

CONCENTRATION OF SELECTED METALLIC ELEMENTS  
IN THE UPPER ILLINOIS RIVER

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## CHAPTER I

### INTRODUCTION

Due to the present emphasis throughout the nation upon clean air and water, and due to the interest in preserving certain waterways as "scenic rivers," many rivers are becoming focal points of interest. The Illinois River is such a river. Arising in the northwestern part of Arkansas in the Fayetteville-Prairie Grove area the Illinois River flows in a northwesterly direction into northeastern Oklahoma at a point near Siloam Springs, Arkansas. From this point it flows west through Adair County, southwesterly through Cherokee County, and south through the western portion of Sequoyah County to its confluence with the Arkansas River about two miles downstream from Gore, Oklahoma.

The clear sparkling waters of this river flow through an area whose surface geology consists of Osagean rocks. These limestones and cherts account for the gravel beds of the river. Because the water is clear it is an attractive force on tourists who flock to the area in spring, summer, and autumn in pursuit of the recreational activities of fishing, swimming, water skiing, canoeing, and boating.

In 1952, approximately thirteen miles above the mouth of the river, Tenkiller Ferry dam was completed. The water began to rise behind the dam and when the lake was filled it covered an area of approximately 12,500 acres. The water of this beautiful lake serves several purposes among which are the following: flood control, power production, water



supply, recreation, and fish and wildlife habitat. In connection with the lake's recreational appeal, the Tulsa Corps of Engineers have estimated that during the year of 1970 the lake was visited by two and a quarter million people and the number of visitors has been increasing ever since.

Farther upstream, at a point just inside the Oklahoma state line, near the town of Watts, is another much smaller lake called Lake Frances. It was constructed in the late nineteen-thirties and presently serves as a source of municipal water for the towns of Siloam Springs, Arkansas and West Siloam Springs, Oklahoma. It, too, attracts its share of fishermen and picnickers.

Because this river system is one of the most beautiful river systems in the Southwest it has been designated by the Oklahoma State Legislature as a "scenic river." At this writing there is a movement afoot to have it designated by the federal government as a "wild and scenic waterway." There is much controversy between the proponents of this plan and the landowners along the river. Flint Ridge, a development project on the river north of the city of Tahlequah, was sued in court in 1974 by The Oklahoma Scenic Rivers Commission and halted construction by court order until studies could be made regarding the amount of pollution which could come from such a settlement (1).

Regardless of the outcomes of these proposals there is a need to know the concentrations of certain chemical elements in the waters of this river. The Public Health Service has designated specific concentrations of various elements in water as safe levels. When these levels of concentration are exceeded the water has detrimental effects upon the animal and plant life of the stream and area. The purpose of this

study is to determine if the concentrations of the elements cadmium, copper, lead, mercury, and zinc in the waters of the upper Illinois River exceed these levels. These elements were selected because of their toxicities to animals and plants. The upper Illinois refers to that portion of the river above Tenkiller Lake. The hypothesis stated in the null form is: The waters of the upper Illinois River are contaminated with the elements cadmium, copper, lead, mercury, and zinc to the point of being harmful to animal life as determined by the public health service.

The data collected in this study will serve as a reference point for future comparisons of the concentrations of these metallic elements in this river system. Pollution studies probably will become more numerous in the future and by comparing the results of future studies with the results of this study one will be able to determine the effectiveness of efforts being made to control pollution of this river system.

In evaluating the worthiness of this project Mr. Richard Orth of the United States Geological Survey, Federal Building, Oklahoma City was consulted, personally. He agreed that the project was not only feasible but also worthwhile. Mr. Mark Coleman, Laboratory Director of the State Health Department was consulted and he, too, was in agreement with the objectives outlined for this study. Dr. Ralph Harkins of the Kerr Water Laboratory of the Environmental Protection Agency volunteered the use of his laboratories, with the most modern equipment, in Ada, Oklahoma for the completion of this study. Chemists at the State Department of Agriculture were also consulted and concurred with the others on the proposed study.

## CHAPTER II

### REVIEW OF LITERATURE

#### Elements

The metallic elements of this study can be classified as heavy metals and also as trace elements. These terms are sometimes used synonymously; however, there is a distinction between the two. The term "heavy metal" is restricted to those metallic elements whose specific gravity is equal to or greater than five. The term "trace element" is used to describe those elements whose abundance is less than or equal to 0.0 percent (1000 mg/kg) of the earth's crust by weight. The densities of these elements in g/ml are as follows: cadmium, 8.65; copper, 8.96; lead, 11.4; mercury, 13.6; and zinc, 7.14. The abundance in parts per million (mg/kg) of these elements are as follows: cadmium, 0.2; copper, 55; lead, 12.5; mercury, 0.08; and zinc, 70 (2). The United States Environmental Protection Agency has classified mercury as hazardous and the others as potentially hazardous pollutants of our water supplies (3).

Cadmium is produced as a by-product in the mining and smelting of zinc ores. It is also found in phosphate and other mineral deposits. The metal is used extensively in the production of nickel-cadmium electrical batteries. It finds a use in the combined form in agriculture as a pesticide. This is one of the sources of cadmium pollution of our natural waters. Methylated forms of cadmium are unstable. For this

reason the movement of this metal through the environment depends upon the solubility of its salts.

The body contains about one microgram of cadmium at birth and may concentrate the element to such an extent that at the age of fifty there have been measured amounts as much as thirty milligrams. Shellfish concentrate this metal in their soft tissues by a factor of 900-1600 times (4). Physiologically it damages the kidneys, affects bone metabolism, and has been the cause of emphysema when inhaled. It is known to interfere with zinc and copper metabolism and has been suspected of being a cause of cardiovascular disease and hypertension.

Copper is second most abundant of the metals of this study. It is found both free and combined in nature. The free metal is found in Michigan where deposits are practically depleted and in Bolivia. The ores of copper are found in five principal areas as follows: the western United States, the Andes of South America, the Ural Mountains of the Soviet Union, Central Africa, and the Canadian shelf. The ores of copper are of three types: (I) free copper, (II) sulfide ores, and (III) oxidized ores. The most abundant ore of copper is chalcopyrite, a compound of copper, iron and sulfur.

Copper is used in greater amounts than any other metal except iron and aluminum. The most extensive use of the free metal is in electrical conductivity. Combined with tin it forms the alloy known as bronze which increases the hardness of the copper and is used in castings. Because it is resistant to the action of acids and because it forms a protective oxide coat it has been used for utensils and in pipes for conducting water and fuel gases. In compounds it is used as

insecticides an example of which is Paris Green, cupric acetoarsenite. It is used in the form of cupric sulfate to control the algae growth in swimming pools and in farm ponds.

In minute amounts copper as the ion  $\text{Cu}^{++}$  is essential to life of vertebrates and invertebrates as well. In invertebrates it is used in the form of hemocyanin for oxygen transport. In man copper is present in several enzymes whose functions range from the utilization of iron to the pigmentation in the skin. These enzymes known as metalloenzymes and metal-ion-activated enzymes contain the metal ion deeply embedded in the protein. The function of the metal ion in these enzymes seems to be to maintain the proper conformation of the protein, to bind substrate to the protein, or to transfer electrons to or from the substrate. Cytochrome oxidase is one such enzyme whose responsibility is to transfer electrons to oxygen in the metabolic process forming water. It is an intricate organic molecule containing two copper atoms and two heme groups both of which transfer electrons. Other examples of copper containing enzymes and their functions are: ceruloplasmin, iron utilization; lysine oxidase, elasticity of aortic walls; and tyrosinase, skin pigmentation (5).

Copper itself probably has little or no toxicity, although there are conflicting reports in the literature. Soluble salts, notably copper sulfate, are strong irritants to skin and numerous membranes (6). Copper oxide fumes can cause metal fume fever which results in pulmonary edema and damage to the respiratory tract. This condition is accompanied by fever, chills, nausea, vomiting, muscular aches, and weakness. Renal damage may also occur. Copper is readily eliminated in the urine; hence chronic poisoning does not occur.

In spite of its relative scarcity in the earth's crust, abundance of 12.5 mg/kg lead has been mined and worked by men for millenniums. Properties that make it so useful are: low melting point, softness, malleability, alloys with other metals easily, high density, and chemically it forms a protective oxide coat which enhances its wide variety of uses. The principal ore galena,  $PbS$ , is found in many parts of the world.

Industrial use of lead has been a factor in contaminating the environment. Production of lead storage batteries for use in automobiles consumes the largest quantity of lead annually. Other industrial uses include ammunition, bearing metal, cable covering, caulking compounds, sheet lead, solder, type metal, and low-melting alloys for use in fire alarms, automatic fire sprinkler systems and electrical fuses. Pure lead is used in pipes designed to carry corrosive chemicals and in sheets used to line sinks or vats exposed to corrosive chemicals in industrial and educational laboratories.

Compounds of lead have been used as paint pigments because they have low water solubilities, good coverability, and a variety of colors. White lead,  $Pb(OH)_2 \cdot 2PbCO_3$ , was the most widely used for this purpose. Others were red lead,  $Pb_3O_4$ , and chrome yellow,  $PbCrO_4$ . Another oxide of lead,  $PbO$ , is used in ceramics to give a glaze that is not obtainable with other oxides. Lead tetraethyl has been used in formulating anti-knock gasoline and has been found to be a source of atmospheric lead pollution.

Exposure of the general public to lead from the atmosphere, in water supplies and in diets amounts to only minute amounts and at present is a question but not too great a concern. The more immediate concern

is to control the exposure to lead of well defined groups that are known to be directly at risk. One of such is children who live in houses of a pre-1940 vintage and have a tendency to ingest chips of the lead-pigmented paints. Another is a group of illegal whiskey drinkers who are exposed to lead from the lead pipes and radiator cores used in the distilling process of the illicit whiskey production. A third group consists of those who eat or drink from improperly lead glazed earthenware. Acidic foods or drinks have a tendency to leach the lead from the glaze. The last group consists of those workers in small-scale industries where exposure to lead is not controlled.

Through post-mortem analysis it has been established that lead concentrations in the bone increase with age, although its concentrations in the soft tissues seem to stabilize at an early age. This concentration of lead in the bone along with excretion through the kidneys is a mechanism by which the concentrations of lead in the soft tissues may be regulated. The bones serve as accumulation sites because of the similarities between the  $\text{Ca}^{++}$  and  $\text{Pb}^{++}$  ions, with the lead ions replacing some of the calcium ions in the bone.

Lead poisoning has been classified as acute and chronic. Acute poisoning results from a short intense exposure, while chronic results from a build-up of lead in the blood due to recurring intense exposures. The usual daily dietary intake of lead is about 0.3 milligrams. The usual daily respiratory intake is estimated to be between five and fifty micrograms. About 10% of the gastro-intestinal lead passes into the blood stream with about 90% being eliminated from the body with the intestinal wastes. Of the 10% that enters the blood stream some is stored in the bones and some is excreted through the kidneys leaving only

a very small amount for the normal blood level from ingested lead. Of the lead inhaled from the atmosphere, the lungs pass 30-40% into the blood stream. Thus, in spite of lower levels of lead in air than in food and water, as much lead may be absorbed into the body through the lungs as through the digestive system.

Whole blood levels in the normal healthy population vary from 15 to 40 micrograms of lead per 100 ml of blood. If this level is increased to about 80 micrograms per 100 ml, mild symptoms of lead poisoning may be apparent. When the level due to intense exposure rises to 120<sup>+</sup> micrograms per 100 ml severe symptoms and long term after effects are probable.

Anemia is one of the first symptoms and is a result of the lead in the body interfering with the production of heme. Lead is implicated specifically in the metabolism of delta-aminolevulinic acid and in the final formation of heme from iron and protoporphyrin (7). Increases in the concentrations of delta-aminolevulinic acid and coproporphyrin in the urine is almost always observed before the occurrence of symptoms of lead poisoning. The presence of either of these two substances in urine is an important diagnostic characteristic. In the blood it is possible to see a direct cause and effect relationship between the metabolic disturbance and the functional disturbance. The cause is a decrease in production of heme and the functional effect is anemia. The decrease in the production of heme leads at first to a shortened lifespan for red blood cells, then to a decrease in numbers of red cells. To compensate for this the body steps-up its production of red cells and immature red cells, reticulocytes and basophilic stippled cells appear in the blood. The presence of the stippled cells in the blood



is the most characteristic symptom of a patient with lead poisoning. This type of anemia is reversible and the blood cell count returns to normal when the patient is removed from the source of the excessive amounts of lead.

Another result of lead poisoning is the effect lead has on the kidneys. The tubular cells of the kidney are damaged by the presence of excessive levels of lead in the blood and fail to reabsorb phosphates, amino acids and glucose. This results in an excessive excretion of these substances with the urine. The resulting low level of phosphates in the blood trigger a mobilization of phosphates from the bone to compensate for the loss from the blood. Lead may be mobilized from the bone and increase the concentrations in the blood and soft tissues as the phosphate is mobilized. The effect of acute lead poisoning on the kidneys, as in the blood, is reversible and improves when the patient is removed from the source of exposure.

