PROTON-INDUCED X RAY FLUORESCENCE ANALYSIS OF TRACE ELEMENTS IN WHEAT FLOUR

by

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Major Professor

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CHAPTER I

INTRODUCTION

During the past few years, technological developments in the area of high resolution solid state x ray detectors have allowed x ray fluorescence spectroscopy to become an important method for the determination of the amount of trace elements in various materials. Several studies have been made to determine trace element concentrations in blood, water and industrial wastes, and in metals using x ray fluorescence.[1,2,3]

In cooperation with the Department of Grain Science and Industry, we have applied the technique of proton-induced x ray fluorescence to the problem of determining the amount of trace elements in wheat flour using the Kansas State University tandem Van de Graaff accelerator.

The original motivation for this study was to find an alternate method to determine bromine residue in flour. The United States Department of Agriculture requires a chemical analysis that is reliable to concentrations of a few parts per million. Since fumigation of grain siloes with methyl bromide is a common practice, an analysis of the bromine concentrations is an appropriate concern. Ordinary chemical analysis of bromine levels in thr region of parts per million is a time consuming and painstaking endeavor. Using proton-induced x ray fluorescence we have been able to detect bromine concentrations of one to ten parts per million with relative ease in a time period of

thirty minutes to one hour.

Another advantage of x ray fluorescence analysis is that during the thirty minutes to one hour analysis, not only bromine, but nearly all elements from phosphorous to lead are simultaneously detected and the concentrations can be determined. Since multi-element analysis is possible using x ray fluorescence, we have determined the concentrations of phosphorous, calcium, sulfur, chlorine, potassium, iron, zinc, and bromine in twenty four flour samples taken from various stages of processing in the flour mill at Kansas State University. By identifying these and any other elements that may be present in the flour, the Department of Grain Science and Industry can determine whether the flour is suitable for commercial uses such as baking, cereals, and animal foods. Some of these elements are detrimental to health if they are present in large quantities, and they also affect the baking properties and suitability for processing the wheat flour for commercial uses.

CHAPTER II

EXPERIMENTAL PROCEDURE

In this experiment, the technique of proton-induced x ray fluorescence was employed to determine the concentrations of various trace elements in wheat flour. As a source of energetic protons, the Kansas State University tandem Van de Graaff accelerator was used. A proton energy of four MeV was found to be the optimum energy at which to perform this experiment.

The principle of x ray fluorescence is relatively simple. The process consists of ejecting an inner shell electron in an atom by bombarding it with energetic projectiles such as protons, electrons, alpha particles, or x rays. Electrons and x rays, when used as incident projectiles, give a large background to peak ratio, thus making data analysis quite difficult. An x ray source, produces a high background due to scattering off of other materials in the target area. The large amount of background radiation when using light projectiles such as electrons, is a result of the projectile slowing down in the target material. This process is known as Brehmsstrahlung radiation. When protons or alpha particles are used as a projectile, Bremsstrahlung radiation is reduced due to the lower velocities of these particles as compared to electrons for a given energy. Thus the reduced background radiation makes data analysis somewhat simpler.

The ion source at the tandem Van de Graaff is not equipped to produce alpha particles, so protons became the logical choice

for a projectile. Other projectiles such as oxygen ions have been tried but did not prove to be as suitable as four MeV protons for this type of experiment.[4] When the inner shell electrons of an atom are ejected by incident protons, electrons from outer shells fall into the shell in which the vacancy was produced. The resultant energy loss in this process is given off in the form of photons with wavelengths in the x ray region of the spectrum. These photons are termed characteristic x rays since their wavelengths, hence their energies, are determined by the level spacings of the atom from which they were produced. If the vacancy is produced in the K-shell of the atom the x rays given off are termed K-series x rays and if the vacancy occurs in the L-shell these x rays are termed L-series x rays. If a K-shell vacancy occurs, giving rise to a K-series x ray, this is necessarily followed by x rays of the L-series, M-series and higher order series. In this experiment K-series and L-series x rays were observed. K-series x rays were observed for detection of elements from phosphorous to strontium and L-series x rays were observed for elements from strontium to lead. The $K\alpha$ x ray for phosphorous is 2.013 keV and the $K\alpha$ x ray for strontium is 14.143 keV.[5] X ray energies for elements of higher atomic number than strontium are in the range such that the detector efficiency is minimized. The $L\alpha$ x ray for zirconium is 2.07 keV so that by observing the L- series x rays of the elements of atomic number greater than strontium, one may stay in the range of x ray energies which allows for reasonable detector efficiency.[5] A table of $K\alpha$

x ray energies and Lα x ray energies for elements from lithium to lead is shown in table 1.[5] A calculation was made to determine the absorption of various Kα x rays produced at a depth x in the target and the result is shown in the appendix.

The targets that were used in this experiment were flour samples obtained from the Department of Grain Science. The targets were prepared in the following manner. First, a few drops of distilled water were added to the flour and mixed until a flour paste consistency was achieved. The paste was then applied to an aluminum target backing and allowed to dry for twenty four hours. After the mixture had dried sufficiently, it was easily removed from the aluminum backing and reapplied with a drop of polystyrene. The reason polystyrene was selected to affix the flour wafer to the aluminum backing, is that the heaviest element in polystyrene is oxygen and the K-series x rays from oxygen are below the limit of detectability of the lithium-drifted silicon detector used in this experiment. The target was allowed to remain in air for approximately twenty four hours to allow the polystyrene to dry. The target was then placed in a vacuum dessicator for another twenty four hours. After this three day process, the targets were ready to be placed in the chamber and data were able to be taken. If the targets were dried at a faster rate, it was found that they would crack very badly.

Calibration targets were also prepared to test the limits of detectability and to determine the x ray production from a known amount of contaminant. To prepare the calibration targets,

Table 1 X Ray Energies

Element	Kα x ray energy	Element	Lα x ray energy
Li	.0543 keV	Y	1.947 keV
Be	.1085 keV	Zr	2.070 keV
B	.1833 keV	Nb	2.196 keV
C	.2770 keV	Mo	2.327 keV
N	.3924 keV	Tc	2.462 keV
O	.5249 keV	Ru	2.600 keV
Fl	.6768 keV	Rh	2.743 keV
Ne	.8486 keV	Pd	2.889 keV
Na	1.041 keV	Ag	3.040 keV
Mg	1.254 keV	Cd	3.195 keV
Al	1.487 keV	In	3.354 keV
Si	1.740 keV	Sn	3.444 keV
P	2.013 keV	Sb	3.605 keV
S	2.307 keV	Te	3.769 keV
Cl	2.622 keV	I	3.938 keV
A	2.957 keV	Xe	4.110 keV
K	3.313 keV	Cs	4.286 keV
Ca	3.690 keV	Ba	4.466 keV
Sc	4.089 keV	La	4.651 keV
Ti	4.509 keV	Ce	4.840 keV
V	4.950 keV	Pr	5.034 keV
Cr	5.412 keV	Nd	5.230 keV
Mn	5.895 keV	Pm	5.432 keV
Fe	6.400 keV	Sm	5.636 keV
Co	6.925 keV	Eu	5.846 keV
Ni	7.472 keV	Gd	6.057 keV
Cu	8.041 keV	Tb	6.273 keV
Zn	8.631 keV	Dy	6.495 keV
Ga	9.243 keV	Ho	6.720 keV
Ge	9.876 keV	Er	6.949 keV
As	10.53 keV	Tm	7.180 keV
Se	11.21 keV	Yb	7.416 keV
Br	11.91 keV	Lu	7.656 keV
Kr	12.63 keV	Hf	7.899 kev
Rb	13.37 keV	Ta	8.146 keV
Sr	14.14 keV	W	8.398 keV
		Re	8.652 keV
		Os	8.912 keV
		Ir	9,175 keV
		Pt	9.442 keV
		Au	9.713 keV
		Hg	9.989 keV
		Tl	10.27 keV
		Pb	10.55 keV

