Development of a System for Water Quality Analysis Using Particle Induced X-Ray Emission

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DEVELOPMENT OF A SYSTEM FOR WATER QUALITY ANALYSIS
USING PARTICLE INDUCED X-RAY EMISSION

by

James Albert Andrus

A Thesis
Submitted to the
Faculty of The Graduate College
in partial fulfillment
of the
Degree of Master of Arts
Department of Physics

Western Michigan University
Kalamazoo, Michigan
August 1980
DEVELOPMENT OF A SYSTEM FOR WATER QUALITY ANALYSIS
USING PARTICLE INDUCED X-RAY EMISSION

James Albert Andrus, M.A.
Western Michigan University, 1980

Particle induced x-ray emission (PIXE) has been in use for several years at Western's accelerator laboratory. Its primary purpose has been to provide trace element analysis of various types of solid samples. The analysis of water samples has not been done because of problems involving target preparation for the accelerator. A process called vapor filtration, developed at Purdue University, allows adequate sample preparation for the accelerator. This process is being adapted for use here at WMU. When completely operational, this system will give the WMU accelerator program the additional capability of performing water quality analyses to concentrations of parts per billion. This thesis tells how the system was developed, details its operation and presents some preliminary results of analyses on waste water samples.
I wish to thank Dr. Stephen Ferguson for the hard work and advice which he gave during the course of this project. There are many other people who have been of great assistance to me. I would like to mention Dr. Larry Oppliger, who donated a portion of his laboratory, Mr. Nick Bock, who donated the calibration standards, Dr. Stanley Derby, who donated the equipment which I needed to make the deionized water, and Mr. Stanley Steele, our machinist, who put a great deal of time and work into making the apparatus.

James A. Andrus
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ANALYSIS USING PARTICLE INDUCED X-RAY
EMISSION.

WESTERN MICHIGAN UNIVERSITY, M.A., 1980
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CHAPTER I

INTRODUCTION

The purpose of this study is to develop a system for water quality analysis using Western Michigan University's tandem Van de Graaff accelerator, and to determine what problems need to be solved before this system is put into routine use. The water samples are prepared by the use of "vapor filtration," a technique developed at Purdue University by Simms and Rickey (Si 78). These samples are then analyzed by Particle Induced X-ray Emission (PIXE).

PIXE is not new at Western Michigan University. It has been used in the past for analysis of mud from Austin Lake, tracing migration routes of Indians (Gi 77), and analysis of solid sludge samples. Using PIXE for water quality analysis is new, however, and the process of vapor filtration is what makes it usable for the WMU accelerator. One major problem with accelerator based water analysis is fabrication of a suitable target from a water sample. For instance, the water could not be held in a container while being bombarded because one would only obtain an analysis of the container. When a water quality analysis is performed, only the contaminants in the water are of interest, not the water itself. If the contaminants could somehow be removed from the water, they could perhaps be made into a suitable target. This is what vapor filtration does. It removes the water from the samples and deposits the contaminants...
on a cellophane backing which can easily be made into a target for the accelerator.

Vapor filtration (explained in Chapter IV) has several advantages as a sample preparation method. It is a closed system so dust cannot get into the sample while it is being prepared. There is no transfer or loss of solid, so good quantitative results can be obtained. Also the water is not agitated (as in boiling) so no material is lost through water droplets leaving the surface (Ri 77).

After the system was built, realistic samples were tested. These samples consisted of waste water from a paper mill. The results showed that this technique provides a multielemental analysis to parts per billion. The results also show that there are contamination problems involving the deionized water, which was used in the calibration of the detector. This problem must be solved before the system is put into full working order.

The addition of water quality analysis to Western Michigan University's accelerator program will, we hope, bring more users into the program and provide more operating funds. This addition will also attract many segments of the University community as it provides a new way to analyze water samples; a way which in some situations may be preferable to some of the older methods of analysis.
CHAPTER II

REVIEW OF PIXE THEORY

PIXE is a commonly used acronym for "Particle Induced X-ray Emission." For this project, the "particles" are protons, so the acronym is still applicable. PIXE theory is well known and detailed development can be found from many sources (Jo 76). The following brief review of PIXE theory is divided into two topics: (a) production of x-ray spectra, (b) production of background.

