YOUNGSTOWN STATE UNIVERSITY

GRADUATE SCHOOL

THESIS

Submitted in Partial Fulfillment of the Requirements

For the Degree of Master of Science

TITLE DETERMINATION OF TRACE ELEMENTS IN THE MAHONING RIVER WATER SYSTEM FROM YOUNGSTOWN TO LOWELLVILLE BY NEUTRON ACTIVATION ANALYSIS

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Chemistry
Program

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Dean of the Graduate School Date

YOUNGSTOWN STATE UNIVERSITY

August, 1972

ABSTRACT

DETERMINATION OF TRACE ELEMENTS IN THE MAHONING RIVER WATER SYSTEM FROM YOUNGSTOWN TO LOWELLVILLE BY NEUTRON ACTIVATION ANALYSIS

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Master of Science in Chemistry
Youngstown State University, 1972

An investigation of trace elements present in the Mahoning River Water System in northeastern Ohio with reference to the area from Youngstown to Lowellville has been carried out using Neutron Activation Analysis, with Californium-252 as the neutron source, and Ge(Li) Spectrometry. Detailed measurements of the levels of ten elements present in the water and sediment were made at major effluent sources.

This study demonstrates a rapid, accurate, and inexpensive method for the detection and measurement of trace elements in a river system. Understanding the role of trace elements in hydrologic systems will help evaluate the influence of man's activities on these systems.

The results show the following variations in the quantities of the elements detected.

Element	Variation in Concentration	
	Water	Sediment
Br	0 - 2.1 ppm	74 - 2,646 ppm
Mn	0.20 - 1.22 ppm	45 - 2,566 ppm
Mg	2.3 - 51 ppm	223 - 10,151 ppm
Cu	0 - 5 ppm	58 - 378 ppm
Na	27 - 113 ppm	50 - 2,482 ppm
V	0 - 0.024 ppm	0.30 - 35 ppm
K	0 - 363 ppm	686 - 4,879 ppm
Cl	30 - 96 ppm	0 ppm
Al	0 - 3.1 ppm	957 - 30,540 ppm
Ca	17 - 115 ppm	537 - 40,892 ppm

The large variation in the concentrations of all these elements demonstrates the effect of the steel mills, chemical and metal-finishing plants, and sewage treatment plants on the river along the sampling area.

It is evident from the results that Californium-252 Activation Analysis using a Ge(Li) detector is a valuable tool in yielding stream flow data.

To

My Parents, Brothers, and Sisters

in Lebanon

ACKNOWLEDGEMENTS

The author wishes to express his sincere appreciation to Dr. Inally Mahadeviah for serving as his research advisor. Dr. Mahadeviah was always available for discussions and offered many valuable suggestions as well as spending long hours at the counting laboratory. Without his aid, this work would not have been possible.

Thanks are due to the author's committee members, Dr. Edward Mooney, Jr., and Dr. Robert Smith for their guidance and suggestions. The author would also like to thank his fellow graduate students, Peter Cordon and Richard Muntean for their help.

The author wishes to acknowledge the financial assistance provided by the Chemistry Department and the Graduate School at Youngstown State University in the form of a Graduate Assistantship.

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

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Introduction

In recent years, the uncontrolled manner of disposing of unwanted by-products within man's mechanized, industrialized and urbanized environment has created a giant problem, that of pollution. Polluted water and air, as well as other types of environmental contamination, present a real danger to all forms of life on earth. Providing solutions to the pollution problem before it reaches the point of no return is one of the hardest tasks facing mankind now and in the years to come.

Practically every major river system in the United States is affected by pollution. The area chosen for this study, the Mahoning River System, which includes a drainage area of 1200 square miles in northeastern Ohio, has a long history of extensive industrial and sewage use and is considered to be highly polluted.[1] The river lies in the heart of the steel district, the fourth largest in the United States, and is used for domestic and industrial water supply, as well as for disposal of municipal and industrial wastes.[1,2] Besides being heavily industrialized, the Mahoning River Valley is densely populated.[2]

Most major studies[1,2,3,4,5] of the past twenty years have failed to provide any information on specific trace elements present in the river. Much work is needed in this area before the quality of this water can be improved substantially. It will be the function of the recently-created Ohio Environmental Protection Agency, in cooperation with the Federal Environmental Protection Agency, to safeguard the water and air in the state from further contamination. Trace element analyses can provide them with useful information.

In a preliminary study, Cordon[6] has recently determined the presence and concentration in parts per million of four elements which appear to be contributing to the pollution of the Mahoning River. The technique used in his work was Neutron Activation Analysis (N.A.A.) with Californium-252 as the neutron source. N.A.A. has proven to be a powerful analytical method in detecting many elements existing in trace amounts in a river system.[6,7,8,9] However, Cordon was limited in the number of elements he could determine due to the low resolution detector system used, a 2x2 in. Thallium-activated Sodium iodide scintillation crystal [NaI(Tl)].

In the present study, a systematic and thorough investigation of trace elements present in the river with reference to the area from Youngstown to Lowellville has been made using N.A.A., Californium-252, and a high resolution Lithium-drifted Germanium semiconductor detector [Ge(Li)]. This work will show that with such a set-up it is possible to detect a larger number of elements.

The reason for choosing the above-mentioned locations is the presence of three steel mills, as well as other industrial plants. In addition, this section of the river has a population of about 190,000.[3] According to officials of the Ohio Department of Natural Resources, this segment is not, at the present time, suitable for boating, fishing and other recreational uses.[2] Thus, data and results from this study on the type, point of origin, and concentration of trace elements could be extremely useful in elucidating the contamination problem in the river.

The United States Atomic Energy Commission's Savannah River Laboratory has recently loaned Youngstown State University 8536 micrograms of Californium-252, which provides the high neutron flux required by N.A.A., as a part of a market evaluation program.

Studies[6,9,10,11] show that this man-made isotope, which was discovered in 1950, is an ideal neutron source for N.A.A. Its long half life (2.646 years), high thermal neutron flux ($\sim 10^8$ n/cm^2/sec), small size, maintenance-free operation and portability make it much more efficient than conventional isotope sources.[6,10,11] The Californium-252 flux was found to be sufficient to make a detailed study of water pollutants in a river system.[6,8,11]

Elements of interest to the water pollution control analyst that can be detected by Californium-252 Activation Analysis[9] include the following:

1. Toxic Pollutants:

   Ag, As, Ba, Br, Cd, Co, Cr, Hg, Ni, Sb, Se, Sn, V

2. Other Pollutants:

   Al, Cl, Cu, F, Fe, Mn, Mo, Na, Nb, Ti, Zn

This information is based on an irradiation time of 60 minutes in a flux of 1.6 x 10^8 n/cm^2/sec using a 3x3 in. NaI(Tl) detector.[9]

Compared to other current analytical methods used in detecting trace elements, N.A.A. is considered the second best method of analysis next to Solids Mass Spectroscopy as far as the total number of elements detected and their sensitivities are concerned (Figure 1).[12] However, N.A.A. offers many advantages[12,13,14,15] over all other methods.

1. It is a non-destructive technique thus permitting the sample to be used for further analysis.

2. It is independent of the physical and chemical state of the element detected.

3. It requires little or no sample preparation, hence, contamination problems are greatly reduced.

4. It provides highly reproducible results, and can be fully automated.

5. It is a simple, rapid and inexpensive method of analysis. Comparison of the cost in dollars/element/sample obtained with Californium-252 to some existing techniques is given in Table 1.[8]

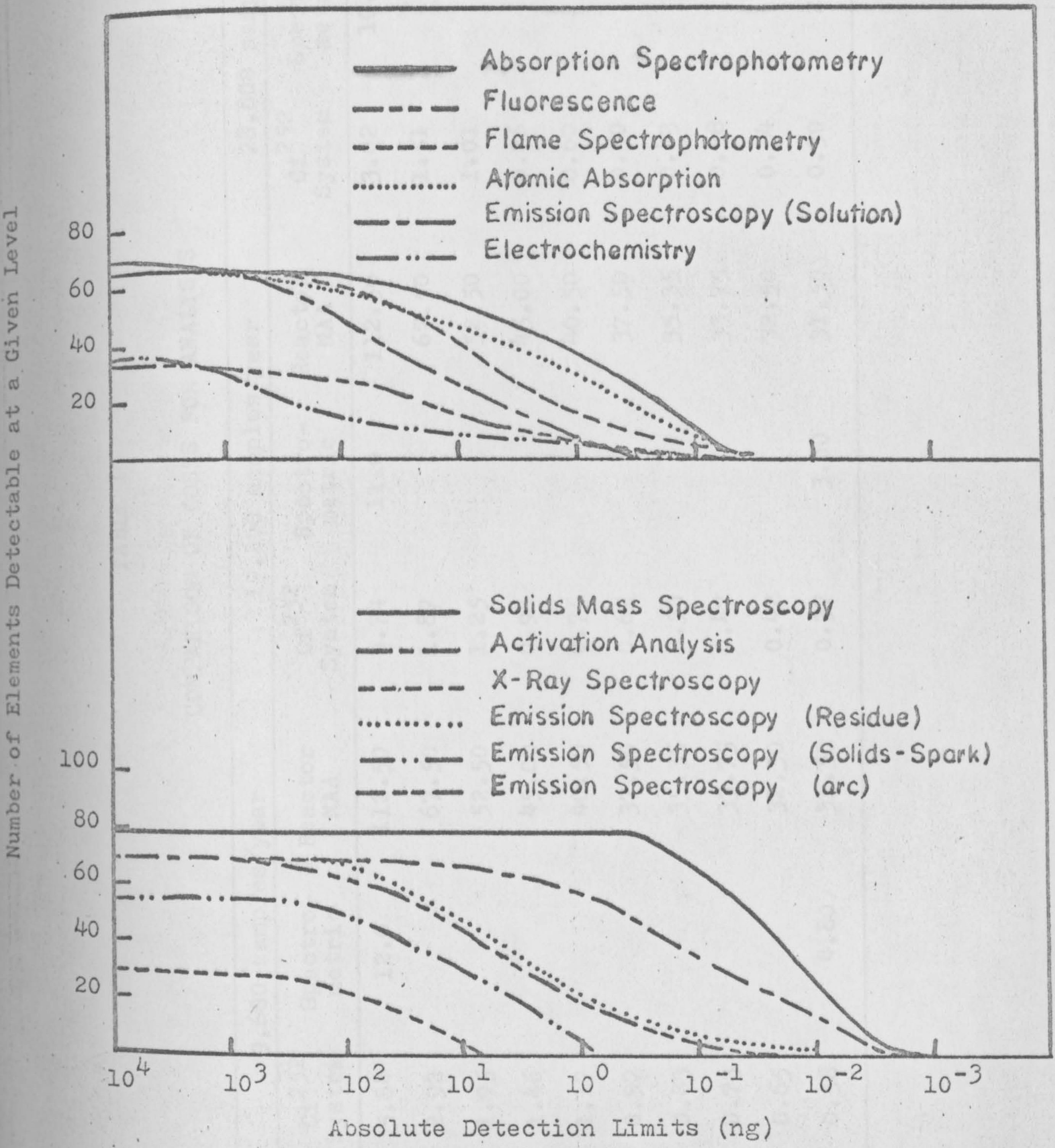

Fig. 1. Detection Scope of Trace Methods of Analysis

TABLE 1

COMPARISON OF COSTS FOR ANALYSIS

mber of ements/ ample	9,600 samples/year			19,200 samples/year			28,800 samples/year		
	Cf^{252} System	Spectro-metric	Reactor NAA	Cf^{252} System	Spectro-metric	Reactor NAA	Cf^{252} System	Spectro-metric	Reactor NAA
1	5.84	12.0	112.50	3.74	11.0	112.50	3.02	10.0	112.50
2	2.92		67.50	1.87		67.50	1.51		67.50
3	1.95		52.50	1.25		52.50	1.01		52.50
4	1.46		45.00	0.94		45.00	0.76		45.00
5	1.17		40.50	0.75		40.50	0.60		40.50
6	0.97		37.50	0.62		37.50	0.50		37.50
7	0.83		35.35	0.53		35.35	0.43		35.35
8	0.73		33.75	0.47		33.75	0.38		33.75
9	0.65		32.50	0.42		32.50	0.34		32.50
10	0.58	4.80	31.50	0.37	3.80	31.50	0.30	2.80	31.50

This study will show that Californium-252 Activation Analysis using a Ge(Li) detector is a valuable tool in pollution studies of a river water system.