a known amount of flour was weighed on an analytical balance and mixed with an appropriate weight of a soluble compound containing the desired contaminant. To determine the weight of compound needed to give a one part in one hundred contaminant to flour ratio the following formula was used:

$$\text{amount of compound needed} = .01\text{gm contaminant} \times \frac{\text{atomic weight compound}}{\text{atomic weight of contaminant}}$$

The desired amount of contaminant was thoroughly mixed with the flour and the drying process was repeated. Targets of one part in one hundred and one part in one thousand contaminant to flour ratio were prepared for several different elements.

Quite often these targets, pure flour and calibration, would crack very badly when prepared in this manner. It was found that when a severely cracked target was used, the data were not always reproduceable. Another problem came when the targets were not completely dry. If the targets were wet, they would outgas when placed in the target chamber, thus ruining the vacuum needed to perform the experiment. This was the best method of target preparation that was found for this experiment.

A schematic of the experimental setup is shown in figure 1. Four MeV protons were allowed to strike a thick target of flour paste inclined at an angle of forty five degrees with respect to the axis of the beam line. The x ray detector, a Kevex lithium-drifted silicon detector with approximately 200 eV resolution, was placed at an angle of ninety degrees with respect to the axis of the beam line. The chamber was insulated from the x ray detector and the beam current was integrated from the entire target and chamber. A tantalum collimation slit was

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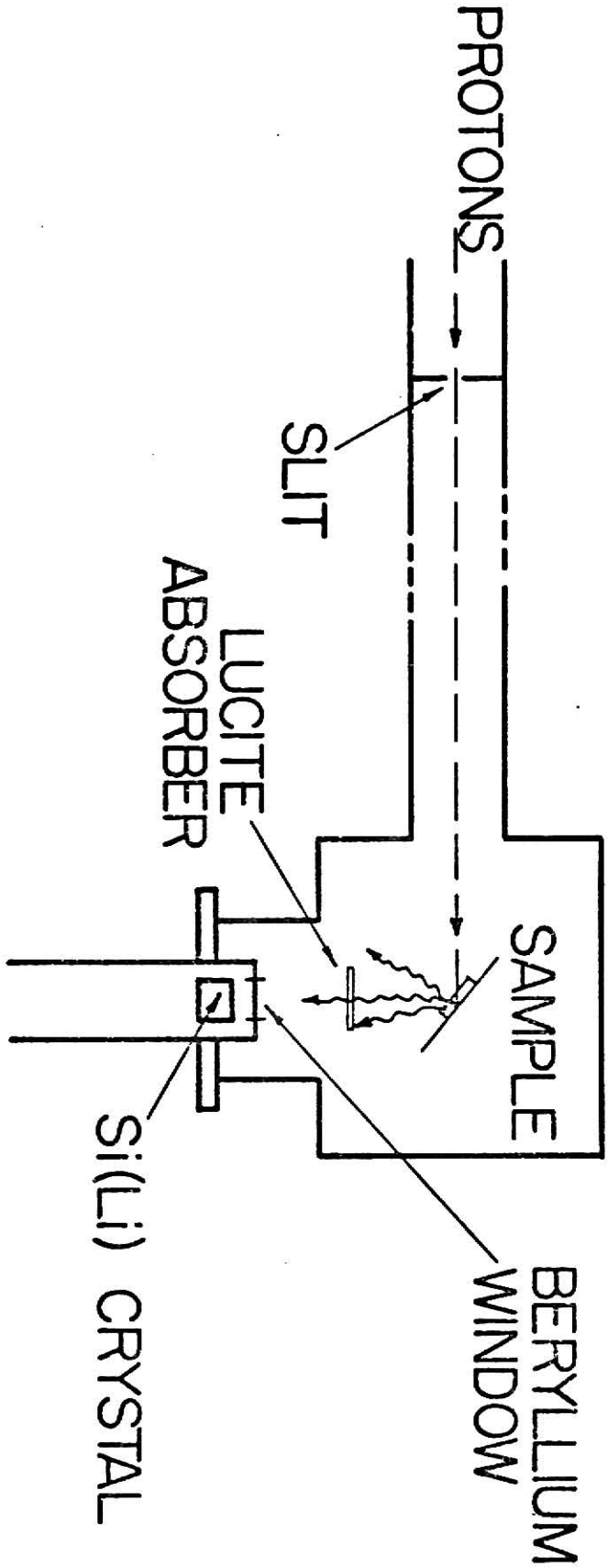


Figure 1. Schematic of experimental setup.

placed approximately three feet upstream from the target chamber. The target holder is designed to accomodate twelve targets, thus reducing the time required to change targets. A retractable one sixteenth inch lucite absorber was placed in front of the Si(Li) detector so that two spectra could be taken from each target. With the lucite absorber in place, x rays from the lighter elements such as phosphorous, sulfur and chlorine were absorbed and a cleaner spectrum for heavier elements such as bromine and zinc was obtained.

A block diagram of the electronics used in this experiment is shown in figure 2. A high resolution x ray detector is needed for this particular experiment. The Si(Li) detector has a resolution of approximately 200 eV. The high resolution of the Si(Li) detector is obtained with circuitry that carefully maintains D.C. bias levels. There is an occasional long reset pulse during which time the detector is cut off and a large pulse occurs in the amplifier. During this interval, the data collecting apparatus must also be cut off, and the integrated beam current must be corrected for this "dead time". The amount of dead time in the detector was measured by gating scalers on or off with the "detector busy" pulse from the amplifier provided by the Si(Li) detector manufacturer. The scalers used to measure dead time were counting pulses from a sixty Hertz pulser. The entire target chamber served as a charge collection region. The beam current on the target was collected and routed to the integrator circuit, which gave a digital pulse proportional to the collected charge.

