

NEUTRON ACTIVATION ANALYSIS OF THE MAHONING RIVER  
WATER USING CALIFORNIUM - 252

YOUNGSTOWN STATE UNIVERSITY

GRADUATE SCHOOL

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TITLE NEUTRON ACTIVATION ANALYSIS OF THE MAHONING RIVER WATER  
USING CALIFORNIUM - 252

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by

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Youngstown State University, 1972

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Chemistry

Program

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Elements

Variation in Concentration

Sodium

26.11 to 67.94 ppm

Chlorine

31.14 to 57.13 ppm

Manganese

0.7 to 7.29 ppm

Copper

.08 to 1.73 ppm

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## ABSTRACT

NEUTRON ACTIVATION ANALYSIS OF THE MAHONING RIVER  
WATER USING CALIFORNIUM-252

Peter James Cordon

Master of Science in Chemistry

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This investigation deals with determination of the neutron flux of 10 mg of californium-252 source and its application to determine certain trace elements in the Mahoning River system.

It has been shown that the system provides a quick, accurate, and inexpensive method of analysis, both qualitative and quantitative, for four elements. The limitation of the number of elements detected was the result of a low resolution detector system, 2 x 2 NaI(Tl) crystal. Preliminary work of a high resolution Ge(Li) detector has demonstrated that many more elements can be detected.

The following were the elements detected.

<u>Elements</u>	<u>Variation in Concentration</u>
Sodium	26.11 to 67.94 ppm
Chlorine	31.14 to 57.13 ppm
Manganese	.07 to 7.29 ppm
Copper	.78 to 1.73 ppm

The change in the manganese and copper concentrations is due to the large and different industries along the river. The variations of sodium and chlorine can be largely accounted for by the sewage treatment plants in the region.

To make a meaningful comparison as to the source of these elements from the industrial and sewage plant effluent, a detailed study above and below each major source of effluent must be made using the Ge(Li) detector.

their help.

The author wishes to acknowledge the work done by Ronald Kline on the sediment samples, and machining of the apparatus used. The author also wishes to thank Jane Wolanin for the infinite work done on the graphs and calculations.

The author would like to acknowledge the loan of 10 mg of californium-252 by the United States Atomic Energy Commission's Savannah River Laboratory.



## ACKNOWLEDGEMENTS

The author is dedicating his work to Jane Ellen Reichert, a beautiful person.

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Californium-252.....	19
Activation Analysis of the Standard Samples..	19
Activation Analysis of Samples.....	26
Site #1 (Meander Crack).....	38
Site #2 (Leavitt's Road Bridge).....	38
Site #3 (Route 28 Bridge).....	39
Site #4 (Liberty Road).....	39
Site #5 (Market Street Bridge).....	39

## TABLE OF CONTENTS

	PAGE
IV. CONCLUSIONS AND SUGGESTIONS.....	
ABSTRACT.....	ii
ACKNOWLEDGEMENTS.....	iv
TABLE OF CONTENTS.....	v
LIST OF FIGURES.....	vii
LIST OF TABLES.....	viii
LIST OF GRAPHS.....	ix
CHAPTER	
I. INTRODUCTION.....	1
II. THEORY AND COMPARISON OF NEUTRON ACTIVATION ANALYSIS WITH OTHER PHYSICO-CHEMICAL METHODS OF ANALYSIS.....	4
Californium-252.....	6
Measurement of Thermal Flux of $^{252}\text{Cf}$ .....	7
Activation Analysis of Water.....	12
Sample Collection.....	12
Preparation of Water and Sediment Samples..	12
Preparation of Standards.....	13
III. RESULTS AND DISCUSSION.....	19
Californium-252.....	19
Activation Analysis of the Standard Samples..	19
Activation Analysis of Samples.....	26
Site #1 (Meander Creek).....	38
Site #2 (Leavitt's Road Bridge).....	38
Site #3 (Route 46 Bridge).....	39
Site #4 (Liberty Road).....	39
Site #5 (Market Street Bridge).....	39

Site #6 (Lowellville Bridge).....	40
IV. CONCLUSIONS AND SUGGESTIONS.....	41
REFERENCES.....	45
2. Cf-252 Storage Tank.....	9
3. Apparatus for Flux Determinations.....	11
4. Detection and Counting System.....	15
5. Sodium Spectrum.....	16
6. Manganese .835 Mev.....	18
7. Mahoning River and tributaries: Sample Sites #1 - 6.....	26
8. Position #4 Using Ge(Li) Detector.....	43

## LIST OF FIGURES

FIGURES	PAGE
1. Cf-252 Storage Tank.....	8
2. Cf-252 Storage Tank.....	9
3. Apparatus for Flux Determinations.....	11
4. Detection and Counting System.....	15
5. Sodium Spectrum.....	16
6. Manganese .835 Mev.....	18
7. Mahoning River and tributaries: Sample Sites #1 - 6.....	36
8. Position #4 Using Ge(Li) Detector.....	43
9. Position #3.....	28
10. Position #4.....	30
11. Position #5.....	31
12. Position #6.....	32
13. Individual Elements.....	33

## LIST OF TABLES

TABLE	PAGE
1. Standards.....	14
2. Weights of Indium Foils.....	21
3. Thermal Flux at Source.....	22
4. Thermal Flux 5 cm Above.....	23
5. Thermal Flux 5 cm Below.....	24
6. Standards.....	25
7. Position #1.....	27
8. Position #2.....	28
9. Position #3.....	29
10. Position #4.....	30
11. Position #5.....	31
12. Position #6.....	32
13. Individual Elements.....	33

## LIST OF GRAPHS

GRAPHS	PAGE
1. Thermal Flux of Californium.....	20
2. Sediment Concentrations.....	35

technological destruction of his environment. This ecological problem has become one of major concern that has witnessed the creation of the Environmental Protection Agency by the United States government. The function of this agency is to safeguard the air and river water from further pollution by our over-zealous industries and our complex municipalities. The cancerous growth of air and water pollution has reached such magnitude that many rivers and lakes are unfit for marine life and beneficial utilization. Extensive investigation into the nature and concentration of environmental pollutants is mandatory to obtain the knowledge needed to combat their detrimental effect on our world.

In this study an attempt has been made to determine the feasibility of using Californium-252 as a source of neutrons in order to determine the point of origin, the type and concentration of elements present in a river system. The river chosen for this purpose was the Mahoning River since its banks support many industries and cities. Any hydrologic system is complex in that a wide variety of processes can occur to affect it. A precise knowledge about chemical composition of a given polluted water system is difficult to obtain, but it is



## CHAPTER I

## INTRODUCTION

During the last decade man has awakened to the technological destruction of his environment. This ecological problem has become one of major concern that has witnessed the creation of the Environmental Protection Agency by the United States government. The function of this agency is to safeguard the air and river water from further pollution by our over-zealous industries and our complex municipalities. The cancerous growth of air and water pollution has reached such magnitude that many rivers and lakes are unfit for marine life and beneficial utilization. Extensive investigation into the nature and concentration of environmental pollutants is mandatory to obtain the knowledge needed to combat their detrimental effect on our world.

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reported that an uncontaminated river system, on the average, would contain 120 parts per million of dissolved solids.<sup>1</sup> These dissolved solids are shown to be as follows: 58 ppm bicarbonate; 15 ppm calcium; 13 ppm silica; 11 ppm sulfate; 8 ppm chlorine; 6 ppm sodium; 4 ppm magnesium; 2 ppm potassium; 1 ppm nitrate; and 0.8 ppm of iron.<sup>2</sup> Since these elements are present in great abundance, there are at our disposal wet analytical techniques to determine their concentration.

The present analytical methods may be sufficient to determine most of the contaminants present in relatively large quantities. It would be highly desirable to detect elements existing in trace amounts and tabulate them so that such information may be eventually used. The present intense interest in mercury and lead is an excellent example of where information, once thought trivial or unnecessary, is now of great importance.

Recently it has been demonstrated that Neutron Activation Analysis (N.A.A.), using a reactor as a source of neutrons, is an excellent analytical technique in determining the variety of trace elements in a river system (the Roanoke River system).<sup>3</sup>

N.A.A. is a much more sensitive analytical method in comparison to traditional analytical methods such as amperometric titration, molecular absorption, u-v visible fluorescence, atomic absorption, flame spectrophotometry, D.C. arc copper spark, and graphite spark.<sup>4</sup>

This thesis represents two firsts in N.A.A.; the use of californium-252 as a source of neutrons for the detection of trace elements in a river system and the use of activation analysis to study the Mahoning River.

Neutron Activation Analysis (N.A.A.) is a fairly new and versatile method. One of the first applications of N.A.A. was by Hevesy and Levi in 1936, to determine the dysprosium in impure yttrium.<sup>5</sup> Another was in 1938 by Seaborg and Livingood<sup>6</sup> using the deuterons produced by the cyclotron at the University of California, Berkeley, to determine the concentrations of copper, phosphorus, sulfur, iron, and arsenic.

In comparison to other methods of analysis, neutron activation has shown great success.<sup>7</sup> This method of analysis allows both qualitative and quantitative determination regardless of the elements' chemical or physical state. Other methods of analysis have many disadvantages. For example: they require destruction of the sample; they are insensitive to a wide range of elements; their reproducibility is low; they require a great deal of sample preparation; and finally, contamination and interfering elements produce many complications. Among these methods can be listed spectrometry, absorption spectrophotometry, and the basic wet analysis.

The technique of N.A.A. requires that a sample be exposed to a flux of thermal neutrons. During this period, a number of nuclei of the element will capture the

## CHAPTER II

THEORY AND COMPARISON OF NEUTRON ACTIVATION ANALYSIS  
WITH OTHER PHYSICO-CHEMICAL METHODS OF ANALYSIS

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The technique of N.A.A. requires that a sample be exposed to a flux of thermal neutrons. During this period, a number of nuclei of the element will capture the

neutrons and become radioactive. The rate at which these nuclei are formed is shown in the following equations.

$$\frac{dN}{dt} = N_0 \sigma \phi (-\lambda N) \quad (1)$$

$$N = \frac{N_0 \sigma \phi}{\lambda} (1 - e^{-\lambda t}) \quad (2)$$

where: N = number of nuclei formed

$N_0$  = number of target nuclei

$\lambda$  = decay constant

$\sigma$  = cross section (tendency to capture a neutron)

$\phi$  = thermal flux of bombarding particles

t = length of bombardment time

Once the sample has been made radioactive it will begin to decay with the emission of characteristic radiation. The knowledge of the energy, type, and the intensity will enable us to identify the element and measure its concentration. A brief discussion of this procedure will be presented in the latter part of this paper.