CHAPTER II

Theory and Practice of Neutron Activation Analysis

The history of N.A.A. dates back to the discovery of artificial radioactivity by the Curies and Joliot in 1933. Hevesy and Levi in Copenhagen, in 1936, used thermal neutrons to determine the content of Dysprosium in impure Yttrium.[15,16] In 1938, Seaborg and Livingood determined the concentration of Gallium in Iron with the use of deuterons produced by the cyclotron at the University of California at Berkeley. This was the first activation experiment to be carried out with charged particles.[17,18]

In N.A.A., the sample to be analyzed is first bombarded with a flux of neutrons. The present study employed neutrons produced by the Youngstown State University Californium-252 source which provided a flux of $\sim 10^8$ n/cm^2/sec (Figure 2).[6,10] The irradiated atoms are converted to radioisotopes in the irradiation process; each of these then decay with the emission of one or more characteristic gamma-ray(s). The gamma-ray energies are used to identify the various elements in the sample. The intensity of the emitted gamma-rays is a measure of the quantities of each of the elements.[13,15]

The basic equation[7] used to calculate the activity of a sample from a given element by thermal neutron irradiation is:

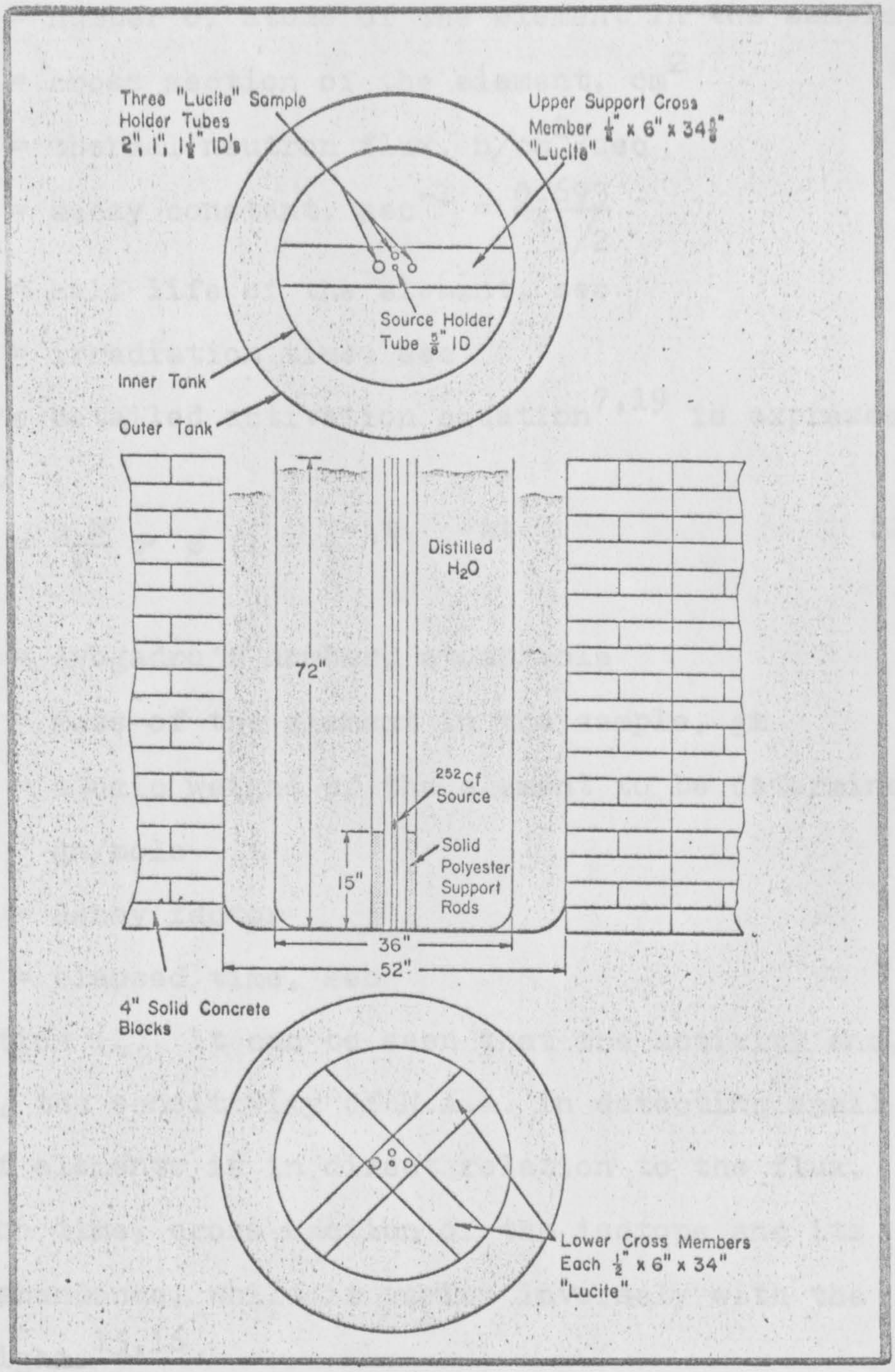

Fig. 2. Californium-252 Storage and Experimental Facility at Youngstown State University

$$A = N\sigma\phi(1 - e^{-\lambda t}) \qquad (1)$$

where,

A = activity, disintegrations/sec

N = number of atoms of the element in the sample

σ = cross section of the element, cm^2

ϕ = thermal neutron flux, $n/cm^2/sec$

λ = decay constant, $sec^{-1} = \frac{0.693}{t_{1/2}}$

$t_{1/2}$ = half life of the element, sec

t = irradiation time, sec

The detailed activation equation[7,19] is expressed as follows:

$$A = \frac{a\,W}{M}\,\sigma\,\phi\,(1 - e^{-\lambda t})\,e^{-\lambda t'} \qquad (2)$$

where,

a = Avogadro's number, atoms/mole

W = mass of the element in the sample, gm

M = atomic weight of the element to be determined, gm/mole

$e^{-\lambda t'}$ = decay factor

t' = elapsed time, sec

From equation (2), it can be seen that the activity and, therefore, the sensitivity of N.A.A. in detecting small amounts of elements is in direct relation to the flux, irradiation time, cross section of the isotope and its relative abundance, while it varies inversely with the atomic weight.[15,16]

In practice, it is usually not possible, for many reasons,[12,20] to make use of equation (2) in activation analysis, instead, a comparative method which employs a standard is used. Under identical irradiating and counting conditions of an element in a sample and in a standard, everything else being constant, the resulting equation[12] is as follows:

$$\frac{\text{A unk (Total activity of element X in sample)}}{\text{A std (Total activity of element X in standard)}} = \frac{\text{W unk (Mass of X in sample)}}{\text{W std (Mass of X in standard)}}$$

Analysis of gamma-ray spectra gives simultaneous determination of the identity and concentration of elements present in the sample. As mentioned earlier, each radioisotope formed by activation decays with the emission of characteristic gamma-rays having specific energies. The main features of the gamma-ray spectrum of Sodium-24 are found in Figure 3.[17] A detailed description of this spectrum will not be given in this work but can be found elsewhere.[13,17]

In this study, the amplifier and multichannel analyzer (see section on apparatus) were set such that the 1.17 mev photopeak of Cobalt-60 occurred at a specific channel, 134, thus placing zero mev in channel zero. Using this calibration, it was possible to assign energy values to the different peaks in the gamma-ray spectra obtained.

In order to calculate the concentration of an element in a sample, the total activity in the prominent photopeak (e.g., the 1.37 mev peak for Sodium-24) of that element was compared to the activity in the same photopeak

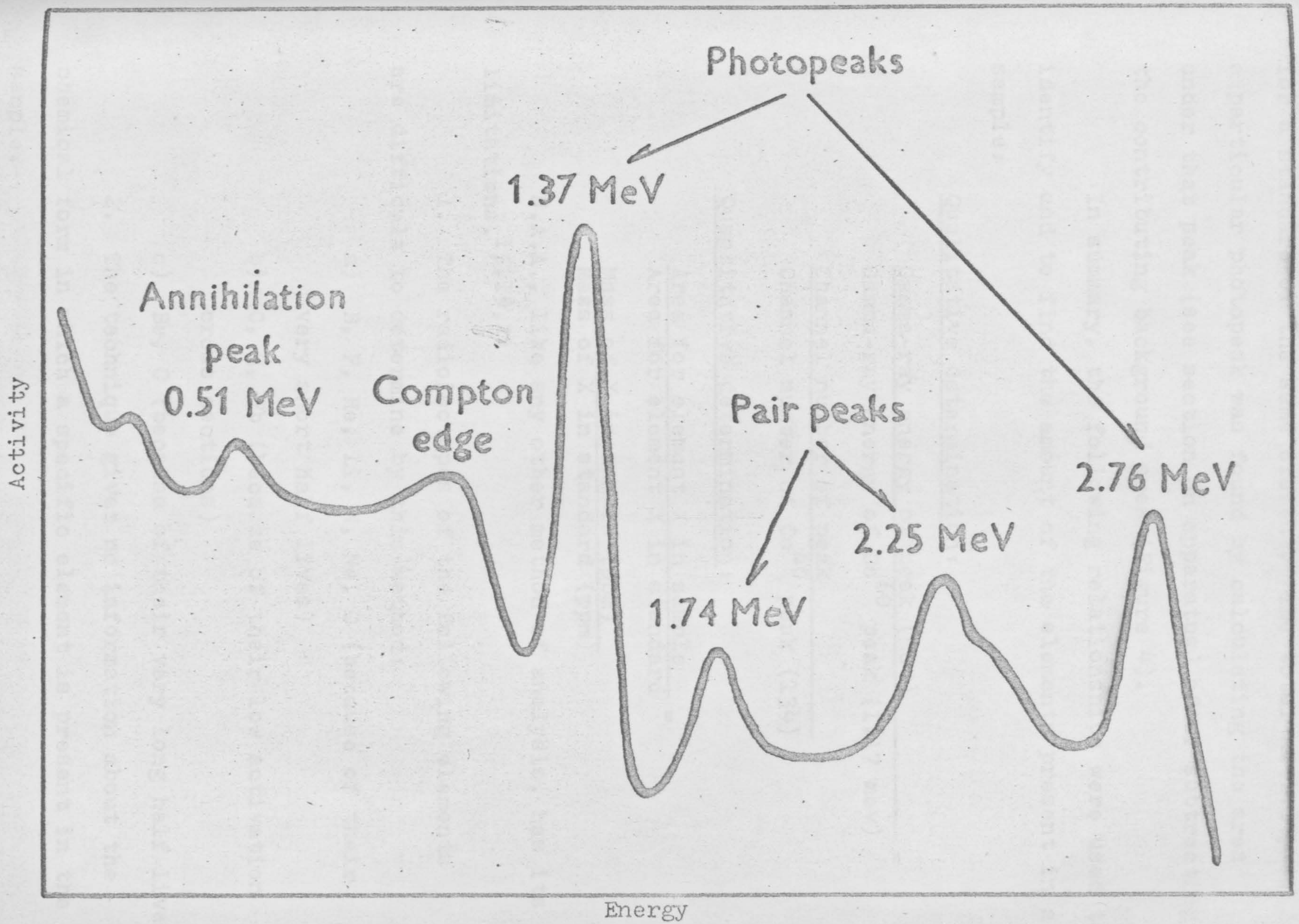

Fig. 3. Sodium-24 Spectrum

for a standard of the same element. The total activity of a particular photopeak was found by calculating the area under that peak (see section on apparatus) after subtracting the contributing background area (Figure 4).

