TRACE ELEMENTAL ANALYSIS OF WATER AND SEDIMENT SAMPLES FROM PRESELECTED SITES ALONG THE MAHONING RIVER VIA NEUTRON ACTIVATION, ATOMIC ABSORPTION, AND WET CHEMICAL TECHNIQUES

By

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ABSTRACT

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Due to the success of the preliminary examinations, additional methods for determining the concentrations of specific trace elements in the same water samples were undertaken. Comparative results were obtained for three elements, calcium, magnesium, and copper, by atomic absorption analyses (via a Perkin-Elmer Model #107 Atomic Absorption Spectrophotometer).

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This method provided values for two other elements, zinc and lead. In addition, wet chemical methods produced comparative results for three elements (calcium, magnesium, and chlorine), while another species (iron) and water hardness were also detected.

The elements examined, methods of detection, and concentration ranges in water and sediment samples are presented in the following tables:

Element	Method of Detection	Variation in Concentration	
		Water	Sediment
Br	NAA	undetected-6.92 ppm	18.4-111 ppm
Mn	NAA	0.095-0.641 ppm	254-8086 ppm
Mg	NAA	undetected-236 ppm	434-2281 ppm
Mg	AA	12.7-303 ppm	not determined
Mg	Wet	96.3-1746 ppm	not determined
Cu	NAA	undetected-3.96 ppm	undetected-183 ppm
Cu	AA	0.08-0.54 ppm	not determined
Na	NAA	15.9-186 ppm	1,042-3,140 ppm
V	NAA	undetected-0.029 ppm	14.6-35.0 ppm
K	NAA	undetected-213 ppm	1,563-5,938 ppm
Cl	NAA	19.5-183 ppm	undetected-155 ppm
Cl	Wet	23.6-208 ppm	not determined
Al	NAA	undetected-1.14 ppm	92.4-160 ppm
Ca	NAA	8.24-398 ppm	160-6,330 ppm
Ca	AA	60-430 ppm	not determined
Ca	Wet	43.2-377 ppm	not determined
Zn	AA	0.105-1,620 ppm	not determined
Pb	AA	0.91-3.01 ppm	not determined
Fe	Wet	0.20-2.98 ppm	not determined
Hardness	Wet	138-2123 ppm	---

Element	Method of Analysis of Water Samples		
	NAA Concentration Range	AA Concentration Range	Wet Concentration Range
Calcium	8.24-398 ppm	60-430 ppm	43.2-377 ppm
Chlorine	19.5-183 ppm	not performed	23.6-208 ppm
Copper	undetected-3.96 ppm	0.08-0.54 ppm	not performed
Magnesium	12.7-303 ppm	12.7-303 ppm	96.3-1746 ppm

The results of the determinations showed that additional techniques could be used (under specified conditions) to obtain concentration data for elements which do not readily respond to neutron activation analysis. Although significantly more susceptible to interferences than NAA, atomic absorption spectrophotometry and wet chemical methods yeild fairly reproducible results for certain elements.

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CHAPTER I

INTRODUCTION

Industrialization has produced a countless number of benefits for the physical and mental well-being of mankind during the last 175 years. However, a negative aspect has arisen with its development which has signaled the start of an ecological demise of our environment. The increased amount of particulates, dissolved matter, and toxic gases which have been added to our air and water as a result of the mechanization produced by modern technology has created a situation whereby every bit of flora and fauna hangs in a delicate balance between life and death. The recycling of waste products may be one answer to the question of pollution, but better methods for the detection and monitoring of effluents must first be found in order to develop systems which will eliminate the potential pollutants at their respective sources.

Many of the important river systems throughout the nation have received their share of contamination in the form of sewage discharged from various municipalities or from effluents contributed by some of the notable fabricating or processing plants. Among these is the system consisting of the Mahoning River and its tributaries, which encompasses a drainage area of 1076 square miles in northeastern Ohio and fifty-five square miles in western Pennsylvania, and serves a population close to half-a-million.[1] It was selected for the present study because of the major industrial role it plays, especially in the area of steel and iron production, for which this region is known.

As Hazari[2] has pointed out, during the last three decades most of the studies performed on the Mahoning River have only been semi-qualitative in nature, with the general conclusion to the extent of pollution being made, but with no idea of which chemical elements were present in trace or major quantities. An organization which is coordinating its efforts in this direction at the present time is the Ohio Environmental Protection Agency (EPA). Compliance of the various fabricating mills to the stringent guidelines set up by the Ohio branch of the EPA, along with construction of secondary and tertiary sewage treatment plants, will undoubtedly reduce the quantities of contaminants being introduced into the river system. But, because of the general feeling that much of their processing equipment is outdated, many manufacturers refuse to install instruments which would control, or even monitor, the effluents arising from their factories, thus resulting in a conflict with the Environmental Protection Agency up to the point where court action is taken.

Cordon[3] performed some of the original work as to the qualitative and quantitative nature of the possible trace contaminants in the Mahoning, utilizing the technique of neutron activation analysis (herein referred to as NAA) in connection with a 2 X 2 inch NaI(Tl) scintillation detector. But, due to the limited number of locations chosen for the selection of samples and the low resolving ability of the sodium iodide detector used, his results proved to be fairly inconclusive since variations in only four elemental concentrations were determined (Cu, Mn, Na, and Cl). Hazari[2] improved upon Cordon's work by using a coaxial lithium-drifted germanium gamma-ray detector having an 8.5% counting efficiency, a peak-to-Compton ratio of 16:1, and a bias voltage of -1400 volts. By this method, the total number of elements detected were increased to ten (Cu, Na, V, K, Br, Mn, Mg, Ca, Cl, and Al). However, Hazari only studied a small industrialized segment of the river in the Youngstown, Ohio, vicinity, relying solely on NAA data for the determination of trace elements in water and sediment samples obtained at various points along the Mahoning. Also, both of the previously mentioned researchers used Californium-252 as a source of neutrons for their NAA determinations.

The present investigation relies on the same detector system for the NAA analyses as that used by Hazari, with application towards another segment of the Mahoning, which flows from the vicinity of Lake Milton Reservoir, where the water is relatively pure, to the city of Niles, Ohio, representing another industrialized region with which the river comes into contact. In addition, the analyses of the same water samples were performed via two other techniques, these being atomic absorption spectrophotometry and wet chemical methods. The section of the river just described has a population around 200,000 and is engaged in such activities as cement and steel production, along with various forms of strip-mining.[4,5] Because of the increased industrialization in this vicinity, the Mahoning River cannot support fish or other forms of aquatic life as one proceeds downstream from Lake Milton. Many years ago, the river was the center of various recreational activities, such as ice skating, boating, sledding, etc., for which it cannot be used at the present time, due to the lack of the ability of the Mahoning to freeze, especially after encountering the manufacturing areas.[1] The thermal pollution problem created by these industries is evident by the dense white clouds of vapor rising from the surface of the river, even in the coldest weather. A combination of the three methods of analysis described above may lead to an understanding why the river behaves as it does at various locations and could also provide an answer to whether or not the damage that has already been done to the surrounding environment by elements introduced into the Mahoning could be rectified by future conservation measures.

In December, 1971, as a part of a market evaluation program, Youngstown State University received a single Californium-252 neutron source (then measuring 9021 micrograms in size) from the United States Atomic Energy Commission's Savannah River Laboratory for use in the activation analyses performed on water and sediment samples taken from the Mahoning River drainage basin. The relatively high flux of approximately 1 X 10^8 neutrons/cm^2-sec and the utilizable half-life of 2.646 years makes Californium-252 an excellent means by which to investigate the trace contaminants present in such a river system.[2,3] Because the university possesses a simply-designed storage facility for the ^{252}Cf source, it can be readily maintained by a small research staff.

As Table 1 illustrates, NAA stands at the forefront among trace analytical techniques, especially insofar as sensitivity, specificity, accuracy, and freedom from contamination are concerned.[6] Besides these obvious advantages, the fact that neutron activation analysis is a non-destructive technique which is not affected by errors due to blank values adds another plus in favor of this type of procedure.[7] However, an aspect of NAA which may be taken as either an advantage or disadvantage by those familiar with it is the non-differentiation of the chemical state of a particular element detected.[8] Neutron activation analysis may be used if only the total elemental concentrations are desired, but if knowledge of a specific form of the element is required, such as the covalent- or ionic-bonded species, another analytical technique should supplement this method. One particularly useful means of investigating the specific form of such an element is to perform standard or wet chemical determinations on the samples being examined. This type of analysis was carried out on the same water samples taken in the vicinity of the river previously described, and will be covered in greater detail later in this section.

Because of the importance attached to atomic absorption spectrophotometry (AA) in the examination of specific

TABLE 1

PARAMETRIC COMPARISONS FOR VARIOUS TRACE ANALYTICAL PROCEDURES

Technique	Several elements simultaneously	Sensitivity (in ppm)	Specificity	Accuracy	Freedom of contamination and interferences	Possibilit of overcom surface co tamination
Activation analysis	in several cases	0.001	good	good	good	good
Atomic absorption and flame spectrophotometry	no	0.01	good	good	bad	reasonable
Emission spectrometry	yes	0.1	good	reasonable	reasonable	reasonable
Gas analysis (reducing fusion)	O_2, N_2, H_2	1	reasonable	reasonable	reasonable	bad
Mass spectrometry	yes	0.01	good	needs stand.	good	good
isotope dilution	no	0.001	good	reasonable	bad	bad
Polarography (cathode ray, pulse)	yes	0.01	reasonable	good	bad	reasonable
Spectrophotometry and fluorimetry	no	0.1-0.01	reasonable	good	bad	bad

elemental concentrations present in a variety of aqueous mixtures, it was decided that this technique would be useful for investigating certain trace elements found by NAA determinations and others which had heretofore been undetermined. A comparison of results received from the two methods was undertaken for calcium, magnesium, and copper, while data for two additional elements (zinc and lead) were obtained from the AA analyses. Some advantages associated with atomic absorption spectrophotometry are the extensive range of sensitivity allied to this method, reaching into the part-per-million (ppm) level; the high accuracy and precision afforded, especially when calibration curves representing a series of different standard concentrations are employed; the relative ease with which the apparatus can be operated; and the moderate cost of the instrumentation required, generally between \$3,000 and \$17,000.[9,10] However, there are also important disadvantages which make this method less desirable as a means for analysis. These include a limited range of application (especially insofar as the non-metals and metalloids are concerned); the formation of stable oxides by certain elements in the flame of the instrument; the fact that, on most equipment, several elements cannot be determined at the same time; and that spectral and chemical interferences, unlike NAA, may occur to a pronounced degree.[10]

As mentioned earlier, standard or wet chemical analyses were also performed on the identical river water samples which were previously investigated by NAA and AA methods. These analyses primarily involved the use of

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complex-forming and/or colorimetric procedures, from which a total of four elements (calcium, magnesium, chlorine, and iron) as well as water hardness were determined for each sample. The highest sensitivity among the elements studied was that obtained for iron, the value being 0.0186 ppm, while the lowest sensitivity was 1.2 ppm, recorded for hardness, making this an excellent means of investigating trace contaminants in a polluted river system such as the Mahoning.[11] But, again, a disadvantage of this method is the number of interferences encountered during the elemental analyses. Generally, these interferences can be represented by reducing or complexing agents such as hydroxylamine hydrochloride and sodium cyanide.[11] Another possible disadvantage, which also appears under the AA investigation, is the fact that no single determination provides data for more than one element.

It is the expressed purpose of this paper to show how other analytical techniques, specifically atomic absorption spectrophotometry and wet chemical methods, may be used in connection with neutron activation analysis in order to expand the number of trace elements investigated and for comparative purposes when a polluted water system like the Mahoning River is studied.

CHAPTER II

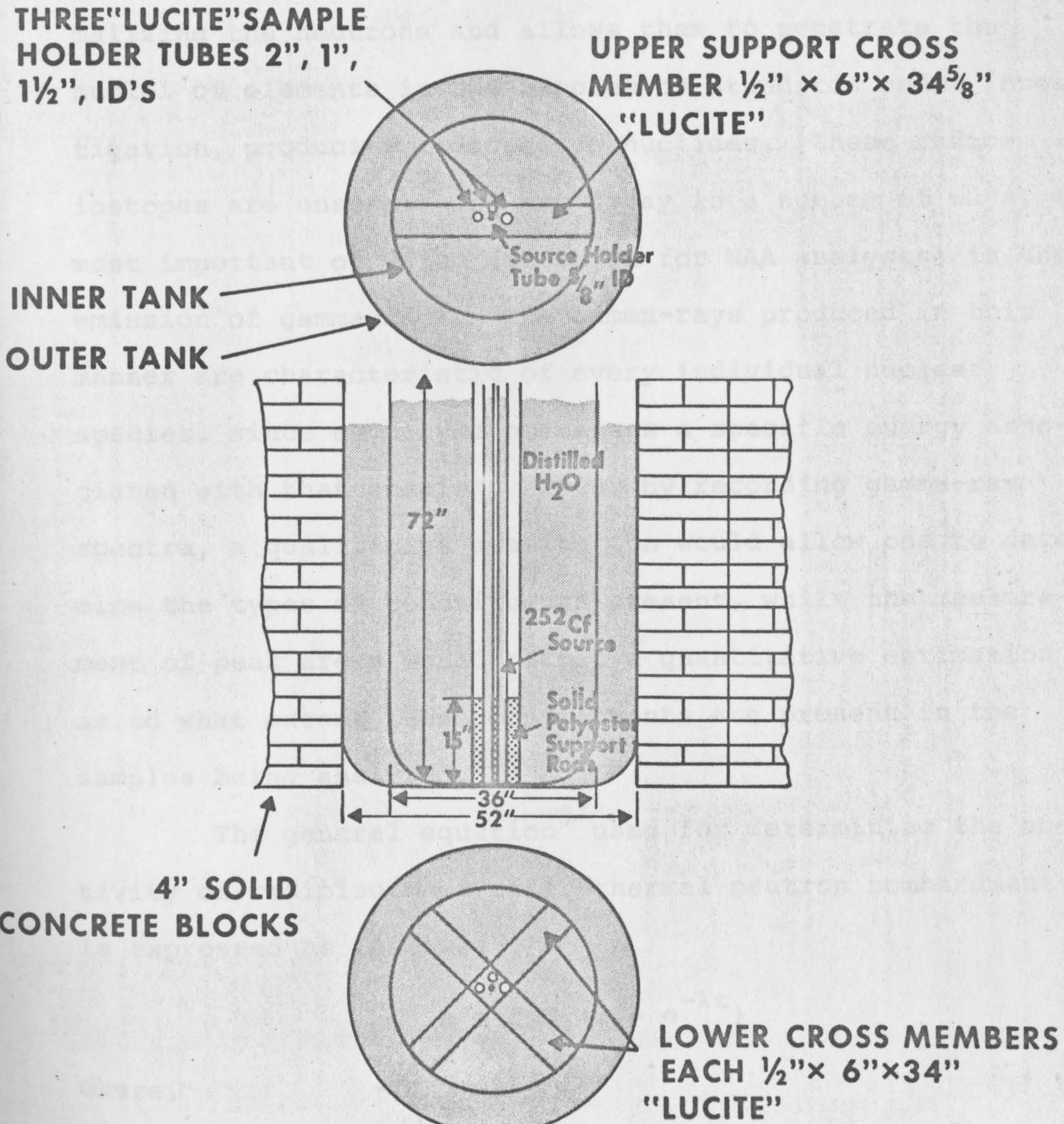
HISTORY OF NEUTRON ACTIVATION, ATOMIC ABSORPTION, AND WET METHODS AND THEIR APPLICATION TO ANALYTICAL CHEMISTRY

Neutron Activation Analysis

Neutron activation analysis was originally theorized by von Hevesy and Levi in 1936 and was followed by charged particle activation studies by Seaborg and co-workers in 1938. But NAA remained an area of limited application until the 1940's, when high reactor fluxes of approximately 10^{12} neutrons/cm^2-sec opened up new possibilities for its use as an analytical tool.[6] In 1968, the United States Atomic Energy Commission made Californium-252, a reactor produced trans-uranium element, available to certain academic and research institutions, presumably for use as a source of thermal neutrons in connection with NAA experimentation.[12] Although the neutron flux was considerably less (of the order of 10^8 neutrons/cm^2-sec) than that produced by a nuclear reactor, the method using ^{252}Cf was sensitive enough to permit trace elemental investigations into the part-per-million range.[2,3]

The facility at Youngstown State University, which makes use of such a Californium-252 source, is depicted in Figure 1. It permits the irradiation of polyethylene bottles

FIGURE 1 CALIFORNIUM - 252 STORAGE AND EXPERIMENTAL FACILITY AT YOUNGSTOWN STATE UNIVERSITY



or vials containing various water or sediment samples and standards by placing them in "Lucite" tubes located at strategic positions with respect to a similar tube containing the source. Water, which moves freely between the source and sample "Lucite" tubes, acts as a moderator for thermalizing the neutrons and allows them to penetrate the nuclei of elements in the samples or standards under investigation, producing radioactive nuclides. These radioiostopes are unstable and may decay in a number of ways, the most important of which (at least for NAA analyses) is the emission of gamma-rays. The gamma-rays produced in this manner are characteristic of every individual nuclear species, since each type possesses a specific energy associated with that species. Thus, by recording gamma-ray spectra, a qualitative examination would allow one to determine the types of constituents present, while the measurement of peak areas would permit a quantitative estimation as to what extent these constituents are present in the samples being analyzed.[13]

The general equation[8] used for determining the activity of radioisotopes after thermal neutron bombardment is expressed as follows:

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

where,

A = rate of disintegration of the radioactive species (in disintegrations/sec);

f = flux of the bombarding particles (in neutrons/cm^2-sec);

σ = activation cross section for the reaction, which is a measure of the tendency of the unactivated atoms to interact with neutrons (in cm^2);

N_i = total number of unactivated atoms;

λ = radioactive disintegration constant (in sec^{-1}) = $\frac{0.693}{t_{1/2}}$;

$t_{1/2}$ = elemental half-life (in sec);

and t = time of irradiation (in sec).

However, the above equation can be expanded[8] to include other important experimental quantities, in order that it may be more easily utilized:

$$A = f\sigma \frac{W\phi}{M}(1 - e^{-\lambda t})(e^{-\lambda t})(6.02 \times 10^{23}) \qquad (2)$$

where,

W = weight of the element present (in g);

ϕ = fractional abundance of the particular elemental isotope desired;

M = atomic weight of the element investigated (in g/mole);

$e^{-\lambda t}$ = decay factor;

t = length of time elapsed after neutron bombardment has ceased;

and 6.02×10^{23} = Avogadro's number.

Because of a variety of reasons, most of which are related to the fact that the quantities A, f, and σ cannot be determined with the desired accuracy, the weight of the element in Equation 2 cannot be precisely calculated. Therefore, a standard containing a measured amount of the element in question is subjected to the same experimental conditions of samples thought to contain that element in unknown amounts. With other things being equal, the following relationship is obtained for the comparator (or standard) and the unknown sample[8]:

$$\frac{\text{weight of element in sample}}{\text{weight of element in standard}} = \frac{C_x \text{ (observed counting rate of the sample)}}{C_s \text{ (observed counting rate of the standard)}} . \qquad (3)$$

In the present investigation, the instrumental system utilized in the NAA analyses (to be described in greater detail later in this work) was calibrated with a sealed Plexiglas tube of Cobalt-60 so that its two gamma-ray energies of 1.17 MeV and 1.33 MeV would be located respectively at positions 117 and 133 on the associated 400 channel multichannel analyzer screen. This was done previous to the determination of the trace constituents in the water and sediment samples taken from the Mahoning River, so that representative energy values could be assigned to the corresponding spectra.[2] By comparing the activity of a particularly pronounced photopeak occurring at a specific channel number in the unknown spectrum to the activity of an identical photopeak in the standard spectrum, one can determine the concentration of that element in the unknown sample. The activities of the samples and standards were obtained from the areas under the peaks associated with these spectra after allowances were made for background radiation.

Hazari[2] noted two equations that were used for his work in the area of neutron activation analysis, which, with minor adaptations, were also utilized for the various NAA determinations contained within this study:

Qualitative elemental determination:

$$\frac{\text{Gamma-ray energy of photopeak (in MeV)}}{\text{Gamma-ray energy of Co}^{60}\text{ photopeak (1.17 or 1.33 MeV)}} = \frac{\text{Channel number of photopeak}}{\text{Channel number of Co}^{60}\text{ photopeak (1.17 or 1.33 MeV)}} \tag{4}$$

Quantitative elemental determination:

$$\frac{\text{Area of desired element photopeak in sample}}{\text{Area of desired element photopeak in standard}} = \frac{\text{Mass of desired element in sample (in ppm)}}{\text{Mass of desired element in standard (in ppm)}} . \tag{5}$$

As noted previously, some obvious disadvantages may limit the success of neutron activation analysis as a technique for trace determinations. The prohibitive cost of maintaining a nuclear reactor and the added care which must accompany such a facility in order to produce the highest sensitivities for NAA work, the restrictions introduced by NAA in answering the question of the forms the element under study possesses, and the general inertness of elements such as carbon, hydrogen, and oxygen, which are of particular interest to organic and biochemists,[14] are several barriers introduced along the way towards a complete understanding of the chemical properties belonging to minor constituents in a natural environment.

Atomic Absorption Spectrophotometry

In contrast to neutron activation analysis, the field of absorption spectroscopy is a well-established area, having its earliest beginnings in the first quarter of the nineteenth century with the study of dark lines in solar spectra by Wollaston and Frauenhofer. Not until 1859, however, was a direct relationship between naturally occurring spectral lines and those produced artificially by the excitation of chemical elements postulated, this being due to the pioneering efforts of Kirchhoff and Bunsen from their observation of the sodium D-line. Work continued in this area into the late 1920's, when Saha began to look into the prospects of determining a quantity known as the oscillator strength, which gives some idea of the desired element's concentration as atoms. But, due to the complex instrumentation involved, it proved to be impractical for use as an analytical method. By 1953, the first efficient atomic absorption spectrophotometer was developed by Walsh, paving the way for future advancements in design, sensitivity, and ease of operation.[15]

Atomic absorption spectrophotometry is a technique which relies on the dissociation of chemical compounds into their constituent elemental atoms, this being accomplished by the heat produced from a flame associated with a specially-designed burner head. Once these atoms have been broken apart in the gaseous phase, a certain fraction of them can absorb radiation of a characteristic wavelength furnished in the form of narrow emission lines by a hollow cathode lamp of the element in question and become electronically excited from their initial ground state to a higher energy level, which is generally the lowest excited state of that element.[16,17] Absorption of radiation by these atoms reduces the intensity of the beam emanating from the cathode lamp, and thus alters the resulting signal to the detector. This process may be described via a pictorial adaptation from Christian and Feldman's text:[16]

$$\underset{\text{(solution)}}{MX_2} \xrightarrow{\text{flame}} \underset{\substack{\text{(gas)}\\ \text{(molecules)}}}{MX_2} \xrightarrow[\text{energy}]{\text{dissociation}}$$

$$M^0 + 2X^0 \text{ (unexcited gas atoms)} \qquad (6)$$

$$M^0\text{(unexcited)} + h\nu \xrightarrow{\text{absorption}} M^* \text{ (excited)} \qquad (7)$$

where MX_2 may be any divalent metal compound.

From the ideas expressed above, an important quantity known as the "degree of absorption" may be defined by the following equation:[10]

$$\int k_\nu d\nu = \frac{\pi e^2}{mc} N_1 f \qquad (8)$$

where,

k_ν = absorption coefficient at frequency ν;

e = charge of an electron;

m = mass of an electron;

c = speed of light;

N_1 = number of unexcited atoms;

and f = oscillator strength of the absorbing line = average number of electrons which can be excited in each atom.[10]

Equation 8 is utilized in most atomic absorption work in preference to the familiar Beer-Lambert law:[10]

$$I_1 = I_0 e^{-kbc} \qquad (9)$$

where,

I_1 = intensity of the transmitted radiation;

I_0 = intensity of the incident radiation;

k = absorption coefficient, as defined above;

b = radiation path length of the sample;

and c = concentration of the species being determined;

since with this method of analysis, it is more common to find situations where there is a non-homogeneous rather than a homogeneous distribution of atoms required for a steady state by the latter relationship.

Besides the advantages listed in the introduction to this work, atomic absorption spectrophotometry has some positive features over its counter-technique, known as atomic emission spectrophotometry. For instance, atomic absorption methods are temperature and wavelength independent, while emission techniques are not. Also, only a small fraction of excited atoms can emit radiation, while a major part of the unexcited atoms can absorb radiation. Finally, in absorption work the I_1/I_0 ratio is the only experimental quantity which really needs to be determined, while in emission work the absolute value of the emitted signal must be measured.[10]

Due to the nature of the instrumental parameters (such as the type of burner, fuel and oxidant ratios, and elemental wavelengths used) and their close association to the actual experimental procedure, a thorough discussion of these topics, as well as additional disadvantages of the method itself, will be deferred until the next chapter. Suffice it to say for the present that the unknown water samples were measured via a comparator technique similar to that used for neutron activation analysis after a linear working range, based upon absorbance readings taken for a series of standards, was found for each element studied.

Wet Chemical Methods

The origins of wet chemical techniques for the analysis of elements, particularly the metals and halogens, lie buried in the archives of analytical chemistry, this being the oldest field in the science.[17] After the development of a balance which would yield a high degree of precision, gravimetric determinations were the first to be utilized for obtaining quantitative information from unknown samples. Following this initial stage, gravimetry was used to prepare standards, which were then applied in connection with finely calibrated glassware so that multiple analyses could be run in short periods of time.[18] Quantitative analysis underwent further changes, especially during the last fifty years, with the introduction of newer and improved optical and electrochemical instrumentation. However, in order to test the reliability of this equipment for chemical analyses, gravimetric and titrimetric procedures, which make up the bulk of standard or wet chemical methods, were applied even though they lacked the precision that was inherent to analytical instrumentation. In addition, many instrumental methods were useless as a means for analysis, since they did not differentiate between an element and others which interfered with its observation. Some wet chemical methods were also guilty of this, but in most instances a chemical reagent could be found which would mask these interferences while the desired element was being determined. Thus, standard methods showed some notable advantages to instrumental methods during the developmental stages of the latter, and this is still the case today.

As mentioned in the previous chapter, complexometric and precipitation titrations which involve visible color changes were the chief means of investigating the calcium, magnesium, chlorine, iron, and hardness contents of the river water samples via standard analyses. Calcium and total hardness were determined by a complexation reaction with disodium ethylenediaminetetraacetate (Na_2EDTA) in the presence of an indicator such as murexide (for calcium) or Eriochrome Black T (for hardness). Magnesium was not determined by an experimental wet analysis method, but by subtraction of the calcium data from the results obtained for total hardness, assuming that water hardness was principally due to the magnesium and calcium components. Total chlorine was not found by this means, since the technique used (the Mohr method) determines chlorine only in the form of the chloride ion. Iron was examined by its complex formation with 2,2'-bipyridine while in the ferrous state. This method required the use of a transistorized Spectronic-20 spectrophotometer, which was initially used in order to determine a linear working range for the unknown water samples from a series of iron standards with the aforementioned complexing agent. Briefly regressing to Equation 9 (the Beer-Lambert law) and rearranging several terms, a familiar quantity used in spectrophotometry (alluded to earlier as the I_1/I_0 ratio and known as transmittance) can be derived[11]:

$$T = \frac{I_1}{I_0} = e^{-kbc} \tag{10}$$

where,

$$T = \text{transmittance} .$$

From this, the definition of an experimental parameter more generally used, the absorbance, can be stated in the form of the following equation[11]:

$$A = -\log_{10} T = -\log \frac{I_1}{I_0} = kbc \tag{11}$$

where,

$$A = \text{absorbance}.$$

Since k and b in the above equation are constant for a particular chemical quantity and the set of prevailing experimental conditions, there is a direct linear relationship between the absorbance (A) and concentration (c) of the absorbing species. However, this linearity may be violated, especially at very high or very low concentrations, due to the lack of monocromaticity of the light passing through the samples being analyzed or from extensive solute-solvent interactions.[18] So, a plot must be made for a series of standards in order to determine the range of linearity inherent to a particular element at the specific wavelength of light used. More will be said about this and the details of the elemental procedures followed for the wet analysis studies in the next chapter. Possible disadvantages or restrictions associated with the method will also be discussed at that time.

