam intensity could be increased. This would lead to several more counts which would decrease the error range the data. The only reason it was so low was due to an inaccurate measurement of the beam radius. The intensity was two orders of magnitude lower than other groups who have successfully analyzed inks.[1, 2]

The beam area could also be decreased by a smaller hole in the collimator. Decreasing the beam area will allow for more accurate aiming of the beam on a spot of

ink. It will also allow for a larger range of choices of where to test. The large beam area forced the use of large ink prints.

More sample runs would also make a difference. Each paper was only tested once away from the ink. Testing the paper without ink multiple times would give a more accurate. Multiple tests and longer tests decrease the statistical inaccuracy in an experiment. Since most of the elements observed are from the paper, a high statistical accuracy is needed in order to distinguish the elements in ink from the elements in paper. Taking more runs will give a statistically better result and help give a better understanding of the true content of ink in contrast to the paper.

One advantage to the research is that the paper can be analyzed. With this large data base of runs that the ink did not significantly affect, we have begun to analyze the paper to determine if the method is effective for distinguishing one paper from another on the basis of the all the same elements (with the exception of lead). Each book was printed in a different state and the paper most likely came from different paper mills. The ability to distinguish one paper from another will still be useful in characterizing the writings of interest in this project.

ACKNOWLEDGEMENTS

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