The concentration of an element that can be determined varies with the element. Using a thermal neutron flux of  $1.6 \times 10^8$  (1 hr irradiation) with a 4 liter sample;<sup>8</sup>

In order for the elements to become radioactive, a source of neutrons is required. Since Youngstown State University does not have a reactor to produce thermal neutrons, another source is needed. The United States Atomic Energy Commission's Savannah River Laboratory

15 $\mu\text{g/ml}$	F
.08 $\mu\text{g/ml}$	Na
.1 $\mu\text{g/ml}$	Al
.8 $\mu\text{g/ml}$	Cl



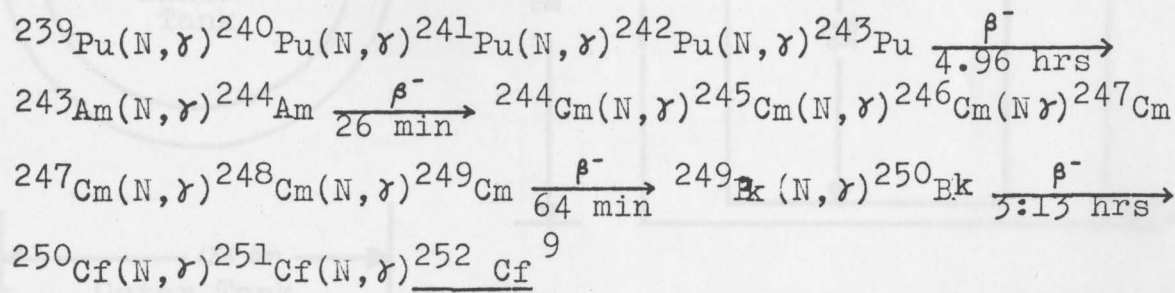
1 $\mu\text{g/ml}$	Ti
.01 $\mu\text{g/ml}$	V
12 $\mu\text{g/ml}$	Cr
.0001 $\mu\text{g/ml}$	Mn
2700 $\mu\text{g/ml}$	Fe
.09 $\mu\text{g/ml}$	Co
5 $\mu\text{g/ml}$	Ni
.03 $\mu\text{g/ml}$	Cu
2 $\mu\text{g/ml}$	Zn
.04 $\mu\text{g/ml}$	As
.6 $\mu\text{g/ml}$	Se
.1 $\mu\text{g/ml}$	Br
8 $\mu\text{g/ml}$	Nb
1 $\mu\text{g/ml}$	Mo
.09 $\mu\text{g/ml}$	Ag
.1 $\mu\text{g/ml}$	Cd
.3 $\mu\text{g/ml}$	Sn
.05 $\mu\text{g/ml}$	Sb
.08 $\mu\text{g/ml}$	Ba
10 $\mu\text{g/ml}$	Hg

#### CALIFORNIUM-252

In order for the elements to become radioactive, a source of neutrons is required. Since Youngstown State University does not have a reactor to produce thermal neutrons, another source was needed. The United States Atomic Energy Commission's Savannah River Laboratory



loaned the University 10 mg of californium-252. Californium-252 is a man-made element that has a half-life of 2.646 years. Prepared in a reactor of high neutron flux, the mode of formation is as follows:



Californium-252 as a source of neutrons is still in a pilot stage. As a source of neutrons perhaps it is unexcelled because of its simplicity and cost-free maintenance. The source arrived on December 13, 1971, at 2:30 p.m. and was finally placed in its permanent storage tank at 4:10 p.m. (Figures 1 and 2).

#### Measurement of Thermal Flux of ${}^{252}\text{Cf}$

Before beginning the activation analysis of the water samples, a study of the thermal flux of our new source of neutrons was made. Neutrons which have slowed down to thermal equilibrium with their surroundings are called thermal neutrons. To calculate the thermal flux the following equations are used.

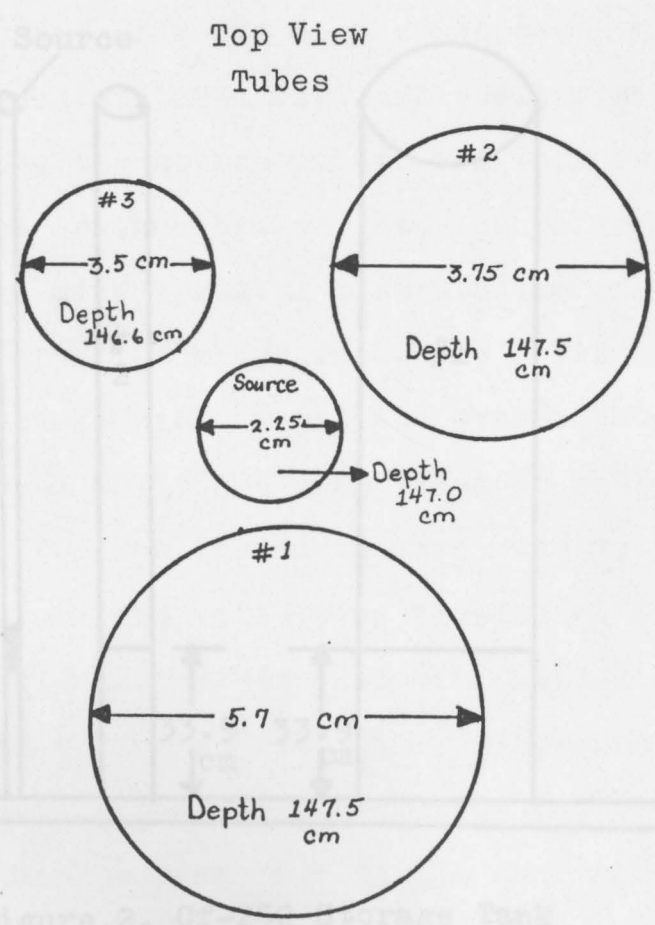
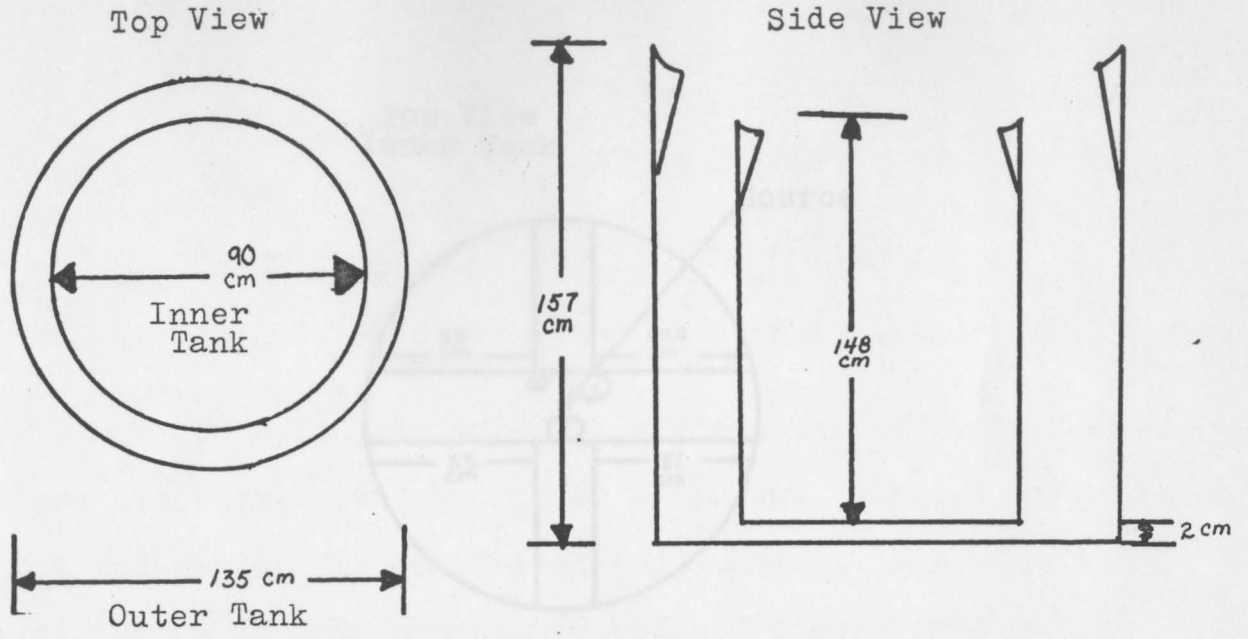