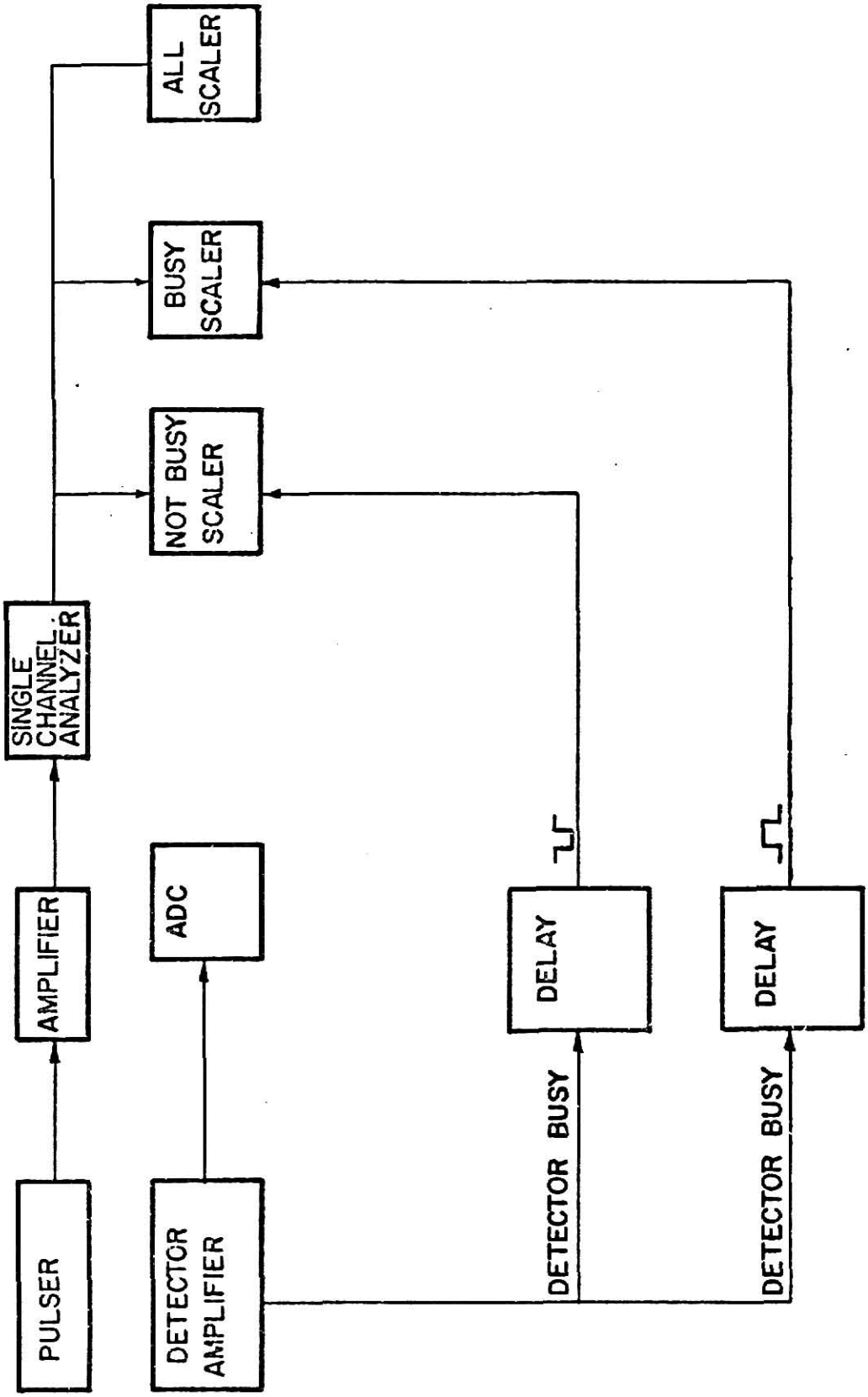


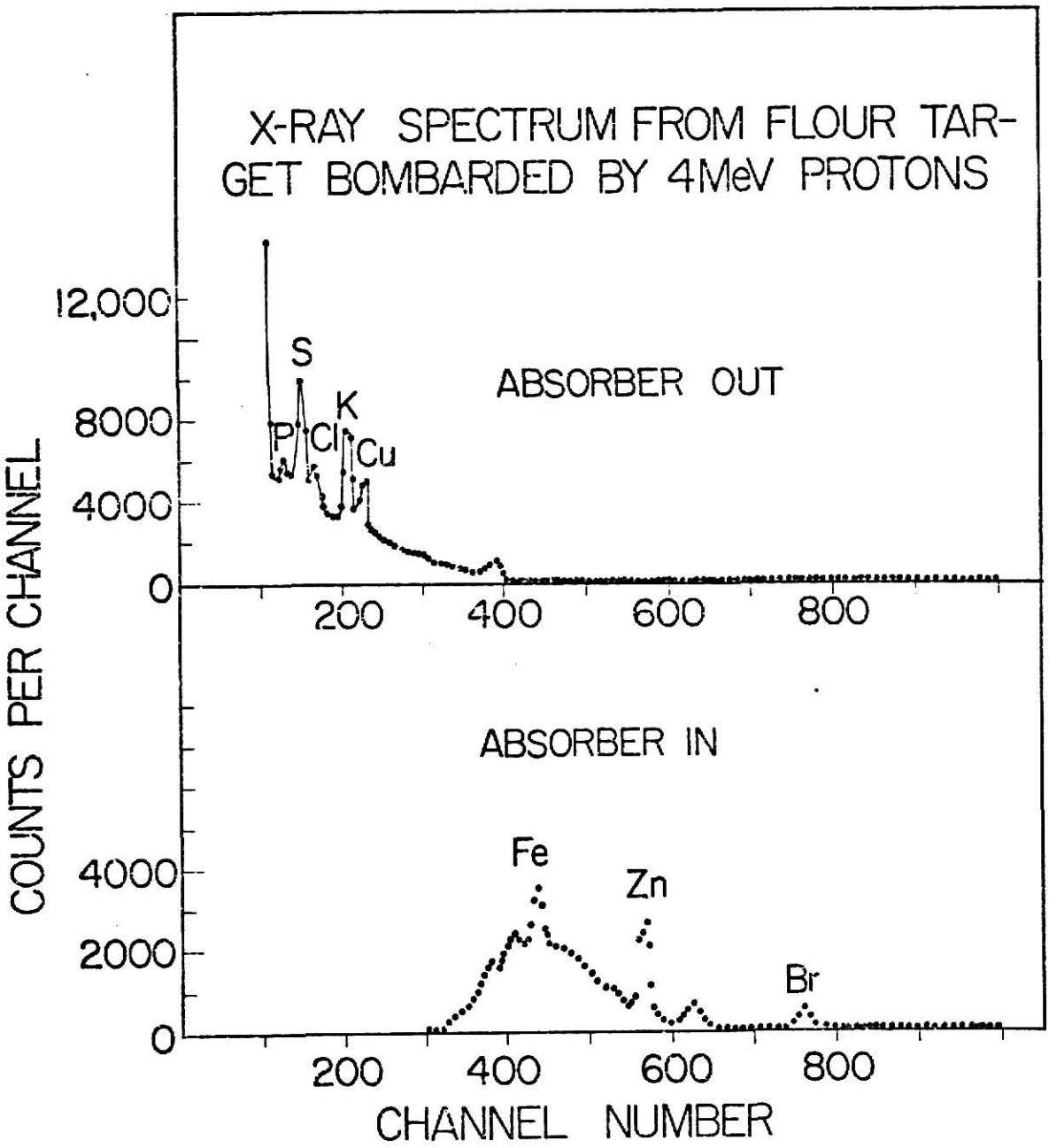
Figure 2. Block diagram of electronics

CHAPTER III

EXPERIMENTAL RESULTS

The data obtained in this experiment were taken on twenty four flour samples obtained from the Department of Grain Science at Kansas State University. Two separate spectra were taken for each sample. One spectrum was taken with the lucite absorber removed and another with the lucite absorber in front of the x ray detector. A typical spectrum with absorber out is shown in figure 3. Elements such as phosphorous, sulfur, chlorine and potassium are readily identifiable. In figure 4, a spectrum with absorber in is shown. The presence of heavier elements such as iron, zinc and bromine become apparent in this spectrum when the absorber is in place. Calibration targets were also prepared and two spectra were taken, one with the absorber in and one with the absorber out. The spectrum of a copper bromide calibration target is shown in figure 5.

As a first step in determining the amount of x ray production due to a known contaminant amount present in the calibration target, the area under the peak must be determined. This was accomplished by a least squares fit program. This program was adapted from Bevington.[6] A Digital Equipment Corporation model PDP-15 computer located at the tandem Van de Graaff facility was used to fit the background of the peak under observation. By appropriate setting of markers on each side of a peak, the background on each side of the peak could be fit.



Figures 3 and 4. X ray spectra from flour targets absorber out absorber in respectively.

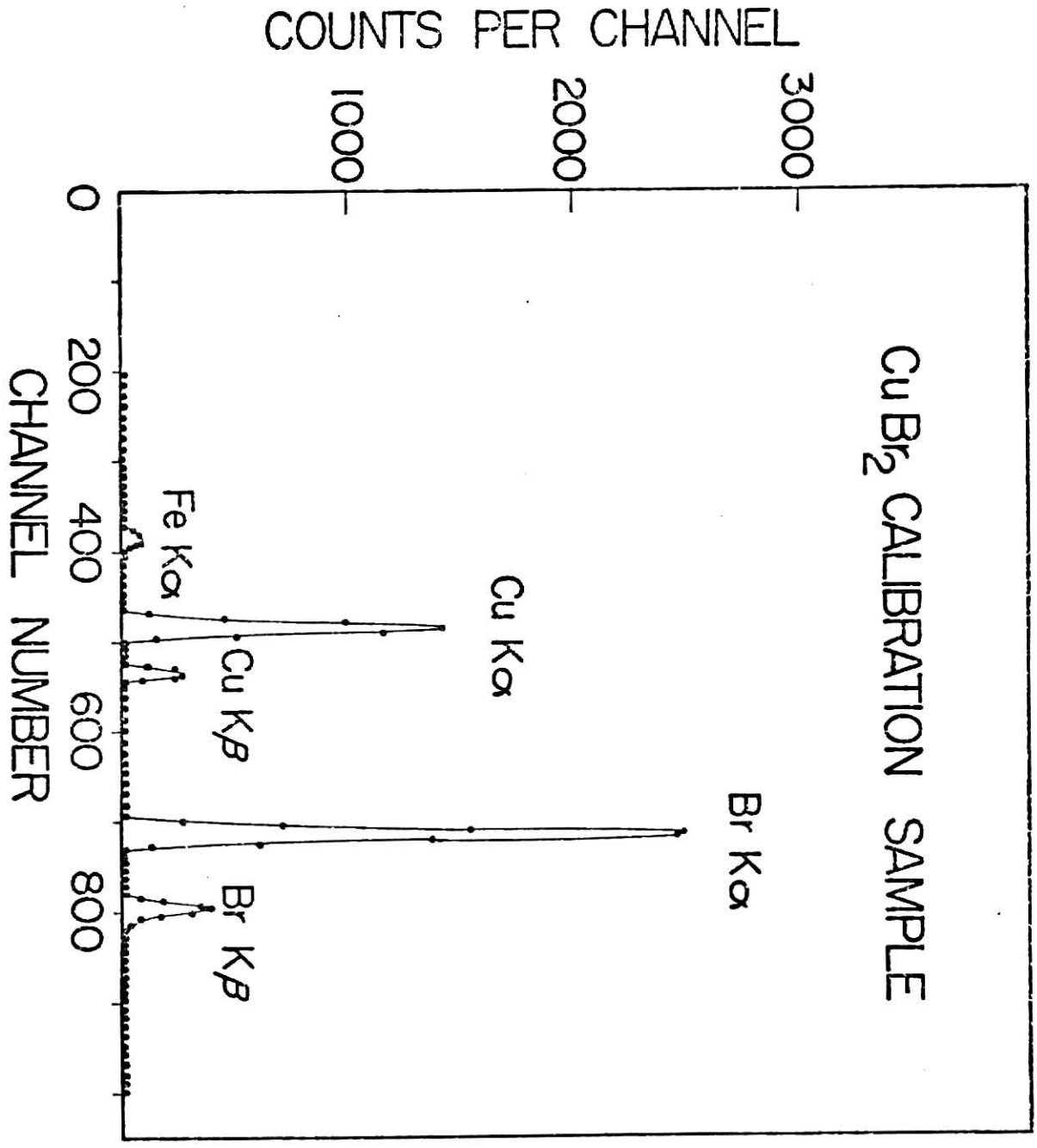