In summary, the following relationships were used to identify and to find the amount of the elements present in a sample:

Qualitative determination:

$$\frac{\text{Gamma-ray energy of peak (mev)}}{\text{Gamma-ray energy of Co}^{60}\text{ peak (1.17 mev)}} = \frac{\text{Channel number of peak}}{\text{Channel number of Co}^{60}\text{ peak (134)}}$$

Quantitative determination:

$$\frac{\text{Area for element X in sample}}{\text{Area for element X in standard}} = \frac{\text{Mass of X in sample (ppm)}}{\text{Mass of X in standard (ppm)}}$$

N.A.A., like any other method of analysis, has its limitations.[15,19,21]

1. The radioisotopes of the following elements are difficult to determine by this method:

    a) B, F, He, Li, N, Ne, O (because of their very short half lives)

    b) C, H, Pb (because of their low activation cross sections)

    c) Be, C (because of their very long half lives)

2. The technique gives no information about the chemical form in which a specific element is present in the sample.

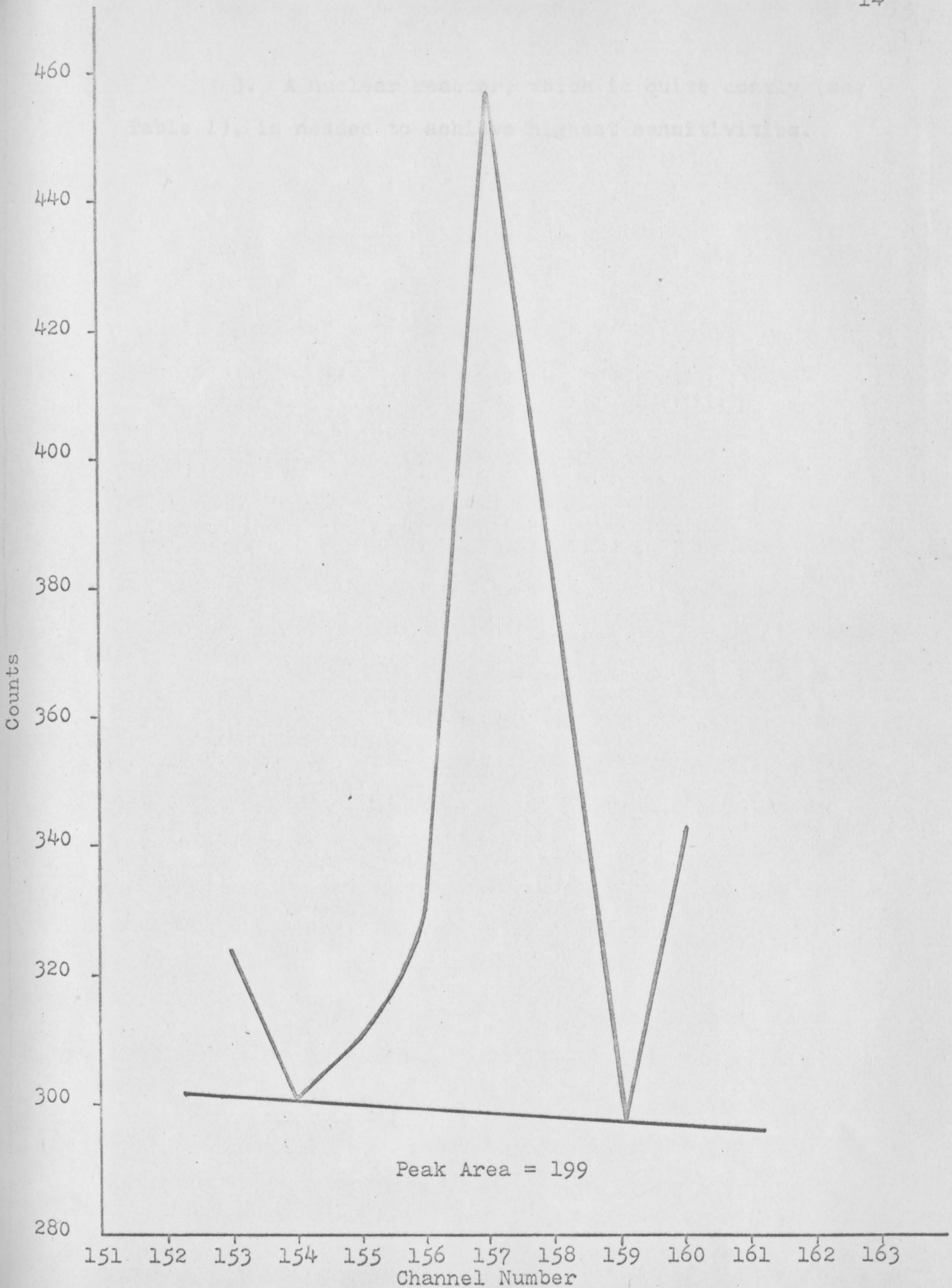

Fig. 4. Sodium 1.37 mev Photopeak

3. A nuclear reactor, which is quite costly (see Table 1), is needed to achieve highest sensitivities.

CHAPTER III

Experimental Techniques

Apparatus

Figure 5 is a block diagram of the detection and counting system used in the present work. The specifications of the instruments are given in Table 2.

The heart of the detection system was a Ge(Li) gamma-ray detector. The first detector of this kind was manufactured in 1962.[22] NaI(Tl) detectors have been in use since the 1940's, however, they have poor resolution.[23] Comparison of the resolution of NaI(Tl) and Ge(Li) detectors is given in Figure 6.[23] The resolution of Ge(Li) is about 15% better than for NaI(Tl).[12] This superiority results in a higher ratio of peak height to background making closely neighboring peaks distinguishable,[24] hence detection of more elements (see Appendix C). Using Ge(Li) eliminates the need for radiochemical separations in a radionuclide mixture analysis which are necessary when employing a NaI(Tl) detector.[23,25]

The problem of calculating photopeak areas (see Chapter II) is simplified in Ge(Li) spectra analysis because the energy region covered by the peak is so small (see Figure 6) that a linear interpolation of the underlying background is possible.[19]

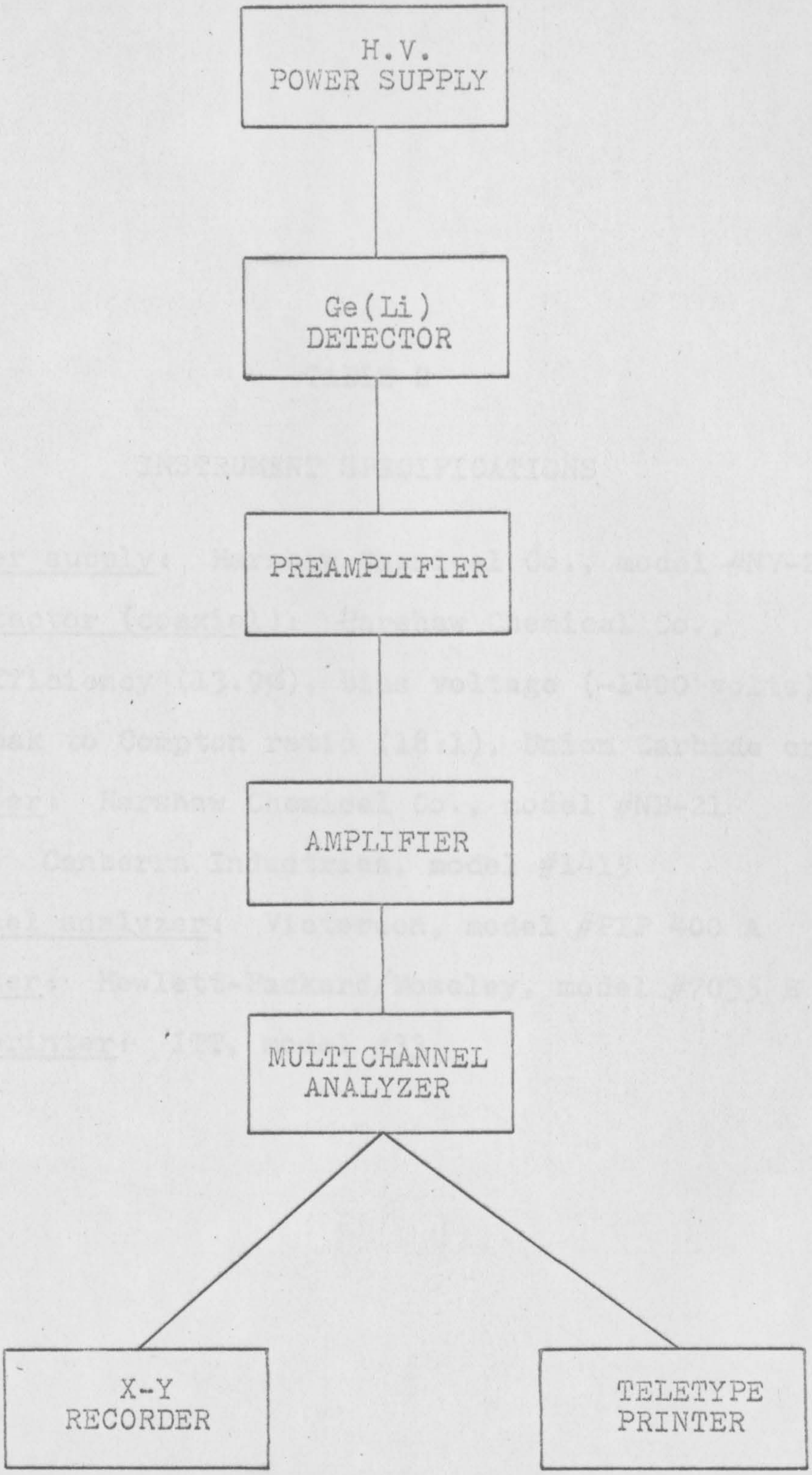

Fig. 5. Detection and Counting System

TABLE 2

INSTRUMENT SPECIFICATIONS

H. V. power supply: Harshaw Chemical Co., model #NV-23

Ge(Li) detector (coaxial): Harshaw Chemical Co., efficiency (13.9%), bias voltage (-1400 volts), peak to Compton ratio (18:1), Union Carbide cryostat