Figure 1. Cf-252 Storage Tank

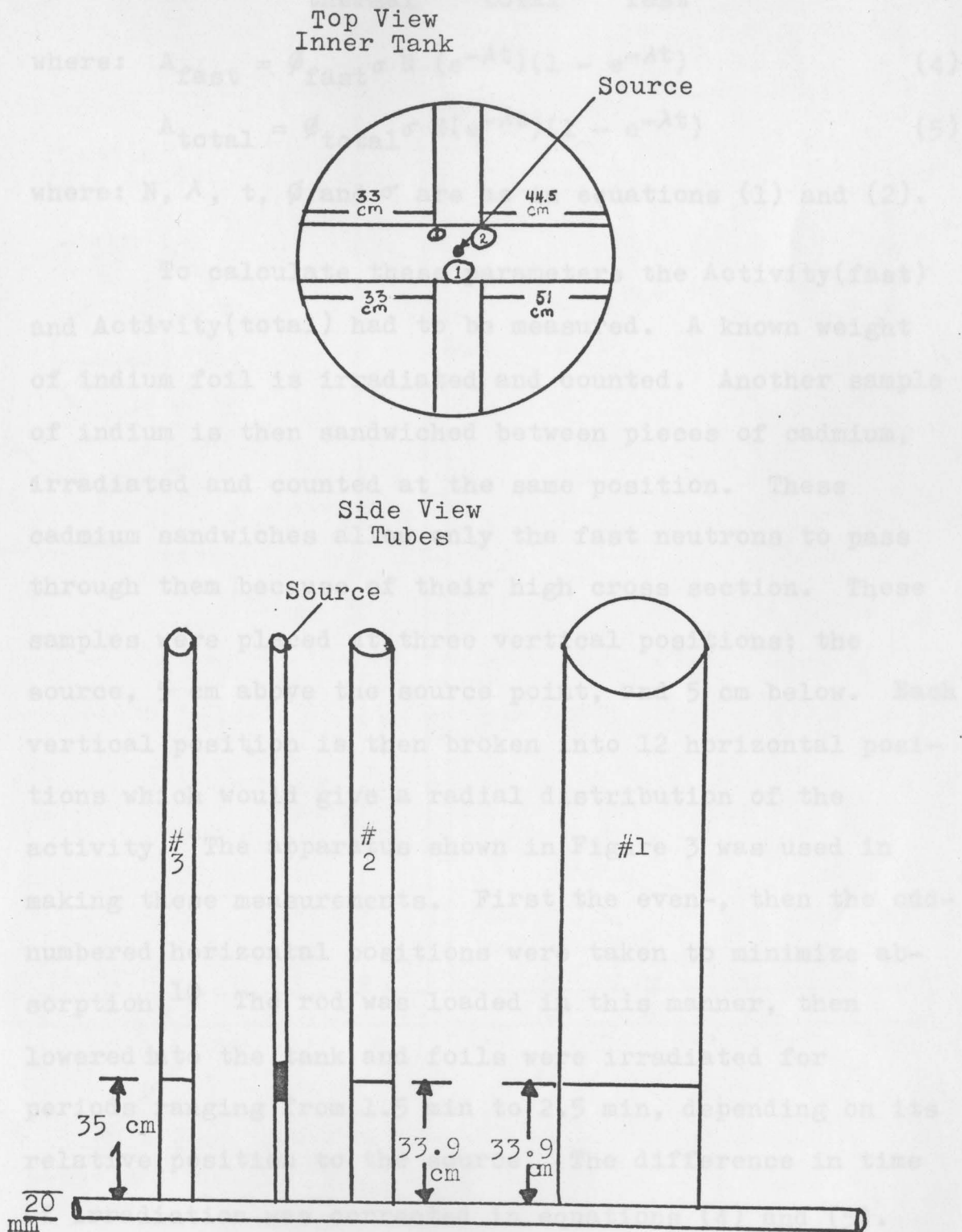


Figure 2. Cf-252 Storage Tank

$$\phi_{\text{thermal}} = \phi_{\text{total}} - \phi_{\text{fast}} \quad (3)$$

$$\text{where: } A_{\text{fast}} = \phi_{\text{fast}} \sigma N (e^{-\lambda t})(1 - e^{-\lambda t}) \quad (4)$$

$$A_{\text{total}} = \phi_{\text{total}} \sigma N (e^{-\lambda t})(1 - e^{-\lambda t}) \quad (5)$$

where:  $N$ ,  $\lambda$ ,  $t$ ,  $\phi$  and  $\sigma$  are as in equations (1) and (2).

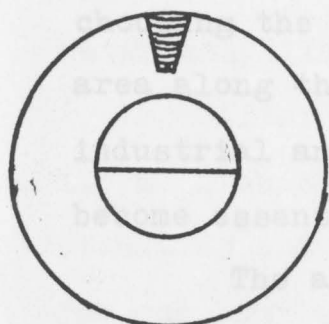
To calculate these parameters the Activity(fast) and Activity(total) had to be measured. A known weight of indium foil is irradiated and counted. Another sample of indium is then sandwiched between pieces of cadmium, irradiated and counted at the same position. These cadmium sandwiches allow only the fast neutrons to pass through them because of their high cross section. These samples were placed at three vertical positions; the source, 5 cm above the source point, and 5 cm below. Each vertical position is then broken into 12 horizontal positions which would give a radial distribution of the activity. The apparatus shown in Figure 3 was used in making these measurements. First the even-, then the odd-numbered horizontal positions were taken to minimize absorption.<sup>10</sup> The rod was loaded in this manner, then lowered into the tank and foils were irradiated for periods ranging from 1.5 min to 2.5 min, depending on its relative position to the source. The difference in time of irradiation was corrected in equations (4) and (5). The foils were then counted on a single channel analyzer made by Nuclear Chicago, Model #186.

ROD ANALYSIS OF WATER

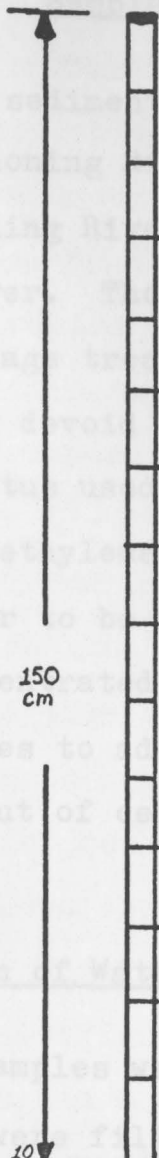
Rod

Collection

Plastic foil holder



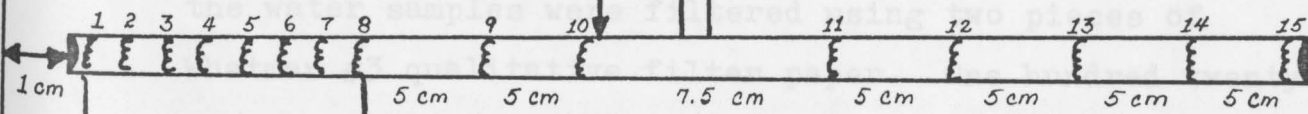
2.5 cm



150 cm

5 cm

125 cm



Distance between each is 1 cm

Figure 3. Apparatus for Flux Determination



## ACTIVATION ANALYSIS OF WATER

### Sample Collection

Water and sediment samples to be analyzed were taken from the Mahoning River system. The reason for choosing the Mahoning River is for the large, industrial area along the river. The river is used to carry away industrial and sewage treatment waste, and thus, it has become essentially devoid of life.

The apparatus used in the collection of samples was a bucket, polyethylene bottles,<sup>11</sup> which were both washed in the water to be sampled, a rope, thermometer, pH paper, and concentrated nitric acid. The acid was added to the samples to adjust the pH to 2. This did minimize plating out of certain trace elements on the walls of the bottles.<sup>12</sup>

### Preparation of Water and Sediment Samples

Once the samples were brought to the laboratory the water samples were filtered using two pieces of Whatman #3 qualitative filter paper. One hundred twenty-five milliliters of each sample was transferred to a 125 ml, pre-washed and rinsed with deionized water, polyethylene vials.

The sediment samples were placed into evaporating dishes and allowed to air dry, then weighed and transferred to 8 ml polyethylene vials.



### Preparation of Standards

Standard solutions of possible ions present were made in order that a simple relative concentration calculation could be made. The standard concentrations were made by dissolving a known weight of the compound in water and diluted to one liter. (Table 1)

After preparation of the standard concentrations, 125 ml of each was transferred to a vial and closed. Both standards and samples were irradiated in tube number one for one hour (Figure 2). Other periods of time for irradiation ranging from 15 min to 3 hr were tried and showed an irradiation time of 1 hr to yield sufficient absorption. Elapsed time between removal of irradiated material from source to counter was kept at 30 sec to eliminate the need for correction of decay time. The irradiated samples were counted for 20 min using a PIP 400 multi-channel analyzer with a 2 x 2 NaI(Tl) crystal as a detector (Figure 4).

Each element has a characteristic gamma ray spectrum as shown in Figure 5.<sup>13</sup> Upon irradiation the element will emit gamma rays which are sensed as pulses or events in the appropriate energy bank or channel. The number of events that occur is directly proportional to the concentration of the element. Using a standard, like the  $^{60}\text{Co}$  1.17 Mev photo peak, each channel can be assigned an energy value. Once standardized the energy of the different photo peaks was determined, thus qualitatively

Figure 1. Detection and Counting System

TABLE 1

## STANDARDS

Elements	PPM	Wgt(grams)/Liter	CPD
Na	200	.713	$\text{NaC}_2\text{H}_3\text{O}_2$
Cl	200	.2391	LiCl
Mg	100	1.0543	$\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$
K	100	.2859	$\text{KNO}_3$
AL	10	.13904	$\text{AL}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$
Mn	10	.037626	$\text{MnSO}_4 \cdot \text{H}_2\text{O}$
Ca	100	.58922	$\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$
Br	100	.1225	$\text{NH}_4\text{Br}$