Production of X-ray Spectra

A PIXE spectrum is produced by striking a target with a beam of protons from the University's tandem Van de Graaff accelerator. When passing through the target, protons in the beam interact with the electrons in the target atoms to produce vacancies in the inner atomic shells. In the deexcitation process that follows, x-rays are emitted. These are detected by a lithium drifted silicon (Si(Li)) detector which produces voltage pulses proportional to the energy of the incident x-rays. Atoms of different elements have different electronic configurations and binding energies. Therefore, "characteristic" x-rays are produced. That is, the energies of the x-rays correspond to the elements from which they were emitted. The x-rays emitted are thus an indication of the elemental make-up of the target. The voltage pulses from the detector are
processed to produce a pulse amplitude, or energy, spectrum. Since the detector plus electronics acts as an energy analyzer, the analysis is multielemental in nature. It will be shown later that this method results in a quantitative as well as qualitative description of the target.

Different energies of x-rays can be emitted from a given element. For instance, when a vacancy in the K-shell is filled by an electron from the L-shell, a "Kα" x-ray is emitted. When the electron is from the M-shell, a "Kβ" is emitted. The Kβ x-ray is higher in energy than the Kα x-rays. When a vacancy in the L-shell is filled with an electron from the M-shell, a "Lα" x-ray is emitted. Using this scheme one can label all the different x-rays from a particular element. Since each element emits various energies of x-rays, there exists the possibility of interference. For example, the "Kβ" x-ray from one element may overlap the "Kα" x-ray from another element. This could lead to an incorrect analysis. This problem will be addressed later in Chapter V.

Production of Background

In this project, the materials to be tested are held on a piece of cellophane, which produces an x-ray background which is present in all samples. Since the background is a factor which limits the sensitivity, the sources of it require some discussion. The three sources of background present in PIXE analysis are: (a) bremsstrahlung from the projectiles, (b) bremsstrahlung from secondary electrons and (c) Compton scattering in the detector of
γ-rays from excited states of target nuclei. The first two are always present in the PIXE spectrum and do not depend on the detector and the near surroundings. Folkmann, Gaarde, Huus and Kemp (Fo 74) give an excellent treatment of background radiation from PIXE analysis. It is summarized below.

Secondary electrons are those which are ejected from the matrix atoms by bombardment with the beam protons. They are then decelerated by the electric field of the matrix atoms, emitting bremsstrahlung radiation before eventually losing their energy through various collisions in their passage through the target. If the target is thin enough, there is a good chance that most of the secondary electrons will escape before being decelerated. However, measurements made by Folkmann, et al. (Fo 74) have shown these thicknesses to be too thin to be practical. This type of background shows up at the lower energies of the x-ray spectrum. The spectrum exhibits a rapid decrease above the maximum energy which a proton can transfer to a free electron. For 3-MeV protons, this is about 6.5 keV (see Figure 1).

Beyond that point, projectile bremsstrahlung is important. It is due to large accelerations which occur during close collisions between the incident protons and the matrix nuclei. Figure 1 is the energy spectrum of a blank cellophane target. It shows both the low energy bremsstrahlung from secondary electrons and the higher energy bremsstrahlung from the incident projectiles.