Preamplifier: Harshaw Chemical Co., model #NB-21

Amplifier: Canberra Industries, model #1415

Multichannel analyzer: Victoreen, model #PIP 400 A

X-Y Recorder: Hewlett-Packard/Moseley, model #7035 B

Teletype printer: ITT, model #33

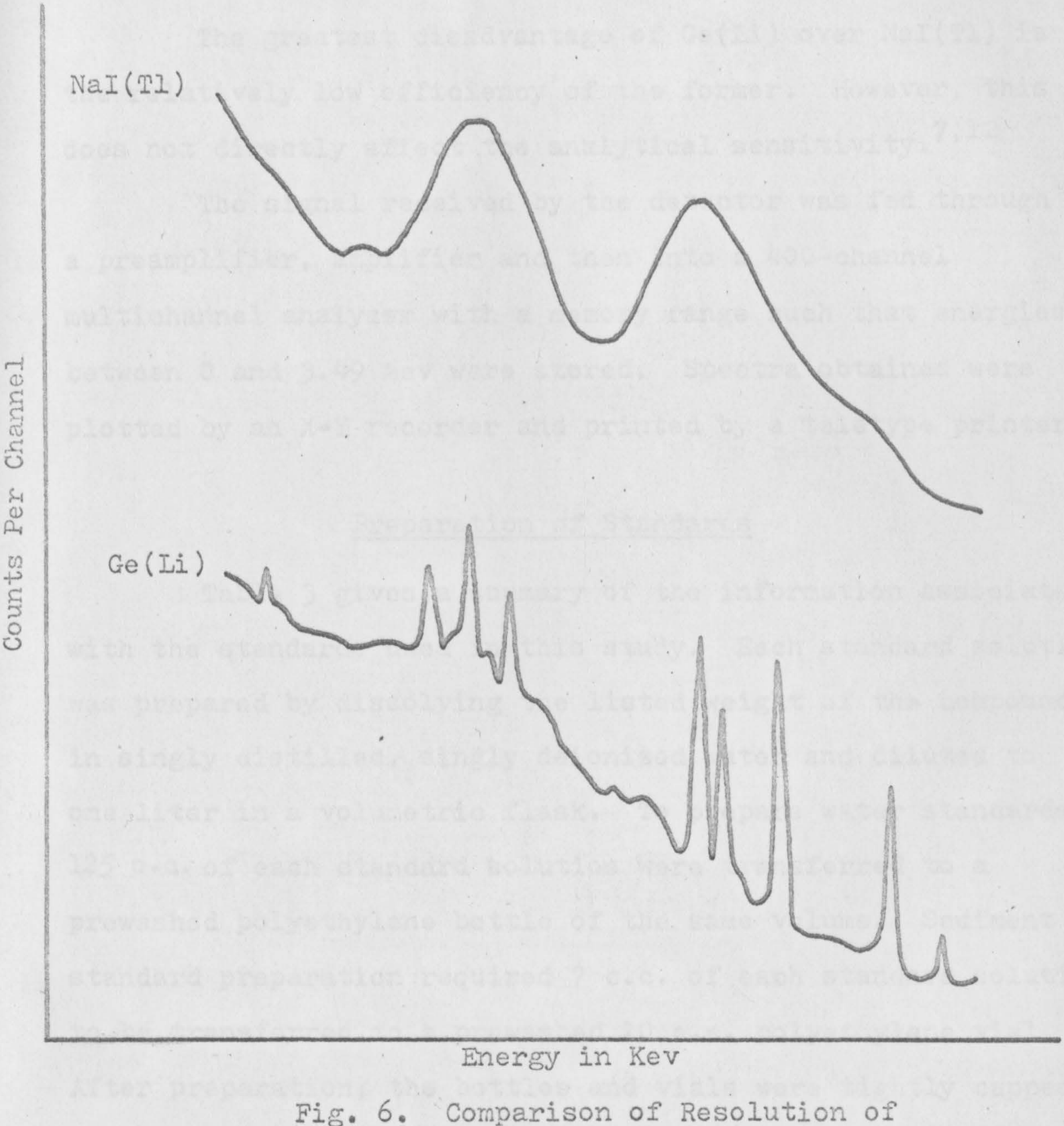

Fig. 6. Comparison of Resolution of NaI(Tl) and Ge(Li) Detection Systems

The Ge(Li) detector has to be stored and operated at about -200°C. To achieve this, the detector is cooled by a copper rod immersed in a liquid Nitrogen cryostat (20-liter Dewar flask) (Figure 7).[19,25]

The greatest disadvantage of Ge(Li) over NaI(Tl) is the relatively low efficiency of the former. However, this does not directly affect the analytical sensitivity.[7,12]

The signal received by the detector was fed through a preamplifier, amplifier and then into a 400-channel multichannel analyzer with a memory range such that energies between 0 and 3.49 mev were stored. Spectra obtained were plotted by an X-Y recorder and printed by a teletype printer.

Preparation of Standards

Table 3 gives a summary of the information associated with the standards used in this study. Each standard solution was prepared by dissolving the listed weight of the compound in singly distilled, singly deionized water and diluted to one liter in a volumetric flask. To prepare water standards, 125 c.c. of each standard solution were transferred to a prewashed polyethylene bottle of the same volume. Sediment standard preparation required 7 c.c. of each standard solution to be transferred to a prewashed 10 c.c. polyethylene vial. After preparation, the bottles and vials were tightly capped and stored until use.

Information on the energies and areas obtained from irradiating and counting of the standards is found in Chapter IV.

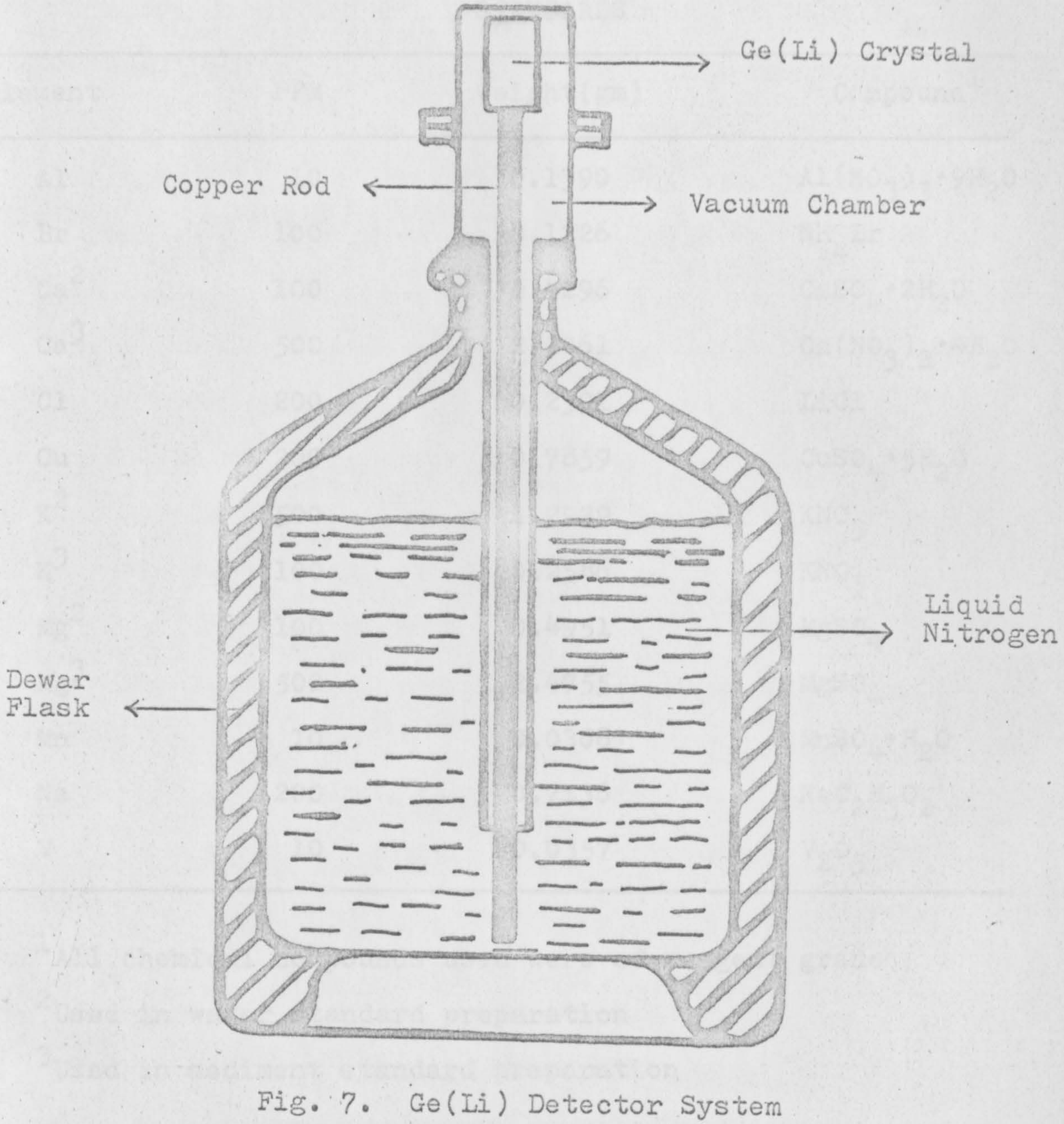

Fig. 7. Ge(Li) Detector System

TABLE 3

STANDARDS

Element	PPM	Weight(gm)	Compound[1]
Al	10	0.1390	$Al(NO_3)_3 \cdot 9H_2O$
Br	100	0.1226	NH_4Br
Ca[2]	100	0.4296	$CaSO_4 \cdot 2H_2O$
Ca[3]	500	2.9461	$Ca(NO_3)_2 \cdot 4H_2O$
Cl	200	0.2391	LiCl
Cu	200	0.7859	$CuSO_4 \cdot 5H_2O$
K[2]	500	1.2929	KNO_3
K[3]	100	0.2586	KNO_3
Mg[2]	100	0.4951	$MgSO_4$
Mg[3]	500	2.4755	$MgSO_4$
Mn	10	0.0308	$MnSO_4 \cdot H_2O$
Na	200	0.7136	$NaC_2H_3O_2$
V	10	0.0357	V_2O_5

[1] All chemical compounds used were of reagent grade

[2] Used in water standard preparation

[3] Used in sediment standard preparation

Sample Collection and Preparation

Water and sediment samples were collected from bridges and, where possible, along the banks of the Mahoning River. The sampling equipment in situ analysis consisted of a galvanized 10-quart pail, one liter polyethylene bottles, large enamel-coated metal funnel, thermometer (all washed prior to collection in water from which the samples were taken), pHydrion paper, rope, and concentrated reagent-grade nitric acid. The pH of the water samples was adjusted to approximately 2 with the acid in order to minimize loss of trace elements by oxidation and (or) precipitation and by adsorption onto the bottle walls.[26,27] After collection, the bottles were tightly capped and stored until use.

Figure 8 shows the Mahoning River drainage basin. The location of sample sites (labelled as A - L) is given in Figure 9. Table 4 is a summary of the pertinent information associated with each collected sample.