Another effect of lead poisoning is on the central nervous system. Here it is least understood. Most of the information comes from clinical observation and post mortem studies. The capillaries of the brain become too permeable and leak causing swelling of the brain which results in damage to the brain tissue due to the increased pressure.

The chronic effects are due to either the after effects of acute plumbism or a slow build-up over a period of years. The best known of these, chronic nephritis, is a disease characterized by a scarring and shrinking of kidney tissue. Chronic lead nephropathy, sometimes accompanied by gout, is seen in persistent, heavy moonshine drinkers and in some people who have had severe industrial exposure. Another result of chronic lead poisoning is peripheral nerve disease, affecting primarily

the motor nerves of the extremities. It has been found that the peripheral nerves do not conduct the impulses as they should in these cases.

Mercury, the only metal which is in the liquid state at room temperature, exists in ores principally as the sulfide, cinnabar. It is a rare element in that it ranks sixteenth from the bottom in abundance. It has a wide variety of uses which are dependent upon its characteristics. A list of its commercial uses in order of decreasing amounts is as follows: electrical apparatus, chlor-alkali industry, paint, instrumentation, dental preparations, agriculture, general laboratory use, catalysts, pharmaceuticals and others.

The greatest use in electrical apparatus is due to the fact that mercury is an excellent conductor and being liquid over a wide range of temperatures makes it convenient to use. The chlor-alkali industry, the second largest consumer, produces chlorine and sodium hydroxide by the electrolysis of aqueous salt, NaCl, solutions. Mercury is used in this process as the cathode of the cell. The mercury then forms an amalgam with the sodium freed during electrolysis. This amalgam is then removed from the reaction chamber and allowed to react with water forming sodium hydroxide. Due to its toxicity to living things, mercury is used in the paint and agriculture industry as a pesticide. Mercury compounds are added to paint which is to be used in humid regions to act as a preservative and a fungicide. In agriculture organo-mercurials are used as seed dressings to inhibit the growth of fungi on the seeds. In 1972, the Environmental Protection Agency restricted the use of numerous mercury-based pesticides resulting in a decrease in this use of mercury compounds.

Mercury is released into the environment through human activity and

also through natural processes. In mining and smelting mercury it is estimated that two to three percent of the mercury contained in the ore is returned to the environment. The burning of coal has recently been identified as a source of environmental contamination. Headlec and Hunter (8) reported mercury in the ashes of a West Virginia coal to average 120,000 ppb. If we assume that the mercury content of the coal is only 0.1 mg/kg and the production of coal in the United States is 600 million tons annually, the mercury released to the environment would be sixty tons. The weathering of rocks is estimated to yield up to 450 thousand pounds of mercury to the environment each year. This mercury enters primarily in the form of particulates.

Industries that produce mercury containing wastes may add to the mercury concentration in the environment from the natural processes. This fact was brought to light in the early 1950's by the Minamata Bay episode. In Japan, in late 1953, fishermen and their families who lived on the shores of Minamata Bay were stricken with a strange neurological malady. As a result of "Minamata disease" forty-four people died and many of those stricken who managed to survive were left paralyzed for life. The mystery of the disorder was solved when it was noticed that sea birds and house cats of the area were suffering from similar symptoms. Upon investigation it was discovered that they had fish and shellfish as foods in common with the people who were suffering from the same symptoms (a progressive weakening of muscles accompanied by a loss of muscular coordination, loss of vision, impairment of other cerebral functions, eventual paralysis, and in some cases coma and death). The bay had received large amounts of methyl mercury compounds in the waste effluents from a plastics factory (9).

Recent studies indicate that the alkyl mercurials are more hazardous to man than are the inorganic mercury compounds. The alkyl mercurials may be released into the environment as bacteria converting  $Hg^{+2}$  to methyl mercury and dimethyl mercury as a method of detoxification.

The normal distribution of mercury in the environment is in such small amounts that unless it is altered by man's activities there is no reason for concern. The only ore containing mercury in sufficient concentration for extraction is cinnabar, the sulfide of mercury. This ore is found in minable quantities around the world, and man was attracted to its use as early as prehistoric times. In medieval times, physicians began to use mercury compounds as medicines. In the Middle Ages, mercurous chloride came into use as a cathartic. Mercury, today, is used on a substantial scale in chemical industries in the manufacture of paints and paper, and in pesticides and fungicides for agriculture. The world production is about 10,000 tons per year and three tenths of this is used in the United States (10). From these large scale uses a considerable amount of mercury wastes is flowing into the air, the soil and streams, lakes and bays.

Plants and animals have a tendency to concentrate mercury in their tissues. Some marine algae, for example, have been found to contain mercury in concentrations more than one hundred times higher than that of the seawater in which they live. Fish from the Minamata Bay contained concentrations of methyl mercury as high as fifty parts per million which is one hundred times the total mercury accepted as safe by the United States Food and Drug Administration.

Zinc, the fifth element of this study, is a constituent of many enzymes and is essential to all living organisms (11). It is highly

toxic to fish and other aquatic organisms. The toxic effects of zinc on aquatic organisms varies with the hardness of the water because calcium has an antagonistic effect. Copper, on the other hand, seems to have a synergistic effect on the toxicity of zinc (12).

The metalloenzymes, of which zinc is a component, are: carbonic anhydrase, essential for formation of  $\text{CO}_2$  and regulation of body acidity; carboxypeptidase, necessary for protein digestion; and alcohol dehydrogenase, required for alcohol metabolism. This element is also a component of the metalloprotein, metallothionein, which is involved in the absorption and storage of zinc in the body (5).

#### Theory of Atomic Absorption

The fact that an element in the atomic state will absorb those wave lengths of electromagnetic radiations which it emits when in an excited condition has been known for quite some time. It was not until 1955, however, that the use of this fact was suggested by Walsh (13) and his co-workers as a tool for measuring the concentration of that element in solutions. Since different elements absorb different wave lengths, this method of analysis is highly selective.

In practice light of a specific wave length, supplied by a hollow cathode lamp, is passed through a sample of the atomized element. The intensity of the light entering the cell ( $I_0$ ) is compared with the intensity of the light leaving the cell ( $I$ ) and from this comparison the transmittance ( $T$ ) is determined by the equation  $T = I/I_0$ . If one defines absorbance ( $A$ ) as the logarithm of the reciprocal of the transmittance, then  $A = -\log T = -\log I/I_0$ . The intensity of the light leaving the cell is directly proportional to the number of atoms in the cell which

absorb the light in going from the ground state to the excited state and also to the intensity of the light entering the cell. For a cell having a fixed length ( $l$ ) the absorbance is proportional to  $l$  and the concentration ( $C$ ) of the atoms of that element in the sample  $A = \epsilon C l$  and  $A = k l C = -\log I/I_0$ . Since  $k$  and  $l$  are constants, the absorbance is directly proportional to the concentration of the element in the sample.

In the range of concentrations found in natural waters the absorbance is a linear function of the concentration. Therefore, if the absorbance of an unknown solution is compared with a series of solutions of known concentrations, the concentration of the unknown solution can be determined within the detectable limits of the atomic absorption spectrophotometer.

Using this method the U. S. Geological Survey analyzed selected surface waters of the United States in October, 1970. Samples taken from the Kiamichi River near Big Cedar were found to contain cadmium, lead and zinc in 8, 84, and 790 parts per billion, respectively. The concentration of mercury was found to be below the detectable limits of the spectrophotometer (14). The concentration of copper in the waters was not included in that study.

## CHAPTER III

### EXPERIMENTAL PROCEDURE

#### Methods of Sampling

A series of six sampling stations were selected at appropriate sites on the river above Tenkiller Lake. The criteria used in selecting these sites were accessibility and proximity to settlements along the river. Sites were selected that were above and below settlements, in an effort to determine if any of the elements of this study were being added to the stream in the effluent waters from the settlements.

The sites were labeled beginning with the downstream site and progressing alphabetically upstream to the next site. Station "A" was chosen at the site of the bridge on Oklahoma State Highway 82 about twelve miles downstream from Tahlequah. The site for station "B" was selected at the point on the river where the water from Tahlequah's disposal plant enters the river about two miles south of Tahlequah. Site "C" was designated as the lower end of the city park at the river east of Tahlequah just above the pumping station for Tahlequah's municipal water supply. Station "D" is up the river at the Chewey bridge below the towns of Watts, Oklahoma and Siloam Springs, Arkansas. Site "E" is at the bridge on 59 Highway north of Watts. The uppermost site, station "F," is in the state of Arkansas where the river is crossed by Highway 16 between Siloam Springs and Fayetteville.

In an effort to collect samples that would be representative of the river during all of its phases, grab samples were taken at these stations monthly for a period of one year. The first series of samples were collected in September, 1972. The last was taken in the month of August, 1973.

The samples were collected in containers which were specially treated to prevent any possible contamination of the samples. The treatment which the containers were subjected to is as follows. After having been thoroughly cleaned with dishwashing detergents and water, the containers were treated with a 1:1 nitric acid-water mixture followed by thoroughly rinsing with tap water and successive portions of distilled water (14).

At the time of collection each sample was filtered through a 0.45 $\mu$  membrane filter and treated with 5.0 ml of concentrated nitric acid per liter of water to preserve the sample. Treatment such as this provides a holding period of six months (15). The holding period is the allowable time lapse between collection of the sample and the analysis of the sample.

#### Procedure for Analyzing Samples for Cd, Cu, Pb, and Zn

The analysis for the elements cadmium, copper, lead, and zinc was obtained by the procedure outlined here. Standard solutions were prepared from commercially supplied stock solutions to be used for preparing calibration or working curves for each element. These standards were freshly prepared each time an analysis or series of analyses was to be made and were discarded after use in order to give best results. A set of three standards and a blank were used for determination of the



working curve. This procedure is possible because absorbance in solutions of low concentrations is directly proportional to the concentration and in these ranges of concentrations is linear. By feeding the output signal into the input of a strip chart recorder the absorbance is converted to peak height. Then by plotting peak height against concentration a working curve can be produced for each element (15).

For the analysis for these elements the sample taken from the river undergoes no further pre-analysis treatment and is aspirated into the burner of the atomic absorption spectrophotometer. Using the proper settings on the A.A. and on the strip chart recorder the sample is sent through the spectrophotometer and the peak height of the recording is measured. The height of this peak is then compared with the working curve to determine the concentration of the element in the sample.

Table I indicates the proper settings and parameters using the Perking-Elmer 403 Atomic Absorption Spectrophotometer for the determination of the concentrations of the elements cadmium, copper, lead, and zinc. It should be noted that the burner type, fuel, oxidant, and type of flame are the same for all of these elements. The difference is in the type of hollow cathode lamp and the wavelengths at which the elements absorb radiant energy.

Table II indicates the sensitivity (mg/l) of the instrument for the particular element in the concentration range of the standards and also the detection limits (mg/l).

#### Procedure for Analyzing Samples for Hg

Organic mercurials as well as inorganic forms of mercury may be present in surface water samples. To make these organo-mercury

TABLE I  
SETTING FOR THE PERKIN-ELMER 403AA

Hollow Cathode Lamp	Cadmium	Copper	Lead	Zinc
Wavelength Setting	2288 A 229 UV	3247 A 325 UV	2833 A 283 UV	2139 A 214 UV
Slit Setting	4 (7A)	4 (7A)	4 (7A)	4 (7A)
Burner Type	B <sup>2</sup>	B	B	B
Fuel	Ac <sup>1</sup>	Ac	Ac	Ac
Oxidant	Air	Air	Air	Air
Type of Flame	0 <sup>3</sup>	0	S0 <sup>4</sup>	0

<sup>1</sup>Ac = Acetylene

<sup>2</sup>B = Boring

<sup>3</sup>0 = Oxidizing

<sup>4</sup>S0 = Slightly oxidizing

TABLE II  
VALUES FOR THE PERKIN-ELMER 403AA IN mg/l

	Cadmium	Copper	Lead	Zinc
Sensitivity	0.004	0.04	0.06	0.02
Detection Limit	0.001	0.005	0.01	0.005

compounds respond to the flameless atomic absorption technique, they are first broken down and converted to mercuric ions by an oxidizing agent.

Standard solutions of mercuric compounds were prepared for use in calibration of the instrument which for mercury was a Coleman 50 Mercury Analyzer System. The standards contained mercury in the following concentrations: 0.05, 0.1, and 0.2  $\mu\text{g}/\text{l}$ . Each of the standard solutions had a volume of 100 ml in a 300 ml BOD bottle. To each was added 1 ml of  $\text{KMnO}_4$  solution and was allowed to stand for a period of fifteen minutes, after which time 2 ml of potassium persulfate to each bottle was added and allowed to stand for an additional thirty minutes to allow time for all the mercury in the solution to be converted to the  $2+$  ion. At this time sodium chloride-hydroxylamine sulfate solution was added in 2-ml increments to reduce the excess permanganate. Treating each bottle individually, 5 ml of the stannous sulfate solution was added and the bottle was immediately attached to the aeration apparatus of the analyzer. At this point the sample was allowed to stand quietly without manual agitation. The circulating pump, which had previously been adjusted to a rate of 1 liter per minute, was allowed to run continuously.