Gamma rays are emitted when the incident particles have enough energy to excite the nuclei in the target. Gamma radiation will
undergo Compton scattering in the detector. The background this produces depends not only on the detector, but also on the material in the matrix as different nuclei have different cross sections for gamma emission. One reason that 3-MeV protons were used was to reduce this background by utilizing lower energy projectiles.
Figure I

Background spectrum from a piece of cellophane. The arrow at the 6.5-keV position indicates the maximum energy which can be transferred from a 3-MeV proton to a free electron.
CHAPTER III

EXPERIMENTAL PROCEDURE

The targets, which consist of PD-215 cellophane attached to a plastic washer (see Chapter IV for the procedure) can be snapped into a custom made target holder in multiples of six. The target holder is inserted manually into the chamber and the samples are bombarded one at a time (see Figure II). Targets are changed manually, requiring a person to go into the target room to slide a new target into place after each run. Cahill (Ca 75) describes a "slide projector" type target holder that automatically changes 100 targets before reloading. Such a device would be desirable and cost effective for this system if it is ever used to any great extent.

Presently the target chamber is kept at atmospheric pressure. This helps to facilitate target changing. Also, it allows the target to cool more readily than in a vacuum. The disadvantage is that a strong argon line is present in the spectrum due to the argon in the air. However, this is not a great problem because the argon line does not interfere with any lines of interest.

The diameter of the sample on the cellophane is 1/4 inch. In making the sample, there is a possibility that it may be collected in greater concentrations near the edge than in the center. Therefore, a homogeneous beam of a larger diameter is required. To achieve this the beam is first sent through a nickel diffusing foil.
and then collimated by two apertures. The beam spot striking the target is set by the apertures to be 3/8 inch. Therefore, the sample is covered sufficiently by the beam. Most of the beam passes through the target, is collected in a Faraday cup and processed by a current integrator. Only a small fraction of the beam is stopped by the target, so there is no need to be concerned about charge build-up on the target.

Calcium and iron are often present in large quantities in environmental samples. If there is a lot of these two elements in a sample, then the sensitivity of the detector is decreased. To keep large amounts of these x-rays from reaching the detector, a "funny filter" (Ca 75) is placed between the target and the detector. This filter is composed of three different layers, each with a different purpose. A layer of aluminum absorbs x-rays in the iron region and a layer of polyethylene absorbs x-rays in the calcium region. A small hole is punched in these two layers to allow a small fraction of these x-rays to pass through, even though most are absorbed. For the aluminum absorber, the hole exposes about 2% of the detector to the radiation and for the polyethylene absorber, about 0.6% of the detector's area is exposed. Finally, a layer of "scotch tape" filters out x-rays from elements lighter than silicon. The system also has a pile-up rejection system using "on demand" beam pulsing to sweep the beam off target while the detection system is processing a pulse. The details of this system were outlined by Gibeson (Gi 77).
The detector is a lithium drifted silicon (Si(Li)) detector. It converts the energy of the x-rays into voltage pulses, which are processed electronically into an energy spectrum of the sample. The initial analysis is done by a PDP-15 computer located in the accelerator facility. For more detailed analysis, the spectra are stored on tapes holding twenty spectra each and taken to the University's PDP-10 computer.
Figure II

Experimental set-up, showing the major components of the beam line, target chamber and analyzing system.
Sample preparation played a particularly important role in this project, as water samples had not previously been analyzed at Western's accelerator facility. The heart of the preparation procedure is a process called "vapor filtration." This process was initially developed at Purdue University and is described by Simms and Rickey (Si 78) in sufficient detail to guide this project. One of the problems incurred while attempting to analyze water samples on the Van de Graaff accelerator is containment. The experimenter must contain the water in something while at the same time striking it with a beam of protons and receiving its x-ray spectrum. This is extremely cumbersome in practice as the container would block both the incoming proton beam and the outgoing x-rays. Vapor filtration sidesteps this problem. When water samples are analyzed, it is actually the trace contaminants that are being measured, not the water itself. Vapor filtration removes the water from the samples and deposits the dissolved and suspended contaminants on a piece of cellophane which then can be used as a target. This is done by pumping the water through a cellophane which is permeable to water vapor but not to water. Thus water evaporates only at the cellophane, so that every nonvolatile contaminant in the water is deposited on the cellophane.
A schematic of the sample preparation system is shown in Figure III. A manifold consisting of thirteen vapor filters is pumped on by a mechanical pump which maintains a filtering pressure of 500 microns or less. A pressure of 4000 microns or less is necessary for the vapor filtration process to work. This pressure is constantly monitored by a thermocouple gauge located between the manifold and the pump. Each vapor filter may be opened or closed to vacuum individually. In addition, there is a master valve in the pump line that controls the vacuum into the manifold. To prevent water vapor from mixing with the pump oil, a cold trap was placed in the pumping line. It is cooled by a refrigerator to a temperature of -60° Fahrenheit. The vapor condenses on the surface of the trap before reaching the pump, thus preserving the integrity of the oil. The trap must be warmed up after fifteen to twenty samples have been pumped. After removing the water from the surface of the trap, it is replaced. The trap is filled with alcohol to insure uniform cooling. On the side of the trap is an air intake valve which allows the system to be brought to atmospheric pressure.