Laboratory preparation consisted of filtering the water samples using a Büchner funnel, air suction, and a double-thickness of Whatman #1 (9 cm.) qualitative filter paper. One hundred and twenty five c.c. of each water sample were then transferred to a prewashed polyethylene bottle of the same volume. Sediment samples were first allowed to air dry in evaporating dishes for two weeks. Seven grams of each were then weighed and transferred to

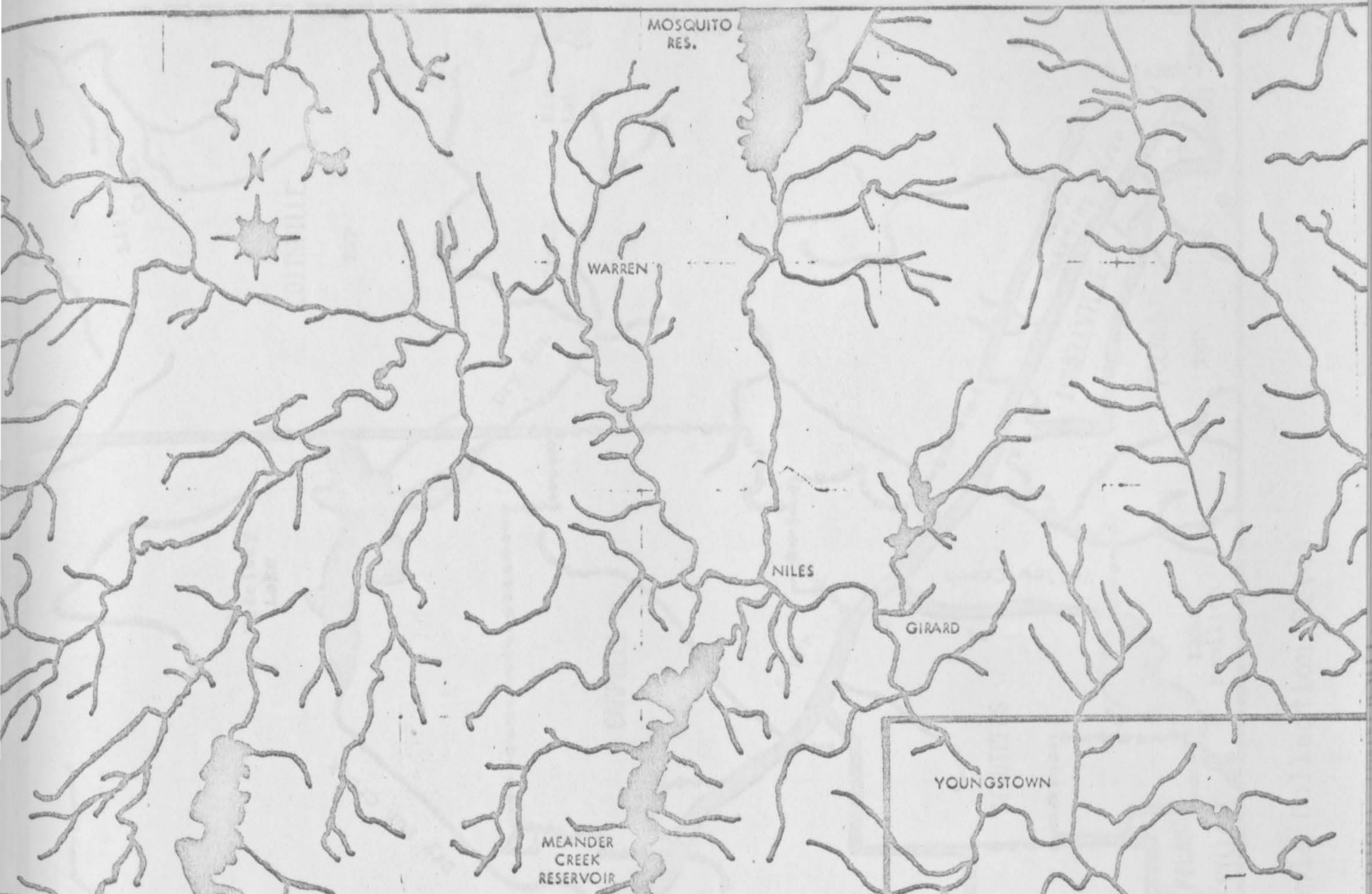

Fig. 8. The Mahoning River Drainage Basin

Fig. 9. Sample Collection Sites

TABLE 4

COLLECTION SITE INFORMATION ON SAMPLES A - L[1]

Sample[2]	Location	Temp. (°C)	Initial pH	Adjusted pH
A	Mahoning Avenue Bridge	31	~6	~2
B	Market Street Bridge	30	~6	~2
C	South Avenue Bridge	31	~6	~2
D	Above Crab Creek and above Youngstown Sewage Treatment Plant	29	~6	~2
E	Below Crab Creek and above Youngstown Sewage Treatment Plant	31	~6	~2
F[3]	Youngstown Sewage Treatment Plant Effluent	23	~6	~2
G	Below Crab Creek and below Youngstown Sewage Treatment Plant	29	~6	~2
H	Center Street Bridge	31	~6	~2
I[3]	Walton Street Bridge	32	~6	~2
J	Bridge Street Bridge	34	~6	~2
K[3]	Struthers Sewage Treatment Plant Effluent	18	~6	~2
L	Lowellville Bridge	31	~7	~2

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[1] All samples were collected on 6/21/1972

[2] See Figure 9

[3] Water sample only

10 c.c. polyethylene vials. After preparation, the bottles and vials were tightly capped and stored until use.

Standard and Sample Irradiation and Counting

All samples were irradiated in the 2 inch tube in the Youngstown State University Californium-252 source facility (see Figure 2) for a period of one hour, then quickly returned to the counting laboratory. Water samples were poured into a prewashed plexiglass cup placed on top of the Ge(Li) detector (Figure 10), while sediment samples were placed on a plexiglass plate (Figure 11). After an elapsed time of 30 seconds, samples were counted for 20 minutes (live time). The elapsed time was kept constant for all samples so as to eliminate the decay factor in equation (2). The dead time of the detection and counting system was between 0 and 10%. After the counting interval, the data was recorded in the form of a plot and a printout.

Sediment sample G was irradiated for fifty hours, allowed to decay for five hours, and finally counted for 20 minutes with the multichannel energy memory range between 0 and 1 mev to determine if additional elements like As, Cd, Hg, Mo, Sn, and Ti were present, but negative results were obtained. If these elements are present, the inability to detect them may be due to the poor shielding of the Ge(Li) detector.