CHAPTER III

METHODS FOR THE ANALYSIS OF WATER AND SEDIMENT SAMPLES

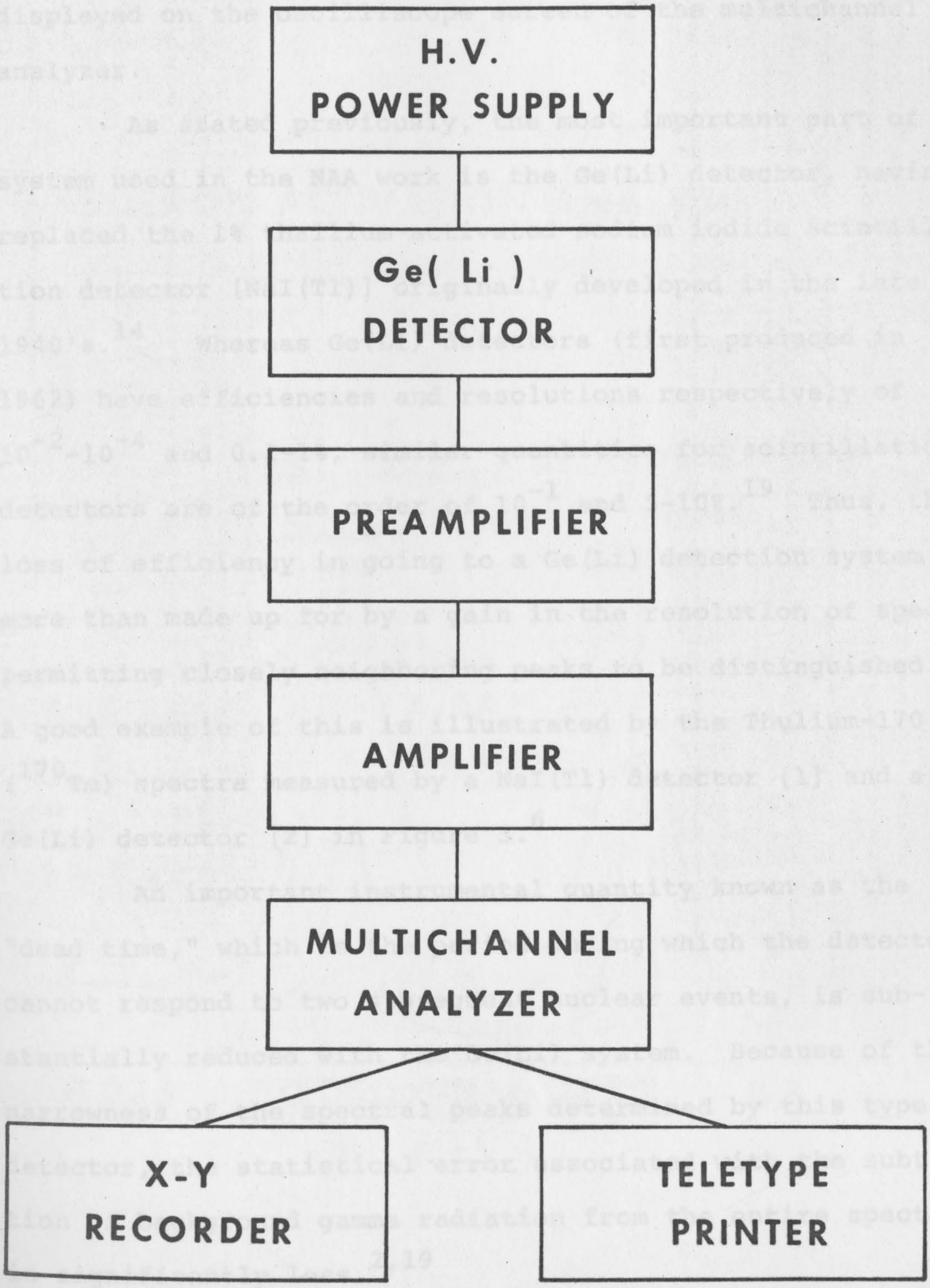
Neutron Activation Analysis

Apparatus

A detailed description of the detection and counting system used at Youngstown State University for the neutron activation analysis studies of Mahoning River water and sediment samples is given in the work by Hazari,[2] so only a brief account of the facilities will be presented here. Figure 2 is a pictorial representation, in the form of a block diagram, of the equipment used. It consists of a Model #NV-23 high voltage power supply linked to a coaxial lithium-drifted germanium [Ge(Li)] gamma-ray detector having an 8.5% counting efficiency, a peak-to-Compton ratio of 16:1, and a bias voltage of -1400 volts, both items being manufactured by the Harshaw Chemical Company. The detector, which is the heart of the system, is then connected to a Harshaw Model #NB-21 preamplifier associated with a Model #1415 amplifier made by Canberra Industries. Next in line is a Victoreen Model #PlP 400 A multichannel analyzer, which is capable of storing data over a series of four hundred memory units having a gamma-ray energy range from 0 to 4 MeV, full scale. Once the experimental data is stored, it can be transferred to a Hewlett-Packard/Moseley Model

Figure 2 - NAA

DETECTION AND COUNTING SYSTEM

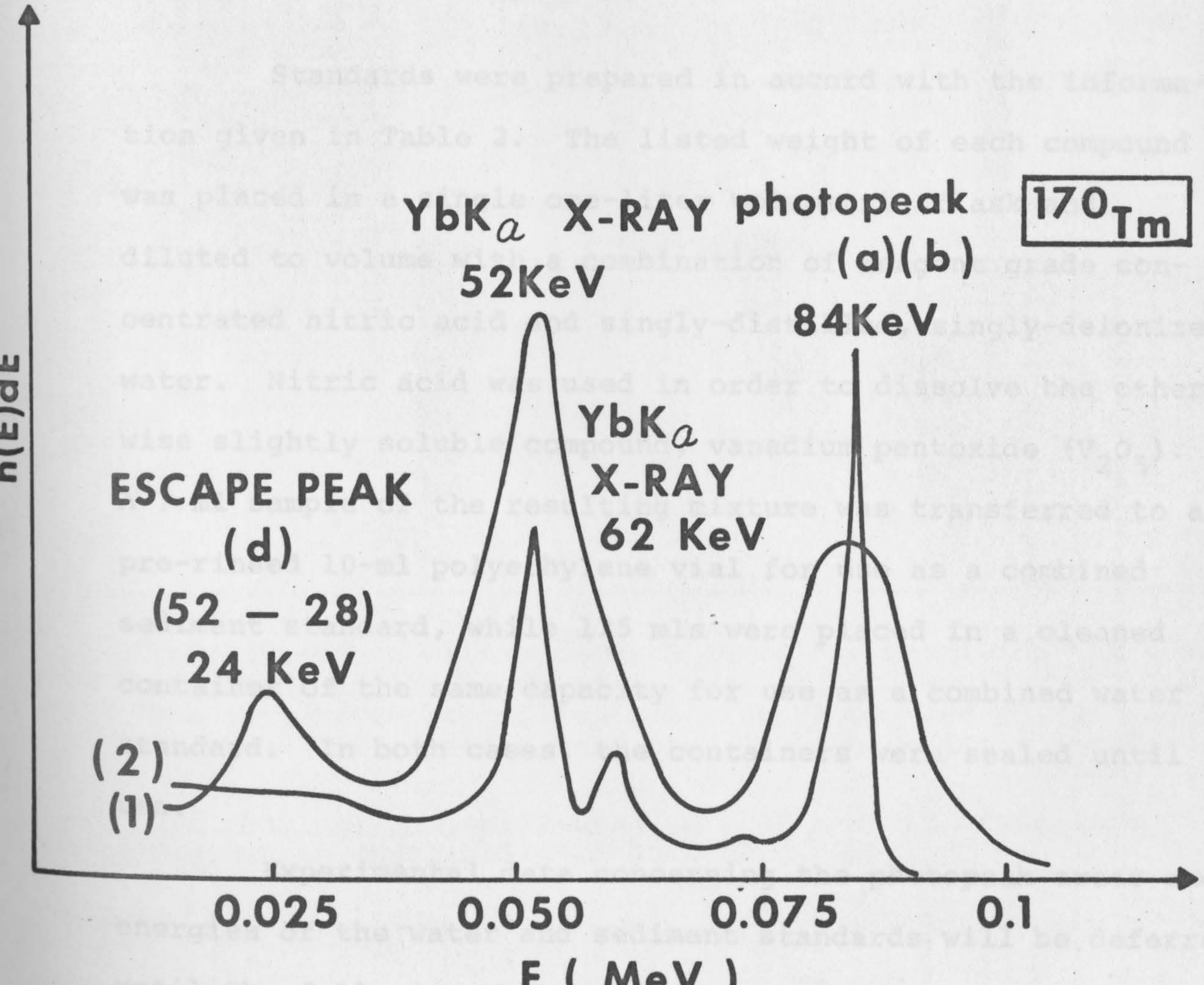


#7035-B X-Y recorder in the form of a gamma-ray spectrum, or to a printed form depicting absolute counts per channel number via an ITT Model #33 teletype printer. In addition, a visual representation of the spectrum is capable of being displayed on the oscilliscope screen of the multichannel analyzer.

As stated previously, the most important part of the system used in the NAA work is the Ge(Li) detector, having replaced the 1% thallium-activated sodium iodide scintillation detector [NaI(Tl)] originally developed in the late 1940's.[14] Whereas Ge(Li) detectors (first produced in 1962) have efficiencies and resolutions respectively of 10^{-2}-10^{-4} and 0.1-1%, similar quantities for scintillation detectors are of the order of 10^{-1} and 5-10%.[19] Thus, the loss of efficiency in going to a Ge(Li) detection system is more than made up for by a gain in the resolution of spectra, permitting closely neighboring peaks to be distinguished.[19] A good example of this is illustrated by the Thulium-170 (^{170}Tm) spectra measured by a NaI(Tl) detector [1] and a Ge(Li) detector [2] in Figure 3.[6]

An important instrumental quantity known as the "dead time," which is the period during which the detector cannot respond to two subsequent nuclear events, is substantially reduced with the Ge(Li) system. Because of the narrowness of the spectral peaks determined by this type of detector, the statistical error associated with the subtraction of background gamma radiation from the entire spectrum is significantly less.[2,19]

Figure 3 NaI(Tl) (I) AND Ge(Li) [2]
GAMMA - RAY SPECTRA FOR THULIUM - 170
NEUTRON ACTIVATION ANALYSIS



One minor inconvenience of using a Ge(Li) detector in place of a NaI(Tl) detector is that the former must be kept at liquid nitrogen temperatures (about 77°K or -196°C) and under a vacuum in order to obtain the best results.[6,14] This is done to prevent the further diffusion of lithium ions out of the germanium core, which destroys the effectiveness of the detector and which is appreciable at room temperature.[14]

Preparation of Standards

Standards were prepared in accord with the information given in Table 2. The listed weight of each compound was placed in a single one-liter volumetric flask and diluted to volume with a combination of reagent grade concentrated nitric acid and singly-distilled, singly-deionized water. Nitric acid was used in order to dissolve the otherwise slightly soluble compound, vanadium pentoxide (V_2O_5). A 7 ml sample of the resulting mixture was transferred to a pre-rinsed 10-ml polyethylene vial for use as a combined sediment standard, while 125 mls were placed in a cleaned container of the same capacity for use as a combined water standard. In both cases, the containers were sealed until use.

Experimental data concerning the photopeak areas and energies of the water and sediment standards will be deferred until the following chapter of this paper.

TABLE 2

NAA STANDARD PREPARATION DATA

Element	PPM[1] (for water standard)	Weight (gm)	Compound[2]
Al	10	0.1390	$Al(NO_3)_3 \cdot 9H_2O$
Br	100	0.1226	NH_4Br
Ca	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	500	1.2929	KNO_3
Mg	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] 1:10 dilutions were made with deionized water for the sediment standards in the cases of Al, Ca, Cl, Cu, Mg, Mn, Na, and V. The same part-per-million concentrations used for Br and K in the water standard were used for the sediment standard.

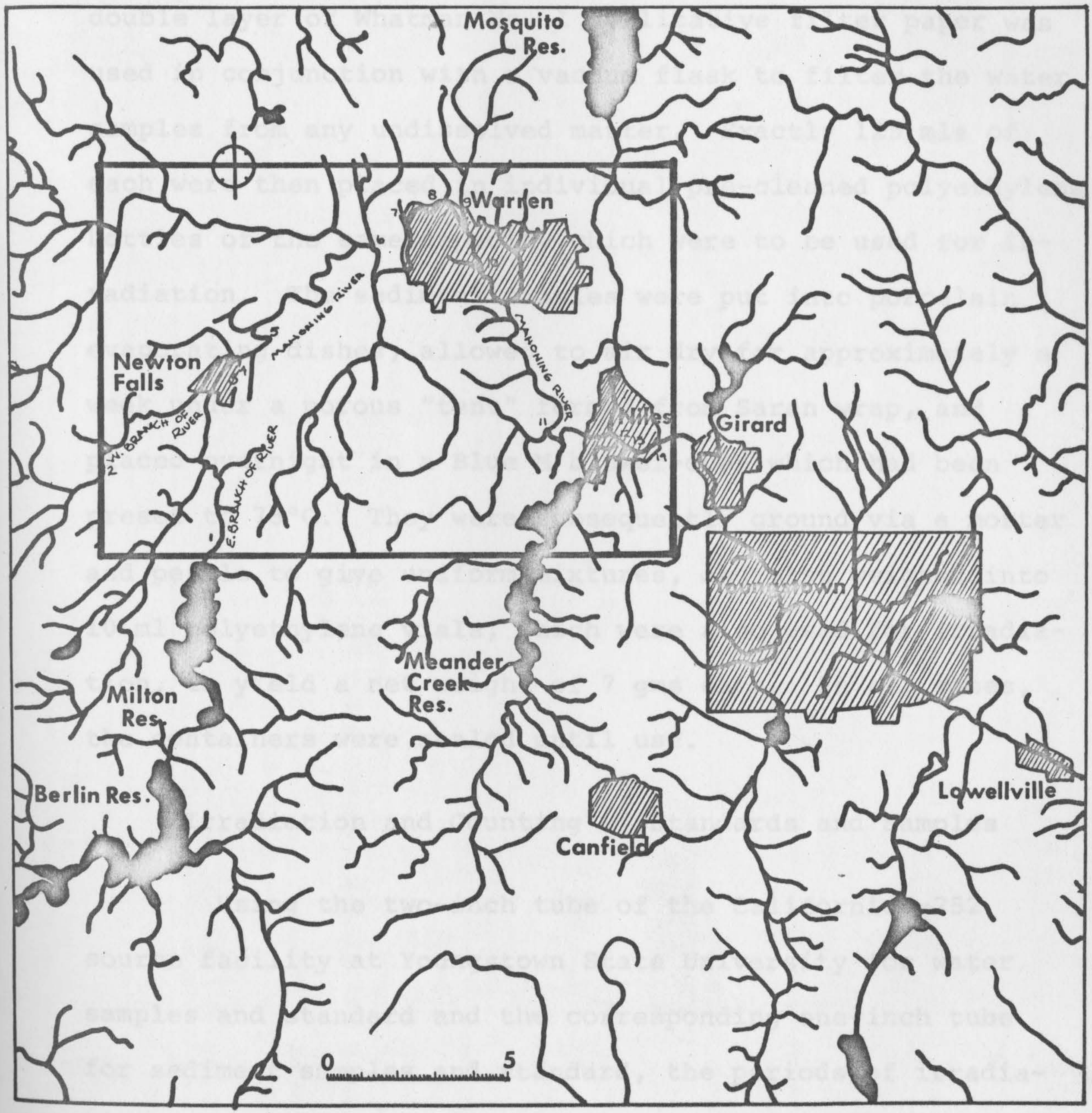
[2] All chemical compounds used were of reagent grade, except V_2O_5 which was labelled "technical".

Collection and Preparation of Water and Sediment Samples

Water and sediment samples were primarily collected from bridges which crossed the Mahoning River or from areas which allowed easy access to it. The vessel used to obtain the samples consisted of a ten-quart galvanized pail weighted symmetrically with several lead discs which was either tossed or lowered to approximate midstream positions by means of a rope so that representative selections could be made. Containers used for the storage of samples were one liter polyethylene bottles having screw-on type caps. These were rinsed several times with river water from the appropriate sites before final collections were made. A funnel and glass rod were utilized in the transfer of sediment samples to the bottles because of their extreme viscosities. In addition, both pH and temperature were determined for the water samples at each of the fourteen locations with the aid of pHydrion paper and a Fisher thermometer which had a range from -10°C to 110°C. The pH of each sample was subsequently adjusted to about two with the aid of reagent grade concentrated nitric acid in order to avoid the precipitation and/or "plating out" of any of the dissolved components onto the container walls upon standing.[2,11]

Figure 4 depicts an overall view of the drainage area encompassed by the Mahoning River. The portion of the river selected for this study is outlined in the figure, with the appropriate sample collection sites being labelled

Figure 4 MAP OF MAHONING RIVER DRAINAGE AREA AND COLLECTION SITES



from 1 to 14. Table 3 is a compilation of data acquired from the on-site analysis of water samples.

Once they were returned to the laboratory, the water and sediment samples were prepared for analysis in an entirely different manner. A Büchner funnel containing a double layer of Whatman No. 1 qualitative filter paper was used in conjunction with a vacuum flask to filter the water samples from any undissolved matter. Exactly 125 mls of each were then placed in individual pre-cleaned polyethylene bottles of the same capacity which were to be used for irradiation. The sediment samples were put into porcelain evaporating dishes, allowed to air dry for approximately a week under a porous "tent" formed from Saran wrap, and placed overnight in a Blue M blower-oven which had been preset to 75°C. They were subsequently ground via a mortar and pestle to give uniform mixtures, and then weighed into 10 ml polyethylene vials, which were also used for irradiation, to yield a net weight of 7 gms each. In all cases, the containers were sealed until use.

Irradiation and Counting of Standards and Samples

Using the two-inch tube of the Californium-252 source facility at Youngstown State University for water samples and standard and the corresponding one-inch tube for sediment samples and standard, the periods of irradiation for the polyethylene bottles and vials were respectively set at one hour and at fifteen minutes. Since the

TABLE 3

COLLECTION SITE INFORMATION ON SAMPLES #1 TO #14[a]

Sample #	Location	Temp. (°C)	Initial pH of Water samples	Adjusted pH of Water samples
1	Bridge located on Mahoning-Trumbull County Line Road (east branch of Mahoning River)	9.5°C	~7	~2
2	Bridge located on Portage County Highway #117 (west branch of Mahoning River)	9.0°C	~6	~2
3[b]	Effluent from North American-Rockwell Plant (east branch of Mahoning River)	16.0°C	~9	~2
4	Approximately 50 feet downstream from Site #3 (east branch of Mahoning River)	10.0°C	~7	~3
5	Bridge located on Ohio State Route #5 (after Ohio Turnpike intersection)	9.3°C	~7	~2
6	Bridge located on Ohio State Route #5 bypass	9.0°C	~7	~2
7[b]	Bridge located on Parkman Road (U.S. Route #422) in the city of Warren, Ohio	9.0°C	~7	~2
8[b]	Effluent from Copperweld Steel Fabricating Plant	10.0°C	~6	~2
9[b]	Bridge located on North West Bridge Street in the city of Warren, Ohio	9.0°C	~6	~2
10	Bridge located on Market Street in the city of Warren, Ohio	9.0°C	~6	~2
11	Bridge located on West Park Avenue Extension (west of the city of Niles, Ohio)	10.0°C	~7	~2
12	River embankment near the intersection of Pratt and River Streets in the city of Niles, Ohio	9.0°C	~6	~2
13	Bridge located on Belmont Street in the city of Niles, Ohio	9.0°C	~6	~2
14	Bridge located on Olive Street in the city of Niles, Ohio	12.0°C	~6	~2

---

[a] All samples were collected on November 12, 1973.

[b] Only water sample collected.

[c] pH adjusted with concentrated HNO_3 to prevent precipitation of aqueous components and/or their "plating-out" onto container walls.

Californium-252 facility was located a short distance from the counting laboratory where all the NAA data was recorded, a thirty-second decay time was allotted for each sample and standard after its removal from the source. This ruled out the detection of prompt gamma rays, which limited the number of elements that could be studied by this method. The water samples and standard were poured individually into a Plexiglas cup having a recessed bottom and capable of fitting over the outside covering of the Ge(Li) detector head, yielding a rather efficient counting geometry. Sediment samples and standard were counted in their vials with the aid of a thin Plexiglas plate which also fit over the surface of the previously mentioned detector head. All samples and standards were counted for a period of twenty minutes each, allowing sufficient time for the photopeaks of the gamma-rays from the longer half-lived isotopes (of several hours each) to appear in the spectra. The "dead time" of the entire system varied between 0% and 10% for the water samples and water and sediment standards, and from 10% to 25% for the sediment samples. As previously mentioned, gamma-ray spectra were recorded in the forms of a graph and a printout sheet in order that a thorough analysis of the data could be made at a later time.

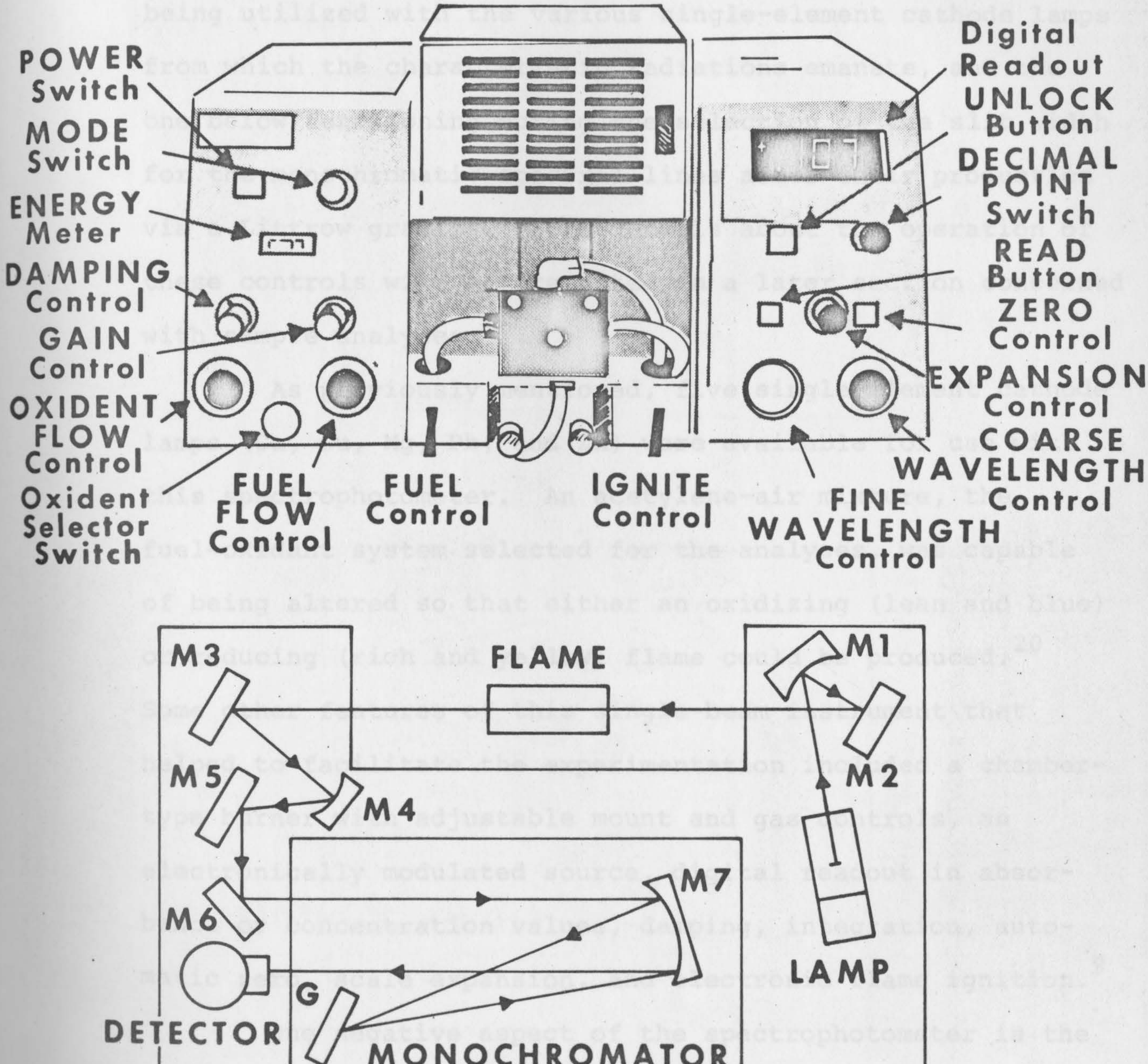
Atomic Absorption Spectrophotometry

Apparatus

A Perkin-Elmer Model #107 Atomic Absorption Spectrophotometer (Figure 5) functioned as the means of

Figure 5

INSTRUMENTAL AND BLOCK DIAGRAMS OF THE PERKIN - ELMER MODEL #107 ATOMIC ABSORPTION SPECTROPHOTOMETER



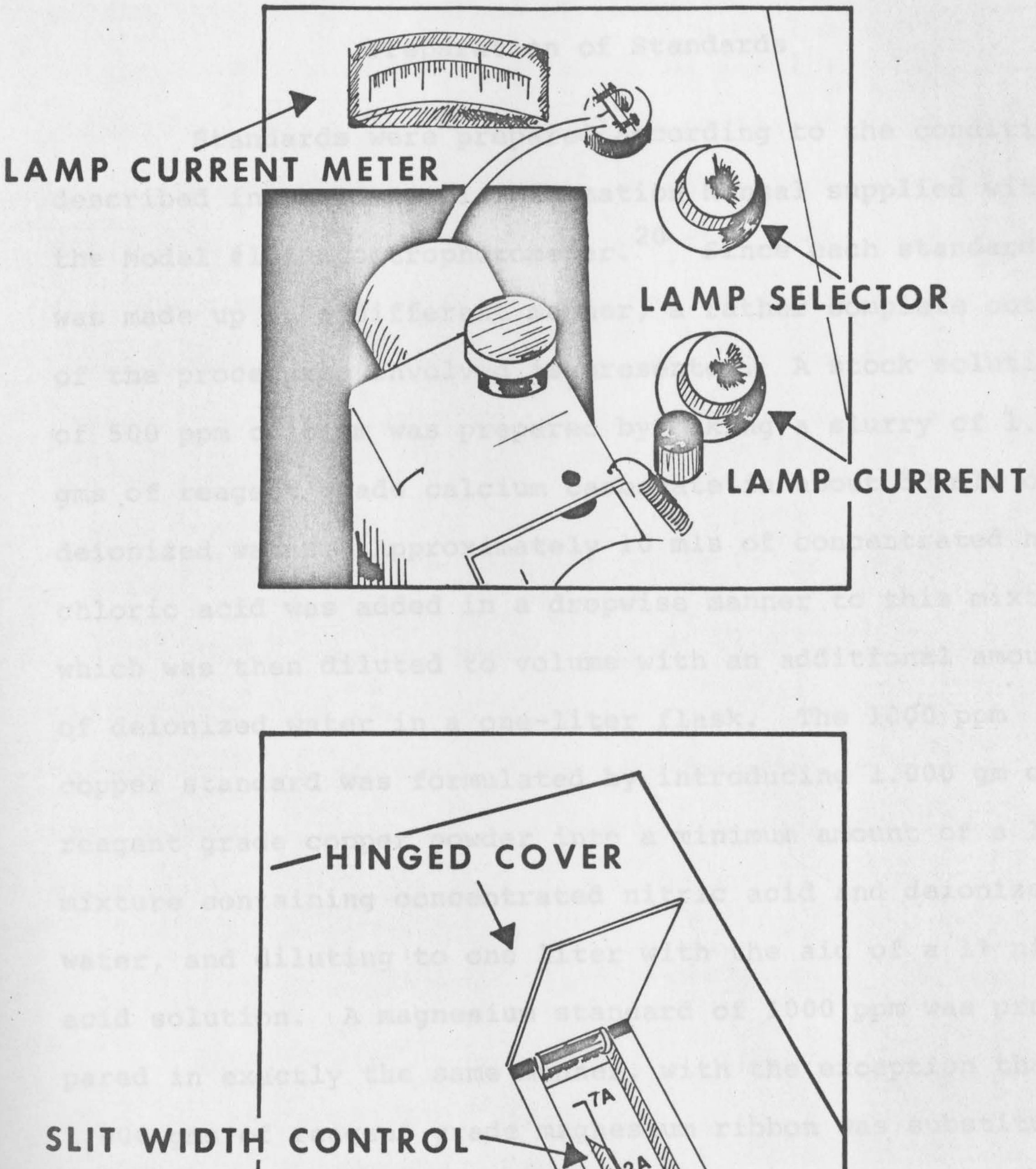
analyzing Mahoning River water samples by AA methods. As outlined in the diagram, the main controls are located to the left or right of the instrument cabinet's face, with the special four-inch flat burner head occupying the central position. In Figure 6 are two additional systems associated with the operation of the spectrophotometer, the one above being utilized with the various single-element cathode lamps from which the characteristic radiations emanate, and the one below functioning during the selection of the slit width for the monochromatic spectral lines after their production via a Littrow grating. More details about the operation of these controls will be presented in a later section concerned with sample analyses.