**Vapor Filtration Apparatus**

A sketch of the filtration apparatus is shown in Figure IV. It consists of two parts, a tube for holding the sample and a target support. The target support is constructed from 3/4 inch Lexan polycarbonate plastic. It was made in the physics machine shop by the machinist, Stanley Steele. Special care had to be taken when machining the target support. Lexan does not conduct heat well, therefore
it can heat up and melt during the machining process. The material had to be annealed periodically by heating it to 220°-250° Fahrenheit for about six hours. In addition, care had to be taken to keep the cutting tool cool with soapy water. All gluing was done with methyl chloride.

The tube for holding the sample was cut from 1/4 inch (inside diameter) plastic tubing. The support collar for the tube is made of 1/2 inch Lexan. This apparatus is resistant to nitric acid, which is necessary as all cleaning was done in an acid bath.

Operation

The operation of the apparatus follows: An O-ring is placed in the O-ring groove inside the target support. The support is then mounted on the manifold pipe which leads to the mechanical pump. A porous plug 5 mm in diameter is placed in its support. The plug is made of polyethylene and was obtained from Fisher and Porter Co. A 3/4 inch circular disk of cellophane is placed on the target holder, above the porous plug. This disk is made of PD-215 cellophane produced by DuPont. It will be the target once the contaminants are deposited on it.

The tube is then placed on top of the target support and held in place by three spring clamps (not shown in the drawing). A carefully measured amount of sample (usually 5 ml) is slowly poured into the tube in such a way that air bubbles do not develop. A piece of aluminum foil is placed over the top of the support to keep dust out, and the apparatus is opened to vacuum. The vacuum is kept
below 500 microns for this procedure. Water cannot exist as a liquid or solid at this pressure, so it turns to a vapor, passing through the cellophane. Since the cellophane is permeable only to water vapor, any contaminants are deposited on the top of the cellophane. After about twenty-six hours, the water has been completely pumped out. The cellophane, with the deposited contaminants, is lifted out by sticking it to a support ring with vacuum grease and placed in a specially made target holder, which holds six targets at once. The target is now ready for analysis.

Cleaning Procedure

The cleaning procedure is vital when preparing samples for PIXE analysis. The target support and tubes are washed in a nitric acid bath between each sample. During the months of sample preparation the following cleaning routine has been developed. The supplies required for cleaning are: (1) nitric acid ACS in 20% solution with deionized water, (2) fresh deionized water, (3) a 250-ml beaker, (4) a 1000-ml beaker, (5) tongs, and (6) proximity to a sink. Below is the procedure used for cleaning the vapor filtration apparatus. Before cleaning commences, everything is rinsed thoroughly with tap water. About 80 ml of a solution of 20% nitric acid is poured into the 250-ml beaker.

Target support: 1) Using the tongs, pick up a target support and immerse it in the acid bath. 2) Remove after about thirty seconds. 3) Rinse completely by pouring deionized water over the support. 4) Then set on a clean surface to dry.
Tube: 1) Hold the tube firmly with the tongs and pour the acid bath through the column, starting at the collar. If many columns are to be washed, one may want to catch the acid solution in the 1000-ml beaker for use on the next column. Provided that all columns are rinsed with water previously, one can rinse as many as four columns without changing the bath. 2) Rinse the column by pouring deionized water through it in the same manner. 3) Set it aside on a clean surface to dry.