Figure 5. X ray spectrum from copper bromide calibration.

By subtracting the background, the area of the peak could be determined. This process is independent of the shape of the peak. A first, second, or third-order fit to the background could be made, enabling one to determine the best fit for each peak. A result of this method of determining peak area is shown in the appendix.

Once the area under a peak and the amount of collected charge were known, a graph of peak area/ microcoulomb of charge/ parts per million of contaminant versus atomic number could be drawn. Graphs of $K\alpha$ x ray production from a known amount of contaminant versus atomic number with absorber in and out are shown in figures 6 and 7 respectively. The $K\alpha$ x ray production from a one part per million concentration can be read off the graph for elements from phosphorous to strontium.

The flour samples were also analyzed to determine the areas under the peaks of all of the elements present in the sample. The amount of collected charge was also determined and a calculation was made to obtain the peak area/ microcoulomb for each element present in the flour sample. By dividing the peak area/ microcoulomb for a given element in the flour sample by the peak area/ microcoulomb/ one part per million of the same element as determined by the calibration graph the amount of a particular element in the flour sample was obtained. The concentrations of phosphorous, sulfur, chlorine, potassium, calcium, iron, zinc and bromine for each of the twenty four flour samples is shown in table 2. The calibration chemicals used and the contaminant studied are shown in table 3.