As previously mentioned, five single-element cathode lamps (Ca, Cu, Mg, Pb, and Zn) were available for use with this spectrophotometer. An acetylene-air mixture, the fuel-oxidant system selected for the analyses, was capable of being altered so that either an oxidizing (lean and blue) or reducing (rich and yellow) flame could be produced.[20] Some other features of this single-beam instrument that helped to facilitate the experimentation included a chamber-type burner with adjustable mount and gas controls, an electronically modulated source, digital readout in absorbance or concentration values, damping, integration, automatic zero, scale expansion, and electronic flame ignition.[9]

One negative aspect of the spectrophotometer is the calibration of its course wavelength control in arbitrary units, with the actual value for the element being obtained

Figure 6 MODEL # 107

CATHODE LAMP AND SLIT WIDTH CONTROLS



SLIT WIDTH CONTROL COMPARTMENT

by comparing the instrumental number to those from a graph of dial reading vs. wavelength provided with the instruction manual.[9]

Preparation of Standards

Standards were prepared according to the conditions described in the General Information Manual supplied with the Model #107 Spectrophotometer.[20] Since each standard was made up in a different manner, a rather complete outline of the procedures involved is presented. A stock solution of 500 ppm calcium was prepared by making a slurry of 1.249 gms of reagent grade calcium carbonate in about 50 mls of deionized water. Approximately 10 mls of concentrated hydrochloric acid was added in a dropwise manner to this mixture, which was then diluted to volume with an additional amount of deionized water in a one-liter flask. The 1000 ppm copper standard was formulated by introducing 1.000 gm of reagent grade copper powder into a minimum amount of a 1:1 mixture containing concentrated nitric acid and deionized water, and diluting to one liter with the aid of a 1% nitric acid solution. A magnesium standard of 1000 ppm was prepared in exactly the same manner, with the exception that 1.000 gms of reagent grade magnesium ribbon was substituted for the equivalent amount of copper. A 1000 ppm lead standard was made up by dissolving 1.598 gms of reagent grade lead nitrate in one liter of a 1% nitric acid solution. The zinc standard of 500 ppm concentration was prepared according to the same procedure as applied to copper and magnesium, but using only 0.500 gm of reagent grade zinc dust in place of the other metals.

To check the ranges of linearity for the operation of the instrument, a series of dilutions (listed in Table 4) of the above standards were run. The resulting calibration curves obtained from the respective series of diluted standards are depicted in Figures 7 to 11. Since the instrument was set to give concentrations directly, these graphs illustrate the relative strengths, as determined by the spectrophotometer vs. the actual strengths of the solutions, prepared via the pipetting and dilution of the more concentrated standards.

Collection and Preparation of Water Samples

Water samples used for atomic absorption experimentation were from the same collections made for neutron activation analysis studies. They were prepared in exactly the same manner as those for the previously described NAA determinations.

Analysis of Water Samples

After their preparation, the water samples were analyzed via the Model #107 Atomic Absorption Spectrophotometer in the following fashion. First, a thirty minute warm-up period was allowed for the proper functioning of the instrument's electronics. This was then followed by the installation of one of the five available single-element cathode

TABLE 4

STANDARD DILUTION SERIES FOR ESTABLISHING ELEMENTAL CALIBRATION CURVES IN ATOMIC ABSORPTION ANALYSIS OF WATER SAMPLES

Calcium Concentrations:	0.5 ppm, 1.0 ppm, 5.0 ppm, and 10.0 ppm
Copper Concentrations:	0.01 ppm, 0.1 ppm, 0.5 ppm, 1.0 ppm, 5.0 ppm, and 10.0 ppm
Magnesium Concentrations:	0.1 ppm, 0.25 ppm, 0.5 ppm, 0.667 ppm, and 1.0 ppm
Lead Concentrations:	0.47 ppm, 0.94 ppm, 1.88 ppm, 3,75 ppm, 7.50 ppm, and 15.00 ppm
Zinc Concentrations;	0.05 ppm, 0.10 ppm, 0.50 ppm, 1.00 ppm, and 1.80 ppm

Figure 7 CALCIUM CALIBRATION CURVE USED FOR ATOMIC ABSORPTION ANALYSES

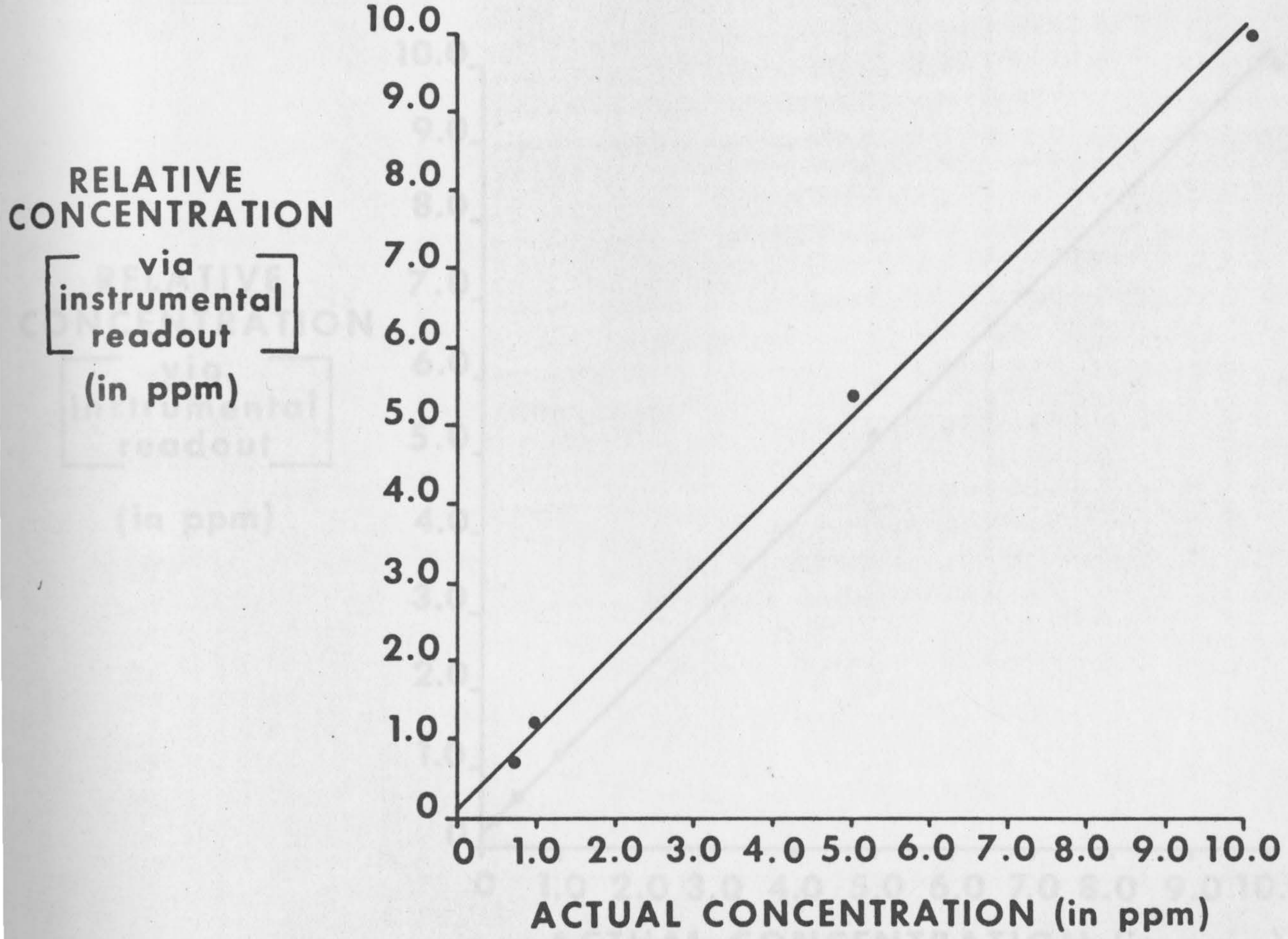


Figure 8 COPPER CALIBRATION CURVE USED FOR ATOMIC ABSORPTION ANALYSES

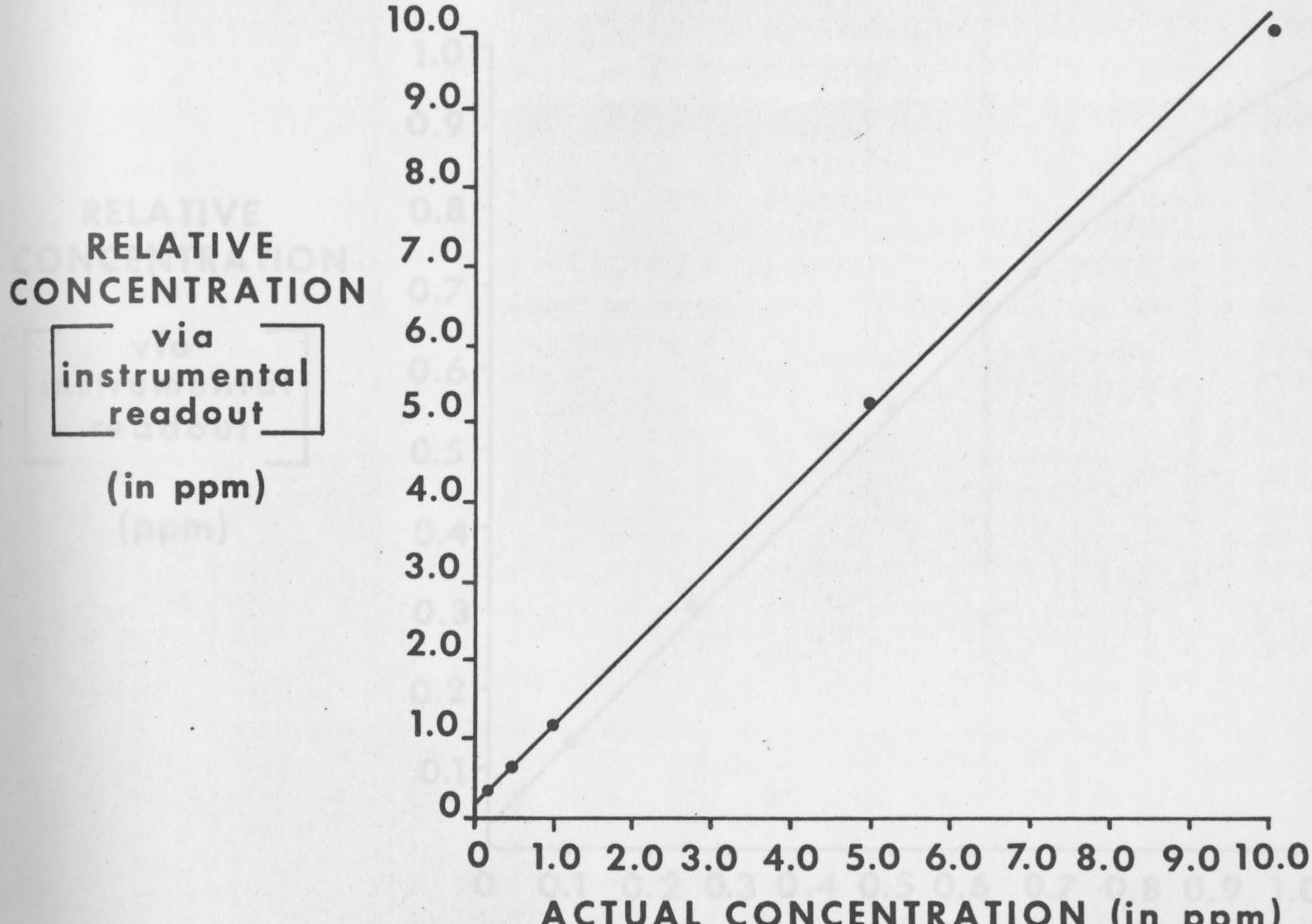


Figure 9

MAGNESIUM CALIBRATION CURVE
USED FOR ATOMIC ABSORPTION ANALYSES

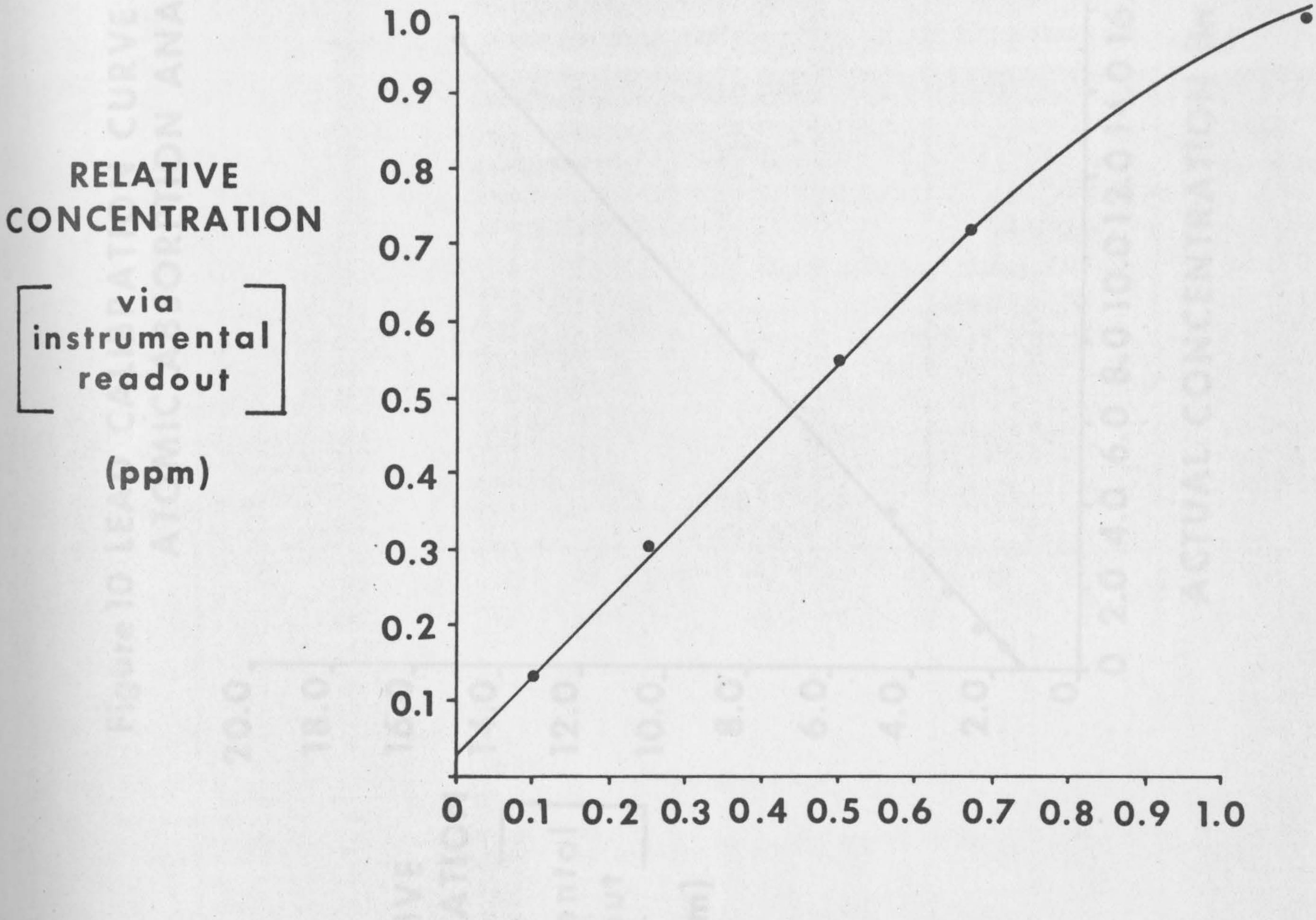


Figure 10 LEAD CALIBRATION CURVE USED FOR ATOMIC ABSORPTION ANALYSES

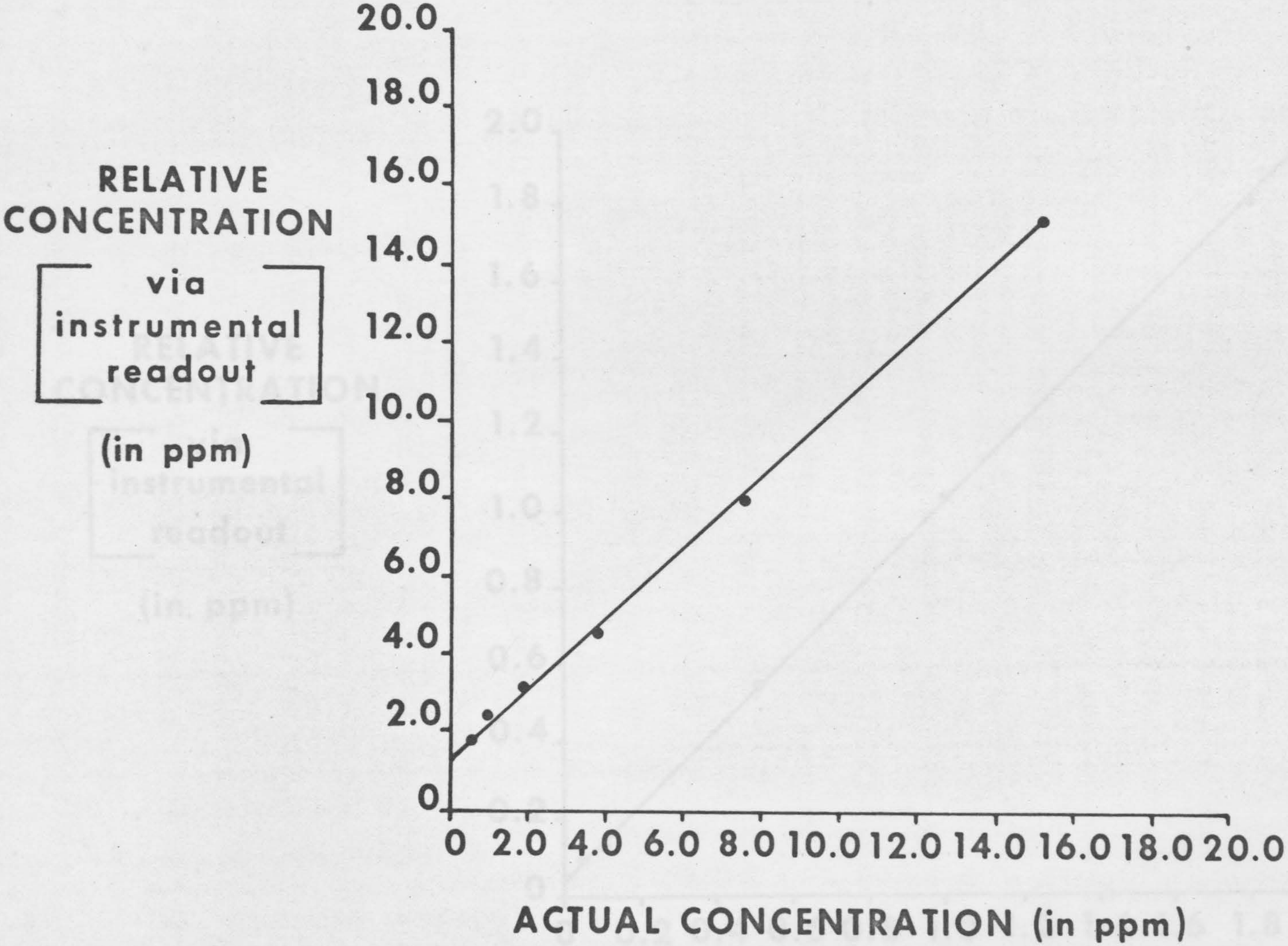
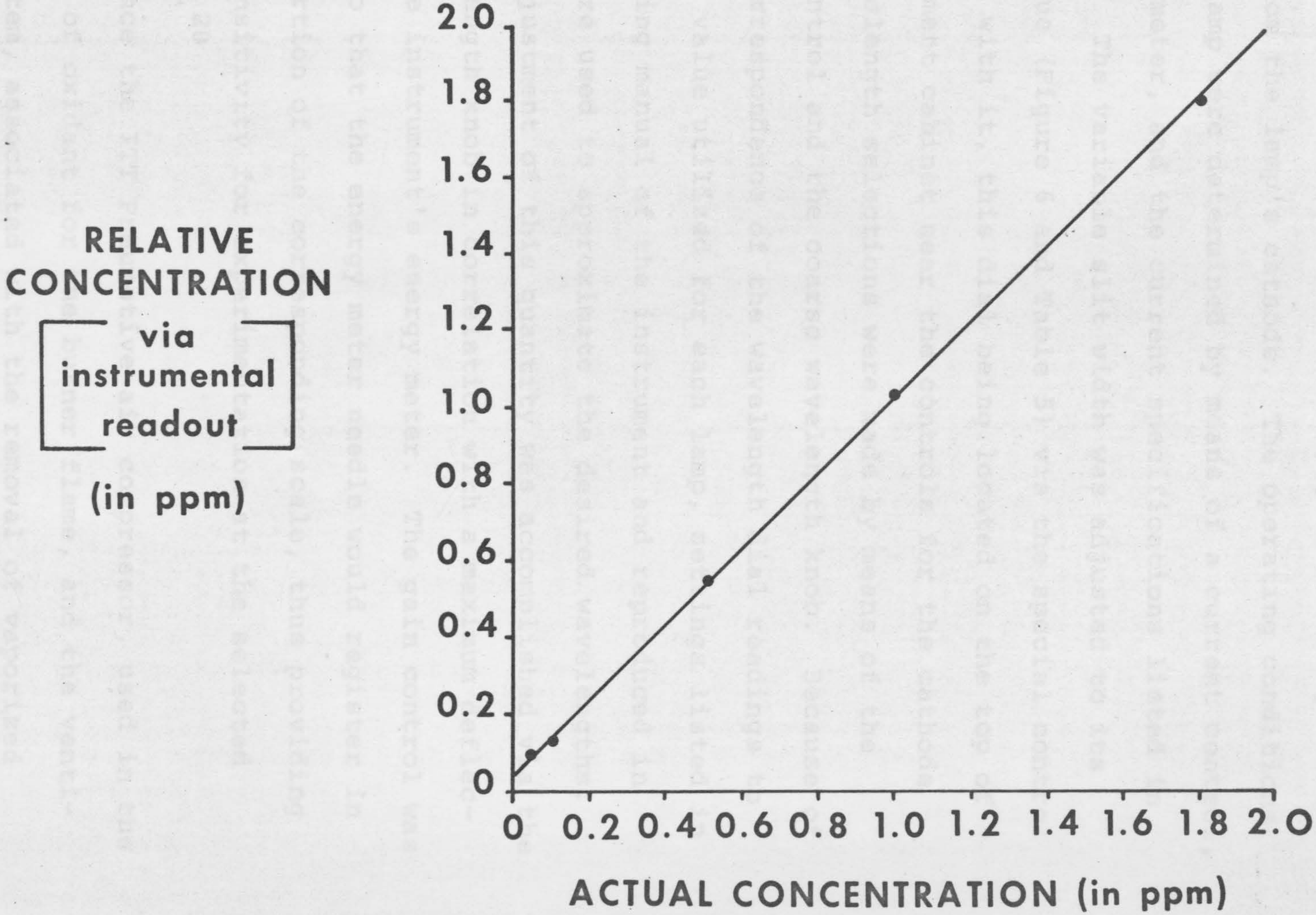


Figure 11 ZINC CALIBRATION CURVE USED FOR ATOMIC ABSORPTION ANALYSES



lamps into a special compartment (see Figure 6). Once it was aligned properly, the selector switch was utilized to find the position at which a luminous glow-discharge would emanate from the lamp's cathode. The operating conditions for each lamp were determined by means of a current control, a current meter, and the current specifications listed in Table 5.[20] The variable slit width was adjusted to its proper value (Figure 6 and Table 5) via the special control associated with it, this dial being located on the top of the instrument cabinet near the controls for the cathode lamp. Wavelength selections were made by means of the damping control and the coarse wavelength knob. Because of the non-correspondence of the wavelength dial readings to the actual value utilized for each lamp, settings listed in the operating manual of the instrument and reproduced in Table 5 were used to approximate the desired wavelengths. Further adjustment of this quantity was accomplished via the fine wavelength knob in correlation with a maximum deflection of the instrument's energy meter. The gain control was adjusted so that the energy meter needle would register in the red portion of the corresponding scale, thus providing maximum sensitivity for experimentation at the selected wavelength.[20]

Since the ITT Pneumotive air compressor, used in the production of oxidant for the burner flame, and the ventilating system, associated with the removal of vaporized components from the flame's vicinity, were connected to

TABLE 5

OPERATING SPECIFICATIONS FOR THE AIR-ACETYLENE FLAME AND SINGLE-ELEMENT CATHODE LAMPS OF THE MODEL # 107 AA SPECTROPHOTOMETER

Type of single-element cathode lamp	Lamp current operating ranges (in milliamperes)	Slit widths (in angstroms)	Wave length dial setting	Actual wave length (in angstroms)	Standard Concentrations used for the analysis of unknown water samples (in ppm)
Calcium (Ca)	5 to 10 mA	7Å	459	4226.7 Å	5.0 ppm
Copper (Cu)	6 to 10 mA	7Å	280	3247.5 Å	5.0 ppm
Magnesium (Mg)	4 to 5 mA	7Å	210	2852.1 Å	0.5 ppm
Lead (Pb)	4 to 5 mA	7Å	206	2833.1 Å	10.0 ppm
Zinc (Zn)	8 to 9 mA	7Å	084	2138.6 Å	0.5 ppm

Type of single-element cathode lamp	Type of Flame Produced	Fuel Flow Control Readings	Oxidant Flow Control Readings
Calcium (Ca)	slightly yellow (rich and reducing)	14.00	14.05
Copper (Cu)	blue (lean and oxidizing)	14.00	12.50
Magnesium (Mg)	blue (lean and oxidizing)	14.00	12.50
Lead (Pb)	blue (lean and oxidizing)	14.00	12.50
Zinc (Zn)	blue (lean and oxidizing)	14.00	12.50

separate electrical circuits, they were placed into operation at this time. The gas cylinder containing acetylene was opened and the fuel pressure meter was set to about 8 lbs/in^2. Appropriate selections (as given in Table 5) were made with the fuel and oxidant flow controls for each set of elemental conditions. The oxidant selector switch was set to the "air" position, the fuel control of the spectrophotometer was opened, and the flame was ignited electronically.[20]

Calibration of the instrument for direct concentration readout was then facilitated. Making sure the mode switch was in the "ABS" (absorbance) position, the expansion control was turned completely clockwise, and the damping selector was set to the "INT 10" position. The selection of this setting, which allows for a ten-second time-averaged integration of the instrumental readout before it is displayed, was made to reduce the amount of instrumental "noise" in the analyses. A cleaned weighing bottle was then filled with deionized water, which served as a blank, and used along with the zero control in order to null the display.[20] Once this was done, standards of specific concentrations (listed in Table 5) were aspirated, and, with a combination of the expansion control and the unlock button, the instrumental readout was adjusted to read the values of those concentrations. Then the water samples were run, with a series of ten concentration readings being taken for each sample. The instrument was rezeroed with deionized water following every set of ten readings. These readings were averaged for every water sample and are tabulated in the following chapter. In the cases of calcium and magnesium, dilution of all the samples (with the exception of Sample #3) to $\frac{1}{100}$ their original values had to be undertaken because of the high concentrations of these elements. Sample #3 was diluted 1:500 with deionized water due to the extreme elevation of the aforementioned metals.

There are several interferences associated with this instrument and AA spectrophotometry, in general, which are related primarily to the calcium and magnesium analyses. Silicon, aluminum, phosphate, and sulfate depress the concentration readings for calcium, while the first two elements listed have a similar effect with magnesium.[20] The addition of specific organic reagents, which were thought to be found in polluted river systems, was conducted with a calcium and a magnesium standard to see what role they played as interfering agents. The results of these tests, as well as the reagents used, are presented in Table 6.

Wet Chemical Analysis

Apparatus

The apparatus used for wet analysis experimentation were relatively simple in nature. They consisted, in part, of what is commonly termed a "visual titration assembly,"[11] made up of a Bausch and Lomb variable-intensity lamp, a 50 ml Kimax graduated buret, a Sargent magnetic stirrer (including a Teflon-coated metallic mixing bar), and a 100 ml

TABLE 6

EFFECTS OF ORGANIC REAGENTS ON ATOMIC ABSORPTION CONCENTRATION VALUES OF CALCIUM AND MAGNESIUM STANDARDS

Type of Standard Utilized	Actual Concentration Values of Standards	Instrumental Display of Standard Concentrations			
		Without Organic Reagents	With Phenol*	With Sodium Acetate*	With Acetic Acid*
Calcium (Ca)	0.5 ppm	1.01 ± .01 ppm	1.27 ± .01 ppm	Not Performed	Not Performed
Magnesium (Mg)	0.5 ppm	0.573± .010 ppm	0.642± .003 ppm	0.788 ± .038 ppm	0.763 ± .029 ppm

*The addition of the organic reagents varied between 0.5 gms (in the case of phenol) and 1.0 gm (in the cases of sodium acetate and acetic acid) per 50 mls of each standard.