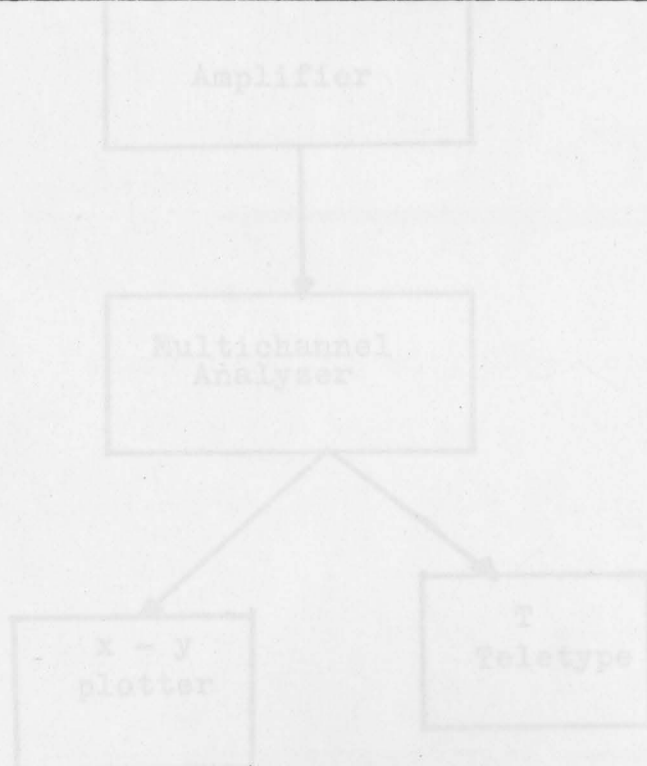
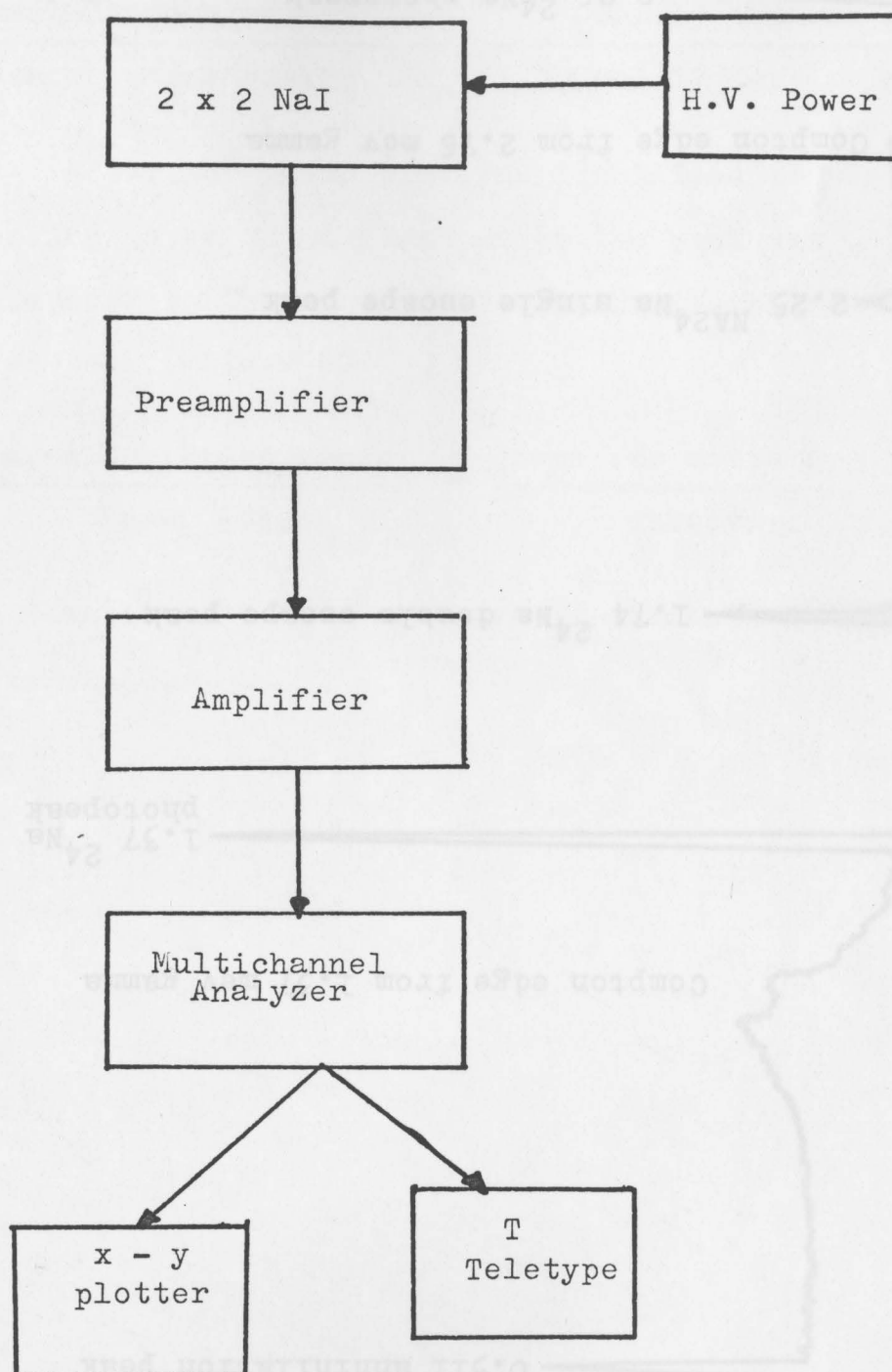


Figure 4. Detection and Counting System



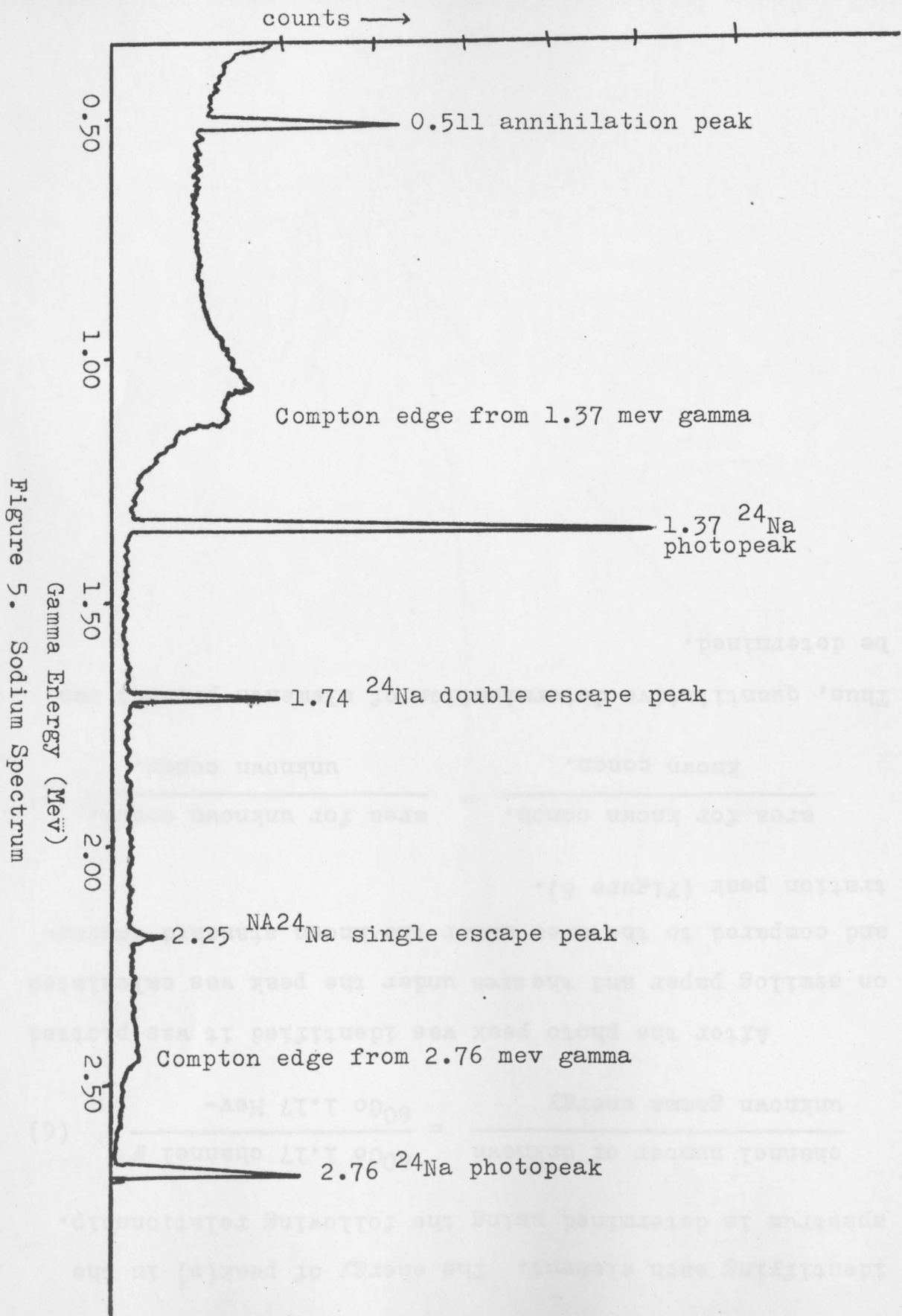


Figure 5. Sodium Spectrum

identifying each element. The energy of peak(s) in the spectrum is determined using the following relationship.

$$\frac{\text{channel number of unknown}}{\text{unknown gamma energy}} = \frac{^{60}\text{Co 1.17 channel \#}}{^{60}\text{Co 1.17 Mev-}} \quad (6)$$

After the photo peak was identified it was plotted on semilog paper and the area under the peak was calculated and compared to the area under the known standard concentration peak (Figure 6).

$$\frac{\text{area for known concn.}}{\text{known concn.}} = \frac{\text{area for unknown concn.}}{\text{unknown concn.}} \quad (7)$$

Thus, quantitative determination of elements present can be determined.