Graduated cylinder: The graduated cylinder, used to measure out the quantity of the sample, must also be washed between samples. 1) Rinse with tap water. 2) Fill it up three times with the acid solution. 3) Rinse with deionized water. 4) Set aside to dry.

There are many different schemes which one could develop for washing the apparatus. This particular method developed naturally through repeated sample preparations and seems to work quite well.

Precautions

There are several precautions which should be taken when preparing samples. First, samples with large concentrations of acid do not work well. Although the tube and supports are resistant to acid, the cellophane is not. Running an acidic water sample through the process tends to make the cellophane brittle and it often breaks, allowing the water to rush through the plug and into the vacuum system. Fortunately, the cold trap is adequate to condense much of the water, but the cellophane is useless as a target. However,
Simms and Rickey (Si 78) report that samples preserved with about 1.5 ml of nitric acid per liter of solution can be used.

Secondly, only water with fairly low concentrations of contaminants should be tested. If high concentration samples of water (sludge samples) are prepared, a cake of material will form on the cellophane. It could very easily fall or flake off, giving erroneous results when analyzed.
Figure III

A schematic drawing showing the major components of the sample preparation system.
Figure IV

A cross sectional drawing of the vapor filtration device (not to scale).
The formula used to determine the amount of a certain element from a specific x-ray peak is found in Johansson and Johansson (Jo 76).

\[ N = \text{An} \sigma_i w \delta \lambda e \]  

Where:

- \( N \) is the number of counts under the peak. This is obtained by subtracting the background from the spectrum and adding up the remaining counts under the peak. For a discussion of this process, see the computer processing section.

- \( A \) is the amount (concentration) of a certain element in the sample.

- \( n \) is the proton flux, which is determined by collecting the beam in the Faraday cup.

- \( \sigma_i \) is the ionization cross section of the \( i \)'th shell. For instance, \( i \) could be K or L depending on the type of x-ray.

- \( w \) is the fluorescence yield, which is the probability that an x-ray is emitted when the vacancy in the K-shell becomes filled.

- \( k \) is the relative transition probability for the particular x-ray transition used in the measurement.
Ω is the solid angle subtended by the detector. This is determined by the geometry of the experiment.

\( t \) is the transmission through the window of the irradiation chamber. Included is the self-absorption factor for the sample and for any other absorbers.

\( e \) is the efficiency of the detector. The quantities \( σ_i, w, k, \ Ω, t \) and \( e \) can all be determined separately, however, we determined them empirically. These quantities were related to the "efficiency factor," \( e \), by:

\[
\frac{1}{e} = σ_i wkΩe.
\]

Then,

\[
N = A n \frac{1}{e},
\]

or

\[
e = \frac{nA}{N}.
\] (2)

This efficiency factor was calculated using commercially made multi-element filters, orchard leaf standards from the National Bureau of Standards and atomic absorption standards donated by Nick Bock of the National Council for Air and Stream Improvement (NCASI). The absorption standards consisted of lead, zinc, copper, chromium, iron, barium, manganese and cadmium. The multielement filters consisted of vanadium, manganese, cobalt, copper, lead, titanium, chromium, iron, nickel, zinc and cadmium. These filters consisted of a uniform amount of material spread throughout an area larger than the beam spot. Therefore, a calibration of the concentration for each of these elements was made for the amount of element within
the area of the beam spot. Once these concentrations were found, the efficiencies were calculated in the usual manner using Equation 2. The orchard leaf standards consisted of manganese, iron, copper, zinc, arsenic, bromine, rubidium and strontium. Since these are solid targets, the efficiencies had to be normalized to the thin target efficiencies. This was done by equating the results for manganese, iron, copper and zinc to those in the thin targets. Then the rest of the elements, arsenic, bromine, rubidium and strontium were multiplied by the proper normalization factor (determined from the rest of the elements) to obtain a thin target efficiency.