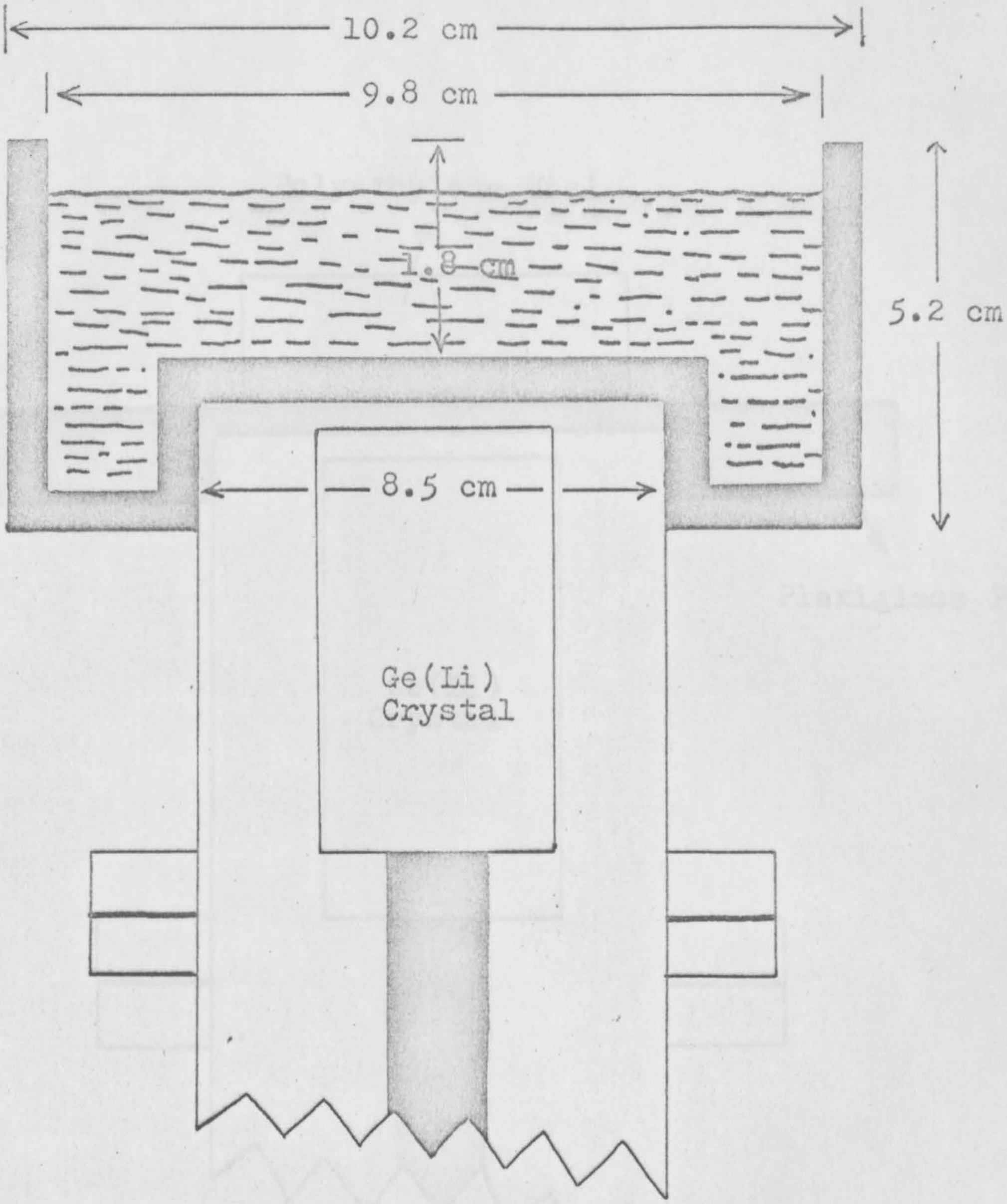

Fig. 10. Cross-Sectional View of Cup Used to Count Irradiated Water Samples

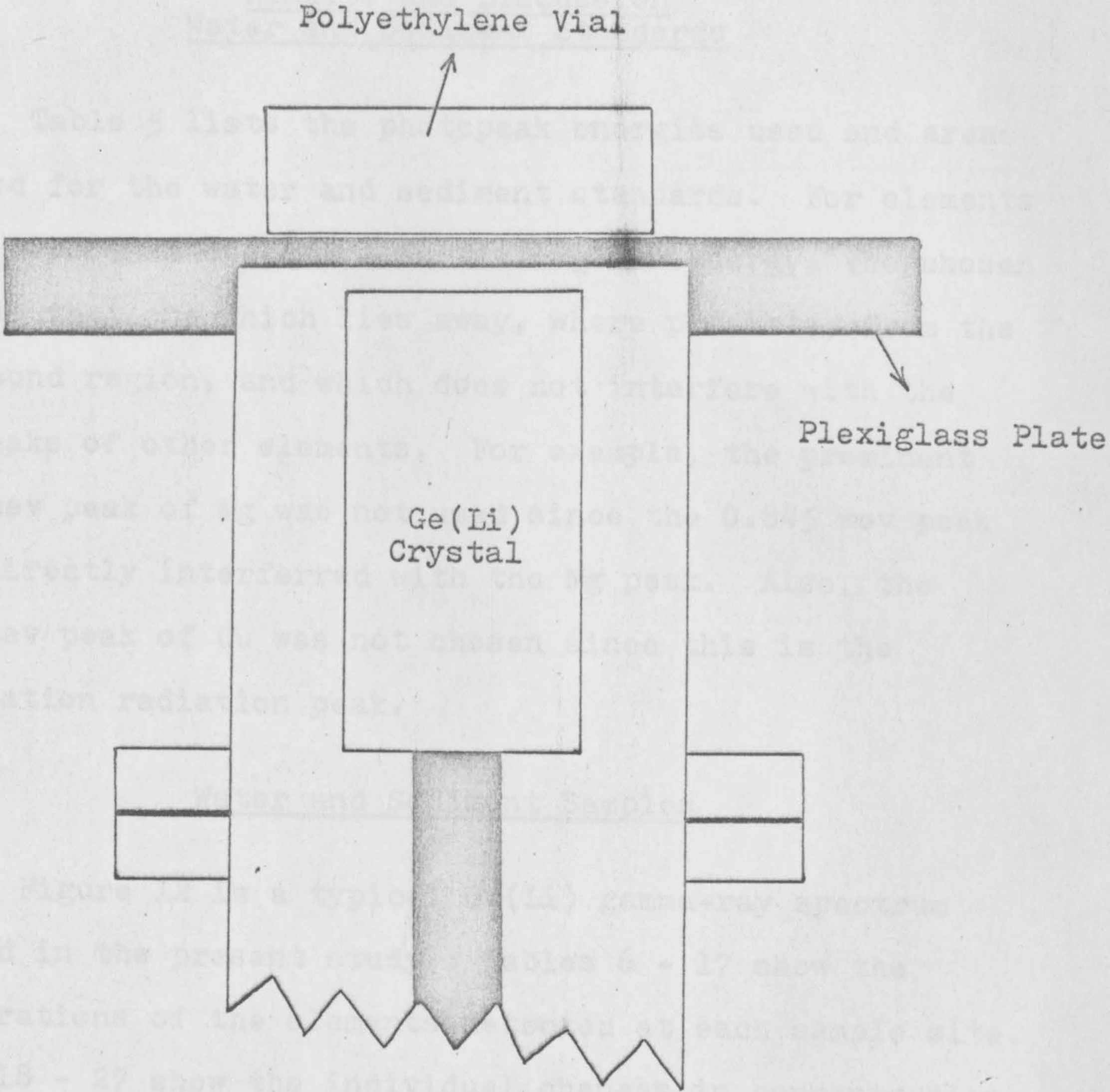

Fig. 11. View of Plate Used to Count Irradiated Sediment Samples

CHAPTER IV

Results and Discussion
Water and Sediment Standards

Table 5 lists the photopeak energies used and areas obtained for the water and sediment standards. For elements having more than one characteristic gamma energy, the chosen peak was that one which lies away, where possible, from the background region, and which does not interfere with the photopeaks of other elements. For example, the prominent 0.842 mev peak of Mg was not used since the 0.845 mev peak of Mn directly interferred with the Mg peak. Also, the 0.511 mev peak of Cu was not chosen since this is the annihilation radiation peak.

Water and Sediment Samples

Figure 12 is a typical Ge(Li) gamma-ray spectrum obtained in the present study. Tables 6 - 17 show the concentrations of the elements detected at each sample site. Tables 18 - 27 show the individual changes in concentration of the elements along the section of the river analyzed.

Site Analysis

Site A (Mahoning Avenue Bridge, Youngstown)

Seven elements (Mn, Mg, Cu, Na, K, Cl, and Ca) were found in the water sample, while nine elements (Br, Mn, Mg,

TABLE 5

STANDARDS

Energy of Photopeak Used (mev)	Element	Water		Sediment	
		Area	PPM	Area	PPM
0.777	Br	2,480	100	85	100
0.845	Mn	34,740	10	3,102	10
1.01	Mg	128	100	103	500
1.04	Cu	2,892	200	240	200
1.37	Na	8,366	200	800	200
1.43	V	14,583	10	1,119	10
1.52	K	494	500	34	100
1.64	Cl	3,813	200	262	200
1.78	Al	386	10	24	10
3.09	Ca	40	100	27	500

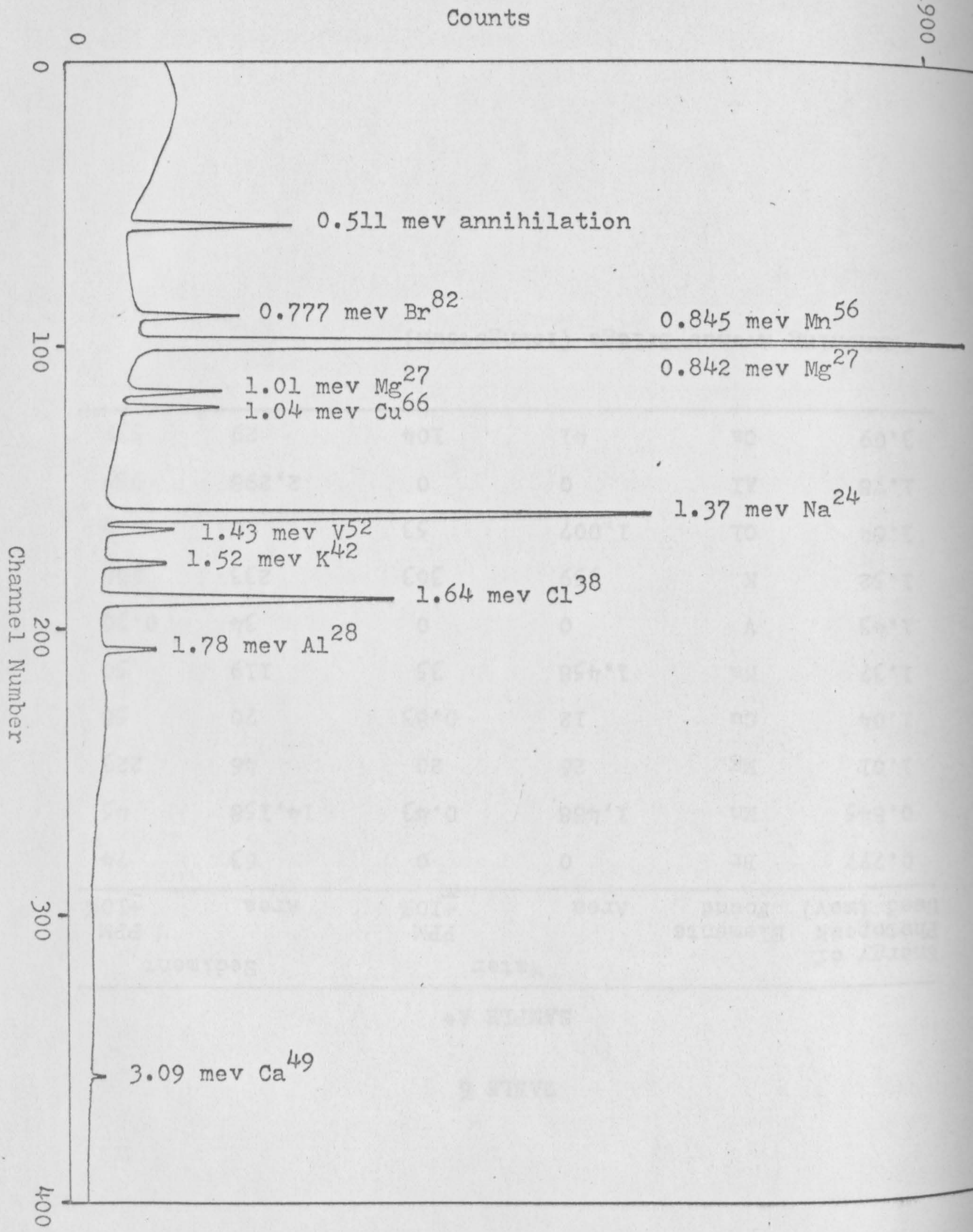

Fig. 12. Typical Ge(Li) Gamma-Ray Spectrum

TABLE 6

SAMPLE A*

Energy of Photopeak Used (mev)	Elements Found	Water		Sediment	
		Area	PPM ±10%	Area	PPM ±10%
0.777	Br	0	0	63	74
0.845	Mn	1,488	0.43	14,158	45
1.01	Mg	26	20	46	223
1.04	Cu	12	0.83	70	58
1.37	Na	1,458	35	119	50
1.43	V	0	0	34	0.30
1.52	K	359	363	233	686
1.64	Cl	1,007	53	0	0
1.78	Al	0	0	2,298	957
3.09	Ca	41	104	29	537

*Mahoning Avenue Bridge (Youngstown)

TABLE 7

SAMPLE B*

Energy of Photopeak Used (mev)	Elements Found	Water		Sediment	
		Area	PPM ±10%	Area	PPM ±10%
0.777	Br	38	1.5	1,521	1,789
0.845	Mn	2,139	0.62	540,512	1,730
1.01	Mg	3	2.3	1,027	4,985
1.04	Cu	34	2.3	288	240
1.37	Na	1,528	37	6,040	1,510
1.43	V	9	0.006	2,345	21
1.52	K	71	72	834	2,451
1.64	Cl	900	47	0	0
1.78	Al	109	2.8	23,896	9,957
3.09	Ca	25	62	669	12,390

*Market Street Bridge (Youngstown)

TABLE 8

SAMPLE C*

Energy of Photopeak Used (mev)	Elements Found	Water		Sediment	
		Area	PPM ±10%	Area	PPM ±10%
0.777	Br	19	0.77	1,107	1,302
0.845	Mn	1,580	0.45	478,516	1,531
1.01	Mg	29	23	1,564	7,592
1.04	Cu	28	1.9	121	101
1.37	Na	1,574	38	6,538	1,634
1.43	V	18	0.012	2,056	18
1.52	K	0	0	619	1,821
1.64	Cl	1,060	56	0	0
1.78	Al	35	0.91	25,710	10,712
3.09	Ca	36	91	486	9,001

*South Avenue Bridge (Youngstown)

TABLE 9

SAMPLE D*

Energy of Photopeak Used (mev)	Elements Found	Water Area	Water PPM ±10%	Sediment Area	Sediment PPM ±10%
0.777	Br	52	2.1	1,565	1,840
0.845	Mn	1,290	0.37	465,735	1,490
1.01	Mg	25	20	1,275	6,189
1.04	Cu	19	1.3	110	92
1.37	Na	1,110	27	8,042	2,010
1.43	V	0	0	480	4.3
1.52	K	0	0	719	2,114
1.64	Cl	572	30	0	0
1.78	Al	0	0	28,861	12,025
3.09	Ca	21	52	485	8,982

*Above Crab Creek and above Youngstown Sewage Treatment Plant (Youngstown).