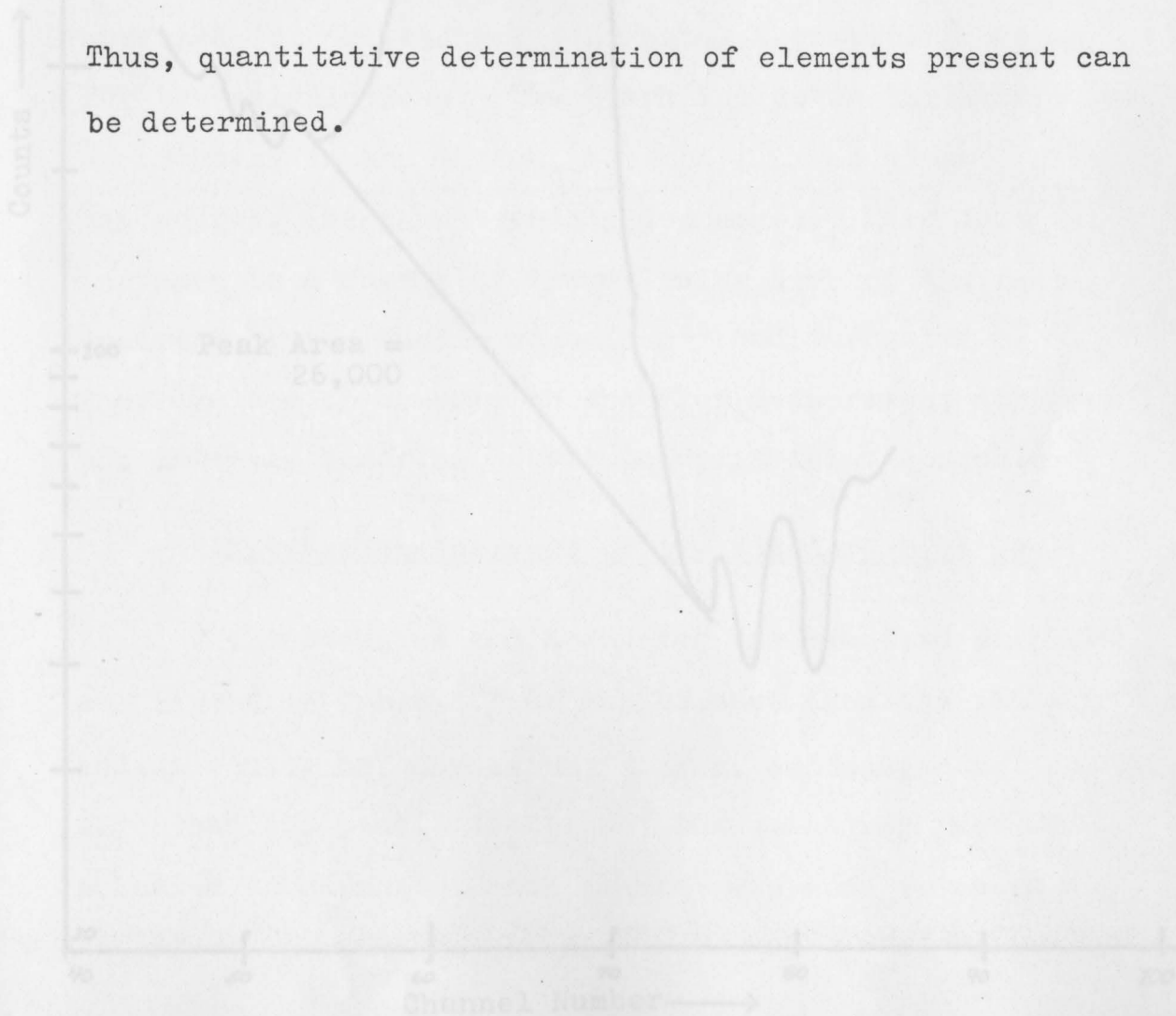
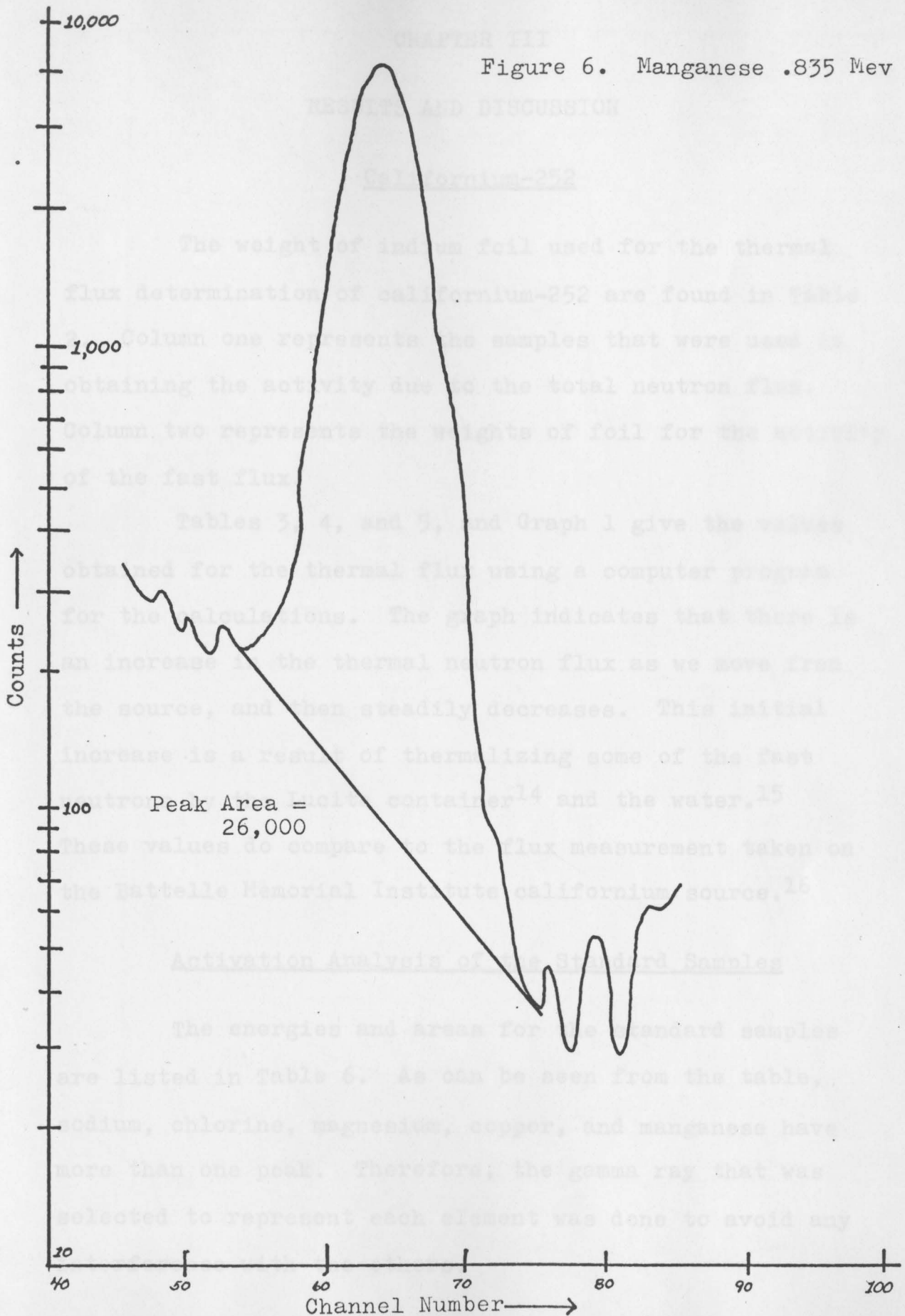


Figure 6. Manganese .835 Mev





## CHAPTER III

## RESULTS AND DISCUSSION

Californium-252

The weight of indium foil used for the thermal flux determination of californium-252 are found in Table 2. Column one represents the samples that were used in obtaining the activity due to the total neutron flux. Column two represents the weights of foil for the activity of the fast flux.

Tables 3, 4, and 5, and Graph 1 give the values obtained for the thermal flux using a computer program for the calculations. The graph indicates that there is an increase in the thermal neutron flux as we move from the source, and then steadily decreases. This initial increase is a result of thermalizing some of the fast neutrons by the Lucite container<sup>14</sup> and the water.<sup>15</sup> These values do compare to the flux measurement taken on the Battelle Memorial Institute californium source.<sup>16</sup>

Activation Analysis of the Standard Samples

The energies and areas for the standard samples are listed in Table 6. As can be seen from the table, sodium, chlorine, magnesium, copper, and manganese have more than one peak. Therefore, the gamma ray that was selected to represent each element was done to avoid any interference with the others.

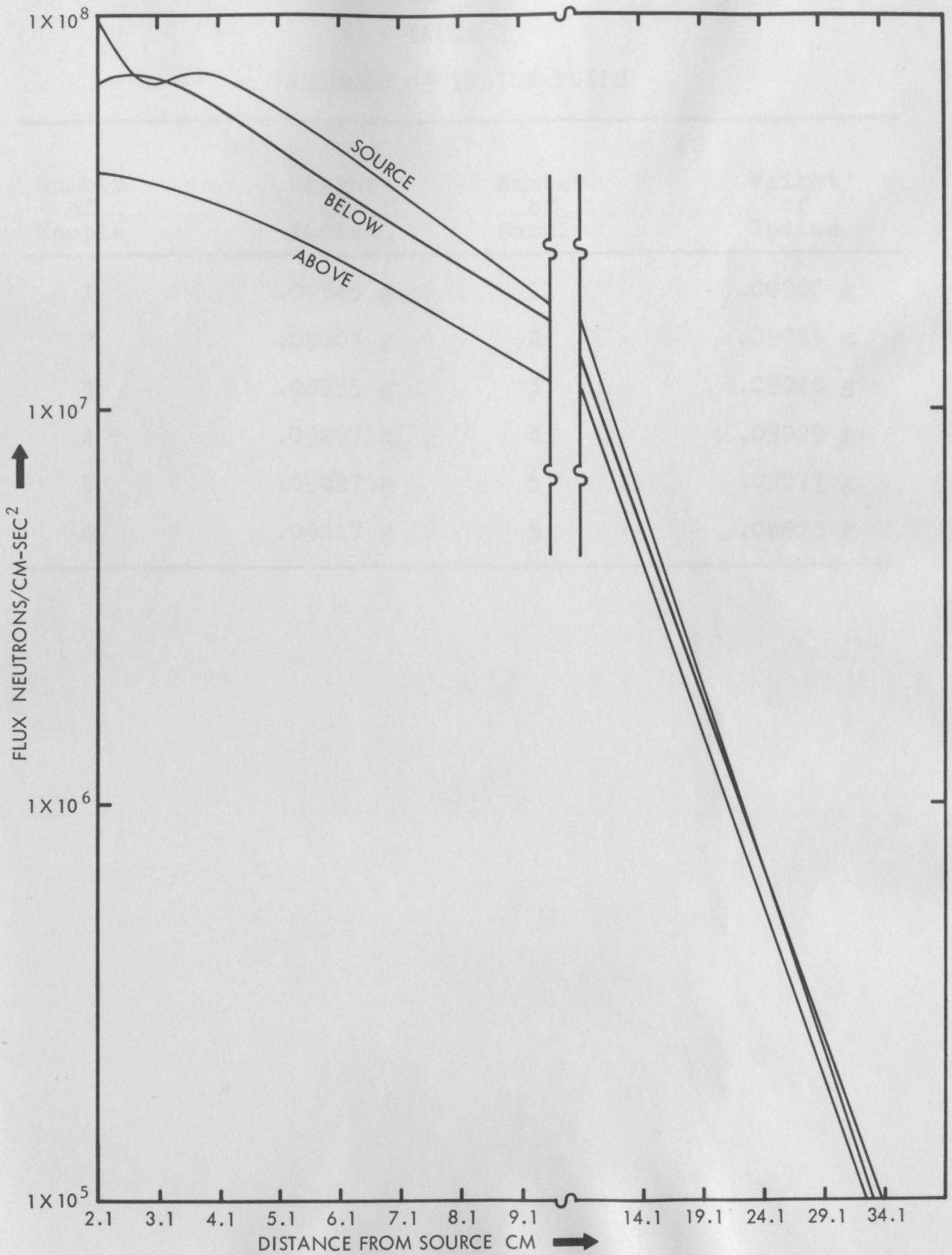


TABLE 2  
WEIGHTS OF INDIUM FOILS

Number of Sample	#1	Weight of Indium	Number of Sample	#2	Weight of Indium
1	3.1	.09345 g	1	.86	.08900 g
2	4.1	.09004 g	2	.41	.09025 g
3	5.1	.08955 g	3	1.0	.09046 g
4	6.1	.09297 g	4	.47	.09029 g
5	7.1	.09027 g	5	1.1	.09077 g
6	8.1	.09217 g	6	.63	.08823 g
8	9.1	$2.13 \times 10^7$		1.2	$\pm 2.5 \times 10^7$
9	14.1	$3.12 \times 10^6$		1.3	$\pm 3.83 \times 10^4$
10	19.1	$2.05 \times 10^6$		2.7	$\pm 5.5 \times 10^4$
11	26.6	$3.45 \times 10^5$		4.5	$\pm 1.53 \times 10^4$
12	31.6	$1.50 \times 10^5$		6.7	$\pm 1.0 \times 10^4$