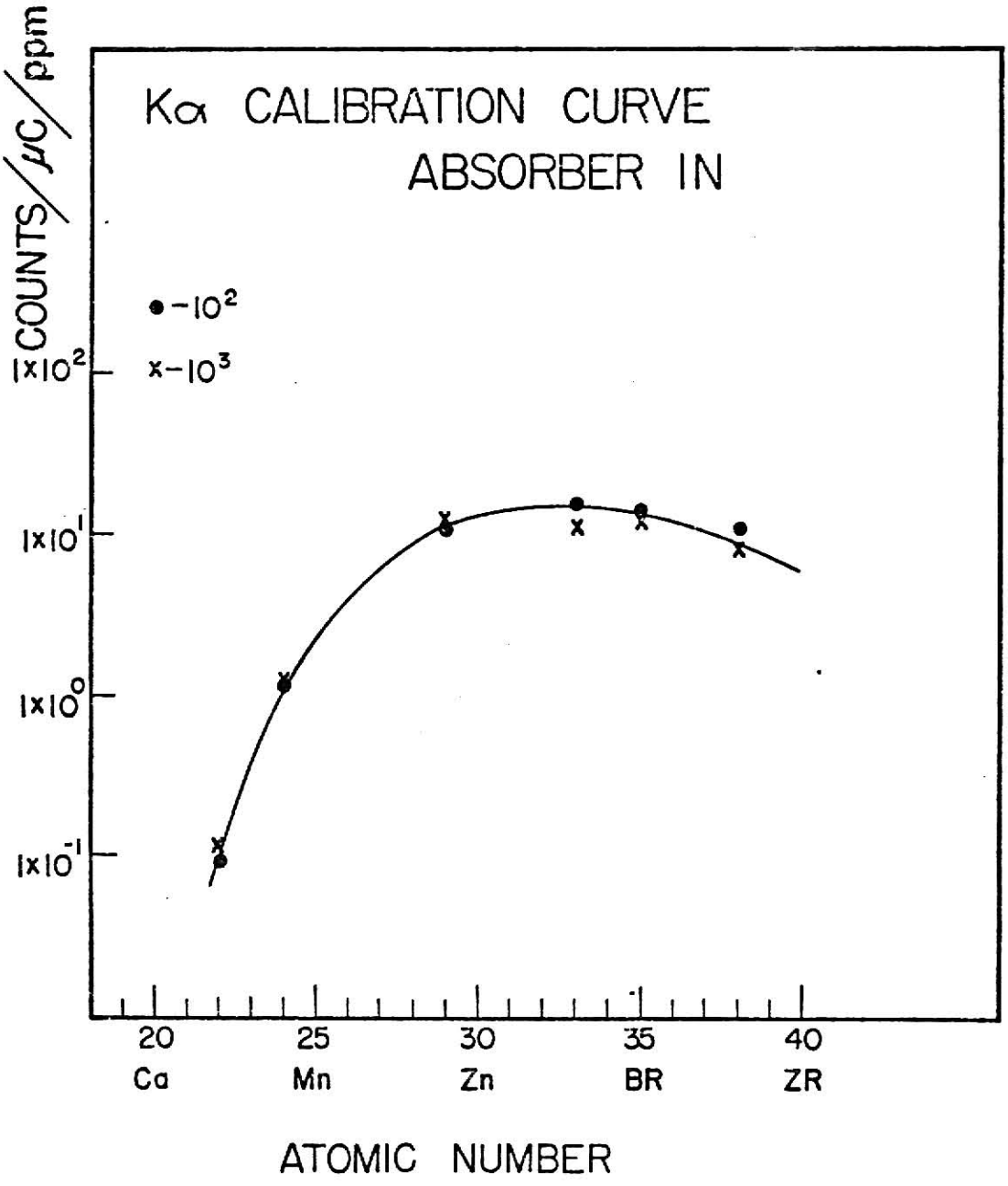


Figure 6. Kα calibration curve absorber in.

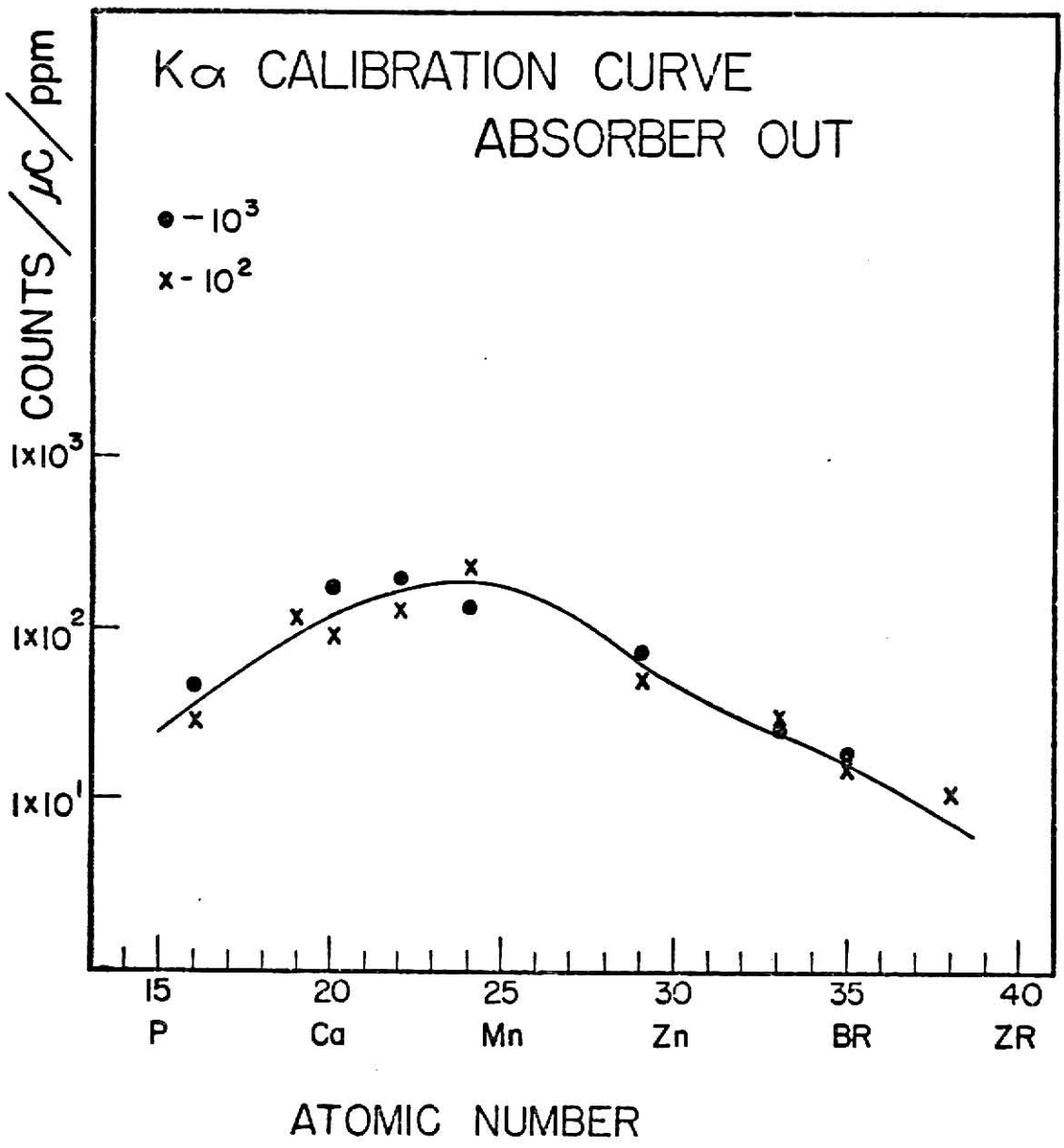


Figure 7. Kα calibration curve absorber out.