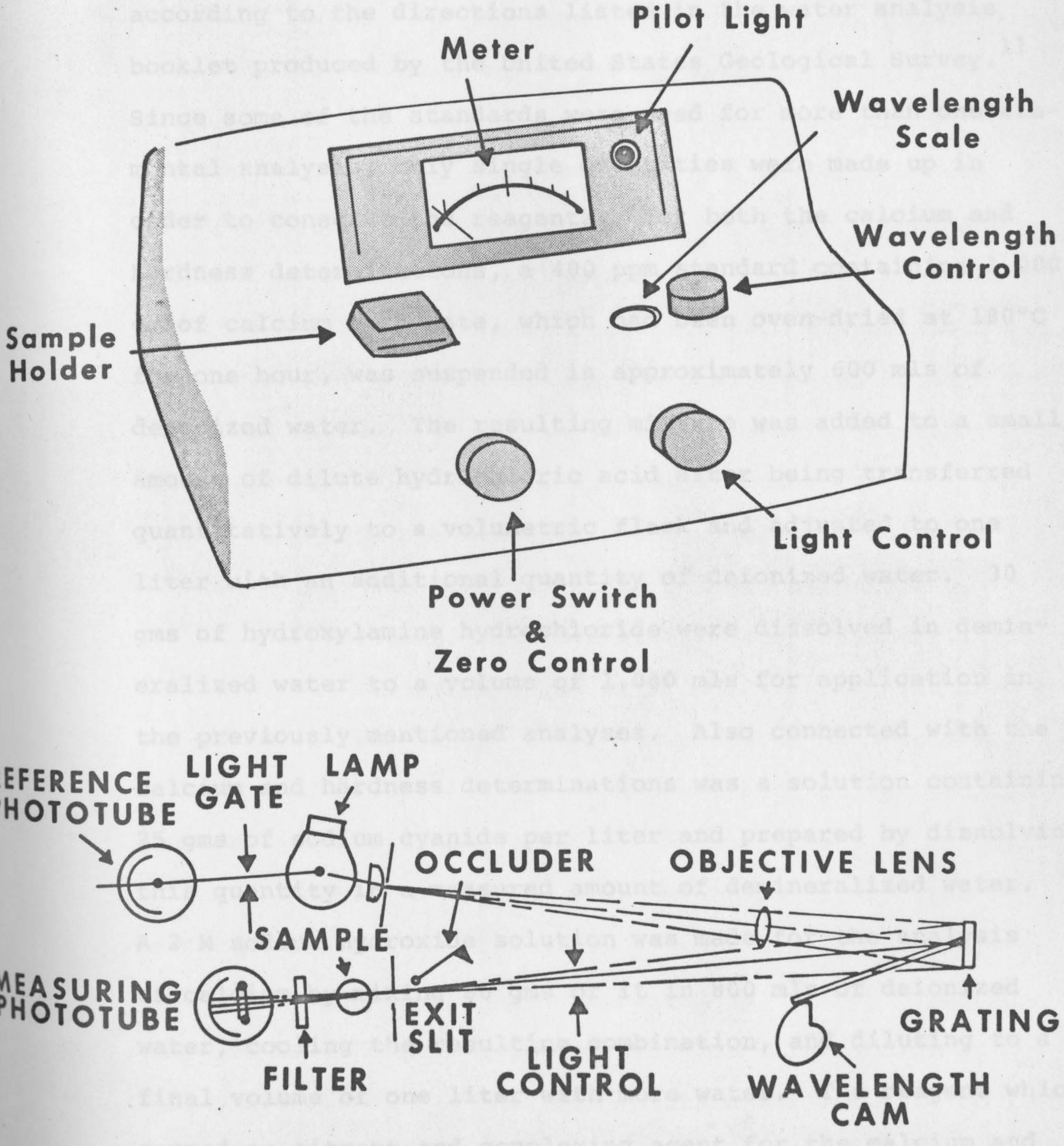
Kimax or Pyrex beaker, and were used exclusively for the calcium and hardness determinations. The latter piece of equipment was replaced by a 15 cm porcelain evaporating dish for the chloride ion analyses. As mentioned previously, magnesium concentrations in the Mahoning River water samples were calculated on the basis of differences between results obtained from the total hardness and calcium determinations, thus eliminating the need for actual experimentation with this element. However, since the iron determinations required the measurement of slight changes in the shades of a series of standards and solutions rather than the visual observation of a sharp color change, a spectrophotometer was utilized for this element.

A transistorized version of the noted Bausch and Lomb Spectronic 20 spectrophotometer (illustrated in Figure 12) was used in the iron analyses. Since the specific wavelength of interest belonged to the visible portion of the spectrum (520 nanometers), a blue phototube was installed in the instrument. Special cuvettes provided with the Spectronic 20 contained the samples and standards during the measurement of absorbance values. More will be said about the functioning of the spectrophotometer in the section on sample analyses.

In addition to the above, five automatic dilutors, with ranges from 0 to 5 mls and 0 to 10 mls, were used during the examination of the aforementioned elements by wet chemical methods, particularly in the case of iron. This facilitated the selection of replicate amounts of a specific

Figure 12

INSTRUMENTAL AND BLOCK DIAGRAMS OF THE SPECTRONIC - 20 SPECTROPHOTOMETER



reagent for a series of water samples or standards and in decreasing the length of time required for the analyses.

Preparation of Standards and Other Analytical Reagents

Standards for wet chemical analyses were prepared according to the directions listed in the water analysis booklet produced by the United States Geological Survey.[11] Since some of the standards were used for more than one elemental analysis, only single quantities were made up in order to conserve the reagents. For both the calcium and hardness determinations, a 400 ppm standard containing 1.000 gm of calcium carbonate, which had been oven-dried at 180°C for one hour, was suspended in approximately 600 mls of deionized water. The resulting mixture was added to a small amount of dilute hydrochloric acid after being transferred quantitatively to a volumetric flask and adjusted to one liter with an additional quantity of deionized water. 30 gms of hydroxylamine hydrochloride were dissolved in demineralized water to a volume of 1,000 mls for application in the previously mentioned analyses. Also connected with the calcium and hardness determinations was a solution containing 25 gms of sodium cyanide per liter and prepared by dissolving this quantity in a measured amount of demineralized water. A 2 M sodium hydroxide solution was made for the analysis of calcium by mixing 80 gms of it in 800 mls of deionized water, cooling the resulting combination, and diluting to a final volume of one liter with more water. The reagent which served as titrant and complexing agent for the calcium and magnesium determinations was sodium ethylenediaminetetraacetate. Solutions of this compound were prepared by drying 10 to 20 gms of it overnight in a desiccator containing concentrated sulfuric acid. Once dried, 4.65 gms were dissolved in a liter of deionized water for use in the calcium analyses, while 3.72 gms were added to the same quantity of water for determining the total hardness. Commercially-prepared reagent grade murexide indicator was used in connection with the calcium portion of the analysis by wet methods, while a solution of Eriochrome Black T indicator, prepared by dissolving 0.40 gms of the crystals in 100 mls of water and diluting this to a liter with 95% ethanol, was applied to the hardness determinations. Reagent grade potassium ferrocyanide crystals and concentrated ammonium hydroxide were also used in the latter case.

The 1000 ppm standard prepared for the chloride ion determinations consisted of 1.648 gms of reagent grade sodium chloride dissolved to a total volume of one liter with demineralized water. Two silver standards were also used for these analyses. The first was prepared by dissolving 23.96 gms of silver nitrate, which had been pulverized via a mortar and pestle and dried for approximately 30 minutes in a 110°C oven, to 950 mls with deionized water. The resulting mixture was stored in a brown bottle in order to retard decomposition and was labelled as "Silver Standard Solution I." "Silver Standard Solution II" was made up by taking 100 mls of the previous solution and diluting to 1000 mls with deionized water, after which it was also stored in a brown bottle until use. In addition to these reagents, an indicator solution was prepared by dissolving 5 gms of potassium chromate in 100 mls of deionized water. A small volume of "Silver Standard Solution II" was added to it until a red precipitate of silver chromate began to form. The solution was left in contact with the precipitate overnight and was purified by gravity filtration on the following day. During this process, the color of the indicator changed from orange-yellow to yellow-green.

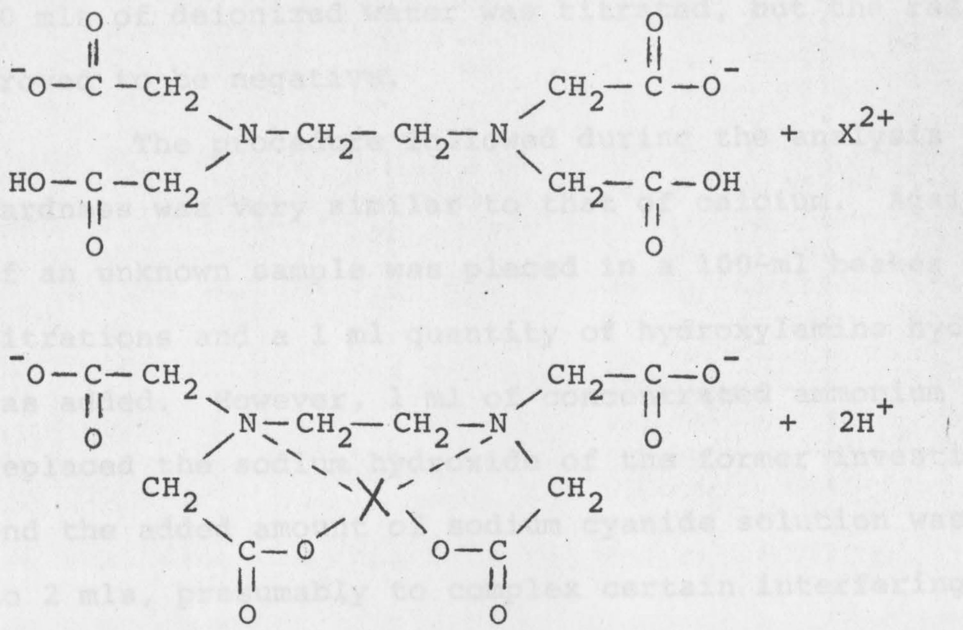
Five reagents were made up for the iron analyses. First, a 500 ml solution containing 1.0 gm of 2,2'-bipyridine in demineralized water was used for the complexation of iron in the aqueous samples and standards. During its preparation, the bipyridine crystals dissolved with great difficulty, but after standing at room temperature (ca. 25°C) for several days, solution was complete. A second hydroxylamine-hydrochloride solution was developed specifically for the iron analyses. It contained 100 gms of the compound dissolved in a minimal amount of demineralized water. 40 mls of concentrated hydrochloric acid and 1 gm of reagent grade beryllium sulfate dihydrate were respectively added to this solution. The resulting mixture was then diluted to one liter total volume. Two standards, one having a 400 ppm and the other a 4 ppm iron concentration, were formulated as follows. The stronger of the two (known as "Iron Standard Solution I") was prepared by weighing out 0.400 gm of reagent grade iron wire, which had been cleaned with dilute hydrochloric acid, rinsed with deionized water, and oven-dried, and dissolving it in a minimum amount of reagent grade hydrochloric acid. Dilution to 1000 ml with deionized water completed the preparation of this standard. "Iron Standard Solution II" was made up by taking 10 mls of the original standard and diluting to one liter with demineralized water. Finally, a nearly-saturated sodium acetate solution containing 350 gms of the compound per liter of solution was prepared with the aid of deionized water for use during the iron analyses of the Mahoning River water samples.

Collection and Preparation of Water Samples

Water samples used for wet chemical experimentation were from the same collections made for neutron activation and atomic absorption studies. They were prepared in exactly the same manner as those for the previously descrived NAA determinations.

Analysis of Water Samples

The water samples and standards were analyzed by a variety of wet chemical methods which will now be discussed in detail. As was alluded to earlier, calcium and total hardness, the latter due primarily to magnesium and calcium ions in the samples, were determined by complexometric titrations involving disodium ethylenediaminetetraacetate (Na_2EDTA) according to the following reaction:[11]



(where X^{2+} = Ca^{2+} or Mg^{2+})

(12)

After the visual titration assembly was set up for the calcium analyses, the following procedure was undertaken. One milliliter each of the previously mentioned hydroxylamine hydrochloride, sodium hydroxide, and sodium cyanide solutions were added to a 100 ml titration beaker containing 10 mls of an unknown water sample. About 0.05 gm of the powdered murexide indicator was added, imparting a burgundy shade to the mixture. The 50-ml buret was filled with the respective EDTA solution, and the titration proceeded with constant stirring until the color of the resulting liquid changed to a deep orchid. During this procedure tiny droplets of solution adhering to the inside edge of the beaker were washed into the bulk of the mixture with deionized water. The above titration was repeated with an individual 10 ml sample from each unknown. In order to determine the concentration of the EDTA titrant, replicate trials involving 25 ml samples of the stock calcium standard were performed. A blank of

50 mls of deionized water was titrated, but the results proved to be negative.

The procedure followed during the analysis of water hardness was very similar to that of calcium. Again, 10 mls of an unknown sample was placed in a 100-ml beaker used for titrations and a 1 ml quantity of hydroxylamine hydrochloride was added. However, 1 ml of concentrated ammonium hydroxide replaced the sodium hydroxide of the former investigation, and the added amount of sodium cyanide solution was increased to 2 mls, presumably to complex certain interfering metal ions. Several small crystals of potassium ferrocyanide trihydrate were added to reduce interferences from manganese. Exactly 2.0 mls of the Eriochrome Black T indicator were introduced to the mixture after a five minute waiting period, and the well-mixed solution was titrated with the respective EDTA solution until the purple color of the indicator changed to a clear blue.[11] Again, two 25-ml samples of the stock calcium standard were titrated in order to determine the exact concentration of the EDTA titrant used. Because of the nature of this investigation, no blank correction was necessary.

Since magnesium was determined by a difference method involving the results of the above two analyses and the assumption that minor interferences such as strontium, barium, manganese, iron, and aluminum are negligible, no experimental method was necessary for this element.

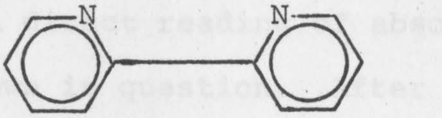
Chlorine was examined as the chloride ion via the Mohr method. This technique involves a relationship between the chloride, silver, and chromate species whereby, at the equivalence point of the first two ions (via the precipitation of insoluble white silver chloride), any excess of silver ions initiates the formation of a reddish precipitate of silver chromate, as the following equations illustrate:

$$Ag^{+} + Cl^{-} \longrightarrow AgCl\downarrow \qquad (13)$$

$$2Ag^{+} + CrO_4^{2-} \longrightarrow Ag_2CrO_4\downarrow \qquad (14)$$

In beginning the determination for chloride ion, 10 mls of an unknown water sample were placed in a 15 cm porcelain evaoprating dish. Ten drops of the potassium chromate indicator solution were then added. While stirring the yellow-tinted mixture constantly, titration with the "Silver Standard Solution II" was initiated. During this process, the silver chloride precipitate imparted a cloudy-white color to the solution after which, with the addition of more titrant, a salmon shade appeared, due to the presence of silver chromate. When the latter color remained for a period of approximately 15 seconds before fading, the titration was terminated. Two 10-ml volumes of the sodium chloride standard were then analyzed in a like manner to check the concentration of the silver solution used. A blank of 50 mls deionized water was also run via the modified visual titration assembly previously described.[11]

The final series of wet analysis studies were performed in order to find the quantity of iron present in the Mahoning River water samples. It consisted of a reaction between the ferrous ion and the complexing agent, 2,2'-bipyridine, which has the following structure:



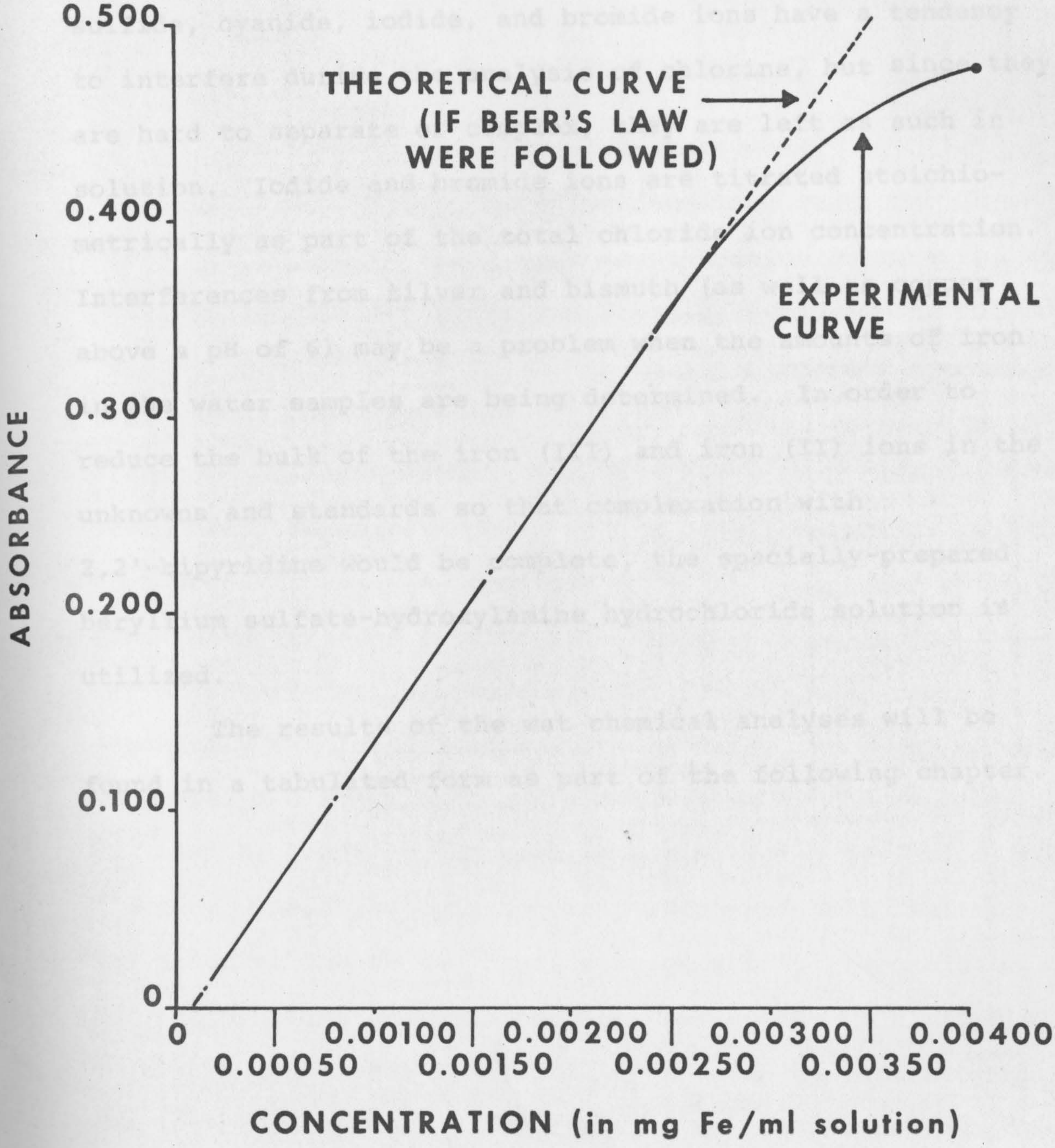
As noted earlier, these determinations required the use of a Bausch and Lomb Spectronic 20 spectrophotometer set at a wavelength of 520 nanometers. In beginning the experiment, the instrument was allowed a warm-up period of approximately twenty to thirty minutes before the analyses were begun. Five milliliters of an unknown water sample were pipetted into a 100-ml beaker to which 20 mls of demineralized water had been added. Into this quantity were mixed, respectively, 1.0 ml of the bipyridine solution and 2.0 mls of the specially prepared hydroxylamine hydrochloride-beryllium sulfate solution. The mixture was allowed to stand for exactly thirty minutes, after which 2.0 mls of the sodium acetate solution were introduced. A previously made blank, prepared by mixing the same amounts of the above solutions with 25 mls of deionized water, was used in connection with the unknown water samples in order to mask any interferences in the absorbance readings contributed by the added reagents.

Once the instrument was operable, the wavelength control (see Figure 12) was adjusted to 520 nanometers. The zero control, which also served as the power switch, was rotated (with the cover to the cuvette compartment closed) until the percent transmittance became nulled. This was followed by the introduction of the cuvette containing the blank solution into the spectrophotometer. The light control was adjusted to 100% transmittance, after which the blank cuvette was replaced in its holder by one containing an unknown water sample. A direct reading of absorbance was then obtained for the unknown in question. After the fourteen sample absorbances were recorded, a series of iron standards (prepared from the stock "Iron Standard Solutions I and II") of 4, 20, 40, 60, 100, and 400 ppm concentrations were run in the above manner to determine a linear working range for the iron-bipyridine complex from a Beer's Law plot of absorbance vs. concentration. The absorbance values of the samples were converted to concentration readings by means of the resulting standard curve (Figure 13).

As is true for most analyses, wet chemical methods are applicable only under a specified set of conditions. For example, the complexometric titrations involving the use of EDTA in the determination of calcium and water hardness may not work with certain polluted waters that contain excessive amounts of heavy metals.[11] The Mohr method for the analysis of the chloride content of the unknowns gives excellent results for natural waters having 10 ppm to 2000 ppm concentrations of the ion. Likewise, the iron-bipyridine technique seems best suited for application to known or unknown solutions containing between 0.05 and 4 ppm of iron.[11]

There are many interferences which would have a sizeable effect on the results of the analyses if certain reagents that preferentially complex or reduce these species were not added. Thus, metals such as iron, manganese,

Figure 13 IRON CALIBRATION CURVE USED FOR WET CHEMICAL ANALYSES



copper, zinc, lead, cobalt, nickel, barium, and strontium interfere with the calcium and hardness determinations. However, their effects are minimized by the addition of sodium cyanide and hydroxylamine hydrochloride. Phosphate, sulfide, cyanide, iodide, and bromide ions have a tendency to interfere during the analysis of chlorine, but since they are hard to separate or complex, they are left as such in solution. Iodide and bromide ions are titrated stoichiometrically as part of the total chloride ion concentration. Interferences from silver and bismuth (as well as copper above a pH of 6) may be a problem when the amounts of iron in the water samples are being determined. In order to reduce the bulk of the iron (III) and iron (II) ions in the unknowns and standards so that complexation with 2,2'-bipyridine would be complete, the specially-prepared beryllium sulfate-hydroxylamine hydrochloride solution is utilized.

The results of the wet chemical analyses will be found in a tabulated form as part of the following chapter.

CHAPTER IV

EXPERIMENTAL RESULTS

Water and Sediment Standards

The predominant elemental photopeaks, selected for the neutron activation investigations, and their corresponding areas are presented along with concentration data of the previously-described water and sediment standards in Table 7. Because of sizable contributions to the gamma-ray spectra from low-energy background radiation, occurring despite the effect of shielding from a two-inch thick lead container which surrounded the main portion of the Ge(Li) detector, peaks that were far removed from this spectral region and which had minor interferences from nearby gammas were utilized. The latter interferences were overcome, for the most part, by permitting the irradiated samples to decay for a period of 24 hours, and reevaluating the activities of the stabler radionuclides by counting the samples again, for a period of 20 minutes. These isotopic species, which had half-lives of the order of one or two days, were generally responsible for the problems encountered with peak areas. The effects mentioned above were substantially reduced by subtracting the interfering agent's contribution to the desired photopeak via a ratio of standard and unknown activities taken before and after the 24-hr. decay period.

TABLE 7

NEUTRON ACTIVATION ANALYSIS STANDARDS

Energy of Photopeak Used (in MeV)	Element	Water		Sediment	
		Area (as counts)	Concentration (in ppm)	Area (as counts)	Concentration (in ppm)
0.777	Br	1,315	100	38	100
0.845	Mn	28,733	10	87	1
1.01	Mg	540	500	40	50
1.04	Cu	2,519	200	39	20
1.37	Na	6,415	200	92	20
1.43	V	11,676	10	105	1
1.52	K	75	500	8	500
1.78	Al	297	10	584	1
2.16	Cl	3,064	200	20	20
3.09	Ca	182	500	5	50

Water and Sediment Samples

In order to depict more clearly the section of the river from which the water and sediment samples were obtained, an enlargement of the area presented previously (Figure 4) is shown in Figure 14. Following this, in Figure 15, is the type of gamma-ray spectrum (minus background) produced by a Ge(Li) detector and normally encountered in NAA work. Tables 8 to 21 list pertinent data for the NAA, AA, and wet determinations, including detectable elements and their concentrations in water and sediment samples obtained from the designated locations. In Tables 22 to 35 are illustrated variations in elemental concentrations as a function of the sample collection sites. These values are reproduced in the form of graphs in Figures 16 to 29 so as to highlight the significant changes occurring with the concentrations of elements in the Mahoning River between Lake Milton Reservoir and Niles, Ohio.