The absorbance increased and reached a maximum, at which time the recorder pen leveled off. The by-pass valve was then opened and the absorbance returned to its minimum value. The by-pass valve was closed, the stopper and frit were removed from the BOD bottle and the aeration was continued.

This process was repeated with the standards and a working curve was constructed by plotting peak height against concentration of mercury

in micrograms per liter. For each series of analyses working curves were constructed in the manner outlined above. These curves were used to determine the concentration of the samples by comparing peak heights of the samples with the peak heights of the standard solutions.

To determine the peak heights of the samples the following method of sample treatment was used. A volume of 100 ml of each sample was transferred to a 300-ml BOD bottle and acidified with 5 ml of concentrated sulfuric acid and 2.5 ml of concentrated nitric acid, mixing well upon each addition to prevent loss of mercury due to excessively heating the sample. One ml of potassium permanganate solution was added to each sample bottle. The bottles were then agitated and additional portions of the permanganate were added as needed for the purple color to persist for a minimum of fifteen minutes. At this point, 2 ml of potassium persulfate was added to each bottle and the bottles were allowed to stand for an additional thirty minutes. Sodium chloride-hydroxylamine sulfate solution was added in 2 ml increments until the purple color of the excess permanganate ion had been reduced to the 2+ oxidation state. Each sample bottle was treated individually from this point on in the analysis. To each bottle a volume of 5 ml of stannous sulfate was added and immediately the bottle was attached to the aeration apparatus of the mercury analyzer. The procedure outlined for the calibration of the instrument was followed from this point on (15).

To determine the concentration of mercury in ng/ml the peak height was determined from the chart of the recorder and the corresponding mercury concentration was read from the standard working curve.

The following is a list of the reagents used in this analysis and how they were prepared:

- Sulfuric Acid, Conc: Reagent grade.
- Nitric Acid, Conc: Reagent grade of low mercury content.
- Potassium Permanganate: 5% solution, w/v.
- Potassium Persulfate: 5% solution, w/v.
- Sodium Chloride-Hydroxylamine Sulfate Solution: Dissolve 12 grams of sodium chloride and 12 grams of hydroxylamine in distilled water and dilute to 100 ml.
- Stannous Sulfate: Add 25 g stannous sulfate to 250 ml of 0.5 N sulfuric acid. This mixture is a suspension and should be stirred continuously during use.
- Stock Mercury Solution: Commercial preparation having a concentration of 1 mg/ml.

## CHAPTER IV

### DATA AND DISCUSSION

Between the months of September, 1972, and August, 1973, inclusive, a total of seventy-two water samples were collected monthly from all six stations situated on the upper illinois as described in Chapter III. Table III indicates the conditions of the river with regard to discharge and turbidity of the water during this expanse of time. A study of this table indicates that during the months of April and May, the river was above its normal flow and that during August, it was below normal. The flow rate for this table was not measured but was visually compared with the normal flow at Tahlequah which is 350 cubic feet per second (cfs) at the United States Geological Society gauging station on the river near Tahlequah (16). Samples were taken during periods of high water, during periods of drought, and during periods of normal flow giving a representative sampling of the river water.

These samples were preserved with 5 ml of concentrated nitric acid per liter of water and then analyzed using the methods prescribed in Chapter III for cadmium, copper, lead, mercury, and zinc content. Table IV gives the results obtained by these analyses. The concentration of each of the elements surveyed was determined to be less than the detectable limit for that specific element under the conditions prescribed. These low concentrations can probably be attributed to the fact that industrial development of the drainage basin of the Illinois has been minimal.

TABLE III  
ALL STATIONS

Date	Conditions	
	Discharge	Turbidity
9-23-72	Normal	Clear
10-21-72	Normal	Clear
11-25-72	Normal	Clear
12-23-72	Normal	Clear
1-20-73	Above Normal	Muddy
2-24-73	Normal	Clear
3-24-73	Normal	Clear
4-21-73	Above Normal	Muddy
5-23-73	Above Normal	Muddy
6-23-73	Normal	Clear
7-21-73	Normal	Clear
8-25-73	Below Normal	Clear

TABLE IV  
ANALYSES OF ALL SAMPLES FROM ALL STATIONS

Sample Number	Station	Concentrations of				
		Cd	Cu	Pb	Zn	Hg
All	All	(a)	(a)	(a)	(a)	(a)

<sup>a</sup>Less than lower limit of detection as follows: cadmium 1 µg/l; copper and zinc, 5 µg/l; lead, 10 µg/l; and mercury, .2 µg/l.

The Public Health Service limits in ng/ml for these elements in water are as follows: Cd-10, Cu-1000, Pb-50, Hg-5, and Zn-5000. Because the concentrations of cadmium, copper, lead, and zinc were well below the limits imposed by the Public Health Service, no further effort to determine the exact concentrations of these elements was made.

Since mercury has demanded such a great amount of attention recently, an effort was made to determine its exact concentration. This was done by using the method of spiked samples. To 100 ml of each sample of the seventh and eighth collections mercury, in the form of  $\text{Hg}^{++}$ , was added in concentrations of 0.2 ng/ml. These samples were analyzed with a Perkin-Elmer Coleman 50 MAS and compared with standards having a mercury concentration of 0.2 ng/ml. Table V gives the results of these analyses. The T-test at the 90 percent confidence level was applied to test the means of the two populations for a significant difference. The results of this test indicated that no significant difference between the spiked samples and the standards exists.

In a similar study on the Kiamichi River, Durum and others (14), found that the concentrations of cadmium and mercury were below detectable limits and those for lead and zinc were 84 and 790 ng/ml, respectively. Bowen (11) reported in other rivers' concentrations of copper varying from 0.6 to 400 ng/ml with a mean of 10 ng/ml. He reported the range for lead to be 0.6 to 120 ng/ml and the mean to be 5 ng/ml. For zinc he found the mean concentration to be 10 ng/ml with a range of 0.2 to 1000 ng/ml. The mean concentration of cadmium was given as 80 ng/ml but the range was not reported. It is evident that some of the rivers whose concentrations Bowen reported were contaminated to an unacceptable extent.



TABLE V  
 T-TEST ON SAMPLES NO. 7 AND NO. 8 SPIKED WITH 0.2 NG/ML  
 HG AT 90% CONFIDENCE LEVEL

Sample No.	Number of Replications	Hg Content (ng/ml)	Mean ( $\bar{X}$ )
$X_1$	7	2.04, 1.87, 1.96	$2.05 \pm 0.01$
	8	1.87, 1.96, 2.13	
$X_2$ --Standard	6	2.21, 2.13, 2.21	$2.05 \pm 0.01$
	4	2.13, 2.13, 1.96	
		2.04, 1.96, 2.04, 1.96	$2.00 \pm 0.01$

(0.2 ng/ml)

$S = 0.12$

$X_1 - X_2 = 2.05 - 2.00 = 0.05$

$$ts \sqrt{\frac{N_1 + N_2}{N_1 N_2}}$$

$$(0.12) \sqrt{\frac{4 + 12}{4(12)}} = 0.14$$

$$X_1 - X_2 < ts \sqrt{\frac{N_1 = N_2}{N_1 N_2}}$$

## CHAPTER V

### SUMMARY, CONCLUSIONS, AND RECOMMENDATIONS

#### Summary of Study

This study was designed to compare the concentrations of cadmium, copper, lead, mercury, and zinc in the waters of the upper Illinois River in Northeastern Oklahoma and Northwestern Arkansas with standard solutions of these elements which had been prepared from commercially supplied stock solutions.

Attempting to insure that the water samples taken were representative of the water in that portion of the river, samples were taken each month for a one-year period from six sites along the river above Lake Tenkiller. These sites were selected by strategic location and by convenience of access. A site was selected above and below Tahlequah, Oklahoma; one above and below the towns of Watts, Oklahoma, and Siloam Springs, Arkansas; and one at each end of the expanse of the river covered by this study.

The collection vessels were thoroughly washed with soap and water, then treated with a 1:1 nitric acid-water mixture. The vessels were then rinsed several times with tap water followed by thorough rinsing with distilled water. This treatment minimizes the chance of contamination of the vessels by those elements.

At the time of collection the sample was filtered and treated with 5 ml of concentrated nitric acid per liter of water. Without further

pre-treatment for all tests except mercury, the sample was aspirated into the flame of a Perkin-Elmer 403 Atomic Absorption Spectrophotometer. The output from the spectrophotometer was fed into a strip-chart recorder and the peak height from the sample was compared with peak heights from the standard solutions previously mentioned. Because in the lower levels of concentration peak height is directly proportional to the concentration and because the curve is linear at these concentrations, the comparison gives the concentrations of the samples.

Because mercury is not detectable using this type of atomic absorption, a flameless type of Atomic Absorption instrument was used. This was the Perkin-Elmer Coleman 50 Mercury Analyzer System. The water requires further pre-treatment to convert all the mercury to the  $Hg^{++}$  state. This was done using the oxidizing chemicals, potassium persulfate and potassium permanganate. After allowing fifteen minutes for these agents to react, sodium chloride-hydroxylamine sulfate solution is added to remove the excess permanganate. The sample is then treated with a stannous sulfate suspension and is then ready to be attached to the aeration apparatus of the analyzer.

After calibration of the instrument using specially prepared standards containing known concentrations of  $Hg^{++}$ , the samples were analyzed and the peak heights were compared with those of the standards for concentration determinations.

### Conclusions

The analyses of the water samples collected indicated that if there is any pollution of these waters by the elements in this study caused by wastes from industrial concerns on or near the upper Illinois River, it

is not detectable by the instruments used. The instruments have limits of detection for the elements cadmium, copper, lead, mercury, and zinc, as noted in Table II. No evidence was collected supporting the hypothesis which was: the waters of the upper Illinois River are contaminated with the elements cadmium, copper, lead, mercury, and zinc to the point of being harmful to animal life as determined by the Public Health Service. Therefore, the hypothesis must be rejected and one must conclude that these waters are not polluted with the elements of this study. These conclusions were verified by a study done in 1976, by the Oklahoma State Health Department (17).

#### Recommendations

Even though there is no immediate danger to the biota of this portion of the river, it is imperative that periodic scrutiny of the river be performed in order to stay abreast of any changes that might occur. Periodic scrutiny is necessary because the opportunity for pollution of the river is increasing daily as Northwestern Arkansas and Northeastern Oklahoma become more and more industrialized. The author recommends that one of the state agencies be assigned this task of monitoring the river annually, or better still, semi-annually. The author also recommends that the findings of such an agency be published in the news media of the area in order to keep the public informed.

#### REFERENCES CITED

1. Scenic Rivers Association and Illinois River Conservation Council v. James T. Lynn, Sect. H.U.D., No. 74-131 (E.D. Okla., Filed April 24, 1974).
2. U.S. Department of the Interior, "Composition of the Earth's Crust," by Raymond L. Parker, U.S. Geological Survey Professional Paper 440-D, 1969, p. D-15.
3. U.S. Environmental Protection Agency, "A Survey of Emissions and Controls for Hazardous and Other Pollutants," by A. J. Goldberg, NTIS Publication PB 223-568, February, 1973, p. 8.
4. Staff Report, "Trace Metals: Unknown, Unseen Pollution Threat," C & E News, July 19, 1971, pp. 29-33.
5. Frieden, E., "The Chemical Elements of Life," Sci. Am., July, 1972, pp. 52-60.
6. Stecher, Paul G., Editor, The Merck Index, Merck and Co., Inc., New York, N.Y., 1968.
7. Chisholm, J. J., Jr., "Lead Poisoning," Sci. Am., February, 1971, pp. 15-23.
8. Headlee, A. J. W., and R. G. Hunter, "Elements in Coal Ash and Their Industrial Significance," Industrial Engineering Chemistry, 1953, Vol. 45, pp. 548-551.
9. Kurland, L. T., S.N. Faro, and H. S. Seidler, Minamata Disease: World Neurologist, 1960, Vol. 1, pp. 320-325.
10. Goldwater, Leonard J., "Mercury in the Environment," Sci. Am., May, 1971, pp.15-21.
11. Bowen, H. J. M., Trace Elements in Biochemistry, Academic Press, New York, N.Y., 1966.
12. McKee, J. E., and H. W. Wolf, Water Quality Criteria, 2nd Ed., California State Water Quality Board Publication, No. 3-A, Sacramento, Calif., 1963.
13. Walsh, A., "The Application of Atomic Absorption Spectra to Chemical Analysis," Spectrochimica Acta, 1955, Vol. 7, pp. 108-117.