Table 2 Flour Sample Concentrations

Sample	P ppm	S ppm	Cl ppm	K ppm	Ca ppm
3M	26,700	1,470	382	817	151
2MT	13,000	2,780	840	1,130	195
1MT		573	427	678	163
3BK	4,140	2,780	603	1,290	182
SUC	4,290	7,680	1,920	4,800	770
CST	8,100	5,250	1,360	2,940	633
Bk.Red	2,030	6,100	1,120	2,600	410
CSB	805	1,430	365	883	147
20	1,820	2,950	512	1,750	254
FSB	177	5,150	1,150	5,460	940
6M	2,020	2,430	545	2,570	445
1MB	690	2,140	572	1,160	287
5BK	3,450	7,370	1,490	3,680	673
1T	2,520	5,030	1,110	3,460	680
PBK	1,670	1,800	237	9,970	114
4BK	1,820	4,430	892	1,140	
BSD	5,350	5,200	1,240	6,290	713
St.Gd	545	2,200	600	1,290	458
2BK	1,390	3,100	1,170	2,740	920
2MB		1,570	4,080	5,470	856
1BK	2,049	8,120	3,110	4,210	965
4M	3,310	1,996	6,790	6,280	1,440
5M	1,140	3,310	1,066	1,300	2,230

Sample	Zn ppm	Fe ppm	Br ppm
3M	2.57	30	3.24
2MT	21.06	18.3	4.23
1MT	8.56	43.1	4.36
3BK	13.44	25.7	2.33
SUC	48.56	151.85	13.75
CST	27.8	58.7	6.55
Bk.Red	7.37	18.8	8.50
CSB	9.25	123.1	5.00
20	17.68	78.7	5.35
FSB	13.8	86.6	10.6
6M	14.9	5.20	7.1
1MB	4.23	81.2	5.00
5BK	16.06	335.2	4.22
1T	9.50	116.8	4.95
PBK	11.56	88.1	4.56
4BK	9.44	235.2	4.7
BSD	53.5	143.5	6.35
St. Gd	15.18	488.8	6.75
2BK	26.6		6.45
2MB	8.87	74.81	2.02
1BK	21.8	142.4	5.4
4M	17.75	383.3	10.16
5M	26.1	81.1	12.05

Table 3 Calibration Chemicals

Chemical Compound	Contaminant
Arsenic Trioxide	Arsenic Z=33
Cupric Bromide	Bromine Z=35
Calcium Bromide	Calcium Z=20
Chromic Chloride	Chromium Z=24
Cupric Bromide	Copper Z=29
Potassium Iodide	Potassium Z=19
Strontium Chloride	Strontium Z=38
Tungsten Sulfide	Sulfur Z=16
Titanic Oxide	Titanium Z=22

The concentrations of phosphorous, sulfur, chlorine, calcium, and potassium are on the average in the one hundred to one thousand parts per million range. Bromine and zinc concentrations however, range from one part per million to one hundred parts per million. Iron shows higher concentrations than either bromine or zinc, but this is most probably due to elastic scattering of the incident protons into the stainless steel target chamber. Such scattering would result in x rays produced from the iron present not only in the flour target, but also the iron present in the target chamber. Aluminum foil was used to line the chamber but some secondary scattering probably occurs.

The Department of Grain Science and Industry analyzed the twenty four flour samples for ash and protein content. The ash content is determined by heating a flour sample at five hundred and fifty degrees Centigrade for twelve to nineteen hours and then weighing the residue. One would expect the presence of heavy metals such as zinc to be related to ash content if the zinc compounds in the flour were non-volatile. A zinc-ash correlation was made and the result is shown in figure 8.

Protein content is measured by nitrogen concentration. The twenty four flour samples were correlated for protein-bromine concentrations and the result is shown in figure 9.

A numerical correlation coefficient was also determined for ash-zinc and protein-bromine concentrations. This correlation coefficient r, is given by:[7] $r = S_{jk}^2/S_j S_k$ where

$$S_{jk}^2 = 1/n-1 \sum (Xij-\overline{Xj})(Xik-\overline{Xk})$$

$$S_i^2 = 1/n-1 \sum (Xij-\overline{Xj})^2 ; \; S_k^2 = 1/n-1 \sum (Xik-\overline{Xk})^2$$