TABLE 10

SAMPLE E*

Energy of Photopeak Used (mev)	Elements Found	Water		Sediment	
		Area	PPM ±10%	Area	PPM ±10%
0.777	Br	0	0	1,179	1,386
0.845	Mn	1,460	0.42	416,458	1,333
1.01	Mg	11	8.6	1,009	4,898
1.04	Cu	29	2.0	339	282
1.37	Na	1,412	34	5,314	1,328
1.43	V	0	0	2,748	24
1.52	K	37	37	803	2,361
1.64	Cl	962	50	0	0
1.78	Al	29	0.75	31,365	13,069
3.09	Ca	38	95	360	6,667

*Below Crab Creek and above Youngstown Sewage Treatment Plant (Youngstown)

TABLE 11

SAMPLE F*

Energy of Photopeak Used (mev)	Elements Found	Water Area	Water PPM ±10%	Sediment Area	Sediment PPM ±10%
0.777	Br	19	0.77	--	--
0.845	Mn	995	0.29	--	--
1.01	Mg	50	39	--	--
1.04	Cu	27	1.9	--	--
1.37	Na	3,510	84	--	--
1.43	V	33	0.023	--	---
1.52	K	25	25	--	--
1.64	Cl	1,836	96	--	--
1.78	Al	75	2.0	--	--
3.09	Ca	16	40	--	--

*Youngstown Sewage Treatment Plant Effluent (Youngstown)

TABLE 12

SAMPLE G*

Energy of Photopeak Used (mev)	Elements Found	Water Area	Water PPM ±10%	Sediment Area	Sediment PPM ±10%
0.777	Br	35	1.4	1,061	1,248
0.845	Mn	1,521	0.44	343,599	1,099
1.01	Mg	4	3.1	2,091	10,151
1.04	Cu	0	0	319	266
1.37	Na	1,861	44	7,259	1,815
1.43	V	5	0.003	1,955	17
1.52	K	74	75	876	2,575
1.64	Cl	1,180	62	0	0
1.78	Al	0	0	44,276	18,448
3.09	Ca	15	37	1,062	19,668

*Below Crab Creek and below Youngstown Sewage Treatment Plant (Youngstown)

TABLE 13

SAMPLE H*

Energy of Photopeak Used (mev)	Elements Found	Water Area	Water PPM ±10%	Sediment Area	Sediment PPM ±10%
0.777	Br	13	0.52	2,250	2,646
0.845	Mn	4,250	1.22	751,513	2,405
1.01	Mg	65	51	1,943	9,430
1.04	Cu	0	0	399	332
1.37	Na	1,797	43	9,928	2,482
1.43	V	35	0.024	3,964	35
1.52	K	40	40	1,660	4,879
1.64	Cl	1,071	56	0	0
1.78	Al	120	3.1	73,296	30,540
3.09	Ca	45	112	1,067	19,770

*Center Street Bridge (Youngstown)

TABLE 14

SAMPLE I*

		Water		Sediment	
Energy of Photopeak Used (mev)	Elements Found	Area	PPM ±10%	Area	PPM ±10%
0.777	Br	0	0	--	--
0.845	Mn	2,019	0.58	--	--
1.01	Mg	45	35	--	--
1.04	Cu	39	2.7	--	--
1.37	Na	1,566	37	--	--
1.43	V	0	0	--	--
1.52	K	71	72	--	--
1.64	Cl	1,146	60	--	--
1.78	Al	6	0.16	--	--
3.09	Ca	46	115	--	--

*Walton Street Bridge (Youngstown-Struthers)

TABLE 15

SAMPLE J*

Energy of Photopeak Used (mev)	Elements Found	Water		Sediment	
		Area	PPM ±10%	Area	PPM ±10%
0.777	Br	0	0	1,212	1,425
0.845	Mn	1,941	0.56	801,843	2,566
1.01	Mg	33	26	1,381	6,704
1.04	Cu	73	5.0	454	378
1.37	Na	1,612	39	5,432	1,358
1.43	V	10	0.007	64,649	5.8
1.52	K	21	21	696	2,046
1.64	Cl	1,092	57	0	0
1.78	Al	59	1.5	5,612	2,338
3.09	Ca	19	47	2,208	40,892

*Bridge Street Bridge (Struthers)

TABLE 16

SAMPLE K*

Energy of Photopeak Used (mev)	Elements Found	Water		Sediment	
		Area	PPM ±10%	Area	PPM ±10%
0.777	Br	49	2.0	--	--
0.845	Mn	708	0.20	--	--
1.01	Mg	39	30	--	--
1.04	Cu	12	0.83	--	--
1.37	Na	4,736	113	--	--
1.43	V	35	0.024	--	--
1.52	K	155	157	--	--
1.64	Cl	1,752	92	--	--
1.78	Al	0	0		
3.09	Ca	33	82		

*Struthers Sewage Treatment Plant Effluent (Struthers)

TABLE 17

SAMPLE L*

Energy of Photopeak Used (mev)	Elements Found	Water		Sediment	
		Area	PPM ±10%	Area	PPM ±10%
0.777	Br	0	0	1,706	2,006
0.845	Mn	1,514	0.44	679,957	2,176
1.01	Mg	5	3.9	633	3,073
1.04	Cu	54	3.7	167	139
1.37	Na	1,875	45	4,501	1,125
1.43	V	17	0.012	1,419	13
1.52	K	79	80	964	2,833
1.64	Cl	1,298	64	0	0
1.78	Al	32	0.83	24,338	10,141
3.09	Ca	7	17	855	15,835

*Lowellville Bridge (Lowellville)

TABLE 18

BROMINE CONCENTRATIONS (PPM)

Sample Site	Water	Sediment
A	0	74
B	1.5	1,789
C	0.77	1,302
D	2.1	1,840
E	0	1,386
F	0.77	--
G	1.4	1,248
H	0.52	2,646
I	0	--
J	0	1,425
K	2	--
L	0	2,006

TABLE 19

MANGANESE CONCENTRATIONS (PPM)

Sample Site	Water	Sediment
A	0.43	45
B	0.62	1,730
C	0.45	1,531
D	0.37	1,490
E	0.42	1,333
F	0.29	--
G	0.44	1,099
H	1.22	2,405
I	0.58	--
J	0.56	2,566
K	0.20	--
L	0.44	2,176

TABLE 20

MAGNESIUM CONCENTRATIONS (PPM)

Sample Site	Water	Sediment
A	20	223
B	2.3	4,985
C	23	7,592
D	20	6,189
E	8.6	4,898
F	39	--
G	3.1	10,151
H	51	9,430
I	35	--
J	26	6,704
K	30	--
L	3.9	3,073

TABLE 21

COPPER CONCENTRATIONS (PPM)

Sample Site	Water	Sediment
A	0.83	58
B	2.3	240
C	1.9	101
D	1.3	92
E	2	282
F	1.9	--
G	0	266
H	0	332
I	2.7	--
J	5	378
K	0.83	--
L	3.7	139

TABLE 22

SODIUM CONCENTRATIONS (PPM)

Sample Site	Water	Sediment
A	35	50
B	37	1,510
C	38	1,634
D	27	2,010
E	34	1,328
F	84	--
G	44	1,815
H	43	2,482
I	37	--
J	39	1,358
K	113	--
L	45	1,125

TABLE 23

VANADIUM CONCENTRATIONS (PPM)

Sample Site	Water	Sediment
A	0	0.30
B	0.006	21
C	0.012	18
D	0	4.3
E	0	24
F	0.023	--
G	0.003	17
H	0.024	35
I	0	--
J	0.007	5.8
K	0.024	--
L	0.012	13

TABLE 24

POTASSIUM CONCENTRATIONS (PPM)

Sample Site	Water	Sediment
A	363	686
B	72	2,451
C	0	1,821
D	0	2,114
E	37	2,361
F	25	--
G	75	2,575
H	40	4,879
I	72	--
J	21	2,046
K	157	--
L	80	2,833

TABLE 25

CHLORINE CONCENTRATIONS (PPM)

Sample Site	Water	Sediment
A	53	0
B	47	0
C	56	0
D	30	0
E	50	0
F	96	--
G	62	0
H	56	0
I	60	--
J	57	0
K	92	--
L	68	0

TABLE 26

ALUMINUM CONCENTRATIONS (PPM)

Sample Site	Water	Sediment
A	0	957
B	2.8	9,957
C	0.91	10,712
D	0	12,025
E	0.75	13,069
F	2.0	--
G	0	18,448
H	3.1	30,540
I	0.16	--
J	1.5	2,338
K	0	--
L	0.83	10,141

TABLE 27

CALCIUM CONCENTRATIONS (PPM)

Sample Site	Water	Sediment
A	104	537
B	62	12,390
C	91	9,001
D	52	8,982
E	95	6,667
F	40	--
G	37	19,668
H	112	19,770
I	115	--
J	47	40,892
K	82	--
L	17	15,835

Cu, Na, V, K, Al, and Ca) were detected in the sediment sample. The concentrations of most of the elements at this location, are low compared to the next eleven sites.

Although, the river flows south through the city of Warren (see Figure 8), past several steel mills, industrial plants and a large land fill, the author feels that any elements introduced along the way are diluted or precipitated before reaching this location.

The trace element concentration in water at all sites is much smaller than in the sediment samples. This is in agreement with John.[8] The K content of the water sample at this location, the highest of all the sites, is so large that the author doubts the existence of any fish in the river at this site, since K is toxic to fish.

Site B (Market Street Bridge, Youngstown)

Ten elements (Br, Mn, Mg, Cu, Na, V, K, Cl, Al, and Ca) were detected in the water, while all these elements except Cl were found in the sediment. This site has proven to be very interesting because of the drastic increase in the concentrations of most of the elements, especially in the sediment samples. This site is located next to two steel mills and a number of chemical and metal-finishing plants.

The presence of Br in the samples could be accounted for by the fact that most industrial wastes contain measurable amounts of this element. This is in agreement with

Brown, Skougstad, and Fishman.[26] Since the Chlorides of all the detected metals are soluble in water, the absence of Cl in the sediment samples at all twelve sites is readily explained.

Although the V and Br concentrations in the water samples are small, their presence in the river water is undesirable, since they are considered to be toxic elements according to Federal laws.[9] It is believed that these two elements are due to the presence of large amounts of petroleum compounds (which contain trace quantities of V and Br) in the sediment. This is evidenced by the petroleum odor noticed while collecting sediment samples at all sites.

The Ca, K, and Mg concentrations observed in water sample B are much lower than their concentrations at site A. This appears to indicate that these elements were precipitated. The presence of Ca, K, and Mg in large amounts in sediment sample B confirms their precipitation.

Site C (South Avenue Bridge, Youngstown)

Nine elements (Br, Mn, Mg, Cu, Na, V, Cl, Al, and Ca) were found in the water sample, while all these elements (with the exception of Cl) and K were detected in the sediment. The precipitation of K in site B is further evidenced by the total absence of this element in water sample C. However, sediment C shows a drop in K which could be accounted for by dilution. This dilution factor is also apparently true for Br, Mn, and Cu.

The author believes that the introduction of the chemical effluent from the steel mills at site B and its observation at site C, explains the increase in Mg and V content of the water and sediment samples. A possible interpretation for the observed increase in Ca in water is the leaching processes occurring in the river.

Site D (Above Crab Creek and above Youngstown Sewage Treatment Plant, Youngstown)

Seven elements (Br, Mn, Mg, Cu, Na, Cl, and Ca) were detected in the water, while nine elements (Br, Mn, Mg, Cu, Na, V, K, Al, and Ca) were found in the sediment sample. The increase in Br (the highest of all the sites) and K (in the sediment only) is believed to be due to industrial wastes from a chemical company at this location. All other elements seem to undergo dilution or gradual precipitation.