TABLE 3  
THERMAL FLUX AT SOURCE

Position	Radial Distance from Square	Thermal Flux N/cm <sup>2</sup> -sec	% Deviation	Deviation
1	2.1 cm	$9.7 \times 10^7$	.37	$\pm 3.5 \times 10^5$
2	3.1	$6.58 \times 10^7$	.86	$\pm 5.5 \times 10^5$
3	4.1	$7.18 \times 10^7$	.41	$\pm 2.83 \times 10^5$
4	5.1	$5.00 \times 10^7$	1.0	$\pm 5.0 \times 10^5$
5	6.1	$4.68 \times 10^7$	.47	$\pm 2.16 \times 10^5$
6	7.1	$3.3 \times 10^7$	1.1	$\pm 3.62 \times 10^5$
7	8.1	$3.02 \times 10^7$	.63	$\pm 1.83 \times 10^5$
8	9.1	$2.13 \times 10^7$	1.2	$\pm 2.5 \times 10^5$
9	14.1	$3.12 \times 10^6$	1.3	$\pm 3.83 \times 10^4$
10	19.1	$2.05 \times 10^6$	2.7	$\pm 5.5 \times 10^4$
11	26.6	$3.45 \times 10^5$	4.5	$\pm 1.53 \times 10^4$
12	31.6	$1.50 \times 10^5$	6.7	$\pm 1.0 \times 10^4$

TABLE 4

## THERMAL FLUX 5 CM ABOVE

Position	Radial Distance from Source	Thermal Flux N/cm <sup>2</sup> -sec	% Deviation	Deviation
1	2.1 cm	$3.97 \times 10^7$	.9	$\pm 3.57 \times 10^5$
2	3.1	$3.75 \times 10^7$	1.1	$\pm 4.00 \times 10^5$
3	4.1	$3.20 \times 10^7$	.98	$\pm 3.13 \times 10^5$
4	5.1	$2.95 \times 10^7$	1.2	$\pm 3.42 \times 10^5$
5	6.1	$2.22 \times 10^7$	1.2	$\pm 2.65 \times 10^5$
6	7.1	$1.97 \times 10^7$	1.4	$\pm 2.67 \times 10^5$
7	8.1	$1.523 \times 10^7$	1.3	$\pm 2.02 \times 10^5$
8	9.1	$1.285 \times 10^7$	1.5	$\pm 1.83 \times 10^5$
9	14.1	$4.77 \times 10^6$	2.6	$\pm 1.25 \times 10^5$
10	19.1	$1.60 \times 10^6$	4.0	$\pm 6.38 \times 10^4$
11	26.6	$3.10 \times 10^5$	6.3	$\pm 1.93 \times 10^4$
12	31.6	$1.13 \times 10^5$	7.0	$\pm 7.83 \times 10^3$

TABLE 5

## THERMAL FLUX 5 CM BELOW

Position	Radial Distance from Source	Thermal Flux N/cm <sup>2</sup> -sec	% Deviation	Deviation
1	2.1 cm	6.96 x 10 <sup>7</sup>	.54	±3.75 x 10 <sup>5</sup>
2	3.1	7.02 x 10 <sup>7</sup>	.63	±4.42 x 10 <sup>5</sup>
3	4.1	5.12 x 10 <sup>7</sup>	.61	±3.12 x 10 <sup>5</sup>
4	5.1	4.90 x 10 <sup>7</sup>	.72	±3.53 x 10 <sup>5</sup>
5	6.1	3.63 x 10 <sup>7</sup>	.82	±2.96 x 10 <sup>5</sup>
6	7.1	3.33 x 10 <sup>7</sup>	.92	±3.00 x 10 <sup>5</sup>
7	8.1	2.30 x 10 <sup>7</sup>	.92	±2.1 x 10 <sup>5</sup>
8	9.1	2.08 x 10 <sup>7</sup>	1.1	±7.00 x 10 <sup>4</sup>
9	14.1	6.16 x 10 <sup>6</sup>	2.02	±1.24 x 10 <sup>5</sup>
10	19.1	1.95 x 10 <sup>6</sup>	3.6	±7.00 x 10 <sup>4</sup>
11	26.6	3.62 x 10 <sup>5</sup>	5.5	±2.0 x 10 <sup>4</sup>
12	31.6	1.30 x 10 <sup>5</sup>	7.1	±9.17 x 10 <sup>3</sup>



TABLE 6

## STANDARDS

Element	Photo Peak (mev.)	Peak Max	Total Area	P.P.M.
Na	.5025	1793	4,208	200
	1.389	2385	27,061	
Cl	1.711	1371	13,190	200
	2.308	827	11,285	
Mn	.830	21248	171,335	10
	1.905	1626	19,504	
	2.295	639	8,296	
Mg	.803	236	1,613	100
	1.003	73	437	
Br	.608	15308	91,586	100
Al	2.648	103	1,135	10
<u>After 24 hrs</u>				
Cu	.511	4141	19,933	200

Cl	—	1.64 Mev
Mn	—	0.845 Mev
Mg	—	1.01 Mev
Na	<	0.511 Mev
	>	1.37 Mev

Both sodium peaks are used because we suspect the presence of copper. Copper has a representative plot peak that lies on top of and close to that of (.511 Mev) sodium. Realizing that sodium has a longer half-life, a ratio between the areas of the two photo peaks should remain constant even after a period of 24 hr. If the sample is allowed to decay for 24 hr or more and the ratio decreases, then copper is present. Subtracting the activity due to sodium from the total peak yields the copper activity. This method requires that the copper standard be counted after 24 hr.

#### Activation Analysis of Samples

Tables 7, 8, 9, 10, 11, and 12 show the concentration of the elements detected at each site. Table 13 shows the individual change in concentration of the elements as we travel down the river. Graph 2<sup>17</sup> shows the sediment concentrations of the elements sodium, copper, and manganese.

The samples sites picked 2 - 6 (Figure 7) allowed us to bracket in the major industrial and municipalities around the river. The author would like to point out at

TABLE 7

POSITION #1

Meander Creek

3/31/72

Initial pH  $\approx$  6 Changed to 2

Photo Peak (mev)	Elements Found	Peak Max.	Total Area	P.P.M. $\pm$ 10%
.507	Na, Cu	831	2193	
.857	Mn	471	1208	.07
1.3806	Na	699	7104	52.50
1.7082	Cl	367	2793	42.35
<u>After 24 hrs decay</u>				
.517	Na, Cu	132	463	
.517	Na		292	52.50
.517	Cu		171	1.768
1.38	Na	180	1939	52.50

TABLE 8  
POSITION #2

Leavitt's Road (Warren)

2/9/72

Initial pH  $\approx$  6 changed to 2  
No sediment, water frozen

Photo Peak (mev)	Elements Found	Peak Max.	Total Area	P.P.M. $\pm$ 10%
.491	Na, Cu	630	1524	
.819	Mn	596	3106	.18
1.372	Na	391	3533	26.11
1.70	Cl	274	2054	31.14
<u>After 24 hrs decay</u>				
.496	Na, Cu	96	330	
.496	Na		179	26.11
.496	Cu		151	1.56
1.388	Na	99	1186	26.11

TABLE 9

POSITION #3

Route 46 Bridge (Niles)

2/9/72

Initial pH  $\approx$  6, changed to 2

Photo Peak (mev)	Elements Found	Peak Max.	Total Area	P.P.M. $\pm$ 10%
.510	Na, Cu	1166	4729	
.832	Mn	1229	6569	.38
1.409	Na	811	4977	36.78
1.722	Cl	511	3534	53.58
<u>After 24 hrs decay</u>				
.506	Na, Cu	128	428	
.506	Na		299	36.78
.506	Cu		129	1.33
1.402	Na	171	1988	36.78

TABLE 10

POSITION #4

Liberty Road (Girard)

2/9/72

Initial pH  $\approx$  6 changed to 2

Photo peak (mev)	Elements Found	Peak Max.	Total Area	P.P.M. $\pm$ 10%
.5062	Na, Cu	1223	4350	
.832	Mn	1128	4605	.26
1.392	Na	867	6208	45.88
1.722	Cl	529	2678	40.60
<u>After 24 hrs decay</u>				
.510	Na, Cu	165	500	
.510	Na		332	45.88
.510	Cu		168	1.73
1.40	Na	213	2210	45.88



TABLE 11

POSITION #5

Market Street Bridge (Youngstown)

2/9/72

Initial pH  $\approx$  6 changed to 2

Photo Peak (mev)	Elements Found	Peak Max.	Total Area	P.P.M. $\pm$ 10%
.5062	Na, Cu	5816	39,585	
.829	Mn	16945	125,016	7.29
1.385	Na	1499	9,193	67.94
1.692	Cl	946	2,330	35.33
<u>After 24 hrs decay</u>				
.506	Na, Cu	165	581	
.506	Na		305	67.94
.506	Cu		276	2.85
1.394	Na	195	2,024	67.94

TABLE 12

POSITION #6

Lowellville Bridge

3/31/72

Initial pH  $\approx$  6 changed to 2

Photo Peak (mev)	Elements Found	Peak Max.	Total Area	P.P.M. $\pm$ 10%
.4992	Na, Cu	1008	2745	
.826	Mn	1068	5306	.30
1.380	Na	679	6633	49.02
1.700	Cl	489	3768	57.13
<u>After 24 hrs decay</u>				
.500	Na, Cu	117	358	
.500	Na		282	49.02
.500	Cu		76	.78
1.38	Na	166	1871	49.02

Table 13 (continued)