The atomic absorption standards come in concentrations of 1000 parts per million (ppm). They were diluted to 10ppm and 1ppm before being used for calibration. In order to dilute these samples, the following procedure was used:

\[ V_1 C_1 = V_2 C_2 \]  

(3)

\( V_1 \) and \( C_1 \) are the volume and concentration for the original solution and \( V_2 \) and \( C_2 \) are for the final solution. When preparing the solutions, everything was diluted with deionized water. Washing of the equipment was done with 20% nitric acid, and to be absolutely sure that no contamination was present between solutions, different beakers were used for each solution. These standards were run through the vapor filtration system just as if they were unknown samples. They were then bombarded and their spectra recorded. These spectra were then analyzed (using the techniques to be discussed later) and the number of counts under the x-ray peaks were determined.
The efficiency factor could then be calculated using Equation 2, where \( \varepsilon \) is the efficiency factor, \( n \) is the total charge incident on the target (in microcoulombs), \( A \) is the concentration (in parts per million) and \( N \) is the number of counts in the peak.

The efficiency factor varies smoothly as a function of atomic number, so a plot was made from the calculations (see Figure V). Several efficiency factors were calculated for each element and there was quite a bit of variance for some of the elements. This could be due to inconsistencies in the preparation of standards or in measuring the amount of the sample for filtering. The mean was calculated for each element and plotted as a dot (●). The mean deviation was then calculated and represented by error bars. Some elements did not have multiple measurements, so error bars were not used. In some instances, the calculated efficiency factor was probably not correct for a specific element, presumably for one of the above reasons. In these cases, the mean was recalculated, leaving out the "incorrect" value and the "good" mean replotted as a circle (○). The curve was drawn with a french curve and fitted to the data by "eye." The values for low Z elements such as calcium and potassium were extrapolated from the curve. They should be experimentally measured before a quantitative analysis is done for these elements. As can be seen, for low and high Z the curve did not fit the data as well as for medium Z. To be conservative, uncertainties of 50% were arbitrarily set for high and low Z elements and uncertainties of 25% were set for middle Z elements, where the curve fit well. The values for \( \varepsilon \) were taken from the curve for...
those elements which were not tested. Once the efficiency factor is known for each element, Equation 2 can be rewritten:

\[ A = \frac{eN}{n} . \]  

This gives the total amount (concentration) of a particular element in an unknown sample.

Computer Processing

In order to determine \( N \) of Equation 4, and thus the concentration of a certain element in a sample, one must sum up the number of counts in the corresponding x-ray peak. This is done by making use of the data analysis programs developed for the PDP-10 computer by Dr. Stephen Ferguson. In order to understand the process, it is best to go through it from the beginning to the end of the analysis.

The operator must first enter a blank spectrum as the background. This is a spectrum which has been obtained from a piece of cellophane without contaminants. The operator now calls up the spectrum from the sample to be analyzed. The operator locates a portion of the spectrum which is just background (i.e. between peaks) and sets two markers to span this region. The computer averages this region and normalizes the background to the spectrum by matching the background and the spectrum in this region. The background is then subtracted from the spectrum.

To obtain a quantitative analysis only the \( K_\alpha \) peaks (\( L_\alpha \) for lead) need to be summed. The operator sets the limits of integration, tells the computer to subtract the background and then
integrates the peak. This process is repeated until all the peaks in the spectrum have been summed.