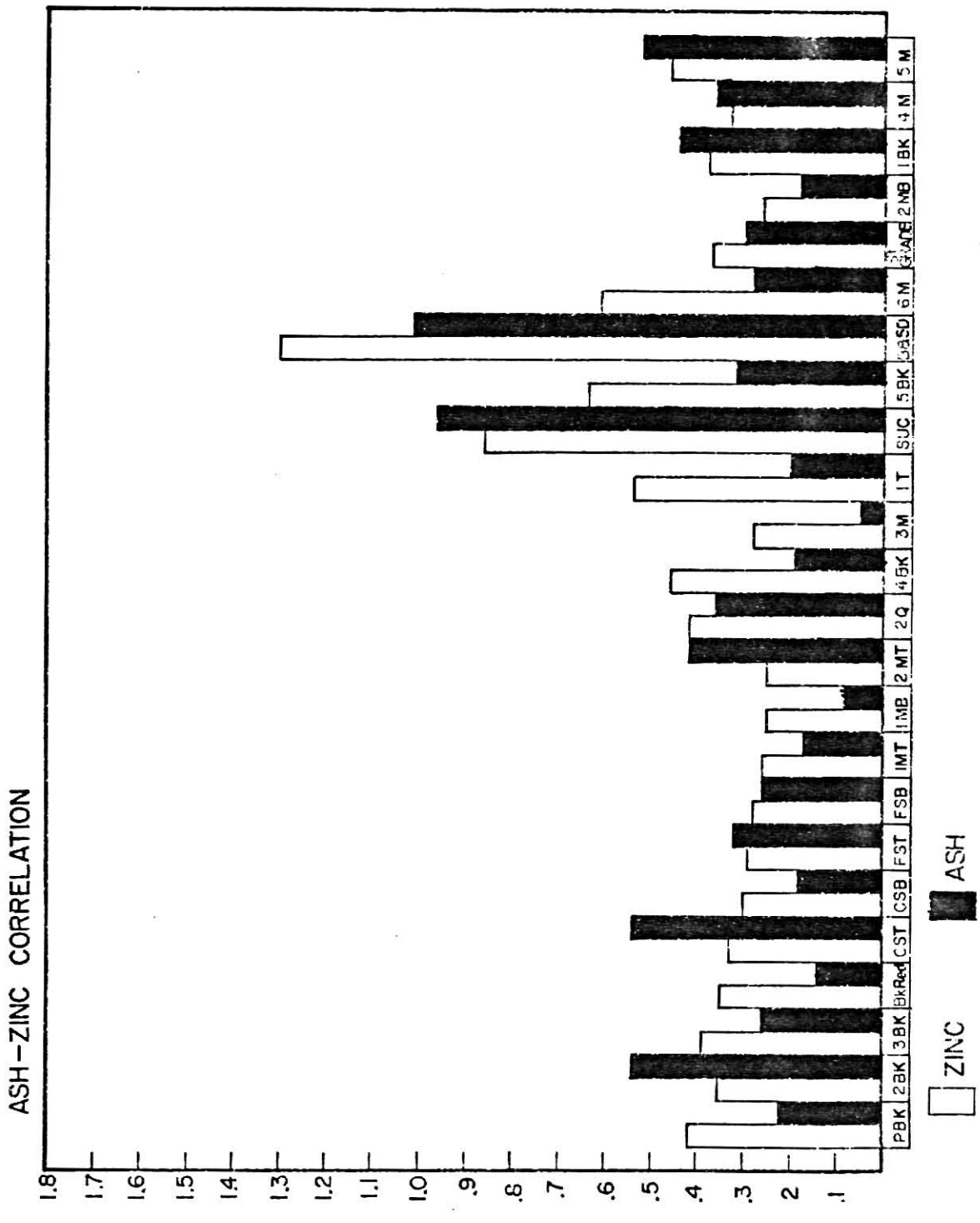


Figure 8. Ash-Zinc correlation.

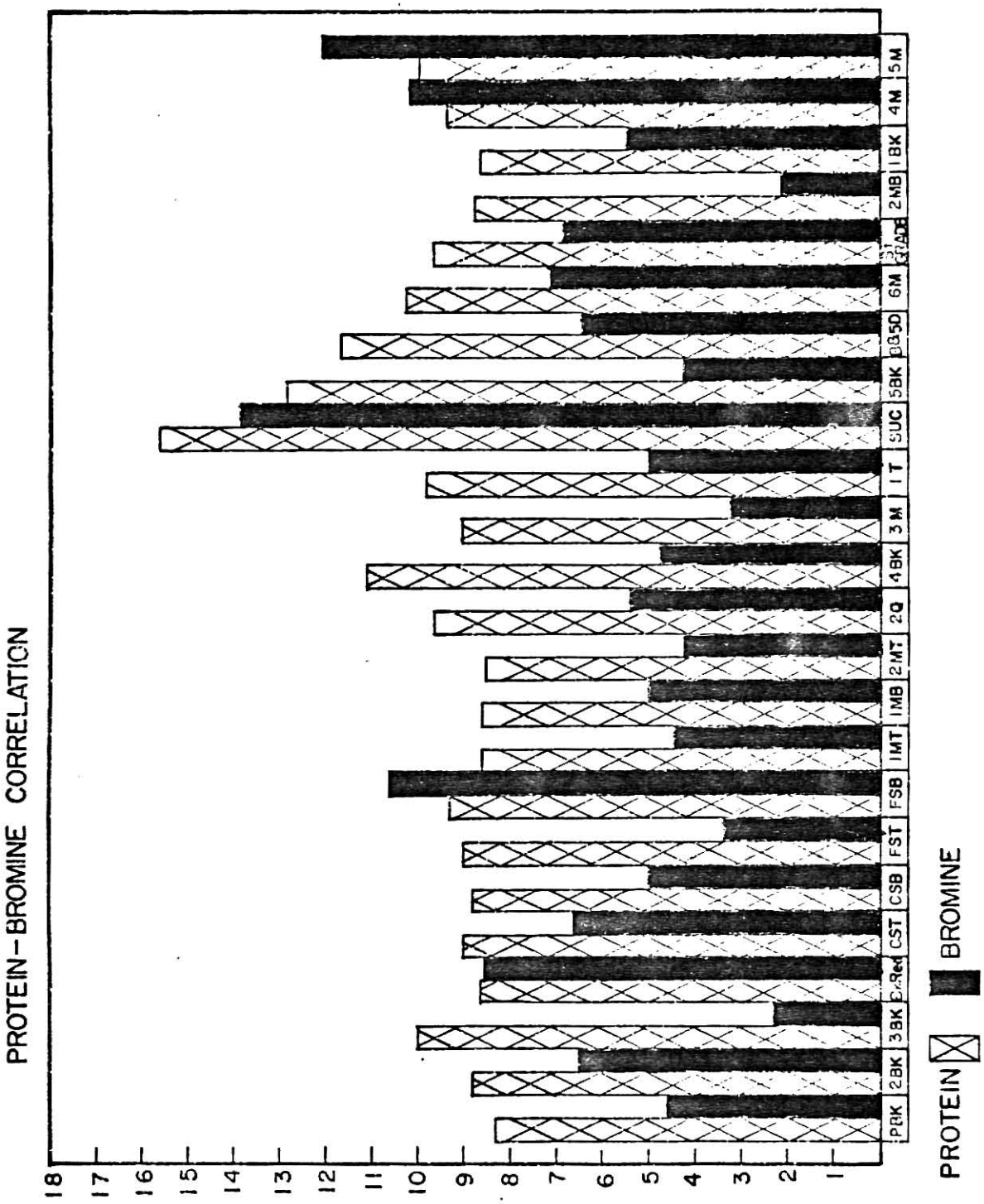


Figure 9. Protein-Bromine correlation.

and n is the number of samples, Xij and Xik are the sums of the individual concentrations Xj and Xk, and $\overline{Xj}$ and $\overline{Xk}$ are the means of the individual concentrations. The correlation coefficient r, for protein-bromine was .411 and the coefficient for ash-zinc was .802.

This says that the flour samples known to have a high ash content, also showed a high zinc content, thus substantiating the assumption that the non-volatile heavy metal content of the flour samples is reflected by the ash content.

The low degree of correlation between protein and bromine implies that one cannot decisively say that a flour sample with a high protein content also has a high bromine content. Perhaps the most effective method of detecting the presence of bromine in various flour samples is by x ray fluorescence since neither ash or protein content seem to give an indication of the presence of bromine.

CHAPTER IV

CONCLUSION

The technique of x ray fluorescence analysis has been shown to be a reliable method for detecting the presence of trace elements in a variety of materials. Experiments have been done on targets such as water with a high degree of success.[1] Concentrations of parts per billion have been reported be these workers using x ray fluorescence techniques.[1] We have shown that biological materials can also be effectively analyzed for the presence of several trace elements with relative ease.