14. Durum, W. H., J.D. Hem, and S. G. Heidel, "Reconnaissance of Selected Minor Elements in Surface Waters of the United States, October, 1970," Geological Survey Circular 643, Washington, D.C., 1971.
15. Environmental Protection Agency, Methods of Chemical Analysis of Water and Wastes, U.S. Government Printing Office, Washington, D.C., 1971.
16. Appraisal of the Water and Related Land Resources of Oklahoma, Oklahoma Water Resources Board, Oklahoma City, Oklahoma, 1971.
17. Water Quality Survey of the Illinois River and Tenkiller Reservoir, Oklahoma State Department of Health, Oklahoma City, Oklahoma, 1977.

APPENDIX

TABLE VI  
 PEAK HEIGHTS FOR CADMIUM STANDARDS USED FOR  
 ANALYZING WATER SAMPLES

Samples	Concentration of Standards in ng/ml	Peak Height (cm)	Average (cm)
1-4	.02	2.0, 2.0, 2.0, 2.0	2.0
	.05	5.4, 5.4, 5.2, 5.3	5.3
	.10	10.3, 10.5, 10.3, 10.4	10.4
6	.05	0.9, 0.9	0.9
	.20	3.5, 3.5	3.5
	.50	9.0, 9.2	9.1
6	.05	1.2, 1.2	1.2
	.20	4.1, 4.1	4.1
	.50	9.9, 9.8	9.9
7-10	.05	1.4, 1.3, 1.5	1.4
	.20	4.6, 4.6, 4.4	4.5
	.50	12.1, 12.1, 12.1	12.1
11-12	.05	1.9, 1.8, 2.0	1.9
	.20	6.3, 6.2, 6.2	6.2
	.50	17.2, 17.2, 17.0	17.1



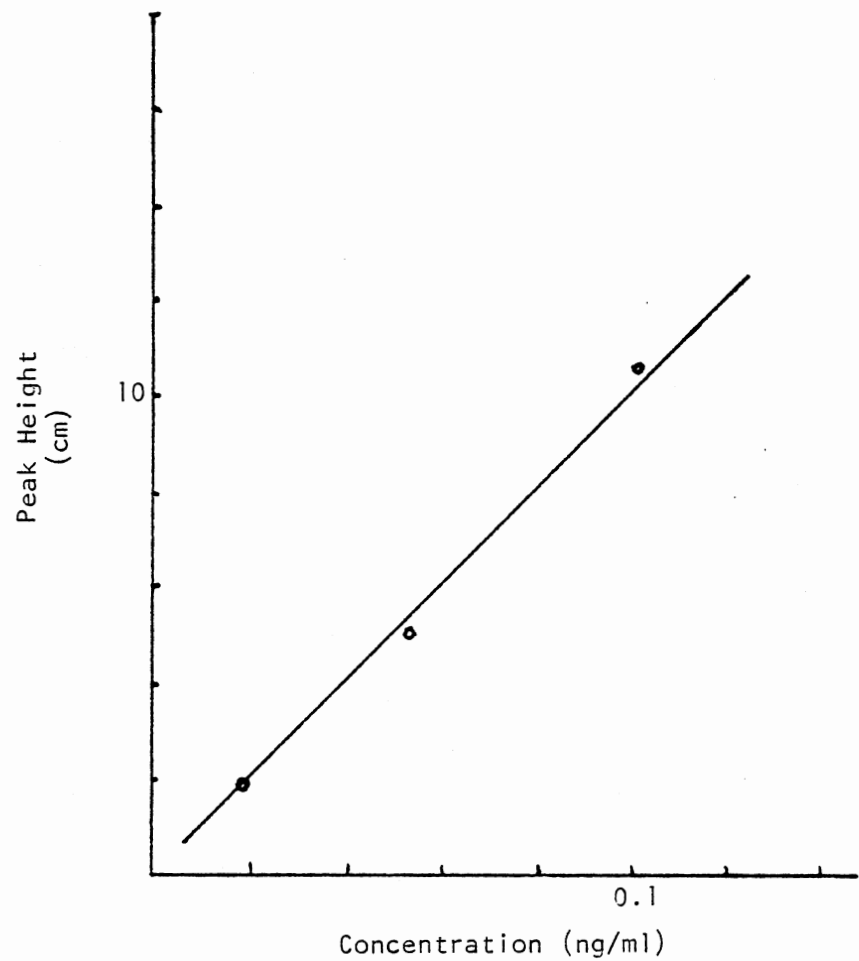


Figure 1. Standard Curve for Cadmium (Samples 1-4)

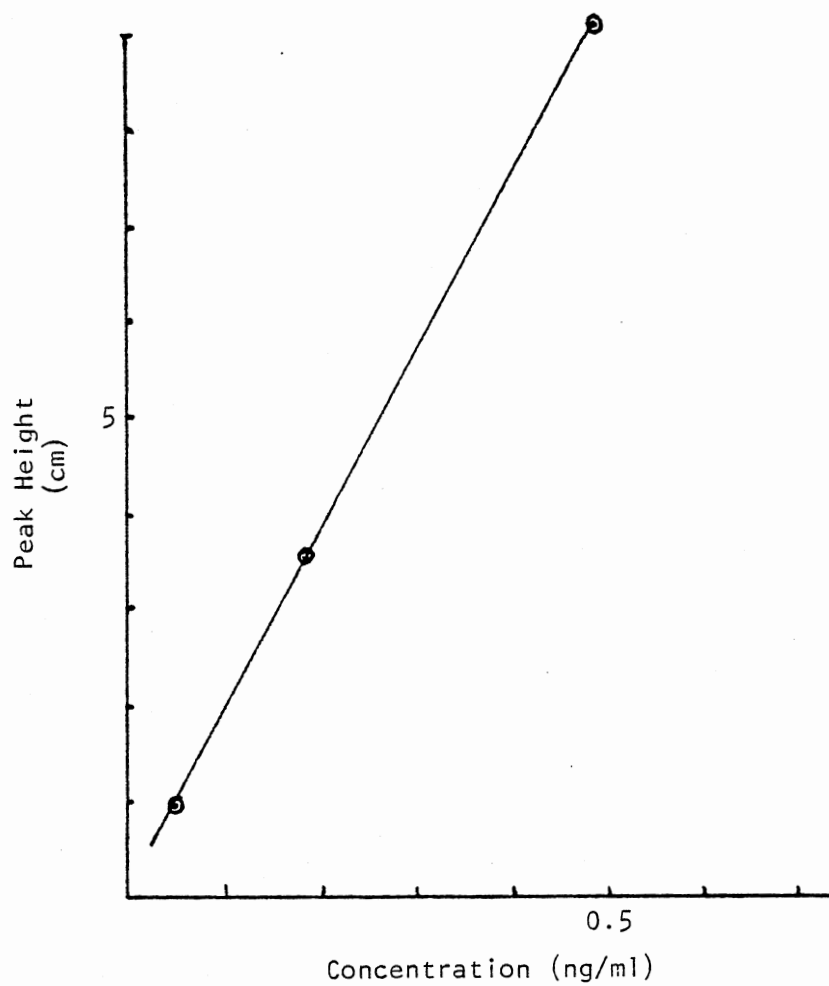


Figure 2. Standard Curve for Cadmium (Sample 5)

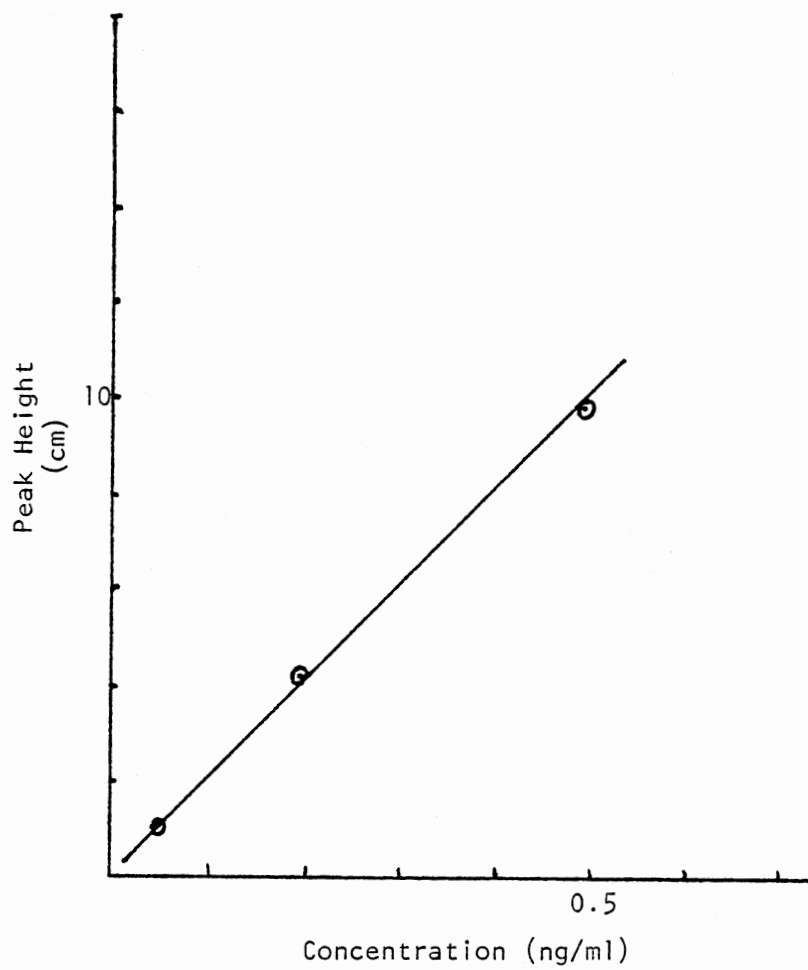


Figure 6. Standard Curve for Cadmium (Sample 6)

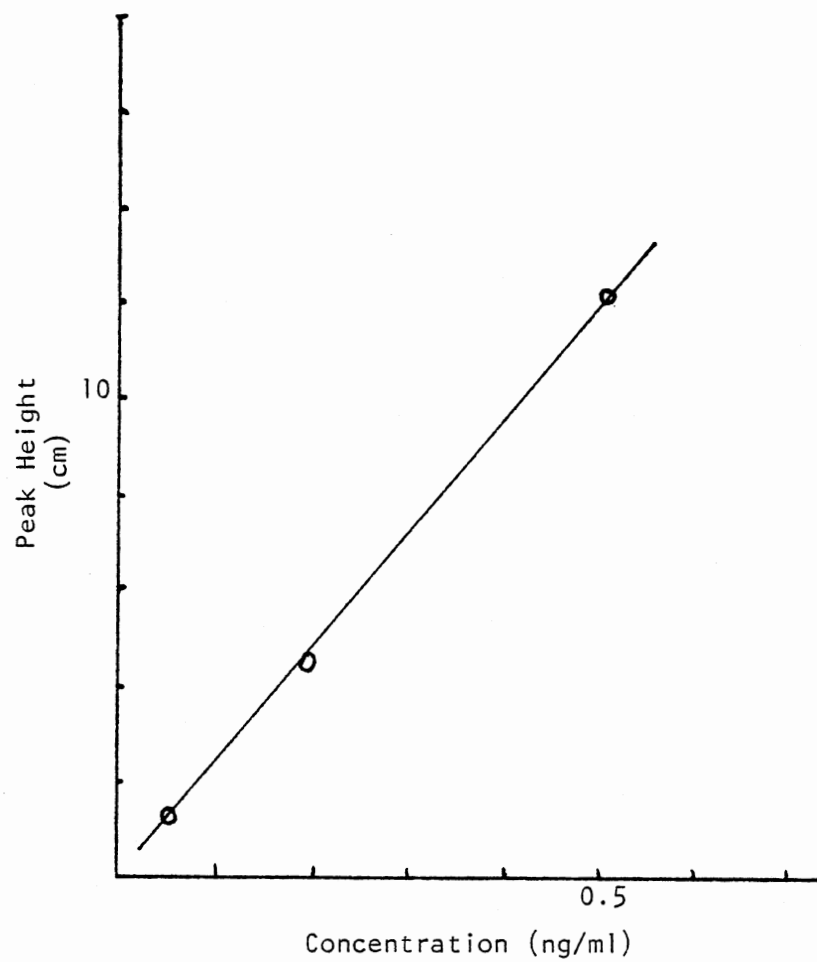


Figure 4. Standard Curve for Cadmium (Samples 7-10)