TABLE 13

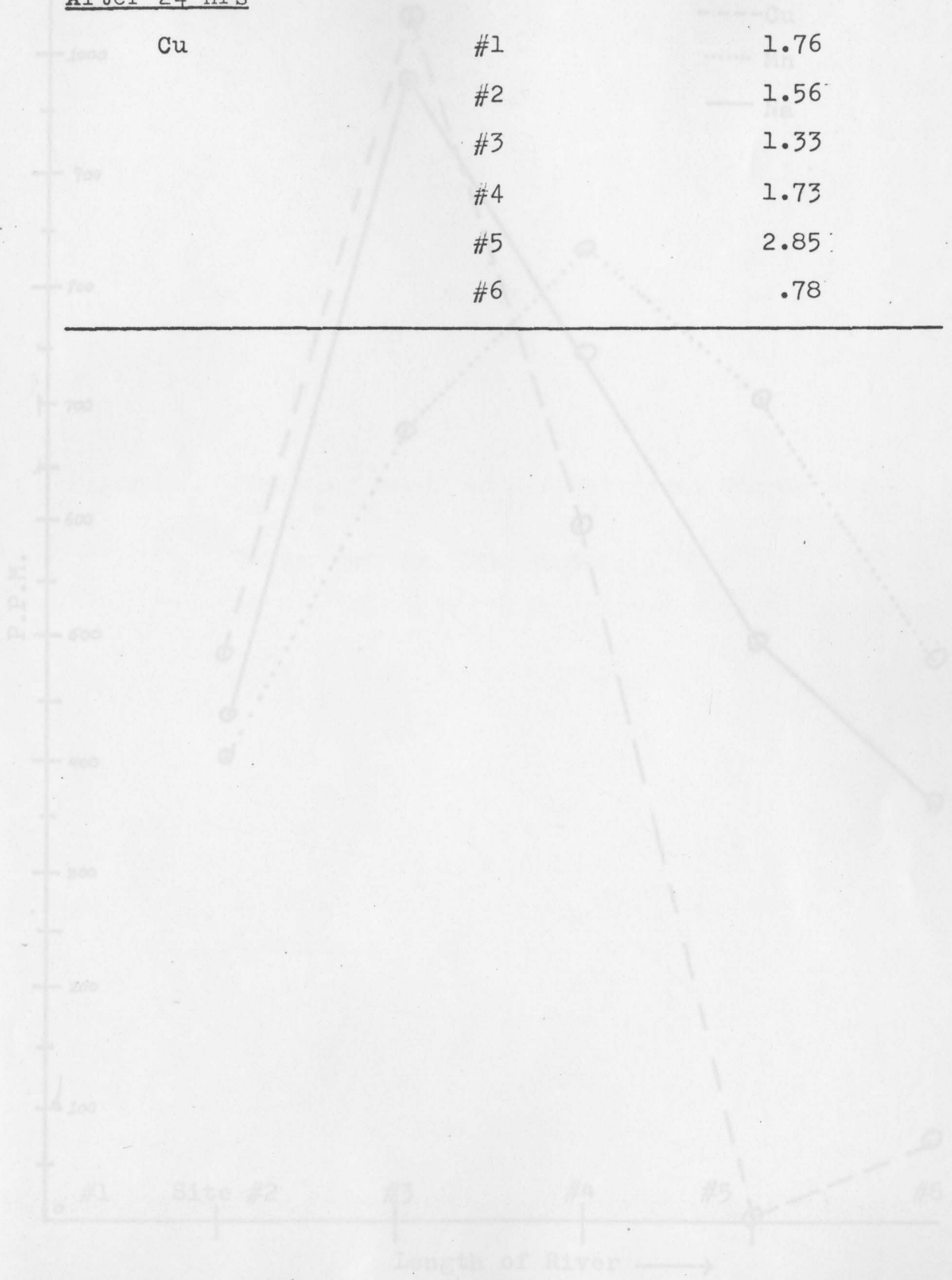
## INDIVIDUAL ELEMENTS

Elements	Position	Concentration P.P.M.
Mn	#1	.070
	#2	.18
	#3	.38
	#4	.26
	#5	7.29
	#6	.30
Na	#1	52.50
	#2	26.11
	#3	36.78
	#4	45.88
	#5	67.94
	#6	49.02
Cl	#1	42.35
	#2	31.14
	#3	53.58
	#4	40.60
	#5	35.33
	#6	57.13

Table 13 (continued)

Graph 2. Sediment Concentrations

After 24 hrs



Cu

#1  
#2  
#3  
#4  
#5  
#6

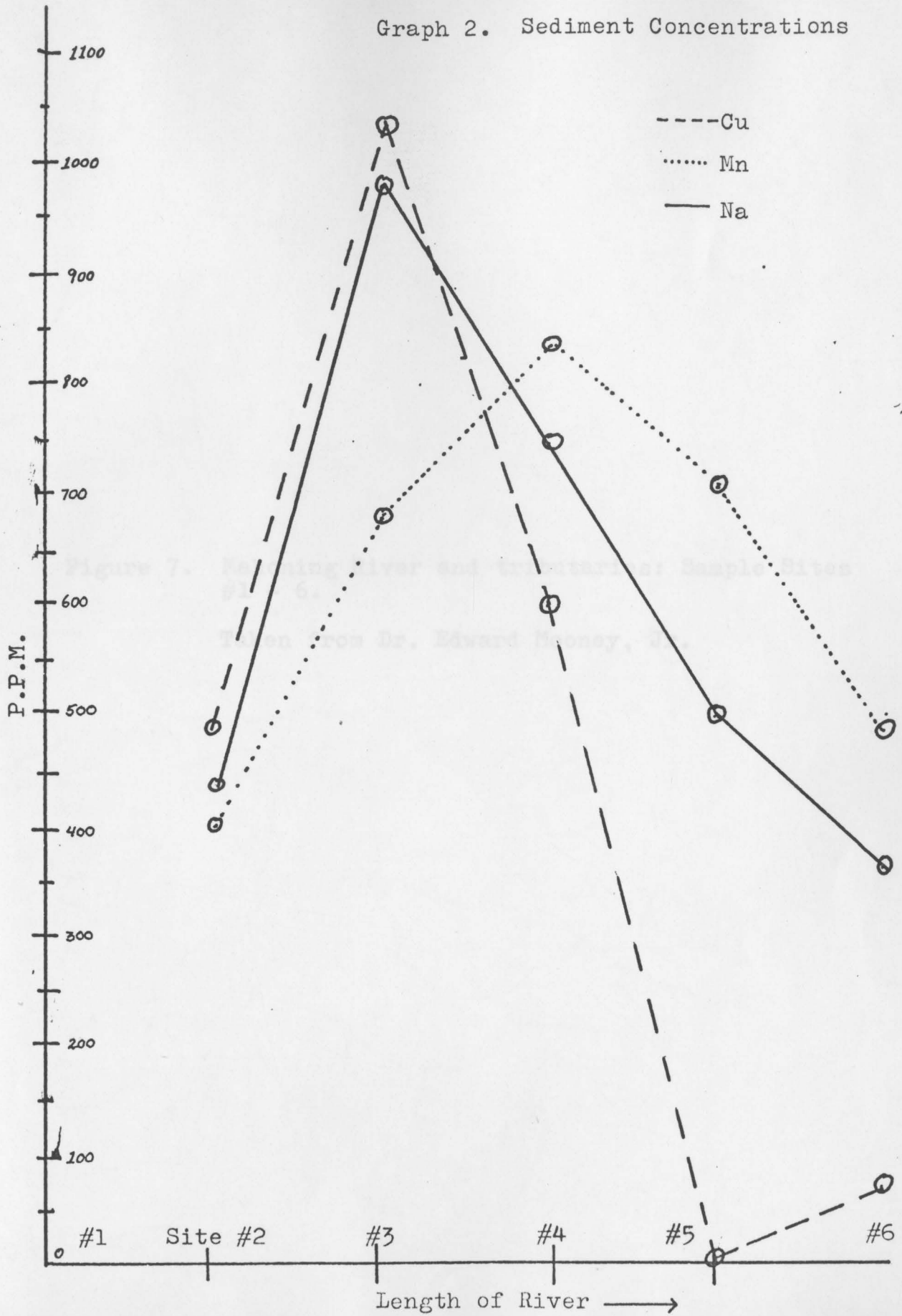
1.76  
1.56  
1.33  
1.73  
2.85  
.78

P.P.M.