Uncertainties are listed with the results for NAA, AA, and wet analyses for iron. The errors for the last two cases were taken as standard deviations from the mean values, while for neutron activation analysis, the uncertainties were obtained on the basis of the following equation:[22]

$$\text{Error} = \left[\frac{\sqrt{A_u}^{\,2}}{tA_u} + \frac{\sqrt{A_s}^{\,2}}{tA_s} \right]^{1/2} W_s \qquad (15)$$

where,

A_u = activity of the unknown sample

Figure 14 ENLARGEMENT OF SAMPLE COLLECTION AREA

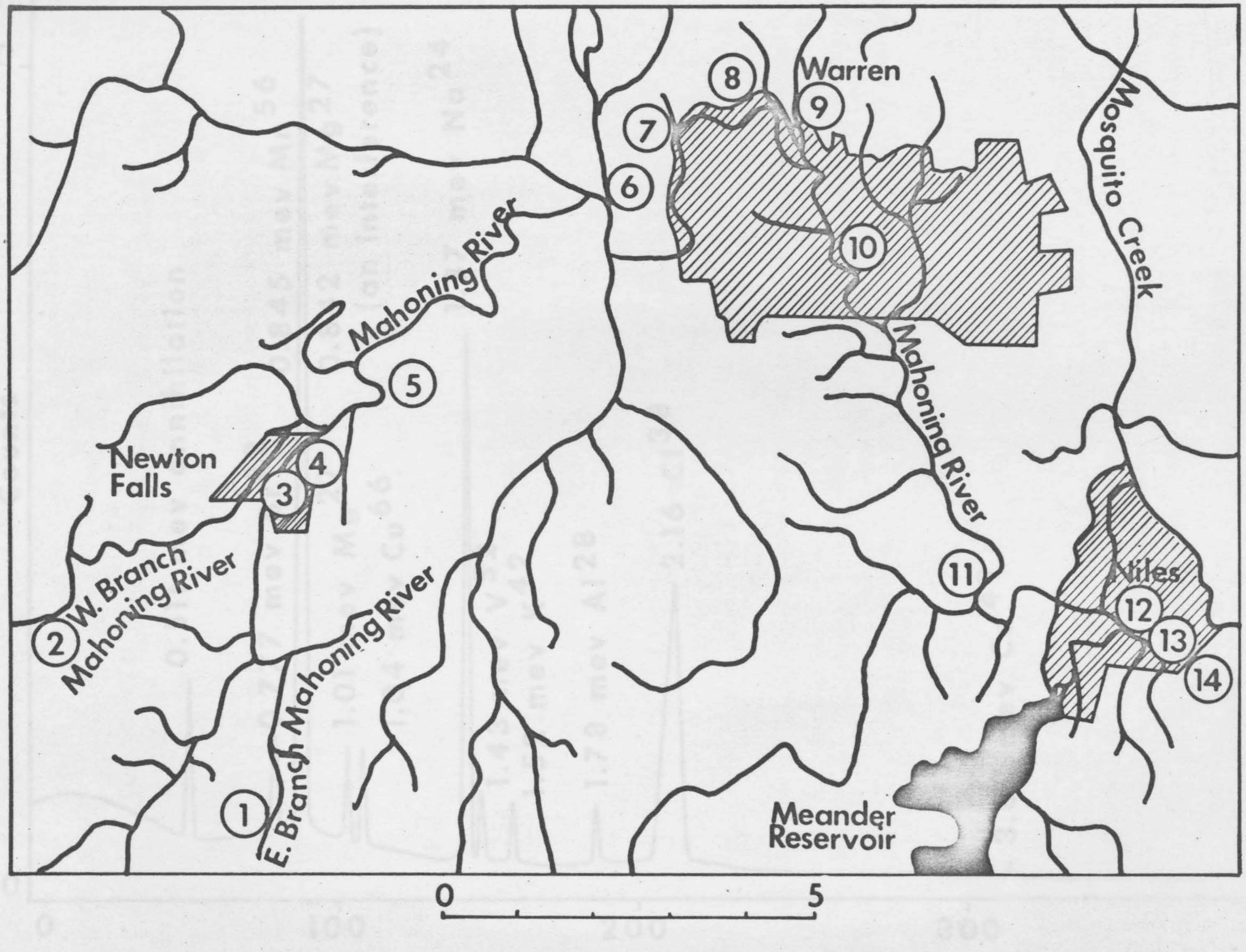


Figure 15 TYPICAL GAMMA - RAY SPECTRUM PRODUCED BY A Ge (Li) DETECTOR

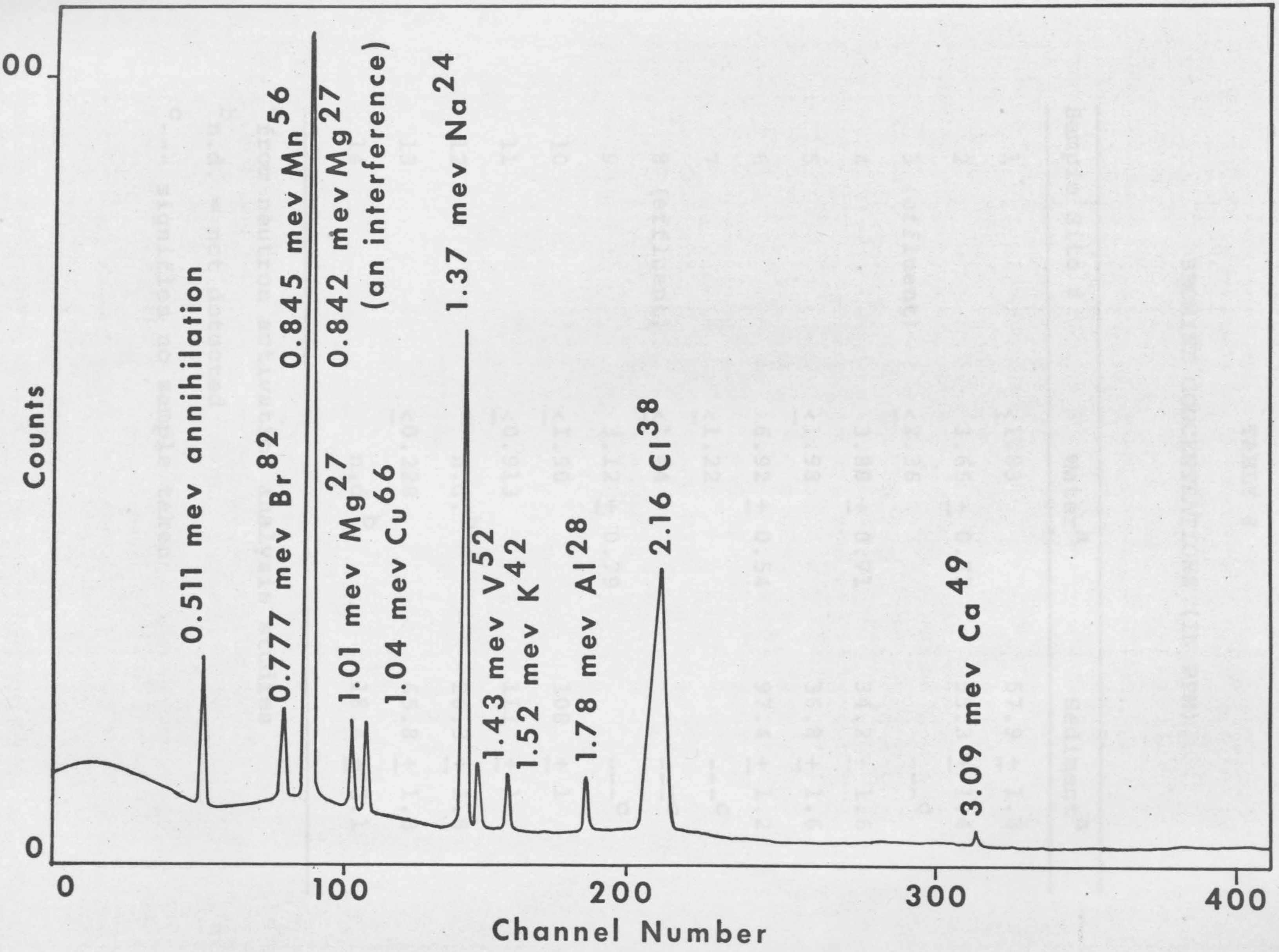


TABLE 8

BROMINE CONCENTRATIONS (IN PPM)

Sample Site #	Water[a]	Sediment[a]
1	≤1.83	57.9 ± 1.3
2	3.65 ± 0.73	55.3 ± 1.4
3 (effluent)	≤2.36	---[c]
4	3.88 ± 0.71	34.2 ± 1.6
5	≤1.98	36.8 ± 1.6
6	6.92 ± 0.54	97.4 ± 1.2
7	≤1.22	---[c]
8 (effluent)	≤1.44	---[c]
9	3.12 ± 0.79	---[c]
10	≤1.90	108 ± 1
11	≤0.913	111 ± 1
12	n.d.[b]	26.3 ± 1.8
13	≤0.228	65.8 ± 1.3
14	n.d.[b]	18.4 ± 2.1

---

[a] from neutron activation analysis studies

[b] n.d. = not detected

[c] --- signifies no sample taken

TABLE 9

MANGANESE CONCENTRATIONS (IN PPM)

Sample Site #	Water[a]	Sediment[a]
1	0.208 ± 0.021	8,086 ± 0
2	0.151 ± 0.024	4,543 ± 0
3 (effluent)	0.243 ± 0.019	---[b]
4	0.630 ± 0.012	3,090 ± 0
5	0.125 ± 0.026	1,472 ± 0
6	0.105 ± 0.029	254 ± 0
7	0.148 ± 0.024	---[b]
8 (effluent)	0.169 ± 0.023	---[b]
9	0.186 ± 0.022	---[b]
10	0.158 ± 0.024	3,048 ± 0
11	0.167 ± 0.023	2,624 ± 0
12	0.641 ± 0.012	1,417 ± 0
13	≤0.0954	1,690 ± 0
14	0.181 ± 0.022	1,559 ± 0

[a] from neutron activation analysis studies

[b] ---signifies no sample taken

TABLE 10

MAGNESIUM CONCENTRATIONS (IN PPM)

Sample Site #	Water[a]	Water[b]	Water[c]	Sediment[a]
1	63.0 ± 3.2	17.2 ± 1.1	143	434 ± 0
2	n.d.[d]	16.4 ± 0.2	100	916 ± 0
3 (effluent)	236 ± 2	303 ± 1	1746	---[e]
4	73.1 ± 3.0	31.2 ± 0.4	215	2,281 ± 0
5	63.9 ± 3.2	19.3 ± 0.4	130	1,070 ± 0
6	≤10.2	12.7 ± 0.5	96.3	1,070 ± 0
7	n.d.[d]	19.8 ± 0.1	127	---[e]
8 (effluent)	≤13.0	27.0 ± 0.4	121	---[e]
9	32.4 ± 4.4	18.4 ± 0.1	129	---[e]
10	n.d.[d]	34.2 ± 0.2	127	1,159 ± 0
11	108 ± 3	20.6 ± 0.2	130	1,569 ± 0
12	≤18.5	17.1 ± 0.2	120	818 ± 0
13	103 ± 3	18.6 ± 0.2	119	1,295 ± 0
14	38.9 ± 4.0	19.0 ± 0.2	124	1,315 ± 0

[a] from neutron activation analysis studies

[b] from atomic absorption analysis studies

[c] from wet analysis studies

[d] n.d. = not detected

[e] --- signifies no sample taken

TABLE 11

COPPER CONCENTRATIONS (IN PPM)

Sample Site #	Water[a]	Water[b]	Sediment[a]
1	$\leq$0.175	0.25 ± 0.05	n.d.[c]
2	$\leq$0.277	0.26 ± 0.04	n.d.[c]
3 (effluent)	n.d.[c]	0.54 ± 0.04	---[d]
4	$\leq$3.88	0.16 ± 0.01	85.1 ± 0.2
5	$\leq$3.94	0.08 ± 0.01	68.2 ± 0.2
6	$\leq$0.712	0.11 ± 0.01	33.3 ± 0.2
7	n.d.[c]	0.15 ± 0.02	---[d]
8 (effluent)	$\leq$3.96	0.25 ± 0.01	---[d]
9	$\leq$0.836	0.24 ± 0.03	---[d]
10	n.d.[c]	0.20 ± 0.02	n.d.[c]
11	$\leq$0.367	0.26 ± 0.03	n.d.[c]
12	n.d.[c]	0.43 ± 0.03	91.2 ± 0.2
13	n.d.[c]	0.34 ± 0.02	183 ± 0
14	n.d.[c]	0.25 ± 0.02	30.3 ± 0.2

[a] from neutron activation analysis studies

[b] from atomic absorption analysis studies

[c] n.d. = not detected

[d] --- signifies no sample taken

TABLE 12

SODIUM CONCENTRATIONS (IN PPM)

Sample Site #	Water[a]	Sediment[a]
1	18.7 ± 0.4	2,072 ± 0
2	20.8 ± 0.4	3,140 ± 0
3 (effluent)	186 ± 0	---[b]
4	29.3 ± 0.3	2,014 ± 0
5	18.8 ± 0.4	2,468 ± 0
6	15.9 ± 0.5	2,346 ± 0
7	18.6 ± 0.4	---[b]
8 (effluent)	20.6 ± 0.4	---[b]
9	18.0 ± 0.4	---[b]
10	19.1 ± 0.4	1,722 ± 0
11	23.2 ± 0.4	1,042 ± 0
12	18.0 ± 0.4	1,388 ± 0
13	19.4 ± 0.4	1,394 ± 0
14	21.5 ± 0.4	1,222 ± 0

---

[a] from neutron activation analysis studies

[b] --- signifies no sample taken

TABLE 13

VANADIUM CONCENTRATIONS (IN PPM)

Sample Site #	Water[a]	Sediment[a]
1	n.d.[b]	14.6 ± 0
2	≤0.00514	19.2 ± 0
3 (effluent)	n.d.[b]	---[c]
4	n.d.[b]	22.5 ± 0
5	≤0.0128	15.8 ± 0
6	n.d.[b]	20.5 ± 0
7	n.d.[b]	---[c]
8 (effluent)	≤0.00771	---[c]
9	n.d.[b]	---[c]
10	≤0.00343	22.4 ± 0
11	≤0.0154	24.4 ± 0
12	≤0.0291	33.5 ± 0
13	≤0.0146	35.0 ± 0
14	n.d.[b]	34.7 ± 0

[a] from neutron activation analysis studies

[b] n.d. = not detected

[c] ---signifies no sample taken

TABLE 14

POTASSIUM CONCENTRATIONS (IN PPM)

Sample Site #	Water[a]	Sediment[a]
1	n.d.[b]	1,938 ± 10
2	107 ± 7	2,813 ± 10
3 (effluent)	213 ± 5	---[c]
4	n.d.[b]	2,563 ± 10
5	80.0 ± 7.8	4,500 ± 9
6	53.3 ± 9.3	1,563 ± 10
7	66.7 ± 8.4	---[c]
8 (effluent)	53.3 ± 9.3	---[c]
9	100 ± 7	---[c]
10	n.d.[b]	4,000 ± 9
11	127 ± 6	5,938 ± 9
12	$\leq$33.3	5,563 ± 9
13	n.d.[b]	2,000 ± 10
14	73.3 ± 8.1	3,125 ± 10

[a] from neutron activation analysis studies

[b] n.d. = not detected

[c] --- signifies no sample taken

TABLE 15

ALUMINUM CONCENTRATIONS (IN PPM)

Sample Site #	Water[a]	Sediment[a]
1	n.d.[b]	93.6 ± 0
2	n.d.[b]	100 ± 0
3 (effluent)	1.14 ± 0.09	---[c]
4	n.d.[b]	92.4 ± 0
5	n.d.[b]	96.9 ± 0
6	n.d.[b]	160 ± 0
7	n.d.[b]	---[c]
8 (effluent)	≤0.404	---[c]
9	n.d.[b]	---[c]
10	n.d.[b]	127 ± 0
11	n.d.[b]	117 ± 0
12	n.d.[b]	130 ± 0
13	n.d.[b]	152 ± 0
14	n.d.[b]	147 ± 0

---

[a] from neutron activation analysis studies

[b] n.d. = not detected

[c] ---signifies no sample taken

TABLE 16

CHLORINE CONCENTRATIONS (IN PPM)

Sample Site #	Water[a]	Water[b]	Sediment[a]
1	21.0 ± 0.6	40.1	n.d.[c]
2	25.3 ± 0.5	41.3	n.d.[c]
3 (effluent)	183 ± 0	208	---[d]
4	39.2 ± 0.4	39.5	26.0 ± 0.3
5	25.1 ± 0.5	24.8	82.0 ± 0.2
6	19.5 ± 0.6	23.6	18.0 ± 0.3
7	22.6 ± 0.6	26.0	---[d]
8 (effluent)	25.5 ± 0.5	30.7	---[d]
9	24.6 ± 0.5	24.2	---[d]
10	23.3 ± 0.6	26.0	trace
11	29.3 ± 0.5	34.8	trace
12	25.4 ± 0.5	34.2	50.0 ± 0.3
13	29.8 ± 0.5	29.5	53.0 ± 0.3
14	31.4 ± 0.5	36.6	155 ± 0

[a] from neutron activation analysis data

[b] from wet analysis data

[c] n.d. = not detected

[d] --- signifies no sample taken

TABLE 17

CALCIUM CONCENTRATIONS (IN PPM)

Sample Site #	Water[a]	Water[b]	Water[c]	Sediment[a]
1	60.4 ± 5.6	70 ± 2	52.7	1,920 ± 1
2	44.0 ± 6.5	60 ± 1	37.8	160 ± 1
3 (effluent)	398 ± 3	430 ± 10	377	---[d]
4	49.4 ± 6.2	95 ± 1	71.6	6,330 ± 1
5	49.5 ± 6.2	89 ± 2	56.2	710 ± 1
6	≤24.7	85 ± 2	44.7	610 ± 1
7	33.0 ± 7.4	93 ± 2	47.2	---[d]
8 (effluent)	68.7 ± 5.3	106 ± 3	62.1	---[d]
9	60.4 ± 5.6	123 ± 3	50.2	---[d]
10	33.0 ± 7.4	143 ± 2	53.2	1,700 ± 1
11	≤8.24	102 ± 3	49.7	1,840 ± 1
12	38.5 ± 6.9	96 ± 1	43.2	2,570 ± 1
13	74.2 ± 5.1	90 ± 3	52.2	1,540 ± 1
14	60.4 ± 5.6	95 ± 2	56.7	5,980 ± 1

[a] from neutron activation analysis data

[b] from atomic absorption analysis data

[c] from wet analysis data

[d] ---signifies no sample taken

TABLE 18

LEAD CONCENTRATIONS (IN PPM)

Sample Site #	Water[a]
1	1.48 ± 0.08
2	0.91 ± 0.12
3 (effluent)	1.21 ± 0.14
4	1.37 ± 0.17
5	1.24 ± 0.14
6	1.32 ± 0.18
7	1.46 ± 0.11
8 (effluent)	1.36 ± 0.11
9	1.75 ± 0.08
10	1.83 ± 0.05
11	1.66 ± 0.03
12	2.19 ± 0.07
13	3.01 ± 0.21
14	2.37 ± 0.11

[a] from atomic absorption analysis data

TABLE 19

ZINC CONCENTRATIONS (IN PPM)

Sample Site #	Water[a]
1	0.131 ± 0.012
2	0.108 ± 0.018
3 (effluent)	0.237 ± 0.028
4	0.200 ± 0.020
5	0.156 ± 0.028
6	0.105 ± 0.007
7	0.181 ± 0.014
8 (effluent)	0.169 ± 0.006
9	0.211 ± 0.016
10	0.114 ± 0.008
11	0.291 ± 0.016
12	1.620 ± 0.026
13	0.246 ± 0.010
14	0.178 ± 0.016

---

[a] from atomic absorption analysis data

TABLE 20

IRON CONCENTRATIONS (IN PPM)

Sample Site #	Water[a]
1	0.26 + 0.02
2	0.26 ± 0.04
3 (effluent)	1.71 ± 0.01
4	0.62 ± 0.01
5	0.20 ± 0.04
6	0.25 ± 0.01
7	0.23 ± 0.01
8 (effluent)	0.81 ± 0.04
9	0.22 ± 0.04
10	0.29 ± 0.02
11	0.47 ± 0.01
12	2.98 ± 0.07
13	0.41 ± 0.01
14	0.49 ± 0[illegible]

[a] from wet analysis data

TABLE 21

TOTAL HARDNESS (IN PPM)

Sample Site #	Water[a]
1	196
2	138
3 (effluent)	2123
4	287
5	186
6	141
7	174
8 (effluent)	183
9	179
10	180
11	180
12	163
13	171
14	181

[a] from wet analysis data

*SITE #1** NEUTRON ACTIVATION ANALYSIS DATA TABLE 22

Energy of Photopeak Used (in MeV)	Elements Determined	Water Area (as counts)	Water Concentration (in ppm)	Sediment Area (as counts)	Sediment Concentration (in ppm)
0.777	Br	29	<1.83	22	57.9 ± 1.3
0.845	Mn	598	0.208 ± 0.021	703,456	8,086 ± 0
1.01	Mg	68	63.0 ± 3.2	347	434 ± 0
1.04	Cu	2	<0.175	——	n.d.[a]
1.37	Na	600	18.7 ± 0.4	1,036	2,072 ± 0
1.43	V	——	n.d.[a]	1,537	14.6 ± 0
1.52	K	——	n.d.[a]	31	1,938 ± 10
1.78	Al	——	n.d.[a]	54,657	93.6 ± 0
2.16	Cl	321	21.0 ± 0.6	——	n.d.[a]
3.09	Ca	22	60.4 ± 5.6	192	1,920 ± 1

ATOMIC ABSORPTION ANALYSIS DATA

Elements Determined	Water Concentration (in ppm)
Ca	70 ± 2
Cu	0.25 ± 0.05
Mg	17.2 ± 1.1
Pb	1.48 ± 0.08
Zn	0.131 ± 0.012

WET ANALYSIS DATA

Elements Determined	Water Concentration (in ppm)
Ca	52.7
Cl	40.1
Fe	0.26 ± 0.02
Mg	143
Hardness	196

[a] n.d. = not detected

* Mahoning Trumbull County Line Bridge (Newton and Milton Townships)

SITE #2* NEUTRON ACTIVATION ANALYSIS DATA TABLE 23

Energy of Photopeak Used (in MeV)	Elements Determined	Water Area (as counts)	Water Concentration (in ppm)	Sediment Area (in ppm)	Sediment Concentration (in ppm)
0.777	Br	48	3.65 ± 0.73	21	57.9 ± 1.3
0.845	Mn	434	0.151 ± 0.024	395,239	4,543 ± 0
1.01	Mg	——	n.d.[a]	733	916 ± 0
1.04	Cu	3	≤0.277	——	n.d.[a]
1.37	Na	668	20.8 ± 0.4	1,570	3,140 ± 0
1.43	V	6	≤0.00514	2,020	19.2 ± 0
1.52	K	16	107 ± 7	45	2,813 ± 10
1.78	Al	——	n.d.[a]	58,552	100 ± 0
2.16	Cl	387	25.3 ± 0.5	——	n.d.[a]
3.09	Ca	16	44.0 ± 6.5	16	160 ± 1

ATOMIC ABSORPTION ANALYSIS DATA

Elements Determined	Water Concentration (in ppm)
Ca	60 ± 1
Cu	0.26 ± 0.04
Mg	16.4 ± 0.2
Pb	0.91 ± 0.12
Zn	0.108 ± 0.018

WET ANALYSIS DATA

Elements Determined	Water Concentration (in ppm)
Ca	37.8
Cl	41.3
Fe	0.26 ± 0.04
Mg	100
Hardness	138

[a] n.d. = not detected

* Portage County Highway #177 Bridge (Paris Township)

NEUTRON ACTIVATION ANALYSIS DATA

Energy of Photopeak Used (in MeV)	Elements Determined	Water Area (as counts)	Water Concentration (in ppm)	Sediment Area (as counts)	Sediment Concentration (in ppm)
0.777	Br	31	$\leq$2.36	—	n.s.c.[b]
0.845	Mu	697	0.243 ± 0.019	—	n.s.c.[b]
1.01	Mg	255	236 ± 2	—	n.s.c.[b]
1.04	Cu	—	n.d.[a]	—	n.s.c.[b]
1.37	Na	5,975	186 ± 0	—	n.s.c.[b]
1.43	V	—	n.d.[a]	—	n.s.c.[b]
1.52	K	32	213 ± 5	—	n.s.c.[b]
1.78	Al	34	1.14 ± 0.09	—	n.s.c.[b]
2.16	Cl	2,802	183 ± 0	—	n.s.c.[b]
3.09	Ca	145	398 ± 3	—	n.s.c.[b]

ATOMIC ABSORPTION ANALYSIS DATA

Elements Determined	Water Concentration (in ppm)
Ca	430 ± 10
Cu	0.54 ± 0.04
Mg	303 ± 1
Pb	1.21 ± 0.14
Zn	0.237 ± 0.028

WET ANALYSIS DATA

Elements Determined	Water Concentration (in ppm)
Ca	377
Cl	208
Fe	1.71 ± 0.01
Mg	1746
Hardness	2123

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[a] n.d. = not detected

[b] n.s.c. = no sample collected

* North-American Rockwell Plant Effluent (city of Newton Falls)

SITE #4* NEUTRON ACTIVATION ANALYSIS DATA TABLE 25

Energy of Photopeak Used (in MeV)	Elements Determined	Water Area (as counts)	Water Concentration (in ppm)	Sediment Area (as counts)	Sediment Concentration (in ppm)
0.777	Br	51	3.88 ± 0.71	13	34.2 ± 1.6
0.845	Mn	1811	0.630 ± 0.012	268,794	3,090 ± 0
1.01	Mg	79	73.1 ± 3.0	1,825	2.281 ± 0
1.04	Cu	49	≤3.88	166	85.1 ± 0.2
1.37	Na	941	29.3 ± 0.3	1,007	2,014 ± 0
1.43	V	———	n.d.[a]	2,359	22.5 ± 0
1.52	K	———	n.d.[a]	41	2,563 ± 10
1.78	Al	———	n.d.[a]	26	92.9 ± 0
2.16	Cl	601	39.2 ± 0.4	53,989	26.0 ± 0.3
3.09	Ca	18	49.4 ± 6.2	633	6,330 ± 1

ATOMIC ABSORPTION ANALYSIS DATA

Elements Determined	Water Concentration (in ppm)
Ca	95 ± 1
Cu	0.16 ± .01
Mg	31.2 ± 0.4
Pb	1.37 ± 0.17
Zn	0.200 ± 0.020

WET ANALYSIS DATA

Elements Determined	Water Concentration (in ppm)
Ca	71.6
Cl	39.5
Fe	0.62 ± 0.01
Mg	215
Hardness	287

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l. = not detected

Approximately 50 feet below North American-Rockwell Effluent source (city of Newton Falls)

*SITE #5** NEUTRON ACTIVATION ANALYSIS DATA TABLE 26

Energy of Photopeak Used (in MeV)	Elements Determined	Water Area (as counts)	Water Concentration (in ppm)	Sediment Area (as counts)	Sediment Concentration (in ppm)
0.777	Br	26	<1.98	14	36.8 ± 1.6
0.845	Mn	359	0.125 ± 0.026	128,075	1,472 ± 0
1.01	Mg	69	63.9 ± 3.2	856	1,070 ± 0
1.04	Cu	50	<3.94	133	68.2 ± 0.2
1.37	Na	602	18.8 ± 0.4	1,234	2,468 ± 0
1.43	V	15	<0.0128	1,661	15.8 ± 0
1.52	K	12	80.0 ± 7.8	72	4,500 ± 9
1.78	Al	—	n.d.[a]	56,571	96.9 ± 0
2.16	Cl	384	25.1 ± 0.5	82	82.0 ± 0.2
3.09	Ca	18	49.5 ± 6.2	71	710 ± 1

ATOMIC ABSORPTION ANALYSIS DATA

Elements Determined	Water Concentration (in ppm)
Ca	89 ± 2
Cu	0.08 ± 0.01
Mg	19.3 ± 0.4
Pb	1.24 ± 0.14
Zn	0.156 ± 0.028

WET ANALYSIS DATA

Elements Determined	Water Concentration (in ppm)
Ca	56.2
Cl	24.8
Fe	0.20 ± 0.04
Mg	130
Hardness	186

[a] n.d. = not detected

*Ohio State Route #5 Brdige (Braceville Township)

*SITE #6**

NEUTRON ACTIVATION ANALYSIS DATA

TABLE 27

Energy of Photopeak Used (in MeV)	Elements Determined	Water		Sediment	
		Area (as counts)	Concentration (in ppm)	Area (as counts)	Concentration (in ppm)
0.777	Br	91	6.92 ± 0.54	37	97.4 ± 1.2
0.845	Mn	301	0.105 ± 0.029	22,084	254 ± 0
1.01	Mg	11	≤10.2	857	1,071 ± 0
1.04	Cu	9	≤0.712	65	33.3 ± 0.2
1.37	Na	509	15.9 ± 0.5	1,173	2,346 ± 0
1.43	V	——	n.d.[a]	2,153	20.5 ± 0
1.52	K	8	53.3 ± 9.3	25	1,563 ± 10
1.78	Al	——	n.d.[a]	93,148	160 ± 0
2.16	Cl	298	19.5 ± 0.6	18	18.0 ± 0.3
3.09	Ca	9	≤24.7	61	610 ± 1

ATOMIC ABSORPTION ANALYSIS DATA

Elements Determined	Water Concentration (in ppm)
Ca	85 ± 2
Cu	0.11 ± 0.01
Mg	12.7 ± 0.5
Pb	1.32 ± 0.18
Zn	0.105 ± 0.007

WET ANALYSIS DATA

Elements Determined	Water Concentration (in ppm)
Ca	44.7
Cl	23.6
Fe	0.25 ± 0.01
Mg	96.3
Hardness	141

[a] n.d. = not detected

* Ohio State Route #5 Bypass Bridge (Warren Township)

*SITE #7** NEUTRON ACTIVATION ANALYSIS DATA TABLE 28

Energy of Photopeak Used (in MeV)	Elements Determined	Water Area (as counts)	Water Concentration (in ppm)	Sediment Area (as counts)	Sediment Concentration (in ppm)
0.777	Br	16	<1.22	——	n.s.c.[b]
0.845	Mn	426	0.148 ± 0.024	——	n.s.c.[b]
1.01	Mg	——	n.d.[a]	——	n.s.c.[b]
1.04	Cu	——	n.d.[a]	——	n.s.c.[b]
1.37	Na	597	18.6 ± 0.4	——	n.s.c.[b]
1.43	V	——	n.d.[a]	——	n.s.c.[b]
1.52	K	10	66.7 ± 8.4	——	n.s.c.[b]
1.78	Al	——	n.d.[a]	——	n.s.c.[b]
2.16	Cl	341	22.6 ± 0.6	——	n.s.c.[b]
3.09	Ca	12	33.0 ± 7.4	——	n.s.c.[b]

ATOMIC ABSORPTION ANALYSIS DATA

Elements Determined	Water Concentration (in ppm)
Ca	93 + 2
Cu	0.15 ± 0.02
Mg	19.8 ± 0.1
Pb	1.46 ± 0.11
Zn	0.181 ± 0.014

WET ANALYSIS DATA

Elements Determined	Water Concentration (in ppm)
Ca	47.2
Cl	26.0
Fe	0.23 ± 0.01
Mg	127
Hardness	174

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[a] n.d. = not detected

[b] n.s.c. = not sample collected

* Parkman Road Bridge (city of Warren)

NEUTRON ACTIVATION ANALYSIS DATA

Energy of Photopeak Used (in MeV)	Elements Determined	Water Area (as counts)	Water Concentration (in ppm)	Sediment Area (as counts)	Sediment Concentration (in ppm)
0.777	Br	13	≤1.44	—	n.s.c.[a]
0.845	Mn	484	0.169 ± 0.023	—	n.s.c.[a]
1.01	Mg	14	≤13.0	—	n.s.c.[a]
1.04	Cu	50	≤3.96	—	n.s.c.[a]
1.37	Na	660	20.6 ± 0.4	—	n.s.c.[a]
1.43	V	9	≤0.00771	—	n.s.c.[a]
1.52	K	8	53.3 ± 9.3	—	n.s.c.[a]
1.78	Al	12	≤0.404	—	n.s.c.[a]
2.16	Cl	391	25.5 ± 0.5	—	n.s.c.[a]
3.09	Ca	25	68.7 ± 5.3	—	n.s.c.[a]

ATOMIC ABSORPTION ANALYSIS DATA

Elements Determined	Water Concentration (in ppm)
Ca	106 ± 3
Cu	0.25 ± 0.01
Mg	27.0 ± 0.4
Pb	1.36 ± 0.11
Zn	0.169 ± 0.006