Site E (Below Crab Creek and above Youngstown Sewage Treatment Plant, Youngstown)

Eight elements (Mn, Mg, Cu, Na, K, Cl, Al, and Ca) were found in the water, while nine elements (Br, Mn, Mg, Cu, Na, V, K, Al, and Ca) were detected in the sediment. The drop in Br and Mg concentrations is an expected one due to the addition of the water (or dilution) from Crab Creek, which empties into the Mahoning a quarter of a mile above this location (see Figure 9). Crab Creek carries along wastes from many industries. Their influence on the river explains the increase in Al, Cu, K, Mn, V, and Cl concentrations in the samples.

The author believes that the movement of the water created during the process of the emptying of Crab Creek into the Mahoning River causes leaching of Na and Ca from the river bed. As can be seen, the concentrations of these elements increase in the water sample, while they decrease in the sediment.

Site F (Youngstown Sewage Treatment Plant Effluent, Youngstown)

Ten elements (Br, Mn, Mg, Cu, Na, V, K, Cl, Al, and Ca) were detected in the Youngstown Sewage Treatment Plant effluent. The author feels that the reason for the presence of most of these elements is due to the disposal of chemicals from a number of different industrial plants into the sewage, which eventually finds its way into the river. Szentirmay[28] has expressed agreement in this matter, on the basis that the Youngstown Sewage Plant is only one of primary treatment type. The plant uses Lime (90% CaO) and Ferric chloride in treating the sewage, and Chlorine gas for its disinfection.[28] As a result, one might expect the Cl concentration to be high.

Site G (Below Crab Creek and below Youngstown Sewage Treatment Plant, Youngstown)

Eight elements (Br, Mn, Mg, Na, V, K, Cl, and Ca) were detected in the water sample, while nine elements (Br, Mn, Mg, Cu, Na, V, K, Al, and Ca) were found in the sediment. It seems that the sewage treatment plant is directly responsible for the increase in the Br, K, Mn, Cl, and Na concentrations.

The drop in Cu and V is apparently due to dilution. In two typical months, the Youngstown Sewage Treatment Plant handled about 38.98 million gallons of sewage per day during April of this year, and 26.51 million gallons per day for the month of May.[29]

The sediment concentrations of Ca, Mg (the highest of all the sites), and Al increased rapidly, signifying that precipitation of these elements has occurred. Part of the increase in Ca sediment concentration might be explained by the fact that there was a bridge construction operation in progress at this location causing the removal of soil and the exposing of underlying limestone, some of which was undoubtedly deposited in the sediment.

Site H (Center Street Bridge, Youngstown)

Nine elements (Br, Mn, Mg, Na, V, K, Cl, Al, and Ca) were detected in the water, while all these elements (with the exception of Cl) and Cu were found in the sediment sample. This site is located at the start of a large steel complex which encompasses sites H - J. Five of the nine elements detected reached their highest concentration at this point on the river. These are Mn, Mg, V, Al, and Ca.

Precipitation of Br (the highest concentration of all the sites), K, Cu, and Na explains the increase in concentration of these elements in the sediment sample.

Site I (Walton Street Bridge, Youngstown - Struthers)

Eight elements (Mn, Mg, Cu, Na, K, Cl, Al, and Ca) were detected in the water sample. Since no sediment sample was collected at this site, because the steel mill officials did not permit it, a detailed analysis could not be made. One point of interest at this location is that the Ca concentration in the water reached its highest value of any of the sites.

Site J (Bridge Street Bridge, Struthers)

Nine elements (Mn, Mg, Cu, Na, V, K, Cl, Al, and Ca) were found in the water, while all these elements (with the exception of Cl) and Br were detected in the sediment. The river at this site has shown no significant change in the concentrations of five of the nine elements. These are Mn, Mg, Na, V, and Cl.

The Cu concentration in the water reached its highest value at this site. The author feels that this element may have been introduced in the water by the steel mill, or the Campbell Sewage Plant (primary treatment).

Site K (Struthers Sewage Treatment Plant Effluent, Struthers)

Nine elements (Br, Mn, Mg, Cu, Na, V, K, Cl, and Ca) were detected in the Struthers Sewage Treatment Plant effluent. The author feels that the high concentration of Br, Mg, Na, V, K, and Ca in the effluent is due to the disposal of chemical wastes in the sewage.

The Struthers Sewage Plant (primary treatment) uses Cl_2 to disinfect the sewage after the removal of the solid wastes. The treated sewage is then pumped out into Yellow Creek which empties into the Mahoning River. For that reason, the Cl content is quite high.

Site L (Lowellville Bridge, Lowellville)

Nine elements (Mn, Mg, Cu, Na, V, K, Cl, Al, and Ca) were detected in the water, while all these elements (with the exception of Cl) and Br were detected in the sediment sample.

As can be seen, the Struthers Sewage Treatment Plant causes an increase in the concentrations of Na, V, K, and Cl in the water. The Lowellville area does not have many industries; so, as expected, the concentration of the elements present in the water should decrease by dilution or precipitation.

Comparison of Data Obtained from Unpolluted and Polluted River Systems

Table 28 is a comparison of the concentrations of elements present in both unpolluted and polluted river water, with the Mahoning (Ohio) and Roanoke (Virginia) Rivers being examples of the latter.

TABLE 28

COMPARISON OF CONCENTRATIONS (IN PPM) OF ELEMENTS PRESENT IN UNPOLLUTED AND POLLUTED RIVER WATER

		Polluted River Water	
Elements Present	Unpolluted River Water	Mahoning[a]	Roanoke[b]
Br		0 - 2.1	
Mn	0.003 - 3.23[c]	0.2 - 1.22	0.008 - 0.448
Mg	4[d]	2.3 - 51	4.81 - 247
Cu	0.01 - 0.280[c]	0 - 5	
Na	6[d]	27 - 113	8.63 - 405
V	0.002 - 0.300[c]	0 - 0.024	
K	2[d]	21 - 363	
Cl	8[d]	30 - 96	1.8 - 65
Al	0.001 - 2.760[c]	0 - 3.1	
Ca	15[d]	17 - 115	3.15 - 74.1

[a] Results obtained from the present work

[b] See reference 7

[c] Concentration range from a limited survey performed by the Environmental Protection Agency[8]

[d] See reference 30

CHAPTER V

Conclusions and Suggestions

The present work has shown that a greater knowledge of the different parameters of river water contamination (geochemical, industrial, and residential) is needed to explain the complex concentration pattern of the trace elements detected. Understanding the role of elements present in trace amounts in ecological systems will lead to solutions of many environmental problems.

Californium-252 Activation Analysis coupled with the Ge(Li) detector has been shown to be a simple and effective tool in detecting trace elements in a river system. This study, if carried on for an extensive period of time under a variety of conditions, would yield valuable baseline data.

The author would like to make several suggestions. First, that a computer program for peak identification and peak area determination be used in the analysis of data. Second, that the Ge(Li) detector be shielded with lead walls in order to detect elements like Hg, As, and Cd (also Mo, Sn, and Ti) which are also considered to be of great interest at the present time.

APPENDIX A

Calculation of the Thermal Flux of a Neutron Source Using a Computer Program

To calculate the thermal neutron flux the following equations,[6] written in FORTRAN IV, were used:

```
D=(((E1(I)-B*X)/W1(I))*EXP(R*T1(I))
    -(((E2(I)-B)*X)/W2(I))*EXP(R*T2(I))
F=D*A/(6.02E23*C*(1-EXP(-R*T)))
```

where:

A = atomic weight of Indium

B = background count (cps)

C = cross section of Indium (cm^2)

D = activity due to thermal flux per gram (cps/gm)

E1 = activity due to total flux (cps)

E2 = activity due to fast flux (cps)

E23 = 10^{23}

F = thermal flux (n/cm^2/sec)

I = number of data points

R = λ = decay constant (sec^{-1}) = $\frac{0.693}{t_{\frac{1}{2}}}$

$t_{\frac{1}{2}}$ = half life of Indium (sec)

T1 = elapsed time of the unsandwiched Indium (sec)

T2 = elapsed time of the sandwiched Indium (sec)

T = irradiation time (sec)

W1 = weight of the unsandwiched Indium (gm)

W2 = weight of the sandwiched Indium (gm)

X = efficiency of detector

APPENDIX B

Neutron Activation Analysis of the Drinking Water at Youngstown State University

Californium-252 Activation Analysis was used to determine trace elements present in the Youngstown State University drinking water. One sample was collected and analyzed as previously mentioned in this paper.

Table 29 shows the results of this study and compares them with three drinking water standards.[31] These include the United States Public Health Service Drinking Water Standards, 1962, the World Health Organization's International Standards for Drinking Water, 1963, and the American Water Works Association's Quality Goals for Potable Water, 1968.

As can be seen, the obtained concentrations of Mn, Mg, Cu, Na, Cl, and Ca are well within the standard limits set by both the United States Public Health Service and the World Health Organization. However, Al is about four times as high as the American Water Works Association's recommended value. No information was given for K (which is quite high here) by any of these three organizations.

TABLE 29

COMPARISON OF RESULTS (IN PPM) FROM THE PRESENT STUDY WITH VARIOUS DRINKING WATER STANDARDS

Elements	Youngstown State University Drinking Water	U. S. Public Health Service, 1962		World Health Organization, International, 1963			AWWA Recommended Potable Quality Water Goals, 1968
		Recommended limit	Tolerance limit	Recommended limit	Acceptable limit	Tolerance limit	
Br	0						
Mn	0.046	0.05	--	0.1	0.5	--	<0.01
Mg	9.4	--	--	50	150		
Cu	0	1	--	1	1.5	--	<0.2
Na	38	--	--	450	850		
V	0						
K	43						
Cl	38	250	--	200	600		
Al	0.21	--	--	--	--	--	<0.05
Ca	57	--	--	75	200		

APPENDIX C

Comparison of Elemental Detection Using Both NaI(Tl) and Ge(Li) Detectors

Cordon[6] has recently used Californium-252 Activation Analysis to determine trace elements at six points on the Mahoning River System. The detector used in his study was a 2x2 in. NaI(Tl) crystal. Due to the low resolution of this detector (see section on apparatus), a limited number of elements were detected.

In the present study, which employed the same method, a larger number of elements were detected because of the high resolution Ge(Li) detector used. The results obtained by using NaI(Tl) and Ge(Li) for two locations, Market Street Bridge (Youngstown) and Lowellville Bridge (Lowellville), are compared in Table 30.

The data presented clearly demonstrates the superiority of Ge(Li) over NaI(Tl) detectors.

TABLE 30

ELEMENTS DETECTED USING NaI(Tl) AND Ge(Li)

Elements Detected	Market Street Bridge (Youngstown)				Lowellville Bridge (Lowellville)			
	NaI(Tl)[6]		Ge(Li)		NaI(Tl)[6]		Ge(Li)	
	Water	Sediment	Water	Sediment	Water	Sediment	Water	Sediment
Br			*	*				*
Mn	*	*	*	*	*	*	*	*
Mg			*	*			*	*
Cu	*	*	*	*	*	*	*	*
Na	*	*	*	*	*	*	*	*
V			*	*			*	*
K			*	*			*	*
Cl	*		*		*		*	
Al			*	*			*	*
Ca			*	*			*	*

*Element detected

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