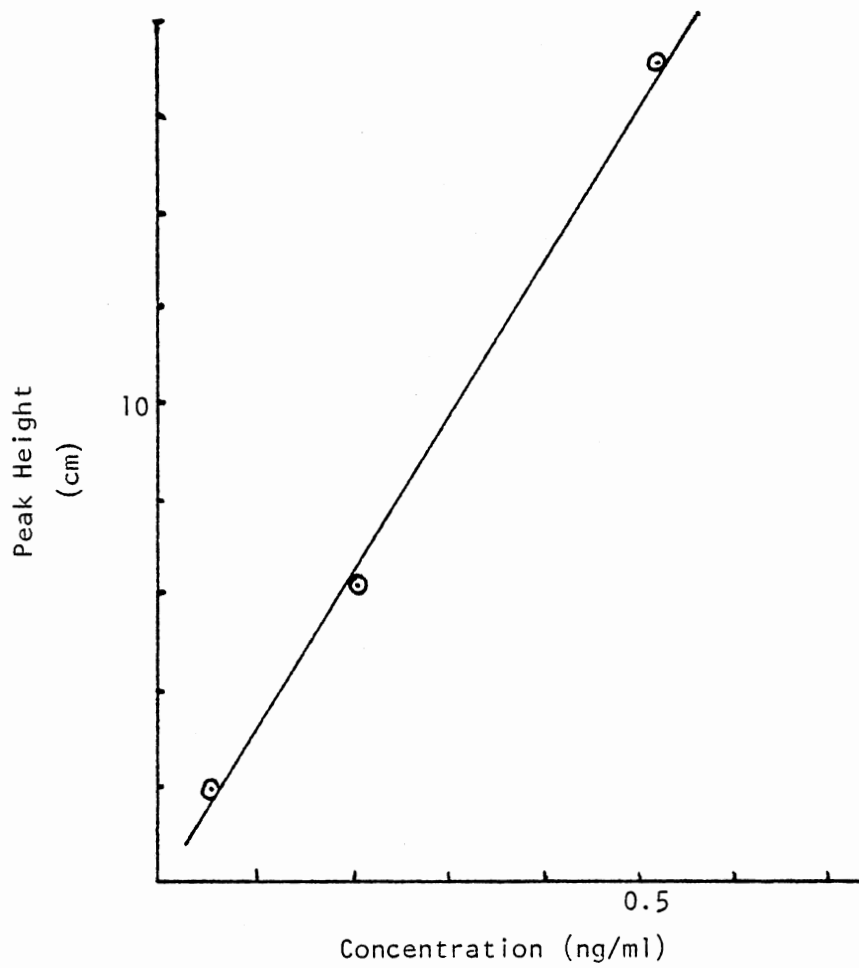


Figure 5. Standard Curve for Cadmium (Samples 11-12)

TABLE VII  
 PEAK HEIGHTS FOR COPPER STANDARDS USED FOR  
 ANALYZING WATER SAMPLES

Samples	Concentration of Standards in ng/ml	Peak Height (cm)	Average (cm)
1-4	0.1	1.5, 1.8, 1.7	1.7
	0.2	3.5, 3.5, 3.5	3.5
	0.5	9.9, 10.0, 9.8	9.9
5	0.1	1.8, 1.8, 1.8	1.8
	0.2	3.9, 4.0, 4.2	4.0
	0.5	10.0, 10.1, 10.1	10.1
6	0.1	1.1, 1.1	1.1
	0.2	2.8, 2.8	2.8
	0.5	8.0, 7.9	8.0
7-10	0.1	1.7, 1.7	1.7
	0.2	2.8, 2.8	2.8
	0.5	8.4, 8.4	8.4
11-12	0.1	2.1, 2.2, 2.1	2.1
	0.2	3.8, 3.8, 3.8	3.8
	0.5	10.4, 10.5, 10.6	10.5

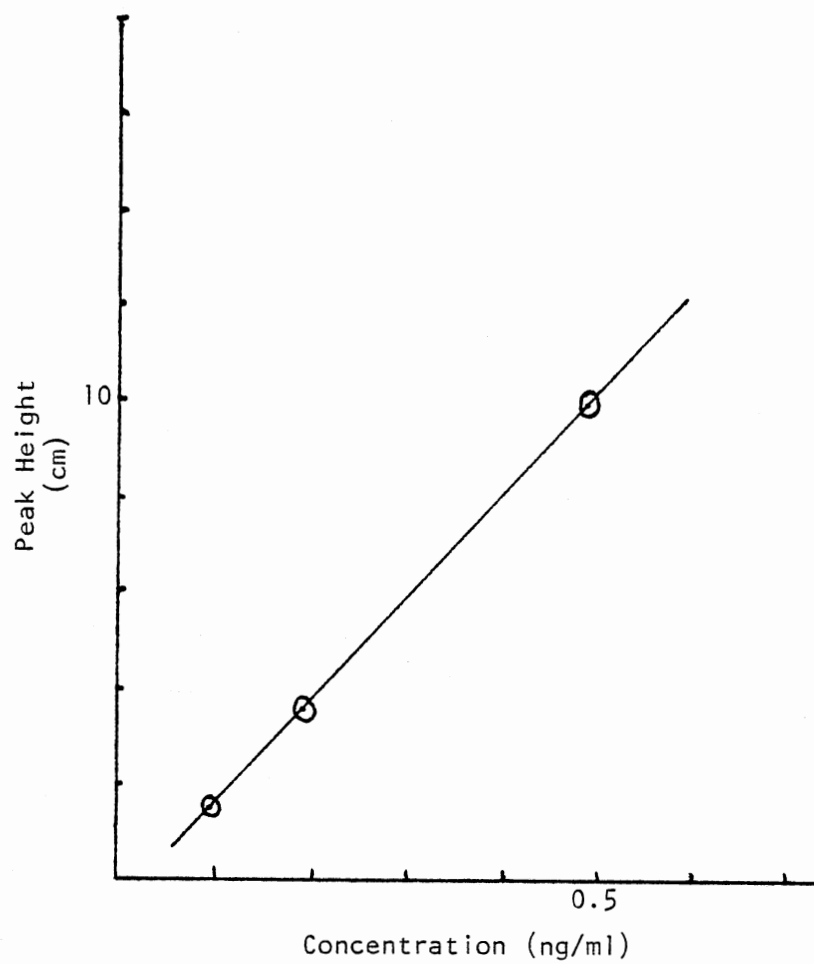


Figure 6. Standard Curve for Copper (Samples 1-4)

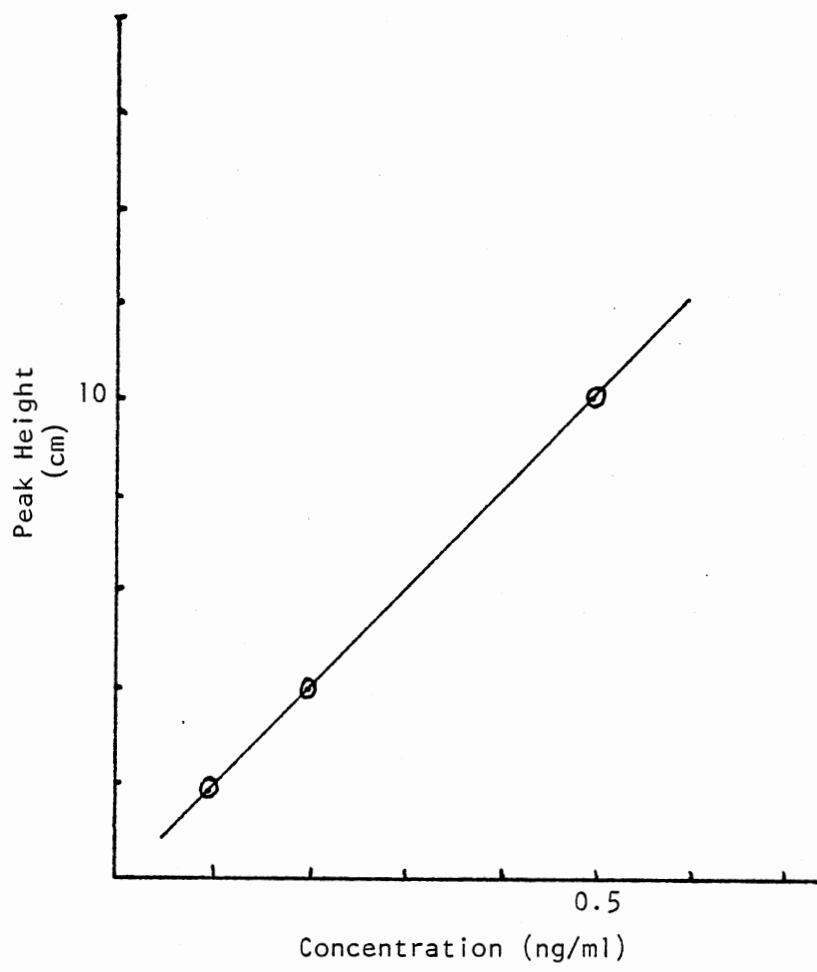


Figure 7. Standard Curve for Copper (Sample: 5).



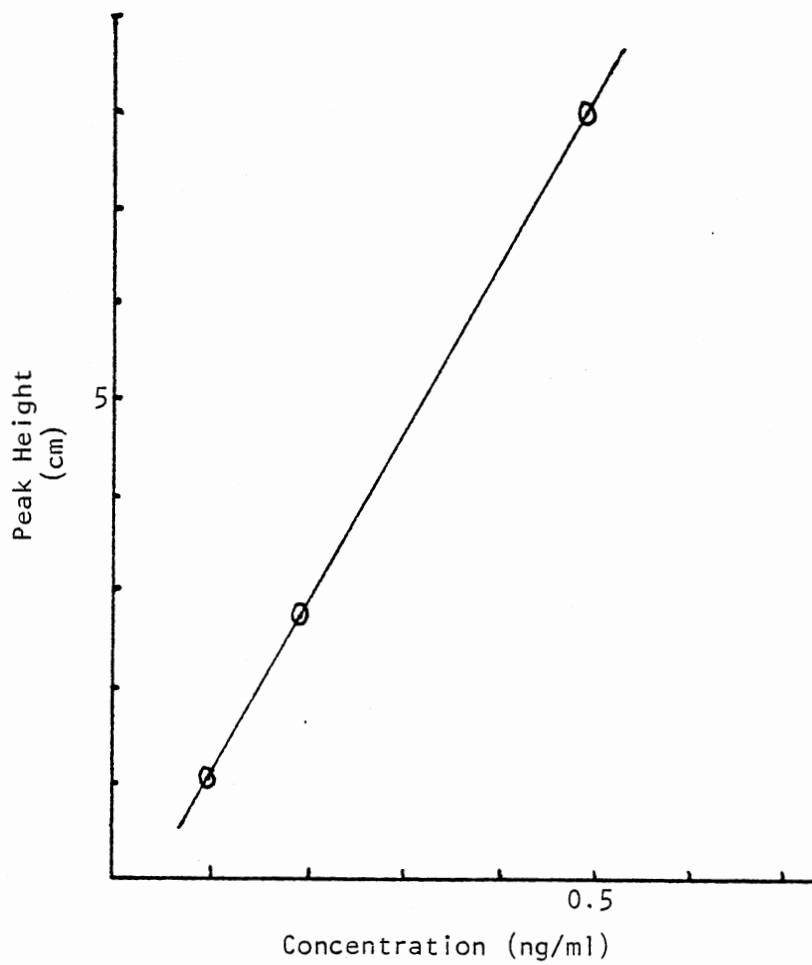


Figure 8. Standard Curve for Copper (Sample 6)

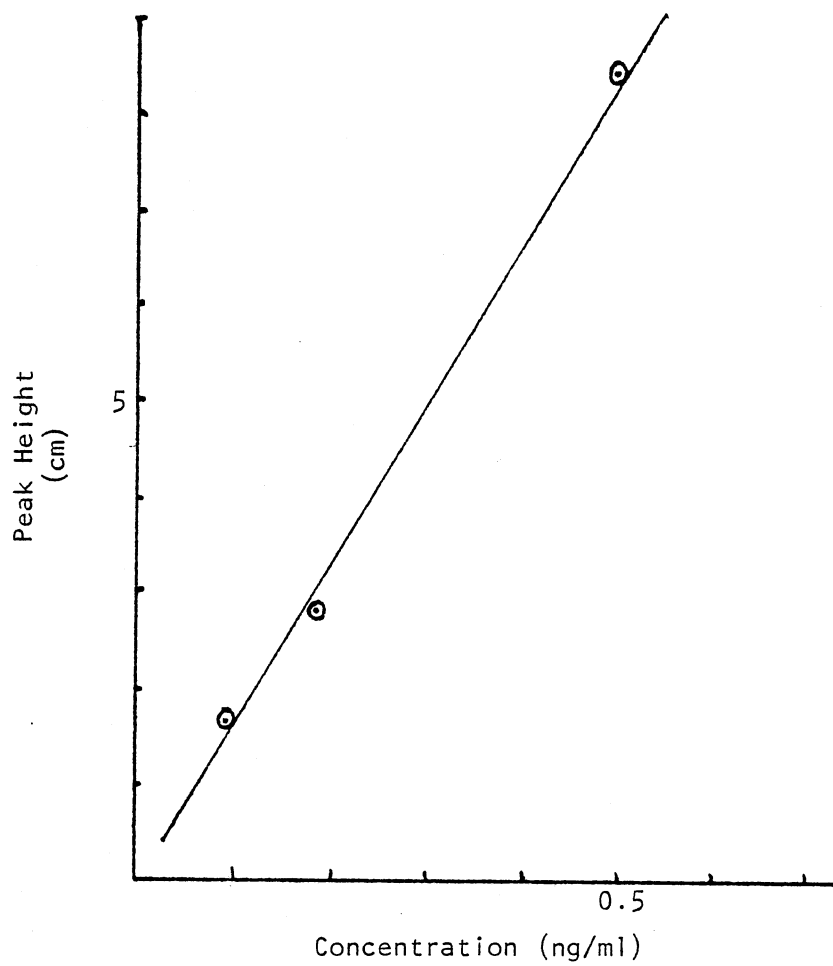


Figure 9. Standard Curve for Copper (Samples 7-10)