In a multielemental sample, there exists the possibility that $K_B$ peaks may interfere with $K_\alpha$ peaks of a different element. If the $K_B$ peak from element "A" interferes with the $K_\alpha$ peak from element "B," the $K_B$ peak must be eliminated from the spectrum before summing up the $K_\alpha$ peak for "B." If it is not, then the wrong concentration would result for element "B" and the analysis would be incorrect. To assist this process, the computer has access to a calibration file, which holds information on efficiency factors, x-ray energies and relative intensities for each element. The efficiency factor, which was found from the standards has already been discussed. The relative intensities are also determined empirically from the standards (Figure VI). No matter how much of a certain element is in a sample the ratio of the intensities of the $K_B$ peak to the $K_\alpha$ peak should be a constant. This ratio was calculated from the standards and stored in the calibration file. Now when the operator wants to eliminate the $K_B$ peak from the spectrum, the computer is ordered to "strip" the peak. The computer then locates where the $K_B$ peak is from the energy calibration, it calculates how intense the $K_B$ peak should be from the relative intensity and then adds it to the background spectrum. The operator can then sum up the $K_\alpha$ peak for element "B" and obtain the correct concentration.

If many of the same type of samples are to be analyzed, the operator can command the computer to repeat the same analysis for
the rest of the samples. They are then analyzed automatically, thus saving much time in the analysis procedure.

Sensitivity

Sensitivity is defined as the smallest detectable concentration in the sample. One of the advantages of PIXE is the high sensitivity which can be obtained. The limits on the sensitivity are:

1) Background: It is impossible to avoid since the projectiles interact with the elements of the matrix as well as the sample. In order to see a characteristic x-ray peak, it must be statistically larger than the background. From Johansson and Johansson (Jo 76),

\[ N_p = 3\sqrt{N_b} \]

where \( N_p \) is the number of counts in the peak and \( N_b \) is the number of counts in the background in the interval equal to the full width half maximum of the peak.

2) Deionized water: Deionized water used in the preparation of standards contained significant amounts of copper, zinc and lead (Figure VII). These concentrations varied from sample to sample. The source of the contamination is not known at this time. However, since the system was calibrated using standards which were mixed in this water, it sets a limit on the sensitivity for the above elements. If there is a large demand for this analysis system in the future, the source of the contamination will have to be found and eliminated.
<table>
<thead>
<tr>
<th>Element</th>
<th>Concentration (ppb), by Run Number</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>62</td>
</tr>
<tr>
<td>Cr</td>
<td>-</td>
</tr>
<tr>
<td>Mn</td>
<td>-</td>
</tr>
<tr>
<td>Fe</td>
<td>3</td>
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<tr>
<td>Cu</td>
<td>17</td>
</tr>
<tr>
<td>Zn</td>
<td>13</td>
</tr>
<tr>
<td>Pb</td>
<td>199</td>
</tr>
</tbody>
</table>

The results from the next chapter give some estimates for sensitivities. For the sample of waste water called NCASI 1, there were several elements in abundance. Chromium, for instance, appeared in concentrations of 3 to 5 parts per billion (ppb). \( N_p \) was 344 and \( N_b \) was 9224. Using Equation 5, \( N_p \) had to be \( \sqrt[3]{9224} \), or 288 or larger to be statistically significant. Of course, 344 is larger than 288 so the system is sensitive enough to detect trace elements in the parts per billion range.

There is another limitation on the sensitivity, however. In NCASI 1, the lead \( L_\alpha \) peak overlapped with the \( K_\alpha \) peak for arsenic. Before summing up the arsenic \( K_\alpha \) peak, the lead \( L_\beta \) peak is summed up first. Then the lead \( L_\alpha \) peak is stripped from the spectrum after which the arsenic \( K_\alpha \) can be summed. The sensitivity is reduced for
lead because the L_β line is weaker than the L_α line. The sensitivity for arsenic is also reduced because the L_α peak from lead has been added to the background making N_b larger. Thus more counts are required in the peak to exceed 3\sqrt{N_b}. This can also happen for other pairs of elements, but lead and arsenic are the only ones to be observed during the course of this project.
Figure V

Graph of efficiency factor vs. atomic number. (●) represents all data. (○) represents "good" data. The curve was fitted to the data by eye.
Figure VI

Graph of the intensity of the $K_\beta$ lines relative to the intensity of the $K_\alpha$ lines vs. atomic number. The curve was fitted to the data by eye.
Figure VII