WET ANALYSIS DATA

Elements Determined	Water Concentration (in ppm)
Ca	62.1
Cl	30.7
Fe	0.81 ± 0.04
Mg	121
Hardness	183

[a] n.s.c. = no sample collected

* Copperweld Steel Plant effluent (city of Warren)

*SITE #9** NEUTRON ACTIVATION ANALYSIS DATA TABLE 30

Energy of Photopeak Used (in MeV)	Elements Determined	Area (as counts)	Concentration (in ppm)	Sediment Area (as counts)	Concentration (in ppm)
0.777	Br	41	3.12 ± 0.79	——	n.s.c.[b]
0.845	Mn	534	0.186 ± 0.022	——	n.s.c.[b]
1.01	Mg	35	32.4 ± 4.4	——	n.s.c.[b]
1.04	Cu	11	≤0.836	——	n.s.c.[b]
1.37	Na	578	18.0 ± 0.4	——	n.s.c.[b]
1.43	V	——	n.d.[a]	——	n.s.c.[b]
1.52	K	15	100 ± 7	——	n.s.c.[b]
1.78	Al	——	n.d.[a]	——	n.s.c.[b]
2.16	Cl	377	24.6 ± 0.5	——	n.s.c.[b]
3.09	Ca	22	60.4 ± 5.6	——	n.s.c.[b]

ATOMIC ABSORPTION ANALYSIS DATA

Elements Determined	Water Concentration (in ppm)
Ca	123 ± 3
Cu	0.24 ± 0.03
Mg	18.4 ± 0.1
Pb	1.75 ± 0.008
Zn	0.221 ± 0.016

WET ANALYSIS DATA

Elements Determined	Water Concentration (in ppm)
Ca	50.2
Cl	24.2
Fe	0.22 ± 0.04
Mg	129
Hardness	179

[a] n.d. = not detected

[b] n.s.c. = no sample collected

* North West Bridge Street Bridge (city of Warren)

Energy of Photopeak Used (in MeV)	Elements Determined	Water Area (as counts)	Water Concentration (in ppm)	Sediment Area (as counts)	Sediment Concentration (in ppm)
0.777	Br	25	≤1.90	41	108 ± 1
0.845	Mn	454	0.158 ± 0.024	265,205	3,048 ± 0
1.01	Mg	——	n.d.[a]	927	1,159 ± 0
1.04	Cu	——	n.d.[a]	——	n.d.[a]
1.37	Na	611	19.1 ± 0.4	861	1,722 ± 0
1.43	V	4	≤0.00343	2,349	22.4 ± 0
1.52	K	——	n.d.[a]	64	4,000 ± 9
1.78	Al	——	n.d.[a]	74,172	127 ± 0
2.16	Cl	357	23.3 ± 0.6	——	trace
3.09	Ca	12	33.0 ± 7.4	170	1,700 ± 1

ATOMIC ABSORPTION ANALYSIS DATA

Elements Determined	Water Concentration (in ppm)
Ca	143 ± 2
Cu	0.20 ± 0.02
Mg	34.2 ± 0.2
Pb	1.83 ± 0.05
Zn	0.114 ± 0.008

WET ANALYSIS DATA

Elements Determined	Water Concentration (in ppm)
Ca	53.2
Cl	26.0
Fe	0.29 ± 0.02
Mg	127
Hardness	180

[a] n.d. = not detected

*Market Street Bridge (city of Warren)

SITE #11* NEUTRON ACTIVATION ANALYSIS DATA TABLE 32

Energy of Photopeak Used (in MeV)	Elements Determined	Area (as counts)	Concentration (in ppm)	Sediment Area (as counts)	Sediment Concentration (in ppm)
0.777	Br	12	≤0.913	42	111 ± 1
0.845	Mn	479	0.167 ± 0.023	228,324	2,624 ± 0
1.01	Mg	117	108 ± 3	1,255	1,569 ± 0
1.04	Cu	5	≤0.367	——	n.d.[a]
1.37	Na	744	23.2	521	1,042 ± 0
1.43	V	18	≤0.0154	2,563	24.4 ± 0
1.52	K	19	127 ± 6	95	5,938 ± 9
1.78	Al	——	n.d.[a]	68,579	117 ± 0
2.16	Cl	449	29.3 ± 0.5	——	trace
3.09	Ca	3	≤8.24	184	1,840 ± 1

ATOMIC ABSORPTION ANALYSIS DATA

Elements Determined	Water Concentration (in ppm)
Ca	102 ± 3
Cu	0.26 ± 0.03
Mg	20.6 ± 0.2
Pb	1.66 ± 0.03
Zn	0.291 ± 0.016

WET ANALYSIS DATA

Elements Determined	Water Concentration (in ppm)
Ca	49.7
Cl	34.8
Fe	0.47 ± 0.01
Mg	130
Hardness	180

[a] n.d. = not detected

* West Park Avenue Extension Bridge (Weathersfield Township)

NEUTRON ACTIVATION ANALYSIS DATA

Energy of Photopeak Used (in MeV)	Elements Determined	Water		Sediment	
		Area (as counts)	Concentration (in ppm)	Area (as counts)	Concentration (in ppm)
0.777	Br	———	n.d.[a]	10	26.3 ± 1.8
0.845	Mn	1,842	0.641 ± 0.012	123,294	1,417 ± 0
1.01	Mg	20	≤18.5	654	818 ± 0
1.04	Cu	———	n.d.[a]	178	91.2 ± 0.2
1.37	Na	578	18.0 ± 0.4	694	1,388 ± 0
1.43	V	34	≤0.0291	3,514	33.5 ± 0
1.52	K	5	≤33.3	89	5,563 ± 9
1.78	Al	———	n.d.[a]	76,162	130 ± 0
2.16	Cl	389	25.4 ± 0.5	50	50.0 ± 0.3
3.09	Ca	14	38.5 ± 6.9	257	2,570 ± 1

ATOMIC ABSORPTION ANALYSIS DATA

Elements Determined	Water Concentration (in ppm)
Ca	96 ± 1
Cu	0.43 ± 0.03
Mg	17.1 ± 0.2
Pb	2.19 ± 0.07
Zn	1,620 ± 0.026

WET ANALYSIS DATA

Elements Determined	Water Concentration (in ppm)
Ca	43.2
Cl	34.2
Fe	2.98 ± 0.07
Mg	120
Hardness	163

[a] n.d. = not detected

*Enbankment near Pratt and River Streets (city of Niles)

*SITE #13** NEUTRON ACTIVATION ANALYSIS DATA TABLE 34

Energy of Photopeak Used (in MeV)	Elements Determined	Water Area (as counts)	Water Concentration (in ppm)	Sediment Area (as counts)	Sediment Concentration (in ppm)
0.777	Br	3	<0.228	25	65.8 ± 1.3
0.845	Mn	274	≤0.0954	146,997	1,690 ± 0
1.01	Mg	111	103 ± 3	1,036	1,295 ± 0
1.04	Cu	—	n.d.[a]	356	183 ± 0
1.37	Na	623	19.4 ± 0.4	697	1,394 ± 0
1.43	V	17	≤0.0146	3,677	35.0 ± 0
1.52	K	—	n.d.[a]	32	2,000 ± 1.0
1.78	Al	—	n.d.[a]	88,566	152 ± 0
2.16	Cl	456	29.8 ± 0.5	53	53.0 ± 0.3
3.09	Ca	27	74.2 ± 5.1	154	1,540 ± 1

ATOMIC ABSORPTION ANALYSIS DATA

Elements Determined	Water Concentration (in ppm)
Ca	90 ± 3
Cu	0.34 ± 0.02
Mg	18.6 ± 0.2
Pb	3.01 ± 0.21
Zn	0.246 ± 0.010

WET ANALYSIS DATA

Elements Determined	Water Concentration (in ppm)
Ca	52.2
Cl	29.5
Fe	0.41 ± 0.01
Mg	119
Hardness	171

[a] n.d. = not detected

* Belmont Sheet Bridge (city of Niles)

*SITE #14** NEUTRON ACTIVATION ANALYSIS DATA TABLE 35

Energy of Photopeak Used (in MeV)	Elements Determined	Water Area (as counts)	Water Concentration (in ppm)	Sediment Area (as counts)	Sediment Concentration (in ppm)
0.777	Br	——	n.d.[a]	7	18.4 ± 2.1
0.845	Mn	520	0.181 ± 0.022	135,668	1,559 ± 0
1.01	Mg	42	38.9 ± 4.0	1,050	1,315 ± 0
1.04	Cu	——	n.d.[a]	59	30.3 ± 0.2
1.37	Na	690	21.5 ± 0.4	611	1,222 ± 0
1.43	V	——	n.d.[a]	3,645	34.7 ± 0
1.52	K	11	73.3 ± 8.1	50	3,125 ± 10
1.78	Al	——	n.d.[a]	85,995	147 ± 0
2.16	Cl	411	31.4 ± 0.5	155	155 ± 0
3.09	Ca	22	60.4 ± 5.6	598	5,980 ± 1

ATOMIC ABSORPTION ANALYSIS DATA

Elements Determined	Water Concentration (in ppm)
Ca	95 ± 2
Cu	0.25 ± 0.02
Mg	19.0 ± 0.2
Pb	2.37 ± 0.11
Zn	0.178 ± 0.016

WET ANALYSIS DATA

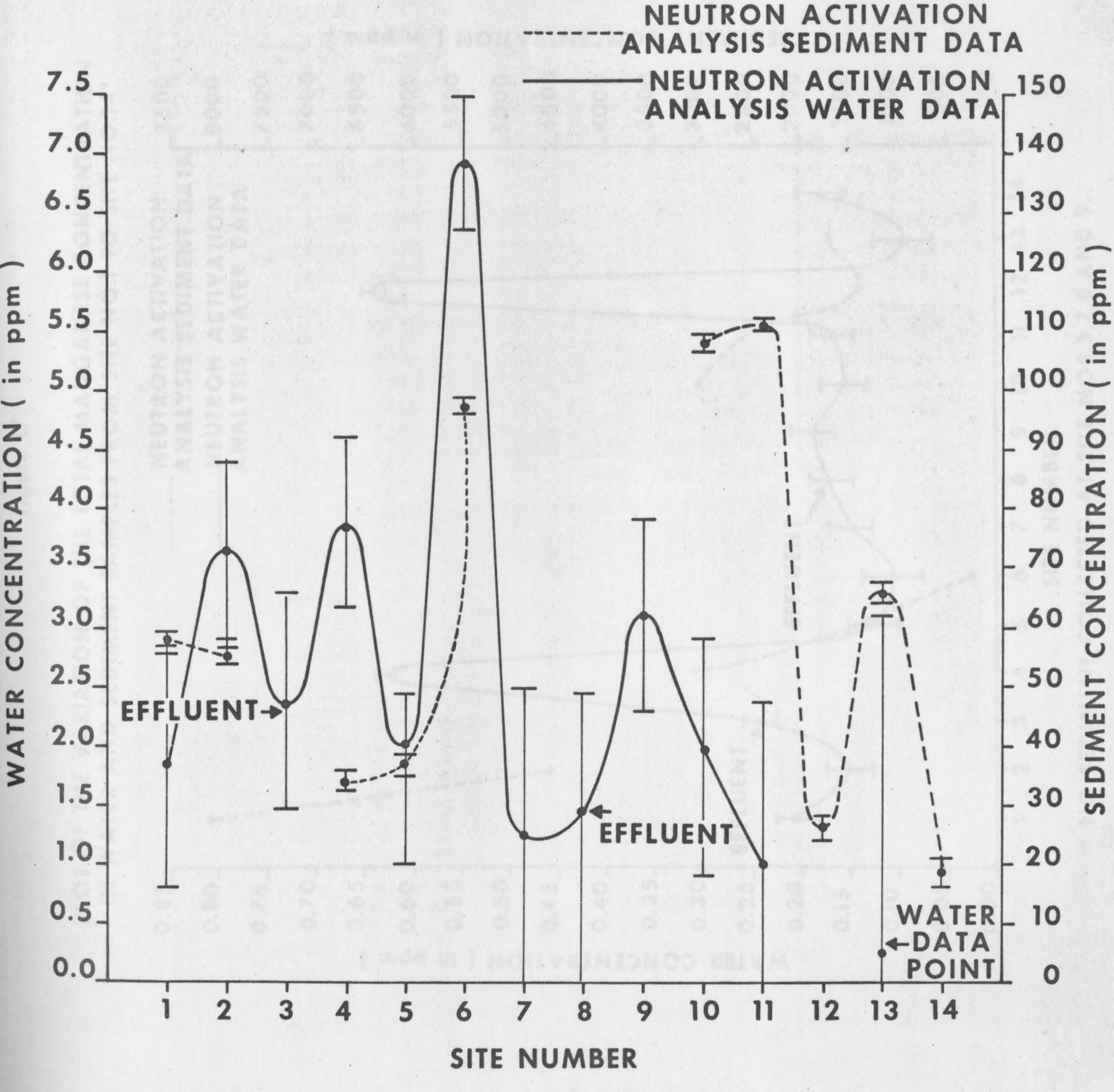
Elements Determined	Water Concentration (in ppm)
Ca	56.7
Cl	36.6
Fe	0.49 ± 0
Mg	124
Hardness	181

[a] n.d. = not detected

*Olive Street Bridge (city of Niles)

Figure 16

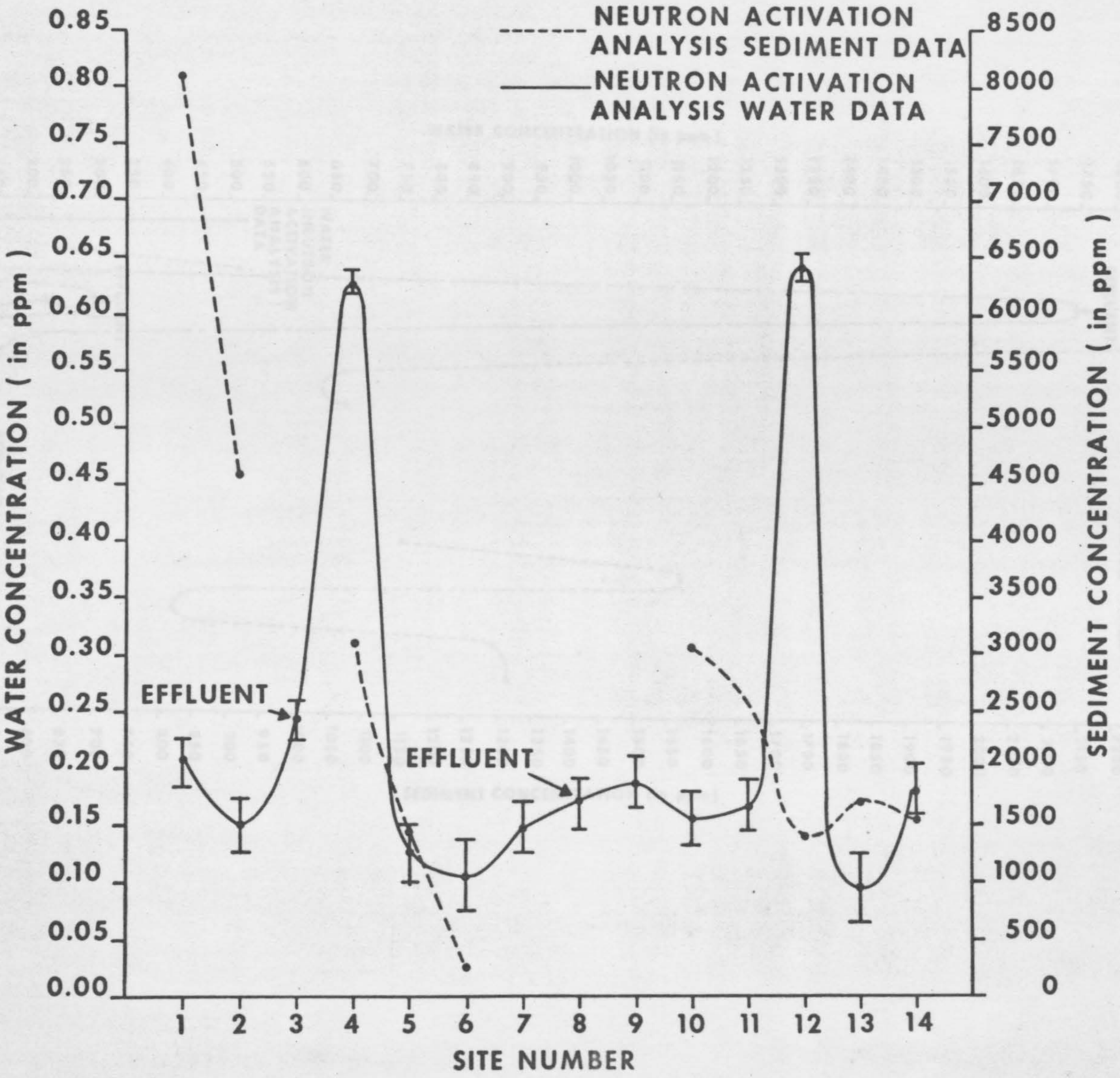
PLOT OF THE VARIATION OF THE TOTAL BROMINE CONCENTRATION IN WATER AND SEDIMENT SAMPLES FROM SITE NO.1 TO SITE NO.14* ‡



* NO SEDIMENT SAMPLES COLLECTED AT SITE NOS. 3,7,8, AND 9.
‡ BROMINE UNDETECTED IN WATER AT SITE NOS. 12 AND 14.

Figure 17

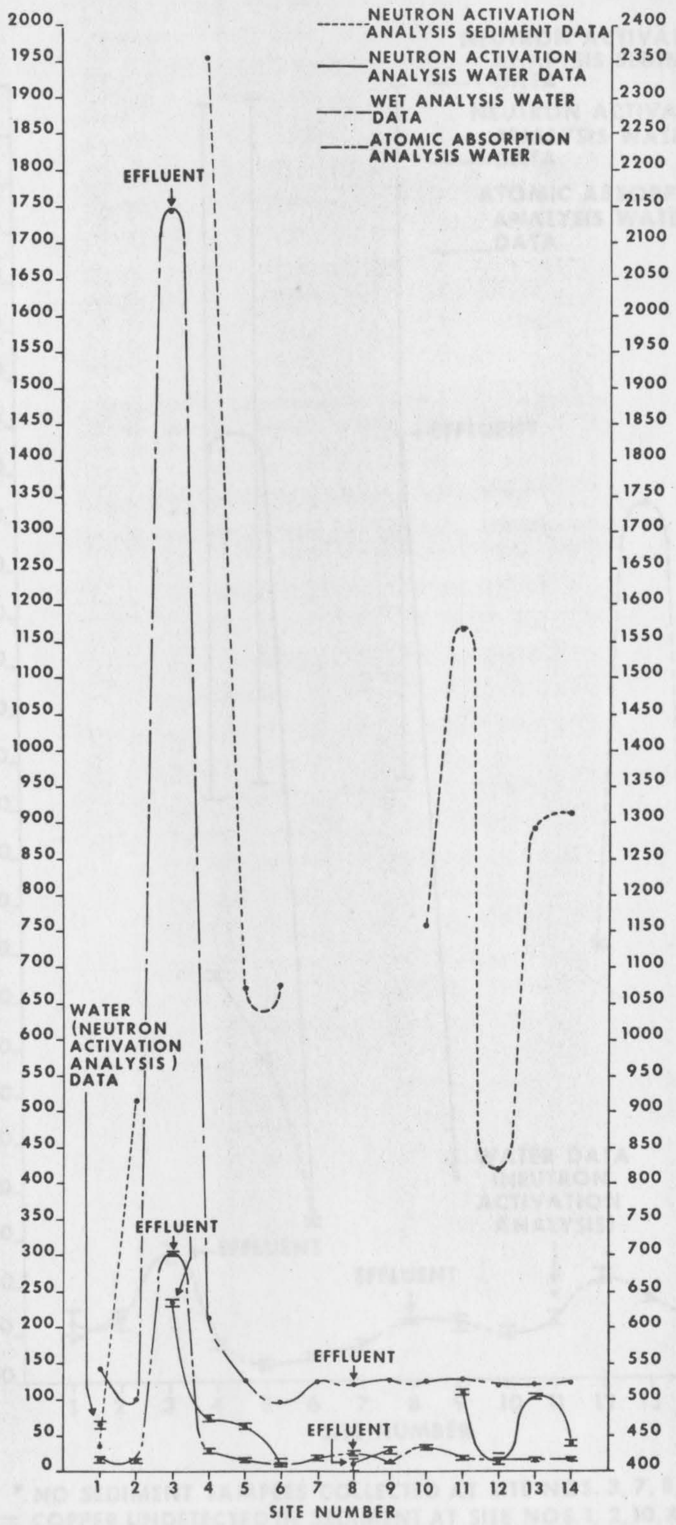
PLOT OF THE VARIATION OF THE TOTAL MANGANESE CONCENTRATION IN WATER AND SEDIMENT SAMPLES FROM SITE NO.1 TO SITE NO.14*



* NO SEDIMENT COLLECTED AT SITE NOS.3,7,8,AND 9.

Figure 18

PLOT THE VARIATION OF TOTAL MAGNESIUM CONCENTRATION IN WATER AND SEDIMENT SAMPLES FROM SITE NO.1 TO SITE NO.14 *‡§



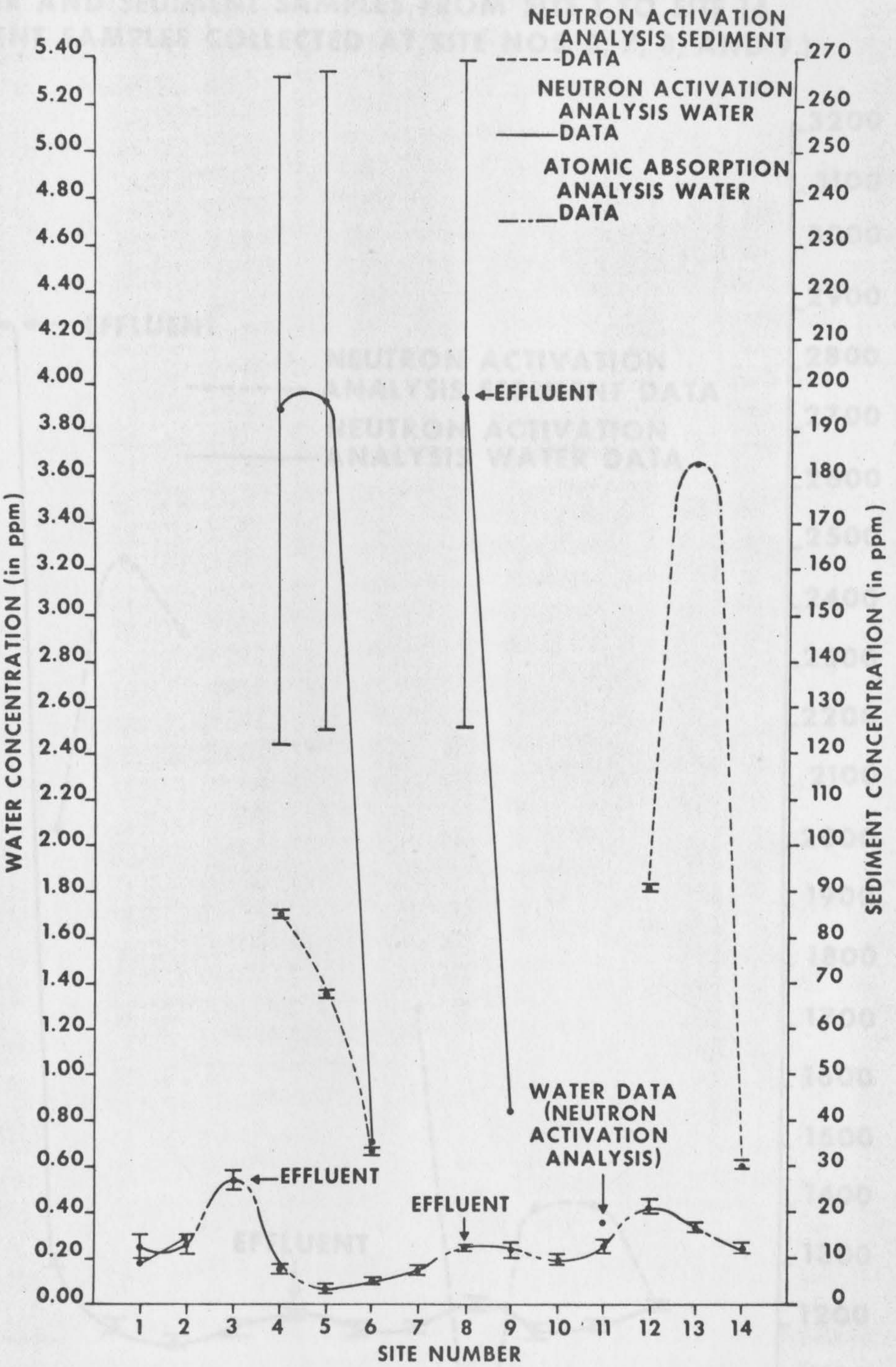
*NO SEDIMENT SAMPLES COLLECTED AT SITE NOS. 3, 7, 8, AND 9.

‡MAGNESIUM UNDETECTED (VIA NEUTRON ACTIVATION ANALYSIS) IN WATER AT SITE NOS. 2, 7, AND 10.

§ WET ANALYSIS DATA OBTAINED BY SUBTRACTING CALCIUM VALUES FROM TOTAL HARDNESS VALUES FOR EACH PARTICULAR SITE.

Figure 19

PLOT OF THE VARIATION OF THE TOTAL COPPER CONCENTRATION IN WATER AND SEDIMENT FROM SITE NO.1 TO SITE NO.14*‡§⊖



* NO SEDIMENT SAMPLES COLLECTED AT SITE NOS. 3, 7, 8, AND 9.

‡ COPPER UNDETECTED IN SEDIMENT AT SITE NOS. 1, 2, 10, AND 11.

§ COPPER UNDETECTED (VIA NEUTRON ACTIVATION ANALYSIS) IN WATER AT SITE NOS. 3, 7, 10, 12, 13, AND 14

⊖ DATA/POINTS FOR NEUTRON ACTIVATION WATER DATA AT SITES 1, 2, 6, 9, AND 11 REPRESENT "MAXIMUM" CONCENTRATION OF COPPER DETECTED.

Figure 20

PLOT OF THE VARIATION OF THE TOTAL SODIUM CONCENTRATION IN WATER AND SEDIMENT SAMPLES FROM SITE 1 TO SITE 14. (NO SEDIMENT SAMPLES COLLECTED AT SITE NOS. 3, 7, 8, AND 9.)