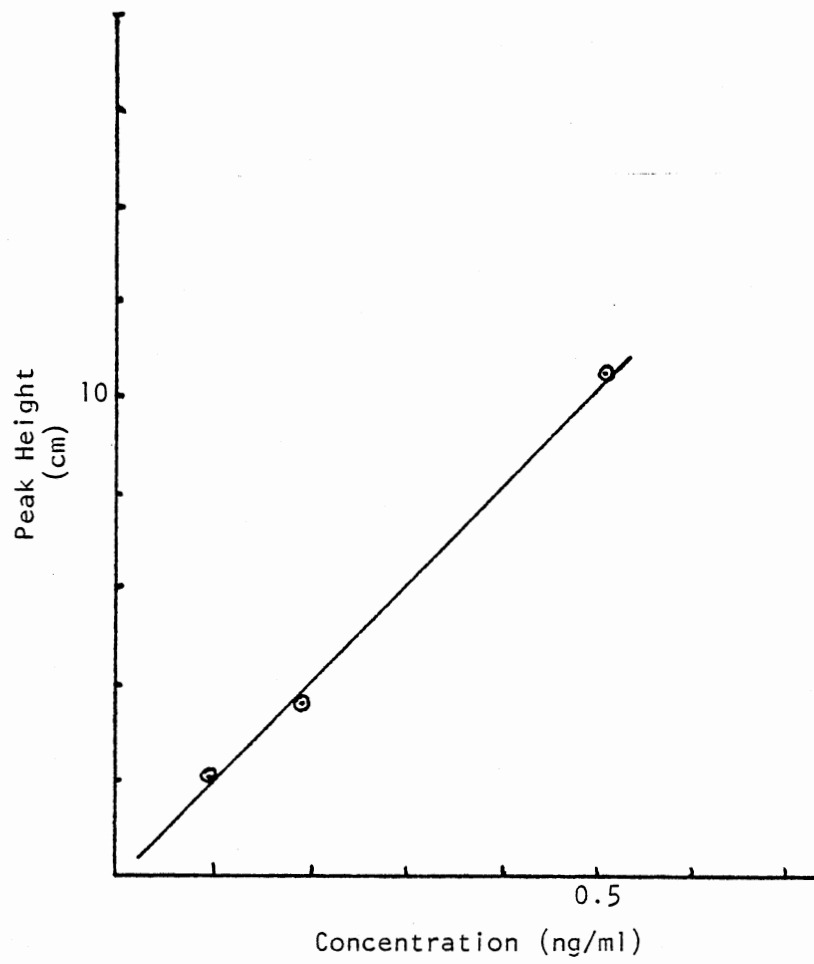


Figure 10. Standard Curve for Copper (Samples 11-12)

TABLE VIII  
 PEAK HEIGHTS FOR LEAD STANDARDS USED FOR  
 ANALYZING WATER SYSTEMS

Samples	Concentration of Standards in ng/ml	Peak Height (cm)	Average (cm)
1-4	0.3	0.8, 0.4, 0.8	0.7
	0.5	1.4, 1.0, 1.2	1.2
	1.0	2.8, 2.9, 2.7	2.8
5	0.3	1.8, 1.8	1.8
	0.5	3.1, 3.1	3.1
	1.0	6.4, 6.4	6.4
6	0.3	0.7, 0.7	0.7
	0.5	1.5, 1.5	1.5
	1.0	2.9, 2.7	2.8
7-10	0.3	0.5, 0.5, 0.5	0.5
	0.5	0.8, 0.8, 0.7	0.8
	1.0	2.0, 2.0, 2.0	2.0
11-12	0.3	0.3, 0.3, 0.3	0.3
	0.5	0.4, 0.4, 0.5	0.43
	1.0	1.0, 1.1, 1.1	1.1

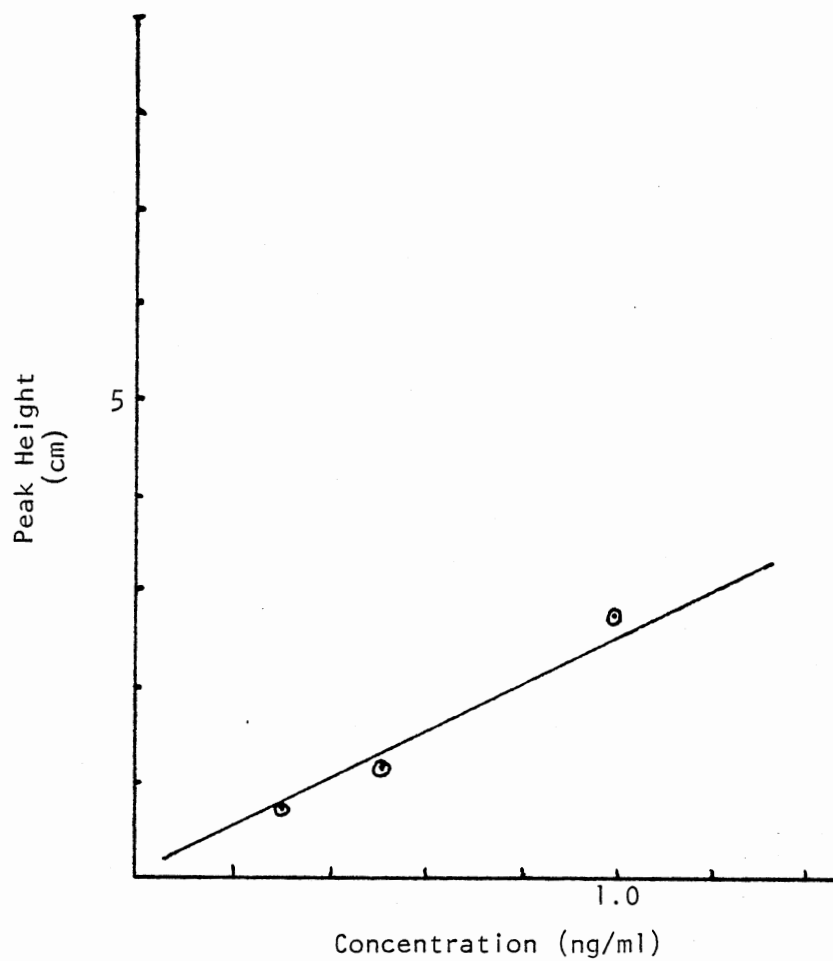


Figure 11. Standard Curve for Lead (Samples 1-4)

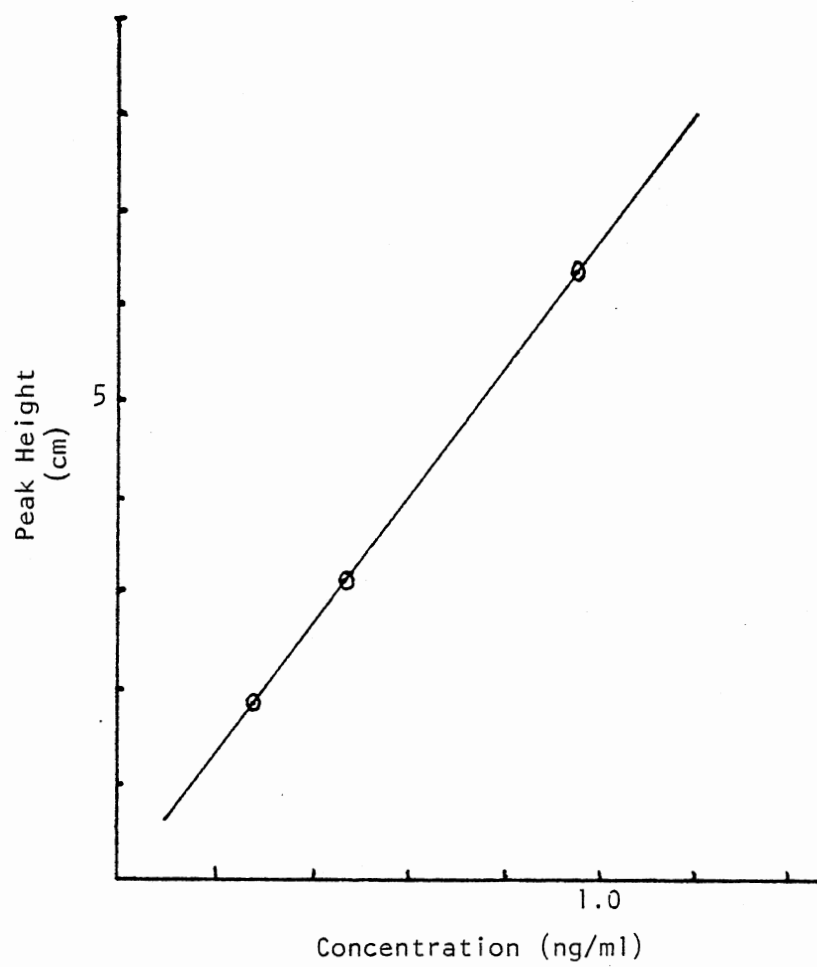


Figure 12. Standard Curve for Lead (Sample 5)

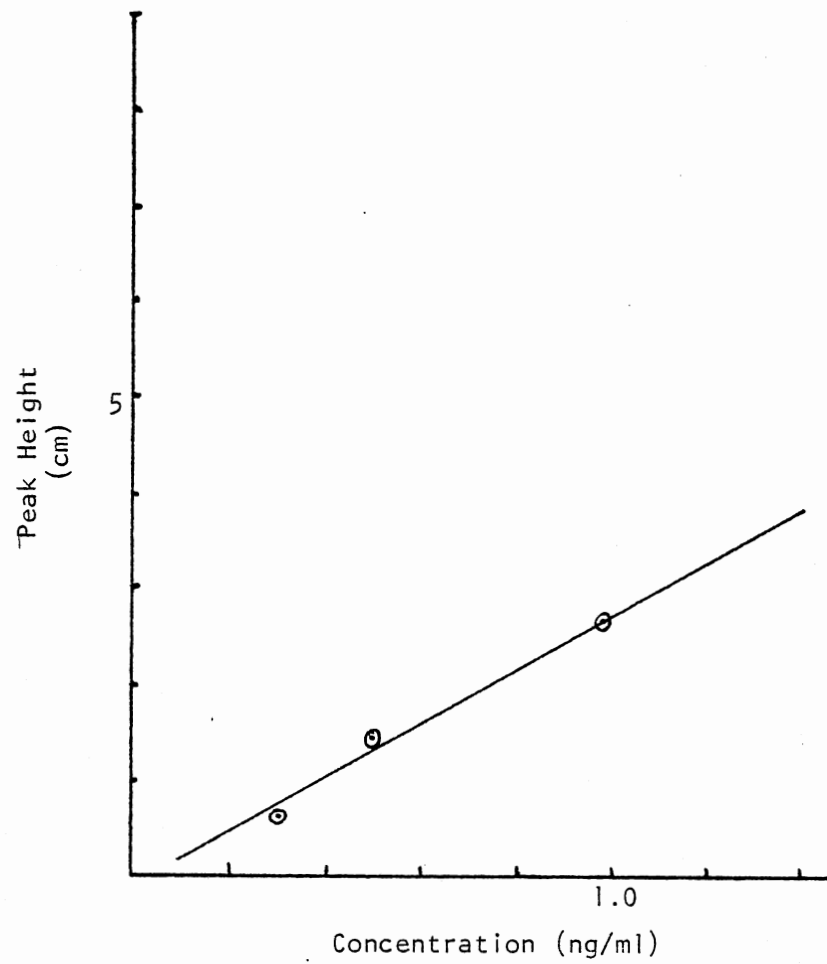


Figure 13. Standard Curve for Lead (Sample 6)