#1 Site #2 #3 #4 #5 #6

Length of River →

Graph 2. Sediment Concentrations



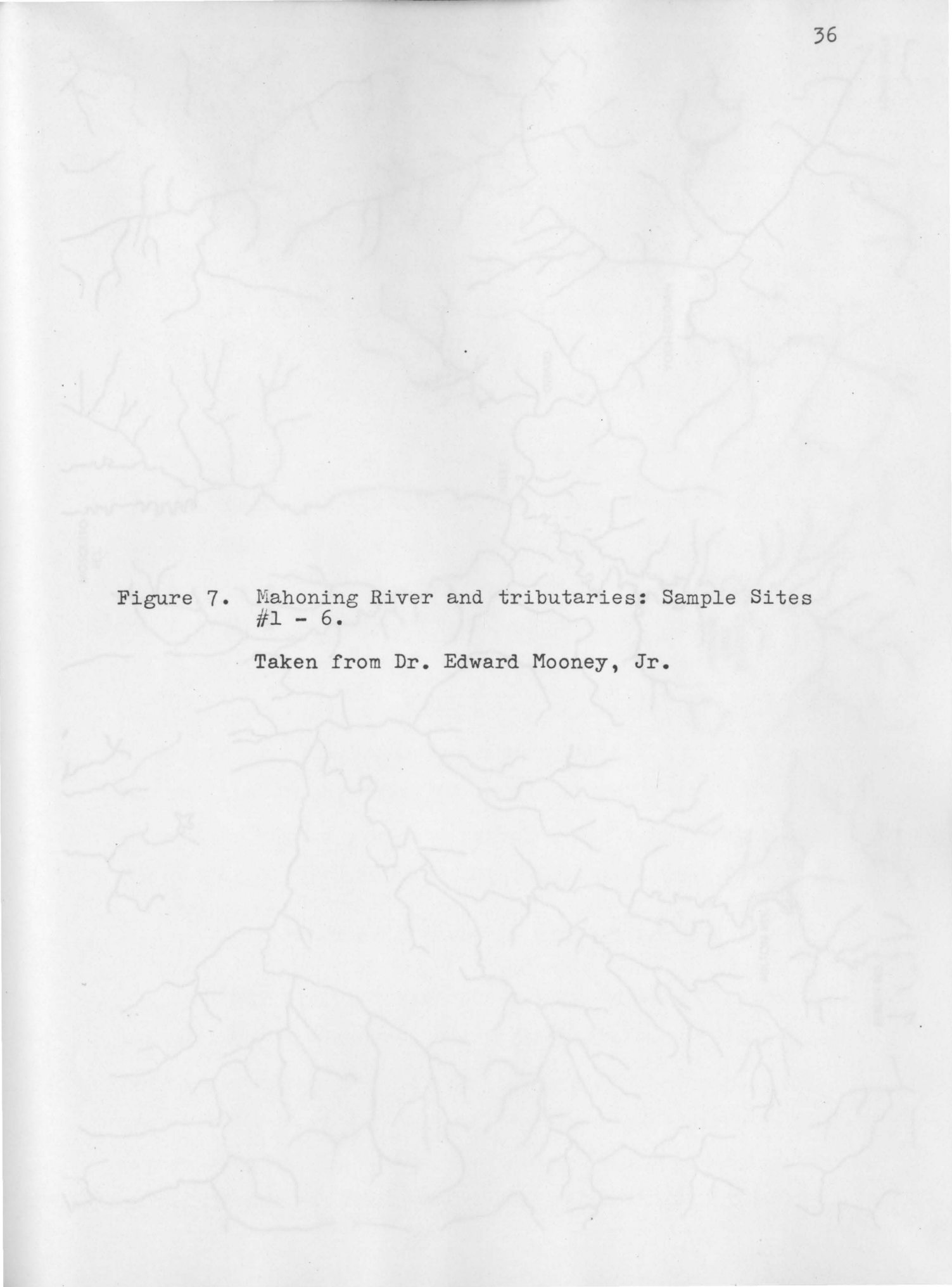


Figure 7. Mahoning River and tributaries: Sample Sites  
#1 - 6.

Taken from Dr. Edward Mooney, Jr.





this time that sites #1 and #6 were not taken the same day as the other four.

#1 Meander Creek, pH  $\approx$  6, 3/31/72

#2 Leavitt's Road Bridge, pH  $\approx$  6, 2/9/72

#3 Route 46 Bridge, Niles, pH  $\approx$  6, 2/9/72

#4 Liberty Road Bridge, Girard, pH  $\approx$  6, 2/9/72

#5 Market Street Bridge, Youngstown, pH  $\approx$  6, 2/9/72

#6 Lowellville Bridge, pH  $\approx$  6, 3/31/72

#### Site #1 (Meander Creek)

Meander Reservoir is the Youngstown area drinking water supply. Any spillage over Meander Dam and chemical wastes that are used by the Meander Treatment plant are allowed to enter Meander Creek which finds its way into the Mahoning River. The concentration of sodium and chlorine can well be explained by the chemical treatment of the water with  $\text{Na}_2\text{SiF}_6$  for teeth and the chlorination for killing of bacteria. Although copper sulfate no longer is used to kill algae, its presence could be leaching from the sediment which has accumulated in the river bed.

#### Site #2 (Leavitt's Road Bridge)

This position was chosen because it is located outside the influence of the major cities and industry. The concentration of all the elements are lower here in comparison except for that of copper. One source of the copper could be General Motors--Lordstown fabrication plant.

Duck Creek flows directly between Lordstown and site #2.

#### Site #3 (Route 46 Bridge)

The crossing of Route 46 and the Mahoning River is located just north of the city of Niles. The river at this position has shown an increase in concentration of all the elements except copper. This increase is to be expected because the river has traveled through the city of Warren, past several mills and a large land fill.

#### Site #4 (Liberty Road)

Site #4 has proven very interesting because of the decrease in the concentration of manganese and chlorine. The author feels the only reason for the decrease could be the precipitation of these elements by the chemicals introduced from sewage treatment plants and Meander Creek.

#### Site #5 (Market Street Bridge)

Market Street is located next to two steel mills and in the heart of the largest of the municipalities. As is expected the river showed a significant increase in concentration for all the elements except chlorine; this is due to the fact that some chlorides are quite insoluble.

### Site #6 (Lowellville Bridge)

At this position a drastic change occurs. All the concentrations except chlorine go down to levels of site #4. Between sites #5 and #6 there is located one large and two minor primary sewage treatment plants. The increase in chlorine is a direct result of the treatment plant. The author also feels that the decrease in the other concentrations could be a dilution factor.<sup>18</sup> The major sewage treatment plant handled during the month of January, on the average of 28.76 million gallons, in the month of February, 29.82 million gallons, and 41.92 million gallons for the month of March.<sup>19</sup>

Since the only other overall study of the river was limited to only 26 ppm organic and 26 ppm inorganic pollutants, there was no comparison made.<sup>20</sup>

This work did show that a greater knowledge of the geological, residential, and industrial areas is essential to explain the complex concentration pattern of some of the trace elements.

It has also been shown that californium can be used as a simple and maintenance-free source of neutrons. The thermal flux provided by the californium is enough to make a detailed study of trace elements in a river system.

## CHAPTER IV

## CONCLUSIONS AND SUGGESTIONS

The gradual increase in sodium between positions 2 through 5 can be attributed to the increase in population and the increase in industrial sources. The change in chlorine concentration is the result of the different sewage treatment and water treatment plants producing the high chlorine concentration near them. Since the samples were taken during the winter, another source of chlorine could be road salts.

The manganese and copper are largely due to the different industries situated along the river. The water is used to cool the ingots of steel and then it finds its way into the river, carrying with it many dissolved elements.

Since the only other overall study of the river was limited to only 26 ppm organic and 26 ppm inorganic pollutants, there was no comparison made.<sup>20</sup>

This work did show that a greater knowledge of the geological, residential, and industrial areas is essential to explain the complex concentration pattern of some of the trace elements.

It has also been shown that californium can be used as a simple and maintenance-free source of neutrons. The thermal flux provided by the californium is enough to make a detailed study of trace elements in a river system.



This is in agreement with Enzo Ricci and T. H. Handley.<sup>21</sup>

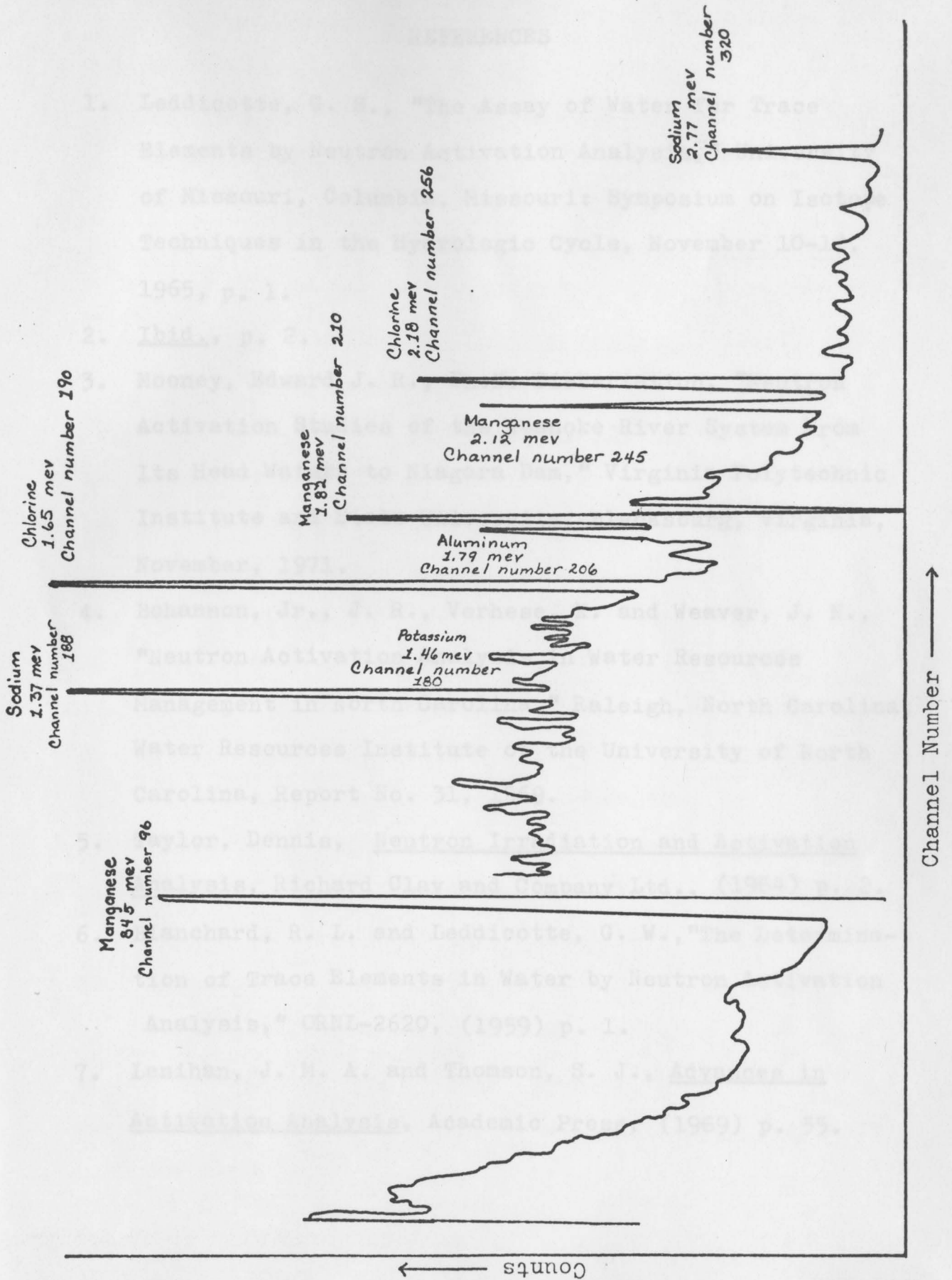
The author would like to make several suggestions. First, that his samples be checked against the new lithium drifted germanium, Ge(Li), gamma-ray detector Youngstown State University has just received. The large photo peaks produced by a 2 x 2 (NaI) crystal tends to mask other elements. Figure 8 shows sample number 5 using the Ge(Li). As can be seen, two more elements, potassium and aluminum, are present.

Second, the author finds two points of interest; the decrease in sites #4 and #6. A detailed study of both of these positions could produce some interesting results.





Figure 8. Position #4 Using Ge(Li) Detector.



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