The major advantages of this technique are that simultaneous multi-element analysis is attainable in a short time period, data reduction and interpretation are relatively simple and that the sample is not destroyed during analysis. Also, it appears that with respect to flour samples, the standard test of determining the ash content, also indicates the presence of heavy metals such as zinc.

The major disadvantages we found in this particular experiment were the preparation of targets and the need for long drying periods to ensure an adequate vacuum. We were also limited in that with the present experimental setup, we could not test liquid samples, gases or dry samples such as flour without altering its natural state.

Preliminary experiments have been done which have allowed us to feasibly use liquid samples and dry samples for analysis by

x ray fluorescence. Such experiments do not require putting the target under vacuum, but allow us to suspend the target outside the beam line by bringing protons through a thin mylar foil, thus striking the target in air. The results from these preliminary experiments seem to be a very promising procedure to analyze a variety of samples using proton-induced x ray fluorescence analysis.

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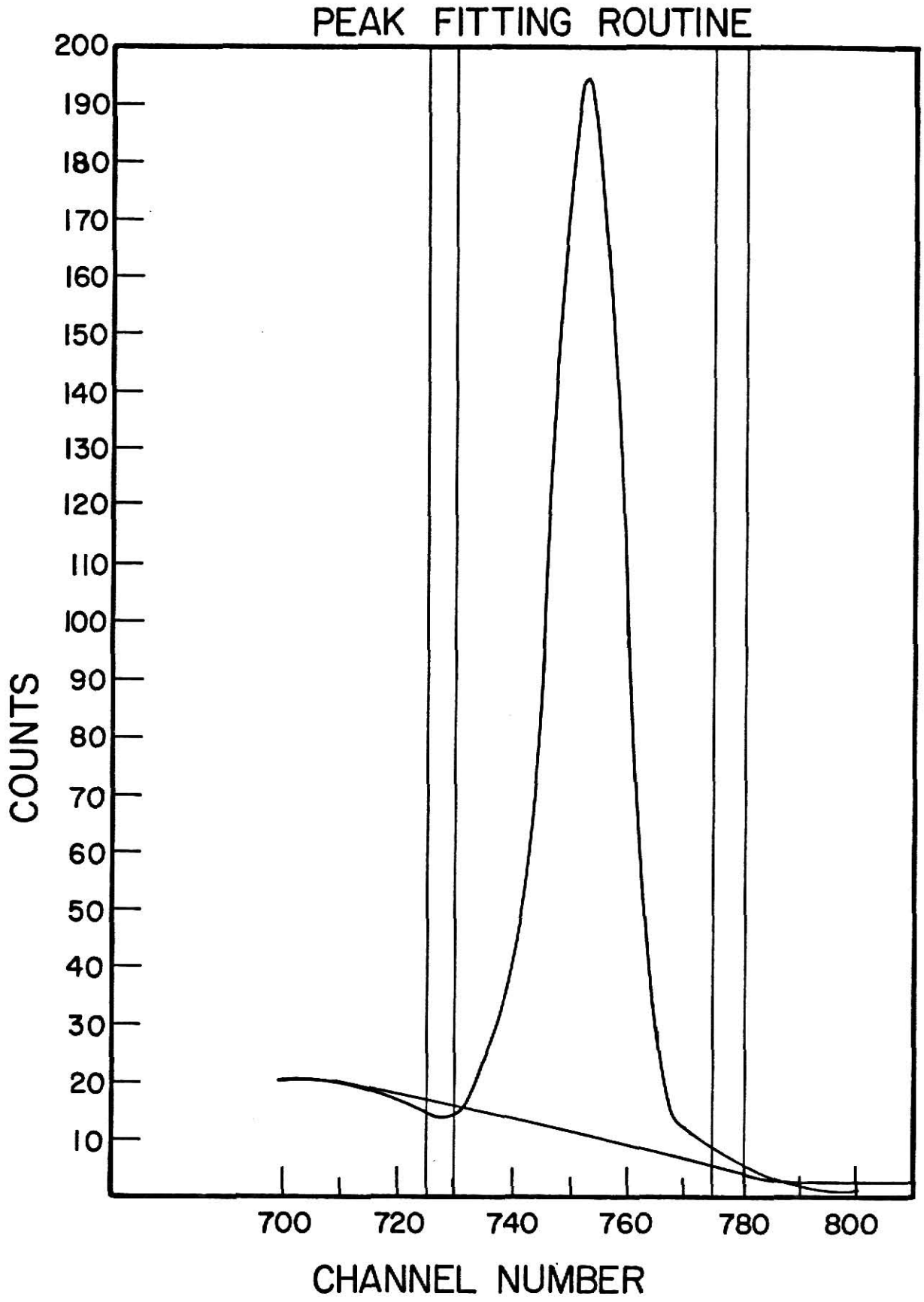
APPENDIX

The x ray production from the trace elements present in the flour target occurs at varying depths governed by the range of protons in the flour targets.[8,9,10] For a four MeV proton in carbon, the range is 27.268 mg/cm^2. By determining at what energy for the proton inside the flour target does the ratio of the cross section at a depth x in the target to the cross section at the surface fall to 10%, another value of range is determined. This was found to be for phosphorous .774 mg/cm^2. Thus by this process, a range for the protons was determined. If a Kα x ray is produced at this depth in the target, the x ray will lose intensity in passing through the target. The absorption coefficient for Kα x rays in carbon from phosphorous, zinc and bromine were determined and also the loss of intensity of the x rays passing through the target using, $I=Io\ e^{-\mu x}$, where x is the depth in the target at which the x ray is produced, μ is the absorption coefficient for a particular Kα x ray in carbon and I/Io is the ratio of the intensity. For a Kα x ray of phosphorous at a range of .0133 cm, I/Io was 2×10^{-6}, I/Io for a Kα x ray of zinc was .899 and I/Io for a Kα x ray of bromine was .961. From this it is seen that the observed x ray production for light elements such as phosphorous occurs mainly at the target surface, while observed x ray production from heavier elements such as zinc and bromine may occur at varying depths in the target.

To obtain the area under a peak in a spectrum, a least squares fit program was used. A typical peak with background markers and a fitted background line is shown in the figure on the following page. The area is determined by subtracting the background from the number of counts in each channel of the peak. A first, second, or third order fit could be made, to ensure an appropriate fit to the background. This process is independent of the shape of the peak and is a relatively simple method of determining the area under a peak.


PEAK FITTING ROUTINE
COUNTS
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CHANNEL NUMBER

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by

RICHARD A. MARTIN

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Department of Physics

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Manhattan, Kansas

1973

ABSTRACT

Using proton-induced x ray fluorescence, twenty four flour samples were analyzed for trace element concentrations. Heavy elements, such as bromine and zinc, were detected and found to be present to extents of one to one hundred parts per million. Lighter elements, such as phosphorous,sulfur, chlorine, calcium and potassium, were found to be present with concentrations from one hundred to one thousand parts per million. Correlations between bromine and protein content and zinc and ash content were also made. This technique of x ray fluorescence analysis has proven to be an efficient method for analyzing the trace elements in wheat flour.