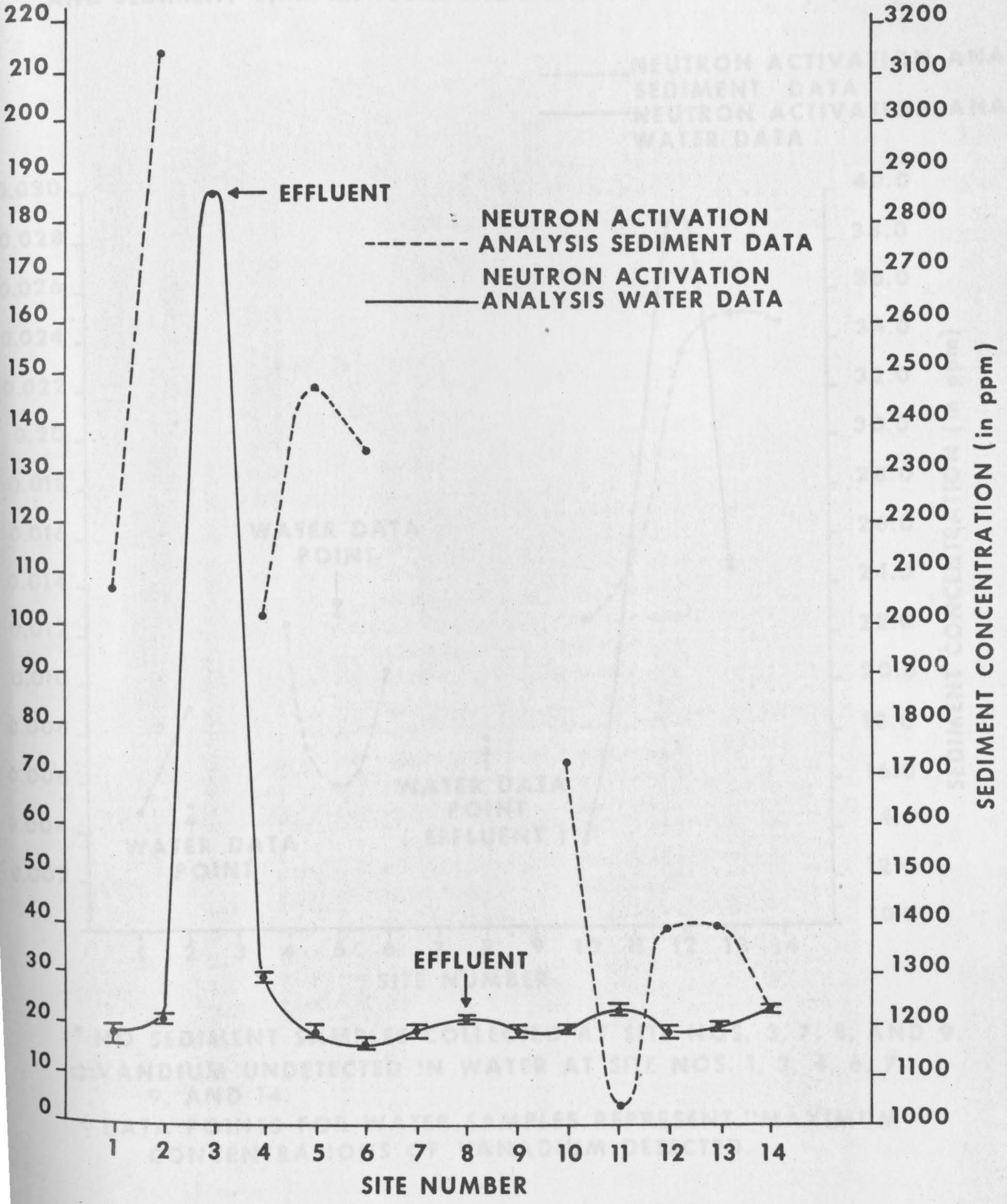
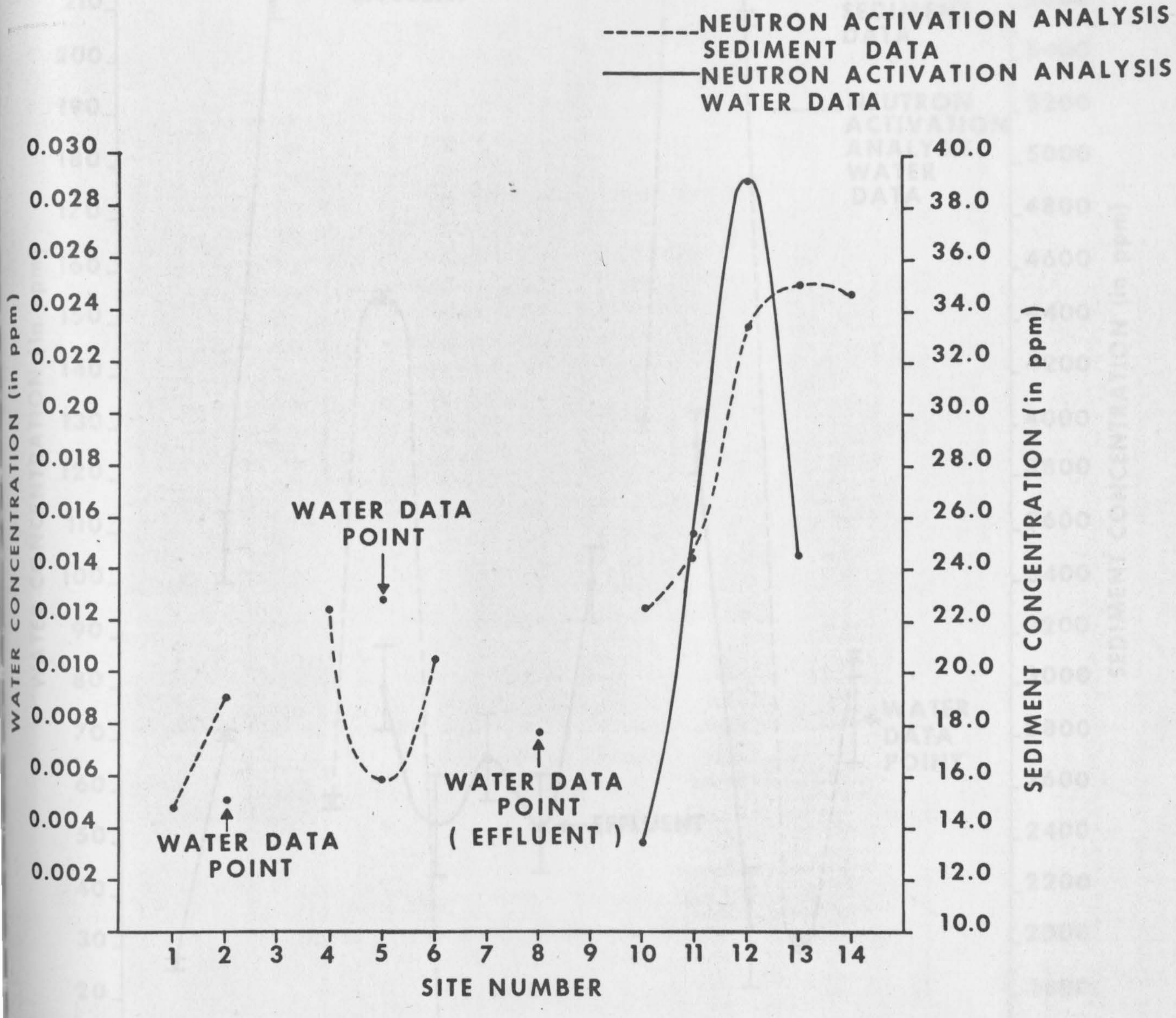


Figure 21

PLOT OF THE VARIATION OF TOTAL VANADIUM CONCENTRATION IN WATER AND SEDIMENT SAMPLES FROM SITE NO.1 TO SITE NO.14 * ‡ §



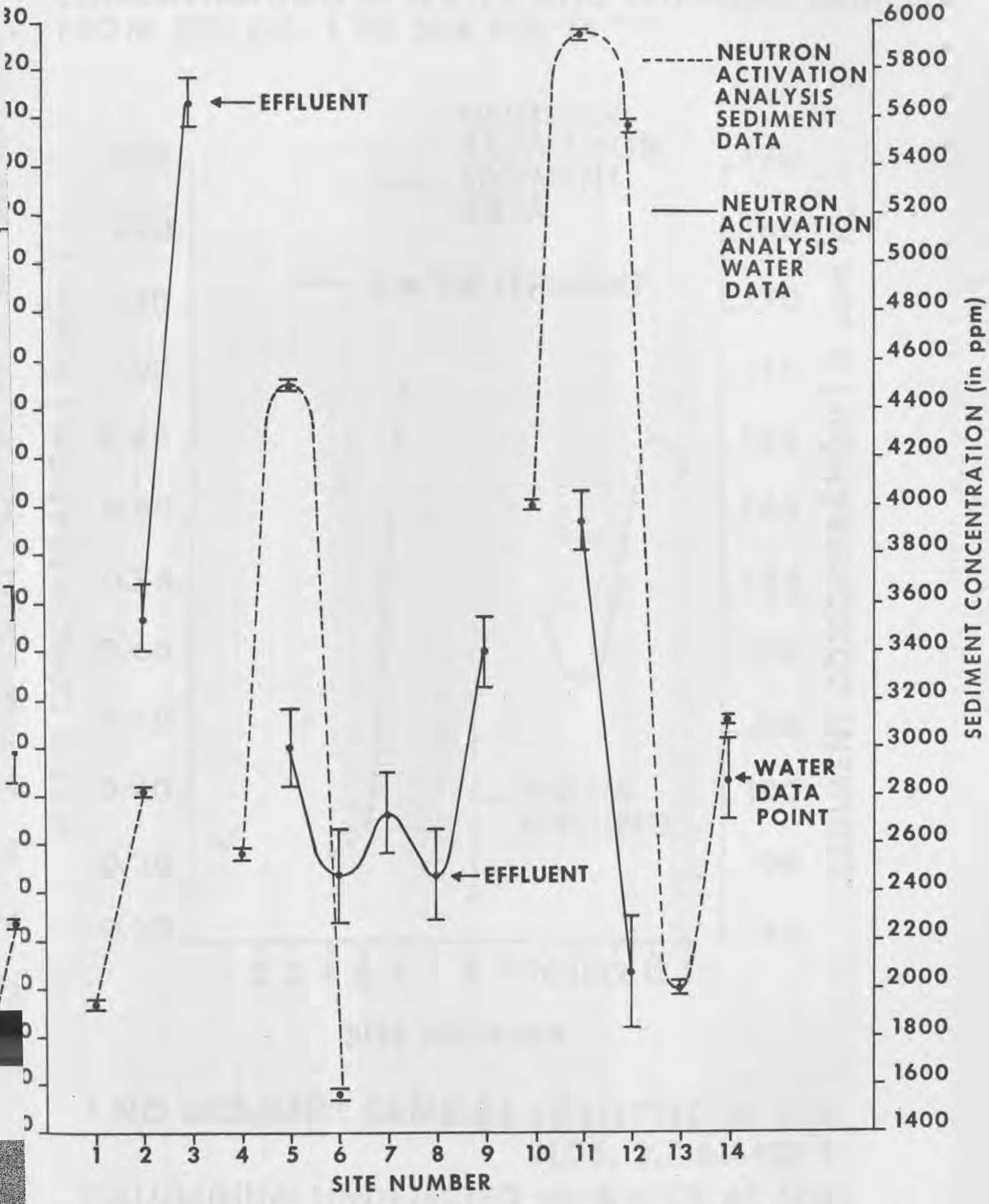
* NO SEDIMENT SAMPLES COLLECTED AT SITE NOS. 3, 7, 8, AND 9.

‡ VANDIUM UNDETECTED IN WATER AT SITE NOS. 1, 3, 4, 6, 7, 9, AND 14.

§ DATA POINTS FOR WATER SAMPLES REPRESENT "MAXIMUM" CONCENTRATIONS OF VANADIUM DETECTED.

Figure 22

PLOT OF THE VARIATION OF THE TOTAL POTASSIUM CONCENTRATION IN WATER AND IN SEDIMENT SAMPLES FROM SITE NO.1 TO SITE NO.14 * ‡

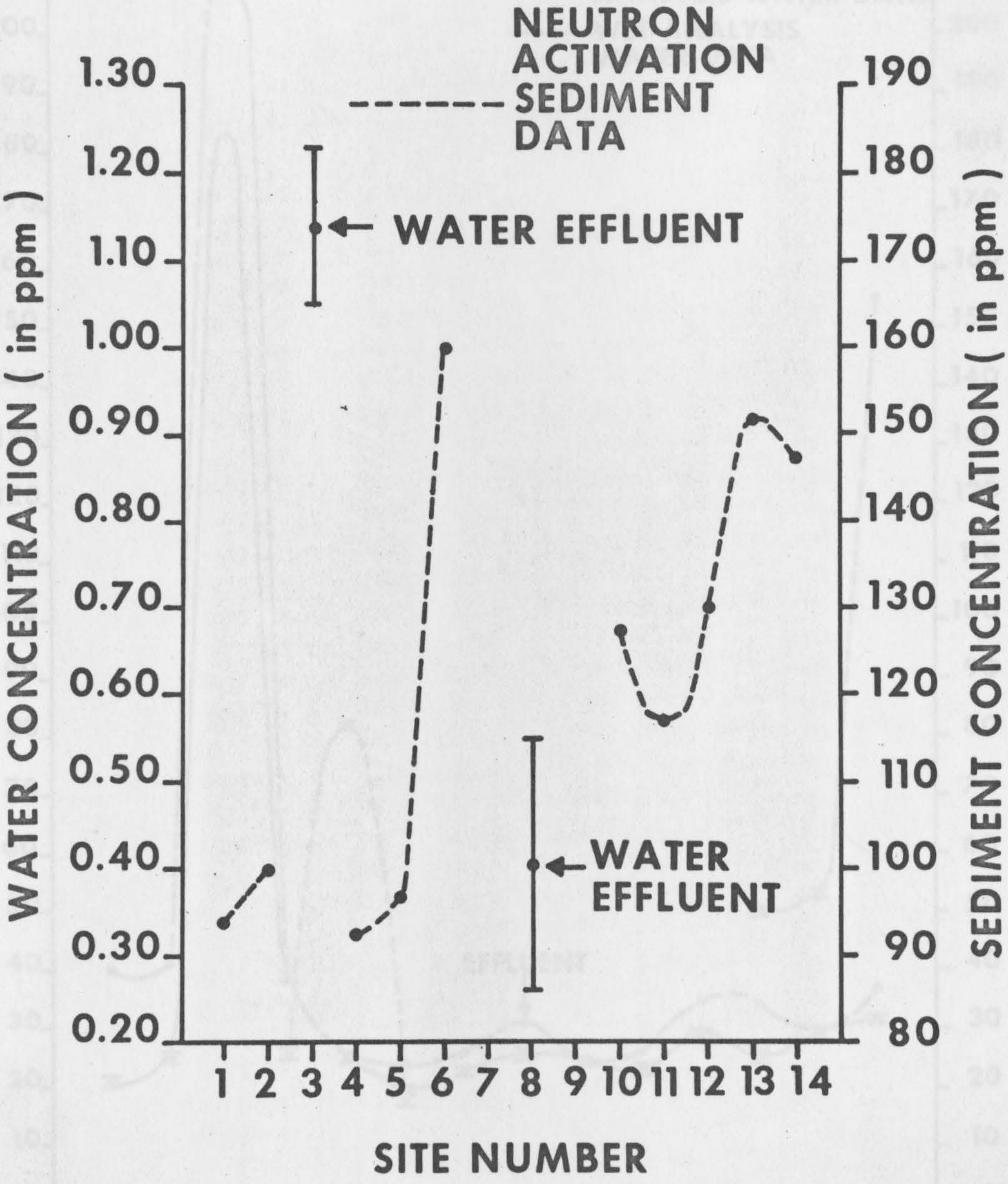


* NO SEDIMENT SAMPLES COLLECTED AT SITE NOS.3, 7, 8, AND 9.

‡ POTASSIUM UNDETECTED AT SITE NOS.1, 4, 10, AND 13.

Figure 23

PLOT OF THE VARIATION OF THE TOTAL ALUMINUM CONCENTRATION IN WATER AND SEDIMENT SAMPLES FROM SITE NO. 1 TO SITE NO. 14 *‡

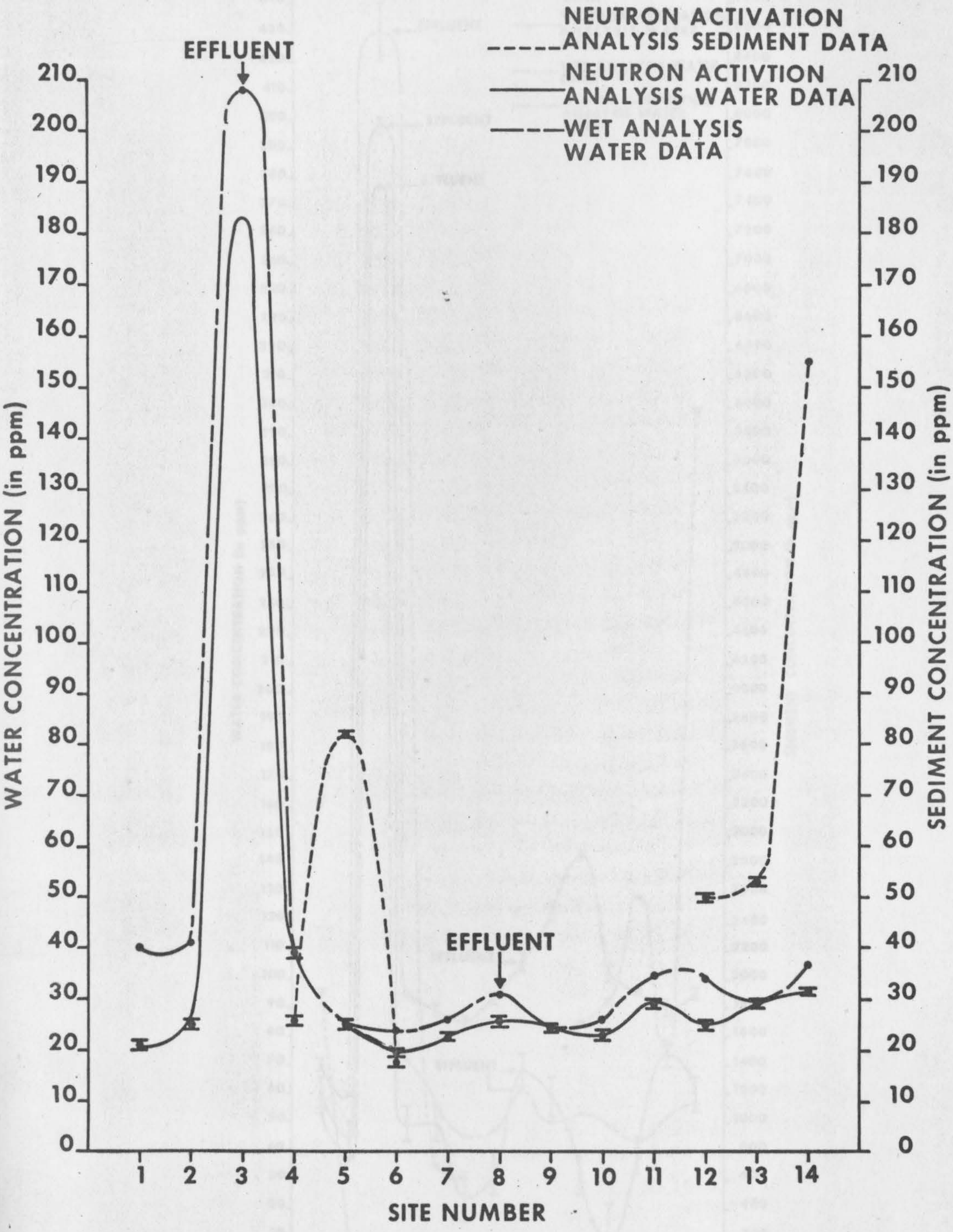


* NO SEDIMENT SAMPLES COLLECTED AT SITE NOS. 3,7,8,AND 9.

‡ALUMINUM UNDETECTED IN WATER AT SITES 1,2,4,5,6,7,9,10,11,12,13,AND 14.

Figure 24

PLOT OF THE VARIATION OF THE TOTAL CHLORINE CONCENTRATION IN WATER AND SEDIMENT SAMPLES FROM SITE NO. 1 TO SITE NO. 14* ‡ §



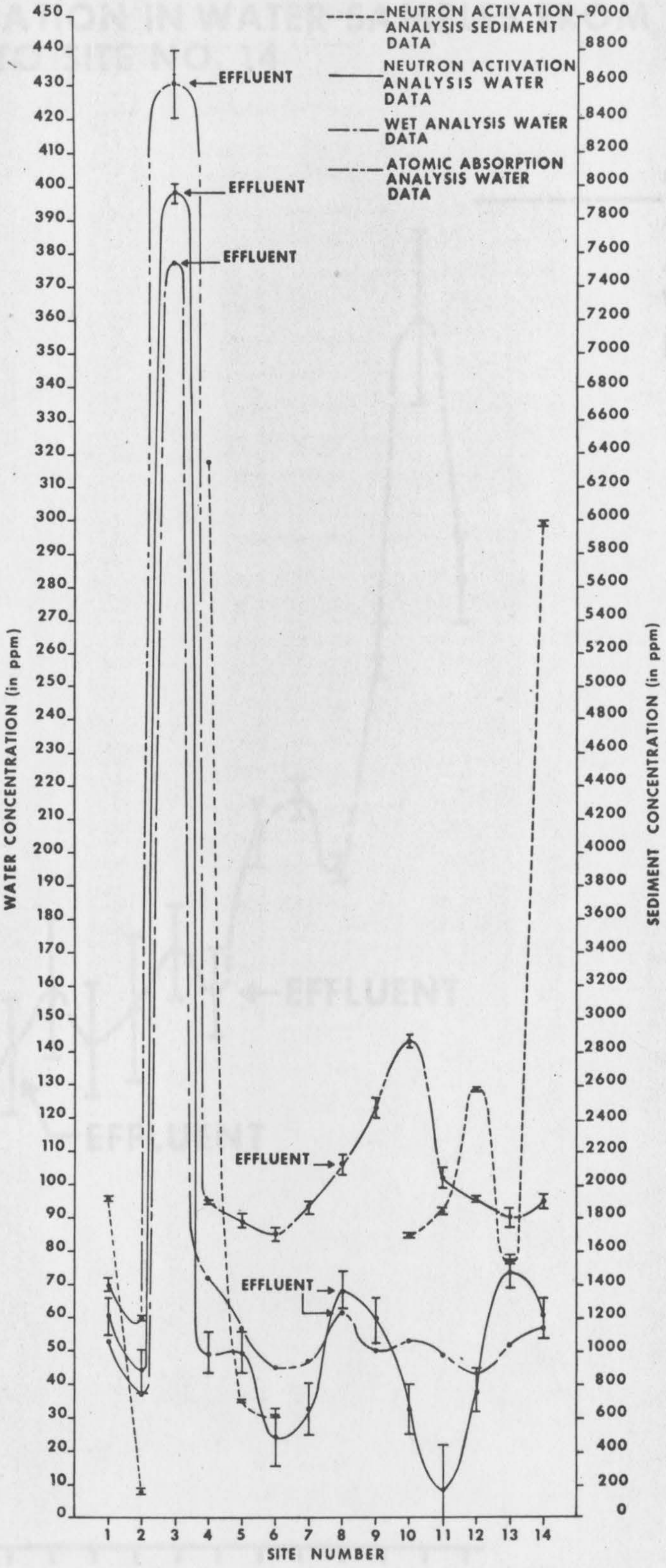
*NO SEDIMENT SAMPLES COLLECTED AT SITE NOS. 3, 7, 8, AND 9.

‡ CHLORINE UNDETECTED IN SEDIMENT AT SITES NOS. 1 AND 2.

§ CHLORINE DETECTED IN TRACE QUANTITIES IN SEDIMENT AT SITE NOS. 10 AND 11.

Figure 25

PLOT OF THE VARIATION OF TOTAL CALCIUM CONCENTRATION IN WATER AND SEDIMENT SAMPLES FROM SITE NO. 1 TO SITE NO. 14*‡



*NO SEDIMENT SAMPLES COLLECTED AT SITE NOS. 3, 7, 8, AND 9.

‡WET ANALYSIS STUDIES SHOW CHLORINE AS "SOLUBLE CHLORIDE" ION WHILE THE OTHER TWO METHODS CONSIDERED TOTAL CHLORINE (INCLUDING MOLECULAR AND COMPLEXED SPECIES).