PIXE spectrum of deionized water, showing peaks due to various contaminants which were found. For an analysis of the concentrations of the contaminants, see Table I.
CHAPTER VI

EXPERIMENTAL RESULTS AND CONCLUSIONS

The National Council for Air and Stream Improvement donated several samples of waste water from paper mills for PIXE analysis. Accompanying the samples were the results of an atomic absorption (AA) analysis done by NCASI for comparison with PIXE results. Many of the samples were digested in acid, so they were too acidic to be put through the vapor filtration process. Other samples contained too much material to be filtered, resulting in "mud cakes" deposited on the cellophane (see Chapter IV). Two samples were prepared, NCASI 1 and NCASI 4. They were both from the same mill, however, NCASI 4 was "spiked" with more material to give larger concentrations.

These samples were PIXE analyzed and their spectra are shown in Figures VIII and IX. A great many elements can be seen on these spectra and the overlapping of $K_{\beta}$ and $K_{\alpha}$ peaks can be observed. This shows that one must indeed be aware of the interference between peaks and to compensate for it in analysis. In addition, the operator must also be aware of the interference between lead and arsenic. The PIXE spectrum for NCASI 4 has more elements in it than the spectrum for NCASI 1. This shows that PIXE is sensitive to the spiking of NCASI 4 with extra material.

The comparison of the PIXE analysis with the AA analysis is
shown in Table II. The values for the concentration are all given in parts per billion. While the AA analysis was done for five elements, the PIXE analysis showed various concentrations of fourteen elements. With PIXE, which is multielemental, one does not need to test separately for each element. All elements which are in the sample in concentrations above parts per billion will show up in the analysis. It is very fortunate that NCASI tested for the very elements which were found contaminating the deionized water. The measured concentrations of copper, zinc and lead were all higher than the values for the same elements when analyzed by atomic absorption. The lead value in particular varied a great deal from AA values. This shows that the water contamination is indeed a problem which needs attention before the system can be put to practical use. Once this problem is solved, WMU will have a new addition to its accelerator program; the capability to perform quantitative water quality analyses to concentrations of parts per billion using PIXE.
Figure VIII

PIXE spectrum for the paper mill waste water sample labeled NCASI 1.
Figure IX

PIXE spectrum for paper mill waste water sample spiked with extra material. Labeled NCASI 4.
Table II
Results for Waste Water Samples

<table>
<thead>
<tr>
<th>Element</th>
<th>NCASI 1</th>
<th>NCASI 1</th>
<th>NCASI 4</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>NCASI 1</td>
<td>NCASI 1</td>
<td>NCASI 4</td>
</tr>
<tr>
<td></td>
<td>68</td>
<td>71</td>
<td>72</td>
</tr>
<tr>
<td>K</td>
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</tr>
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</tr>
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</tr>
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<td>Co</td>
<td>6</td>
<td>5</td>
<td>6</td>
</tr>
<tr>
<td>Ni</td>
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<td>3</td>
<td>4</td>
</tr>
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<td>2</td>
<td>6</td>
</tr>
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<td>Zn</td>
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<td>26</td>
<td>166</td>
</tr>
<tr>
<td>Pb</td>
<td>32</td>
<td>27</td>
<td>34</td>
</tr>
<tr>
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<td>2</td>
<td>2</td>
</tr>
<tr>
<td>Br</td>
<td>14</td>
<td>2</td>
<td>16</td>
</tr>
<tr>
<td>Rb</td>
<td>7</td>
<td>4</td>
<td>5</td>
</tr>
<tr>
<td>Sr</td>
<td>39</td>
<td>3</td>
<td>28</td>
</tr>
</tbody>
</table>

PIXE runs for NCASI 1 are labeled: 68, 71, 72
Atomic absorption analysis for NCASI 1 is labeled: N1

PIXE run for NCASI 4 is labeled: 69
Atomic absorption analysis for NCASI 4 is labeled: N4

This table gives values for concentrations in parts per billion.