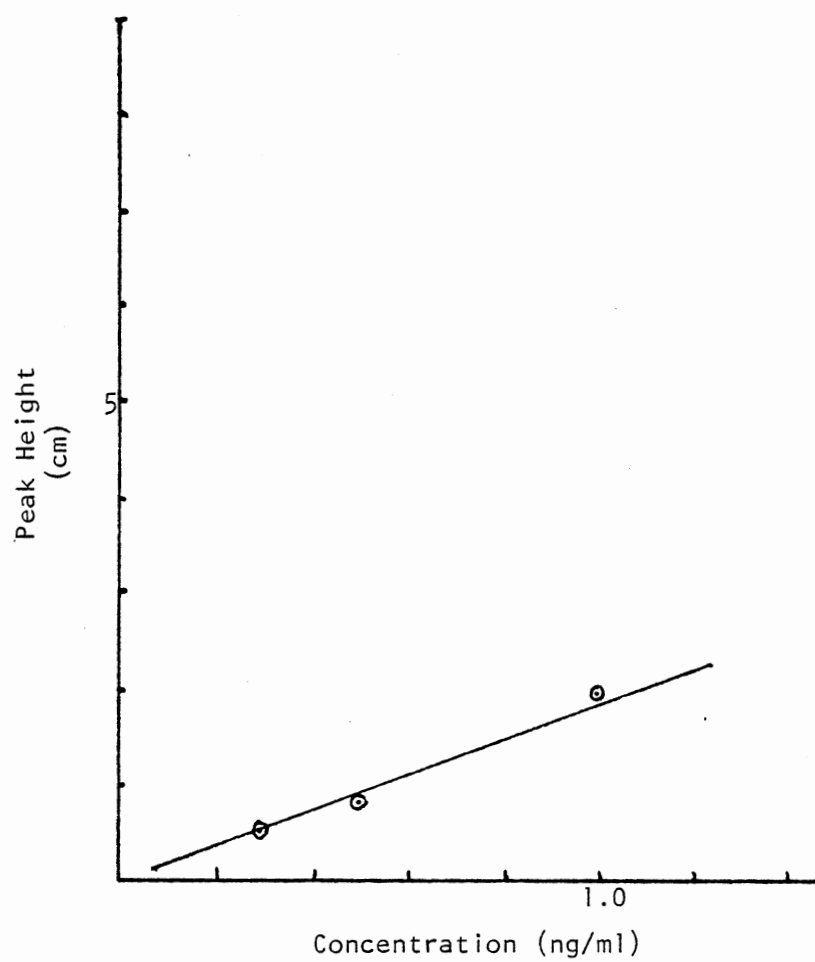


Figure 14. Standard Curve for Lead (Samples 7-10)



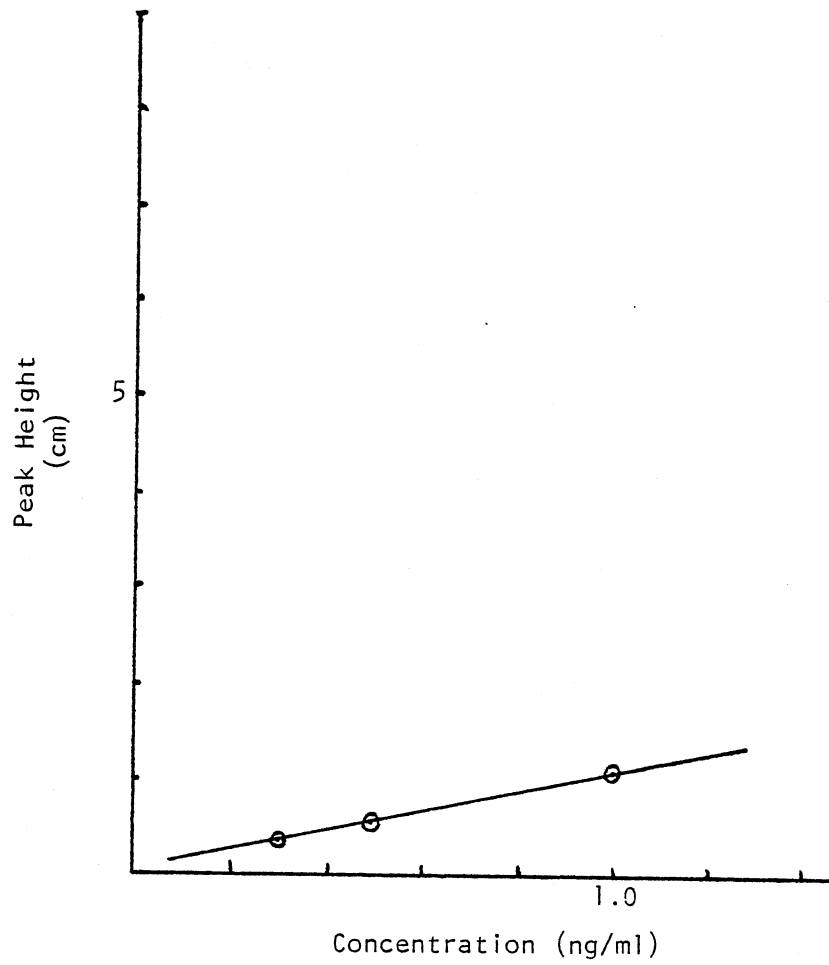


Figure 15. Standard Curve for Lead (Samples 11-12)

TABLE IX  
 PEAK HEIGHTS FOR MERCURY STANDARDS USED FOR  
 ANALYZING WATER SAMPLES

Samples	Concentration of Standards in ng/ml	Peak Height (cm)	Average (cm)
1-4	.05	4.8, 4.7, 4.9	4.8
	.10	6.5, 6.5, 6.5	6.5
	.20	8.8, 8.8, 8.8	8.8
5-6	.05	3.2, 3.2, 3.2	3.2
	.10	4.2, 4.2, 4.2	4.2
	.20	6.4, 6.4, 6.4	6.4
7-8	.05	1.1, 1.1, 1.1	1.1
	.10	1.8, 1.8, 1.8	1.8
	.20	2.8, 2.8, 2.8	2.8
9-10	.05	2.2, 2.2, 2.2	2.2
	.10	3.1, 3.1, 3.1	3.1
	.20	4.8, 4.9, 4.7	4.8
11-12	.05	1.6, 1.6, 1.6	1.6
	.10	3.0, 3.0, 3.0	3.0
	.20	5.5, 5.5, 5.5	5.5

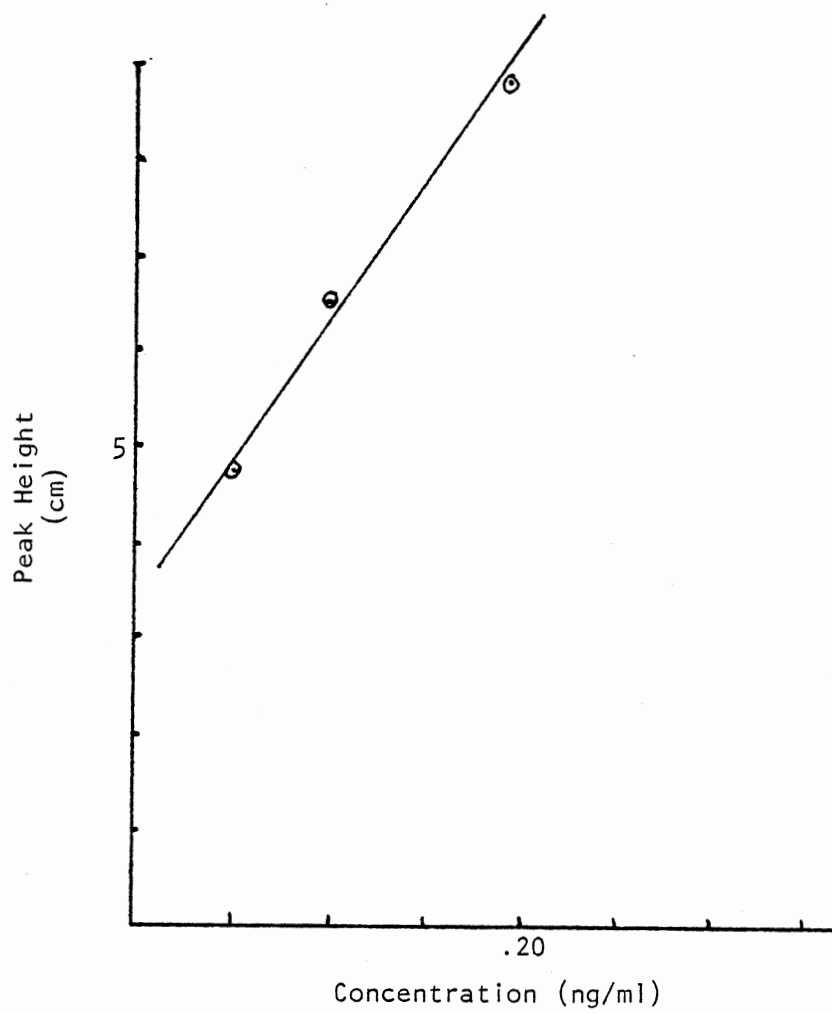


Figure 16. Standard Curve for Mercury (Samples 1-4)

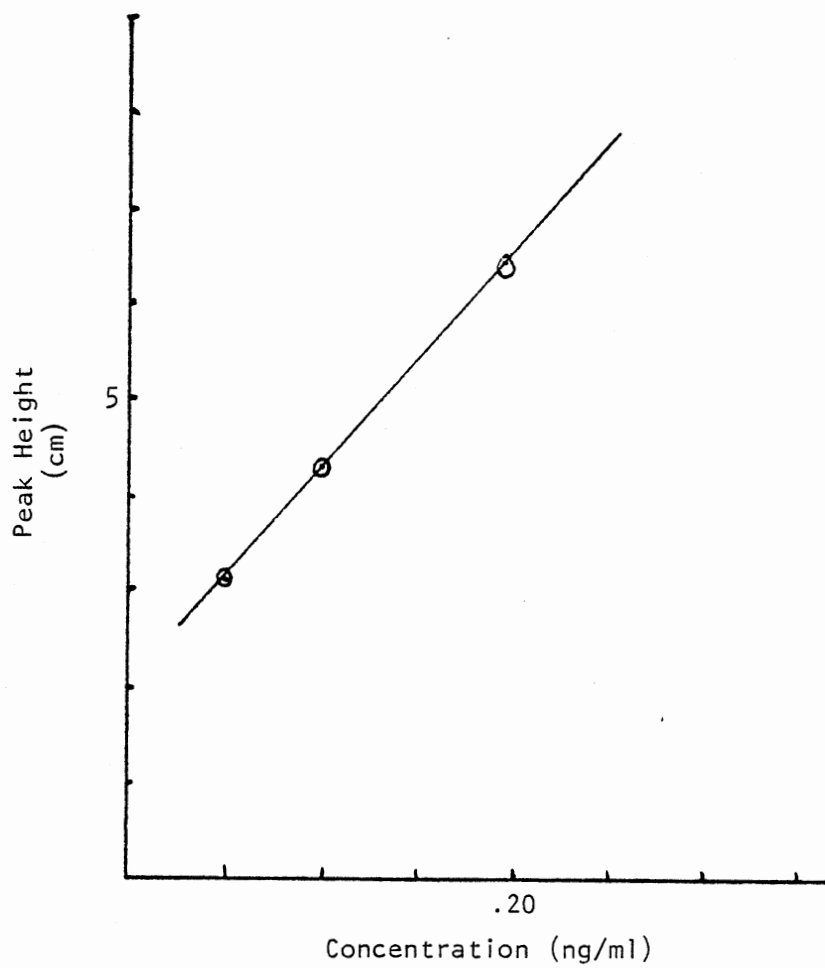


Figure 17. Standard Curve for Mercury (Samples 5-6)

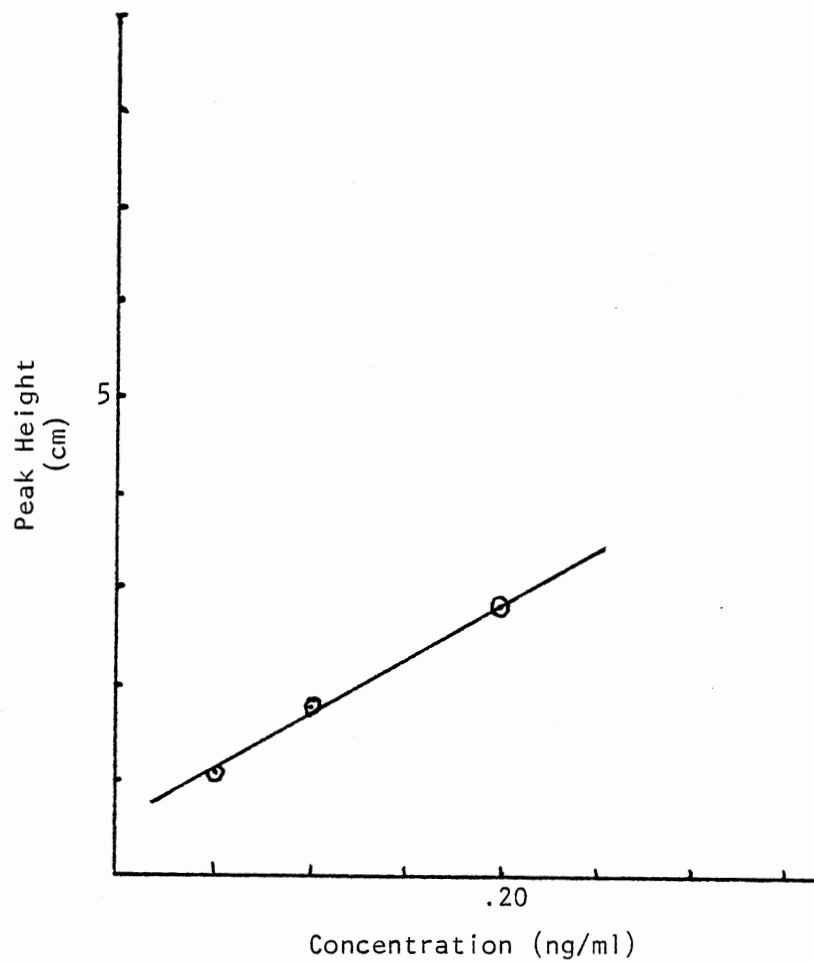


Figure 18. Standard Curve for Mercury (Samples 7-8)