Figure 26

PLOT OF THE VARIATION OF THE TOTAL LEAD CONCENTRATION IN WATER SAMPLES FROM SITE NO. 1 TO SITE NO. 14

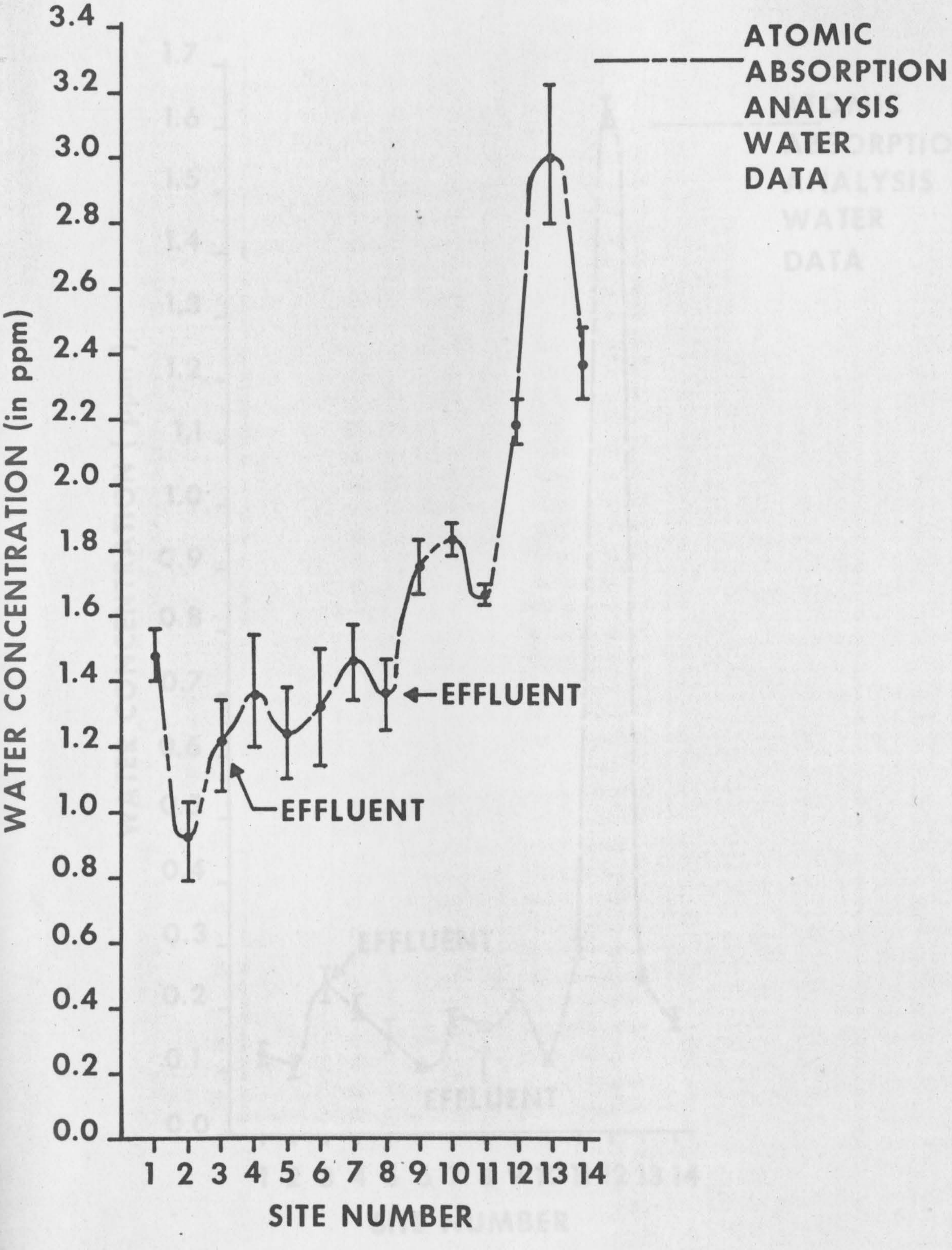


Figure 27

PLOT OF THE VARIATION OF TOTAL ZINC CONCENTRATION IN WATER SAMPLES FROM SITE NO.1 TO SITE NO.14

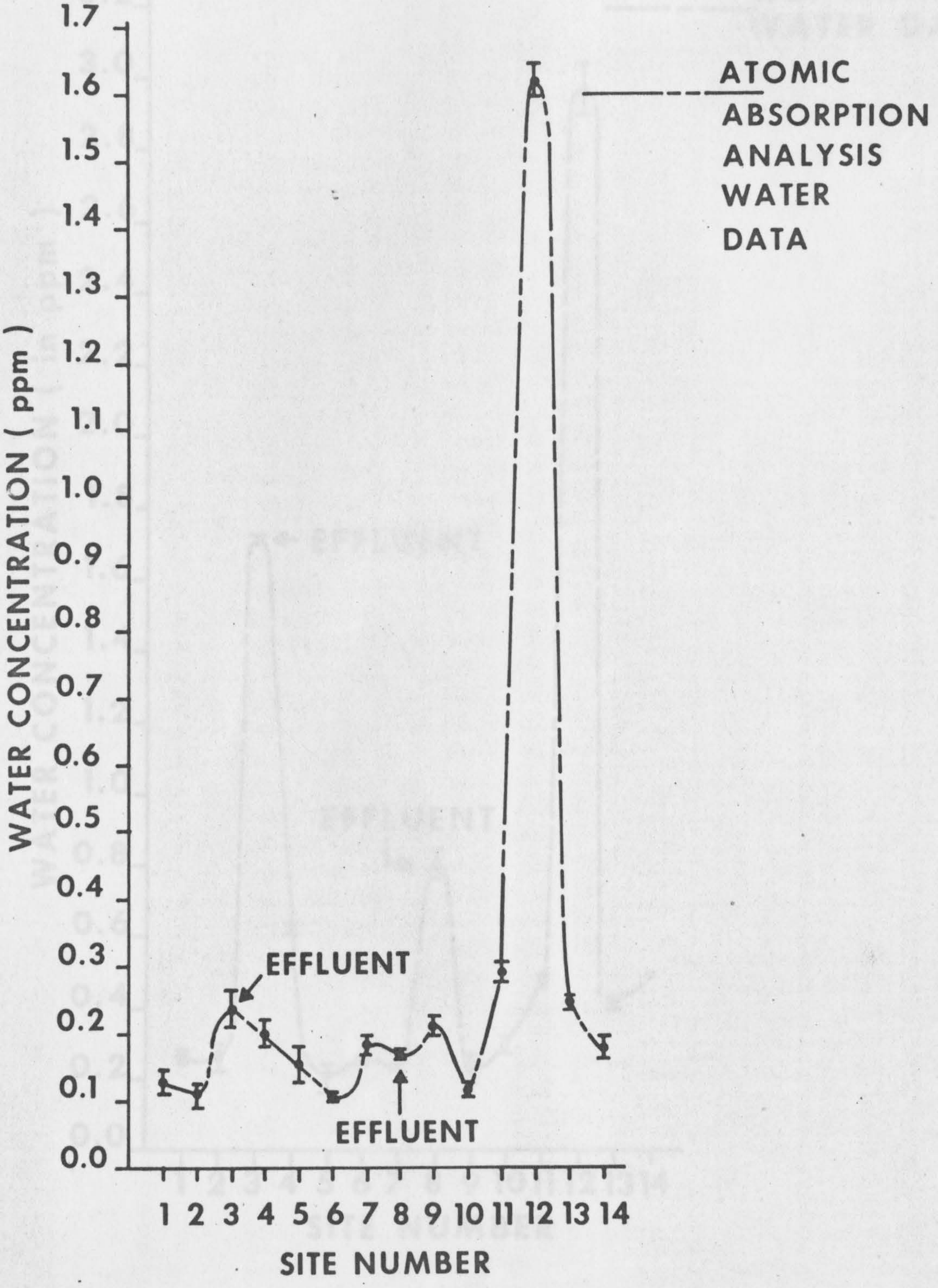


Figure 28

PLOT OF THE VARIATION OF TOTAL IRON CONCENTRATION IN WATER SAMPLES FROM SITE NO.1 TO SITE NO.14

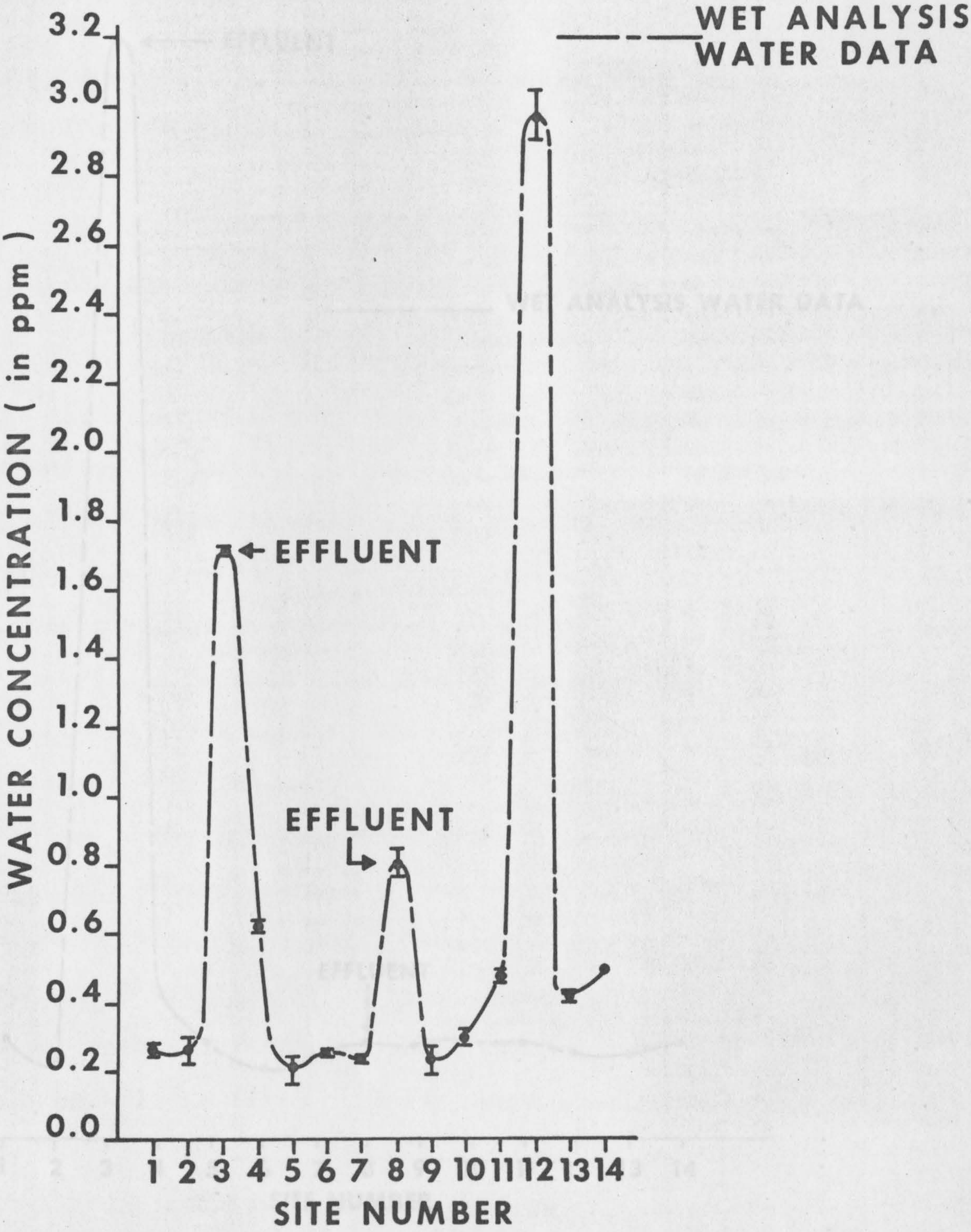
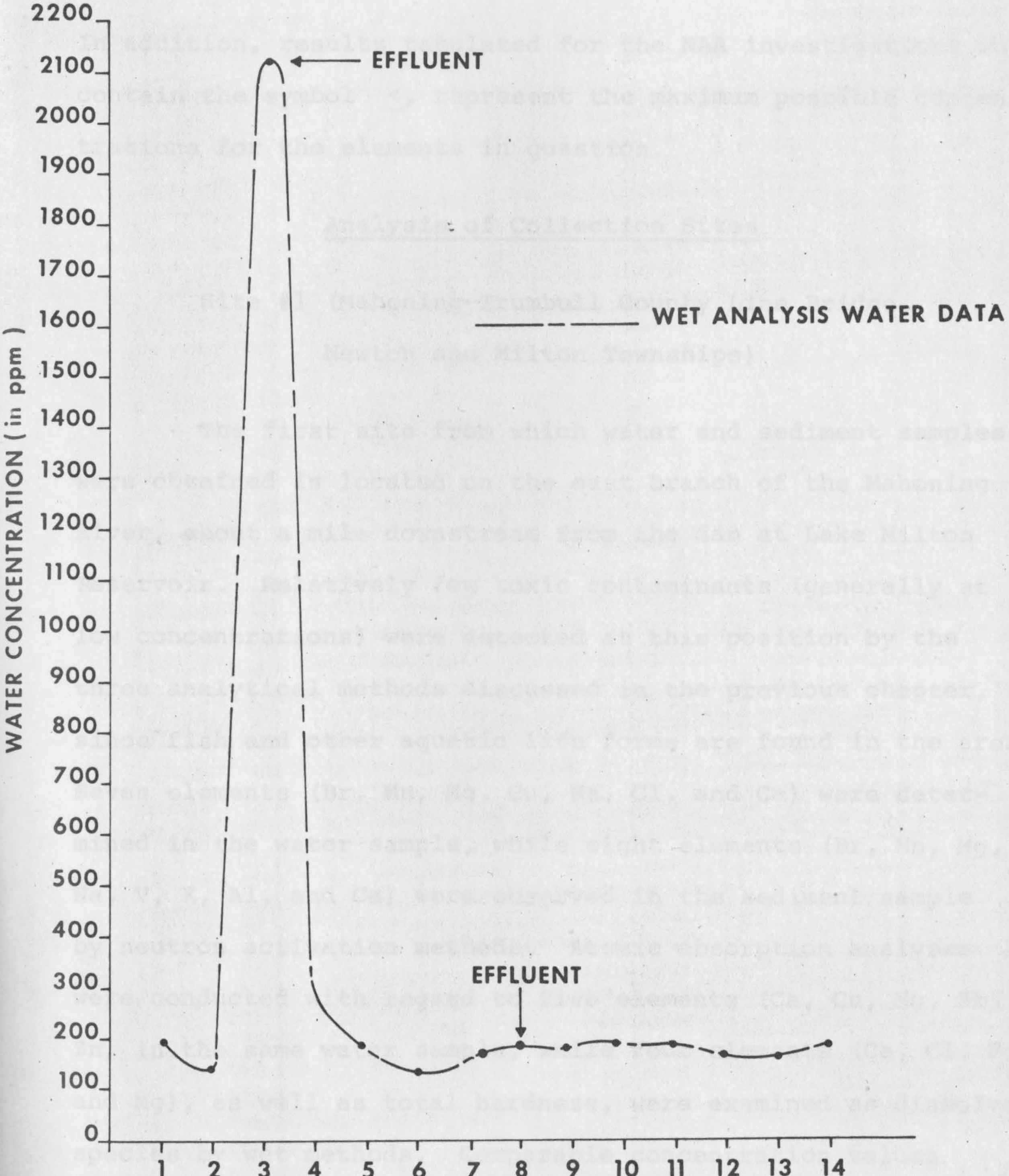


Figure 29

PLOT OF THE VARIATION OF TOTAL HARDNESS IN WATER SAMPLES FROM SITE NO.1 TO SITE NO.14



A_s = activity of the prepared standard
t = counting period of the sample or standard by the Ge(Li) detector (in minutes)
and W_s = concentration of the standard (in ppm)

In addition, results tabulated for the NAA investigations which contain the symbol $\leq$, represent the maximum possible concentrations for the elements in question.

Analysis of Collection Sites

Site #1 (Mahoning-Trumbull County Line Bridge, Newton and Milton Townships)

The first site from which water and sediment samples were obtained is located on the east branch of the Mahoning River, about a mile downstream from the dam at Lake Milton Reservoir. Relatively few toxic contaminants (generally at low concentrations) were detected at this position by the three analytical methods discussed in the previous chapter, since fish and other aquatic life forms are found in the area. Seven elements (Br, Mn, Mg, Cu, Na, Cl, and Ca) were determined in the water sample, while eight elements (Br, Mn, Mg, Na, V, K, Al, and Ca) were observed in the sediment sample by neutron activation methods. Atomic absorption analyses were conducted with regard to five elements (Ca, Cu, Mg, Pb, and Zn) in the same water sample, while four elements (Ca, Cl, Fe, and Mg), as well as total hardness, were examined as dissolved species by wet methods. Comparable concentration values were obtained for calcium and copper from the above analyses, but the results disagreed with one another in the case of magnesium. This may be due to the fact that the wet analysis data for magnesium was determined by a difference between the hardness and calcium results, an assumption which might not always be valid. As is especially true for the alkaline earth elements, depressed values may also have arisen via interferences during the course of atomic absorption experimentation. The discrepancies which result between the NAA and wet data for the element chlorine are a consequence of the total Cl determination by the former method, with the latter means of analysis examining Cl as a sum of chloride, iodide, bromide, phosphate, sulfide, sulfite, and cyanide ions.

Of all the locations which were selected for this study, the highest manganese sediment concentration was observed at this site. This seemingly incredible finding can be explained on the basis of the light-tan sandy-textured particles, which make up a large amount of the river bed material found here, as well as the dissolved particulate matter transferred to the region by air, both of which may contribute to the elevated manganese concentration in the sediment.

Site #2 (Portage County Highway #177 Bridge, Paris Township)

Both water and sediment samples were obtained at Site #2, which is located several miles downstream from the dam at Kirwan Reservoir, on the west branch of the Mahoning River. Because of the surrounding environment, this area was assumed to be free of the pollutants which have an adverse effect on animal and plant life. Low to intermediate concentrations of eight elements (Br, Mn, Cu, Na, V, K, Cl, and Ca) were found in the water, while the same number of elements (Br, Mn, Mg, Na, V, K, Al, and Ca) were detected by NAA in the sediment. All species mentioned previously in regard to the atomic absorption and wet analysis of water samples were also determined here. NAA and AA magensium water concentrations were comparable, but the wet analysis value for the element differed from them by a considerable amount, probably for the same reason as outlined previously. Copper concentrations, also determined by NAA and AA methods, showed excellent agreement, but the same factor which played a part in the divergence of NAA and wet chlorine results in the prior water sample seemed to be involved here.

Since a different branch of the river was selected for obtaining water and sediment samples, no specific conclusions can be drawn from the variation of elemental concentrations with stream flow between the first two sites. The manganese concentration was still pronounced in the sediment, while calcium and hardness were at their lowest levels, apparently due to the granular matrix associated with the samples. Sodium was present in its greatest sedimental concentration, possibly due to the type of structure or to vesicular entrapment, both of which can influence the level of Na in the particles.

Site #3 (North American-Rockwell Plant, Newton Falls)

Site #3 represents the first of two effluent sources encountered along the segment of the Mahoning River included in the present investigation. The plant itself is located north of the town of Newton Falls, Ohio, on the east branch of the Mahoning, into which its industrial by-products are released. An effluent sample was collected at this spot, but no sediment sample was obtained since this was prevented by the aqueous discharge. When the sample was acquired, it was tested with pH paper and found to be rather basic (pH = 9), having a finely-divided white solid suspended in it. Eight elements (Br, Mn, Mg, Na, K, Cl, Al, and Ca) were detected by neutron activation analysis. Atomic absorption and wet analyses were also conducted for the elements previously determined by these methods. Comparable results were obtained for the three techniques in regard to calcium, chlorine, and magnesium concentrations (except for the extremely high wet analysis value for Mg). Copper was not detected by NAA but atomic absorption analysis determined that 0.54 ppm, the greatest Cu concentration for the method, was present.

The highest elemental results for water samples were obtained at this site for magnesium, sodium, chlorine, potassium, aluminum, calcium, and hardness, with elevated concentrations for iron and zinc also being observed. The extreme levels of contaminants present in the effluent would have disastrous effects on the surroundings were it not for dilution by water from the Mahoning. However, this dilution is insufficient (especially during the summer when the water flow is restricted) to control much of the damage being done to the immediate environment.

Site #4 (Below North American-Rockwell Plant, Newton Falls)

In order to discover how the effluent from Site #3 was affecting the nearby locale of the river, water and sediment samples were obtained approximately fifty feet downstream from the previous collection point, again along the east branch of the Mahoning. Seven elements (Br, Mn, Mg, Cu, Na, Cl, and Ca) were detected in the water at Site #4, while ten elements (Br, Mn, Mg, Cu, Na, V, K, Cl, Al, and Ca) were found in the sediment via neutron activation analysis. Atomic absorption and wet analysis methods were again used to determine the specific elements already mentioned. Magnesium, calcium, and copper concentrations in water diverged from each other when compared by the three analytical techniques, but excellent replications were obtained for the NAA chlorine and wet chloride values.

Because of the influence of the previous site, bromine, manganese, magnesium, copper, sodium, chlorine, calcium, iron, and hardness concentrations remained high in the water at Site #4, compared to their values at the first two locations. The aluminum concentration in the sediment, part of which may be considered as silicon due to a neutron-proton interaction with this element during the NAA analyses, is the lowest of all the sites. However, sedimental magnesium and calcium reach extremely high levels here due to their precipitation at this point, to the downstream flow of the river sediment from Site #3, or to a combination of both.

Site #5 (Ohio State Route #5 Bridge, Braceville Township)

The next site at which both water and sediment samples were collected is located approximately three miles downstream from the point where the east and west branches of the Mahoning River combine. Nine elements (Br, Mn, Mg, Cu, Na, V, K, Cl, and Ca) were found in the water sample, while the identical nine elements plus aluminum were detected in the sediment by NAA investigations. As before, calcium, magnesium, copper, lead, and zinc were determined in the aqueous samples by atomic absorption spectrophotometry, while calcium, magnesium, chlorine, iron, and water hardness were examined via wet methods. In nearly all cases, the elemental concentrations were significantly lower than their corresponding values at the previous site. However, dissolved copper remained high according to NAA results, while AA findings showed a much lower Cu content in the water at this location. Again, diverging results were received for magnesium when comparisons between the various analytical methods were instituted, although nearly the same concentrations for NAA and wet determinations of calcium and chlorine were obtained. The aqueous concentration of iron was at its lowest value here, probably because of the isolation of this area from any type of industrialization.

Sodium, potassium, and chlorine remained high in the sediment samples, possibly due to decaying vegitation from the surroundings or to the type of mineral deposits that constitute the soil or sand particles of the river bed.

Site #6 (Ohio State Route #5 Bypass Bridge, Warren Township)

Site #6 is located about two miles west of the city of Warren, Ohio, and represents one of the last collection points were relatively pollutant-free water and sediment samples were obtained previous to entering the highly-industrialized and heavily-populated Warren-Niles area. Eight elements (Br, Mn, Mg, Cu, Na, K, Cl, and Ca) were found in the water, while the same species plus vanadium and aluminum were detected in the sediment, both of which were examined by neutron activation analysis. The same elements mentioned previously were determined by atomic absorption and wet methods. Comparable results were obtained for dissolved magnesium and copper by NAA and AA investigations and for chlorine by NAA and wet analyses. Slightly diverging values were received for aqueous calcium via the three techniques.

Most of the elements were found at low or intermediate concentrations at this location, with the exception of bromine. Among the fourteen sites analyzed, dissolved bromine was at its highest level here, while the sedimental concentration of the element also proved to be elevated. Sodium, magnesium, chlorine, and zinc were at their lowest concentrations in water, while manganese was at a minimum in the sediment. Aluminum was found in its most abundant quantity when the sediment was examined, but this might have been due to silicon via the neutron-proton reaction already discussed. One reason for the extreme bromine levels in both the water and sediment might be the introduction of petroleum into the river, since certain grades of it contain trace amounts of this element.

Site #7 (Parkman Road Bridge, Warren)

This position is located along the northwest periphery of Warren and represents a moderately populated area prior to a region where there is an extensive amount of industry. Because of the large number of rocks and stones forming the river bed, a sediment sample could not be obtained at this site. However, six elements (Br, Mn, Na, K, Cl, and Ca) were detected in the water at low to intermediate levels by neutron activation analysis. Analyses of the specific elements by atomic absorption spectrophotometry and wet methods were reported here. The results for aqueous copper and chlorine concentrations compared well, but those for magnesium and calcium showed some divergence. However, fairly close values were obtained for the latter element via NAA and wet investigations.

A slight increase was observed in the dissolved manganese concentration from that of the previous location, possibly due to the influences already discussed or to a specific type of municipal waste. The rest of the elements remained at low or undetectible levels in the water.

Site #8 (Copperweld Steel Plant, Warren)

The second of the two effluent positions encountered along the segment of the Mahoning River investigated in this paper, Site #8 is located in northcentral Warren immediately outside of the city limits. The petroleum-laden sample that was obtained as it was being introduced into the river emanated from one of the several open pits which the plant uses for the collection of settleable suspended solids. For the same reasons as mentioned in connection with the previous effluent, only a water sample was obtainable at this collection point. Ten elements (Br, Mn, Mg, Cu, Na, V, K, Cl, Al, and Ca) were determined in the water by neutron activation analysis. In addition, the same elements that were examined at prior sites by atomic absorption and wet analytical techniques were observed here. Comparable concentration data were received for the NAA and AA analyses of dissolved magnesium and also for the NAA and wet investigations of aqueous calcium and chlorine. Diverging values were obtained for the NAA and AA determinations of copper in the water.

Most of the aqueous concentrations remained at low to intermediate levels, except for copper, calcium, and iron.

Increases in concentration values for magnesium, manganese, sodium, aluminum, and hardness occurred between this and the previous location, but dilution by river water helped to ease the adverse effects on the environment due to the elevated amounts of these elements in this area. The heightened concentrations for calcium and iron were also a direct consequence of this fact. This was the only other position (along with the effluent at Site #3) where dissolved aluminum was detected. From this, it can be assumed that the element precipitates as it combines with the various components found in the river water.

Site #9 (North West Bridge Street Bridge, Warren)

Site #9 can be found approximately one mile downstream from the previous location, again along the north-central boundary of Warren. Due to the rocky nature of the river bed, only a water sample was capable of being obtained at this point. The water collected here was similar to that observed at the former site, since it also contained a heavy film of oil on its surface. Eight dissolved elements (Br, Mn, Mg, Cu, Na, K, Cl, and Ca) were detected by NAA, while the usual elements were determined in the water by AA and wet methods. The aqueous copper concentrations were similar to each other, but the results for magnesium in water diverged when the data from the three techniques were compared. NAA and wet findings for soluble chlorine and calcium showed good reproducibility, however.

Bromine, manganese, magnesium, potassium, lead, and zinc water concentrations were higher than those at the prior collection point, while the copper, calcium, iron, sodium, chlorine, and hardness results were lower than the dissolved values at the last site.

Site #10 (Market Street Bridge, Warren)

This site is located in the downtown district of metropolitan Warren, and constitutes the beginning of a highly industrialized segment of the river. Both water and sediment collections were made at this position, with the latter having a dark-brown coloration and a viscous texture, unlike that associated with the earlier samples. Six elements (Br, Mn, Na, V, Cl, and Ca) were determined in the water, while nine elements (Br, Mn, Mg, Na, V, K, Cl, Al, and Ca) were detected in the sediment by NAA methods. As before, copper, calcium, magnesium, lead, and zinc were examined by atomic absorption spectrophotometry, with calcium, magnesium, chlorine, iron, and hardness being investigated by wet chemical methods. Diverging values for magnesium, calcium, and copper were obtained by the previously enumerated techniques, but comparable results were observed for chlorine via NAA and wet analyses.

Most of the dissolved elemental concentrations remained low at this location, with moderate increases taking place in regard to sodium, lead, and vanadium and slight elevations occurring with iron and hardness. Decreases in aqueous bromine, manganese, chlorine, calcium, and zinc were evident from experimental data. High sedimental concentrations were received from bromine and potassium, possibly due to the breakdown of specific organic matter containing these compounds or to increases in the crude oil content of the river. Vanadium, which also indicates the extent of contamination by petroleum, was at its lowest level in the water of this site, as was chlorine in the sediment.

Site # 11 (West Park Avenue Extension Bridge, Weathersfield Township)

Site #11 is situated about one-half mile west of the city of Niles, Ohio, a location where industrialization appears to be at a minimum. Both water and sediment samples were obtained from this area, with the latter possessing the light tan coloration and sandy texture characteristic of the first several collections. Nine elements (Br, Mn, Mg, Cu, Na, V, K, Cl, and Ca) were detected in the water, while the same number of species (Br, Mn, Mg, Na, V, K, Cl, Al, and Ca) were found in the sediment by neutron activation analysis. The identical elements examined previously by atomic absorption and wet methods were also determined here. Magnesium and chlorine water concentrations were similar for the NAA and wet analyses, as were the NAA and AA results for dissolved copper. However, the aqueous calcium data for the three techniques showed a large deviation from one another.

Elevations in water concentrations were observed for manganese, magnesium, copper, vanadium, potassium, chlorine, zinc, and iron, possibly due to an increased number of fabricating plants between this and the previous site. Dissolved concentrations for bromine, calcium, and lead were found to be lower. Following along the same lines as Site #10, the highest sedimental concentrations for potassium and bromine were observed here. Increased values for magnesium, vanadium, and calcium were also determined in the soil deposit. Sedimental sodium and chlorine were at their lowest concentrations at this location.

Site # 12 (Pratt and River Streets, Niles)

Located in the heart of Niles, Ohio, Site # 12 was selected because it represents an area where the tributary of Mosquito Creek directly influences the level of pollutants in the Mahoning River itself. Both water and sediment samples were obtained from this collection point, which was overgrown with small trees and underbush. Seven elements (Mn, Mg, Na, V, K, Cl, and Ca) were detected in the water sample, while ten elements (Br, Mn, Mg, Cu, Na, V, K, Cl, Al, and Ca) were determined in the sediment by neutron activation analysis. Atomic absorption and wet methods were applied in order to observe the usual elements. Aqueous magnesium concentration values were comparable in the NAA and AA analyses, but the results for dissolved copper disagreed to some extent. NAA and wet techniques produced similar data for both calcium and chlorine concentrations in water.

Because of the effects of Mosquito Creek, manganese, zinc, and iron were at their highest dissolved levels at this position, most probably due to steel manufacturing which is extensive in the Warren-Niles area. Calcium and lead were found at elevated water concentrations, possibly as a result of the cement industry and municipal plumbing. Aqueous vanadium was at its highest level because of an increased amount of petroleum flowing into the river. Low to intermediate sedimental concentrations of the various elements were also observed.

Site # 13 (Belmont Street Bridge, Niles)

This site is found approximately one-half mile below the previous location and represents the influx of contaminants from another tributary into the Mahoning, that of Meander Creek. Again, collection of both water and sediment samples were instituted. Seven elements (Br, Mn, Mg, Na, V, Cl, and Ca) were detected in the water sample, with ten elements (Br, Mn, Mg, Cu, Na, V, K, Cl, Al, and Ca) being found in the sediment via NAA. In addition, atomic absorption and wet analyses were conducted on the aqueous samples. Comparable concentration data were obtained for dissolved magnesium and chlorine by NAA and wet methods, but diverging values were received for copper and calcium by the applied analytical techniques.

Bromine was at its minimum aqueous level with manganese, vanadium, zinc, and iron having reduced concentrations in water. An increase in the dissolved amount of magnesium, sodium, chlorine, calcium, and hardness was also observed, with lead reaching a maximum value. This could again be due to the type of plumbing located in the general area. Copper reached its highest concentration value, aluminum and magnesium remained elevated, and increased quantities of sodium and chlorine were detected at this location. Calcium was rather low in the particulate matter, however.

Site # 14 (Olive Street Bridge, Niles)

This location, representing the final point of collection for water and sediment samples, is situated about a mile-and-a-half downstream from the previous position. Six elements (Mn, Mg, Na, K, Cl, and Ca) were determined in the water, while ten elements (Br, Mn, Mg, Cu, Na, V, K, Cl, Al, and Ca) were detected in the sediment by neutron activation analysis. The other two analytical methods were also applied to the examination of specific elements in water. Diverging results were obtained for dissolved magnesium and copper via the described techniques. However, calcium had comparable concentration values from the NAA and wet investigations.

An increase in the water concentrations of manganese, sodium, potassium, chlorine, and hardness was observed, while aqueous calcium, magnesium, lead, and zinc levels were found to be lower. The greatest sedimental chlorine value was obtained at this site, while elevations also occurred with magnesium, potassium, aluminum, and calcium in the particulate matter. The increase in concentration of the latter element was probably due to the precipitation of calcium (high in the water at Site #13) originating at the water purification plant located along Meander Creek. The amount of vanadium was found to be lower in this sediment, although it still remained at an overall elevated value. Decreases were also observed for manganese, copper, and sodium concentrations, with the lowest sedimental concentration being reported for bromine.

CHAPTER V

CONCLUSIONS AND SUGGESTIONS

These investigations have shown that it is possible to utilize several analytical methods under specified experimental conditions for detecting trace elements in a polluted river system. Although concentration values obtained via neutron activation and atomic absorption methods did not correspond well in regard to copper, magnesium, and calcium, the neutron activation and wet analytical data showed fairly good agreement for calcium, magnesium, and chlorine. The disagreement between the NAA and AA findings is probably due to the sensitivity limits (0.001 ppm for neutron activation and 0.01 ppm for atomic absorption) inherent to the two methods, and because of certain interferences (silicon, aluminum, phosphate, and sulfate), which are a greater problem with the latter technique than with the former one.[6] Although the sensitivities for elements determined by wet investigations (0.44 ppm for Ca, 1.2 ppm for Cl and hardness, 0.19 ppm for magnesium, and 0.0186 ppm for Fe) are considerably less than those associated with species investigated by the other procedures, comparable results were obtained between this method and neutron activation analysis, since a greater part of the wet chemical interferences were eliminated by complexation and/or reduction.[11] In addition to the above comparisons, several elements not easily detected by NAA (Zn, Pb, and Fe) were capable of being discerned by the other techniques. Thus, concentration data for a number of undetermined trace elements, which may be potentially hazardous to inhabitants of the Mahoning River drainage area, may be obtained by such supplemental methods.

In order to discover the full environmental impact of contamination by trace elements on the Mahoning, a team of scientific researchers, consisting of a chemist, physicist, geologist, and biologist, should study the ecological changes of the river, which would include the periodic collection and analysis of water and sediment samples from various locations. The latter task, which was impossible to perform in the present case, will be easier once data analysis via a mini-computer is instituted.

At this point, the author wishes to make several important and timely suggestions. First, that serious consideration be given to obtaining a new sample of Californium-252 for use as a neutron source, due to the rapid decay of the present one. Second, that additional analytical methods be applied to water and, especially, to sediment samples, with a great amount of emphasis being directed towards x-ray fluorescence. Finally, that further neutron activation analysis studies be accomplished with the instrumental subtraction of background radiation and an increase in the quantity of lead shielding about the Ge(Li) detector.

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