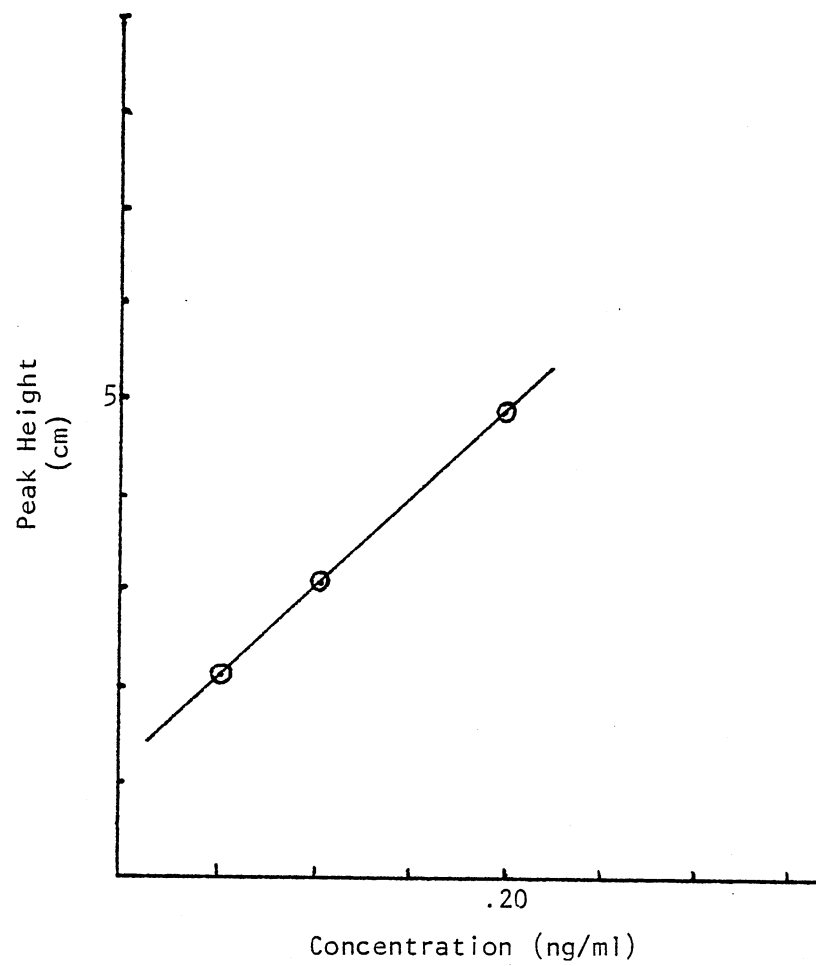


Figure 19. Standard Curve for Mercury (Samples 9-10)

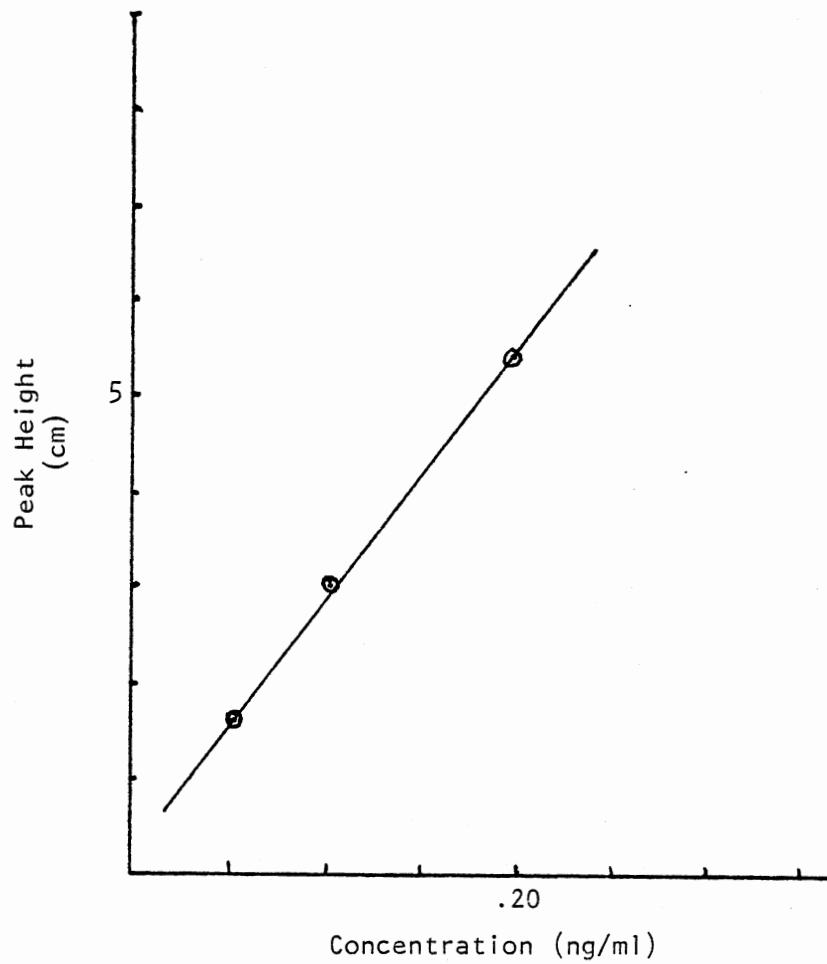


Figure 20. Standard Curve for Mercury (Samples 11-12)

TABLE X  
 PEAK HEIGHTS FOR ZINC STANDARDS USED FOR  
 ANALYZING WATER SAMPLES

Samples	Concentration of Standards in ng/ml	Peak Height (cm)	Average (cm)
1-2	0.10	0.6, 0.6, 0.6	.6
	.50	3.2, 3.1, 3.0	3.1
	1.00	8.2, 8.2, 8.2	8.2
3-4	0.10	1.0, 1.0, 1.0	1.0
	0.40	3.8, 3.8, 3.8	3.8
	1.00	8.8, 8.9, 8.7	8.8
5-6	0.10	0.8, 0.8, 0.8	0.8
	0.50	3.8, 3.8, 3.8	3.8
	1.00	8.9, 9.0, 8.9	8.9
7-10	0.10	0.7, 0.7, 0.7	0.7
	0.50	3.7, 3.7, 3.7	3.7
	1.00	7.4, 7.4, 7.4	7.4
11-12	0.10	1.1, 1.1, 1.1	1.1
	0.50	5.5, 5.5, 5.5	5.5
	1.00	9.9, 9.9, 9.9	9.9



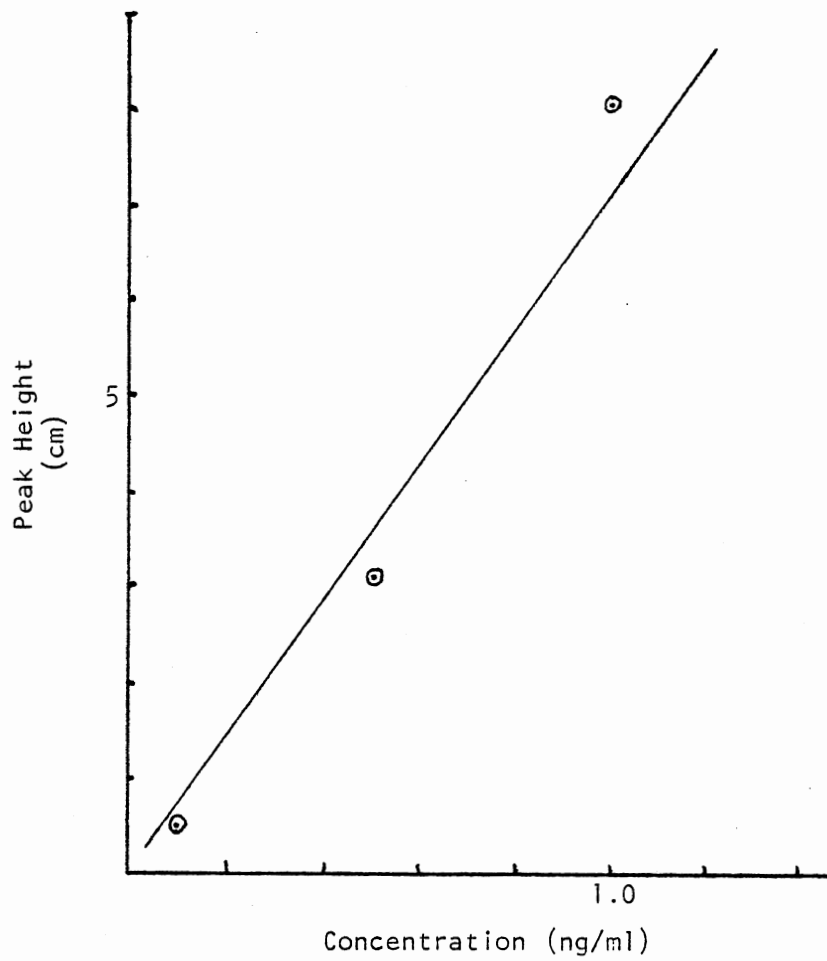


Figure 21. Standard Curve for Zinc (Samples 1-2)

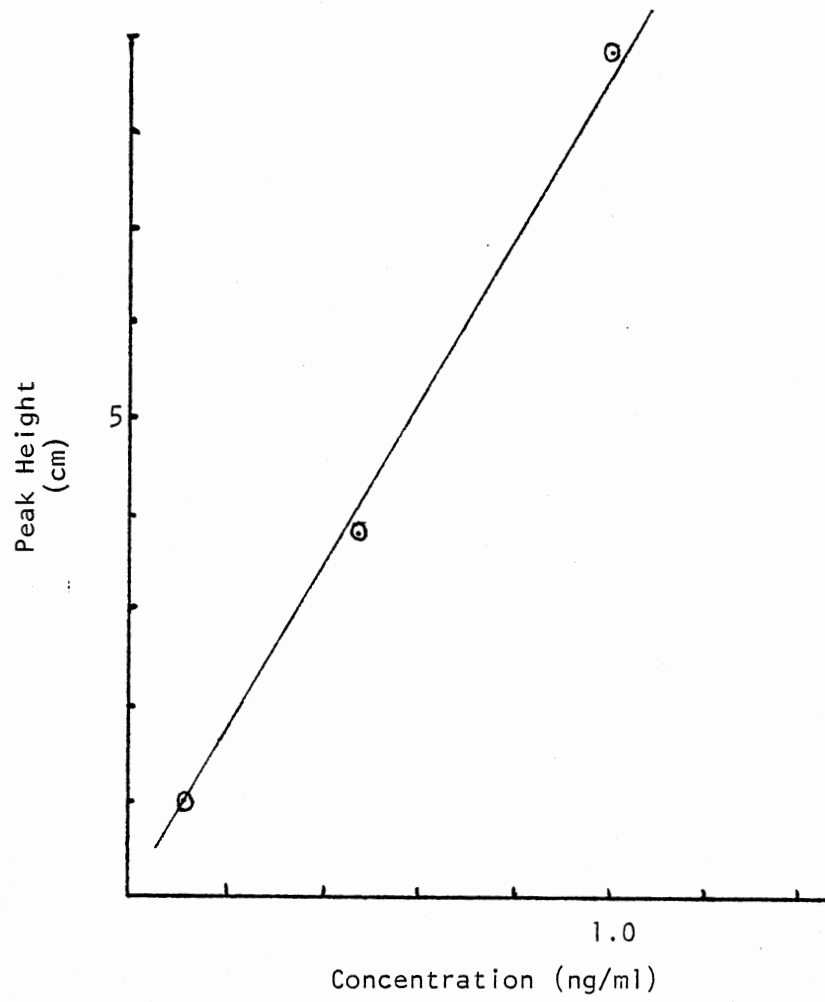


Figure 22. Standard Curve for Zinc (Samples 3-4)

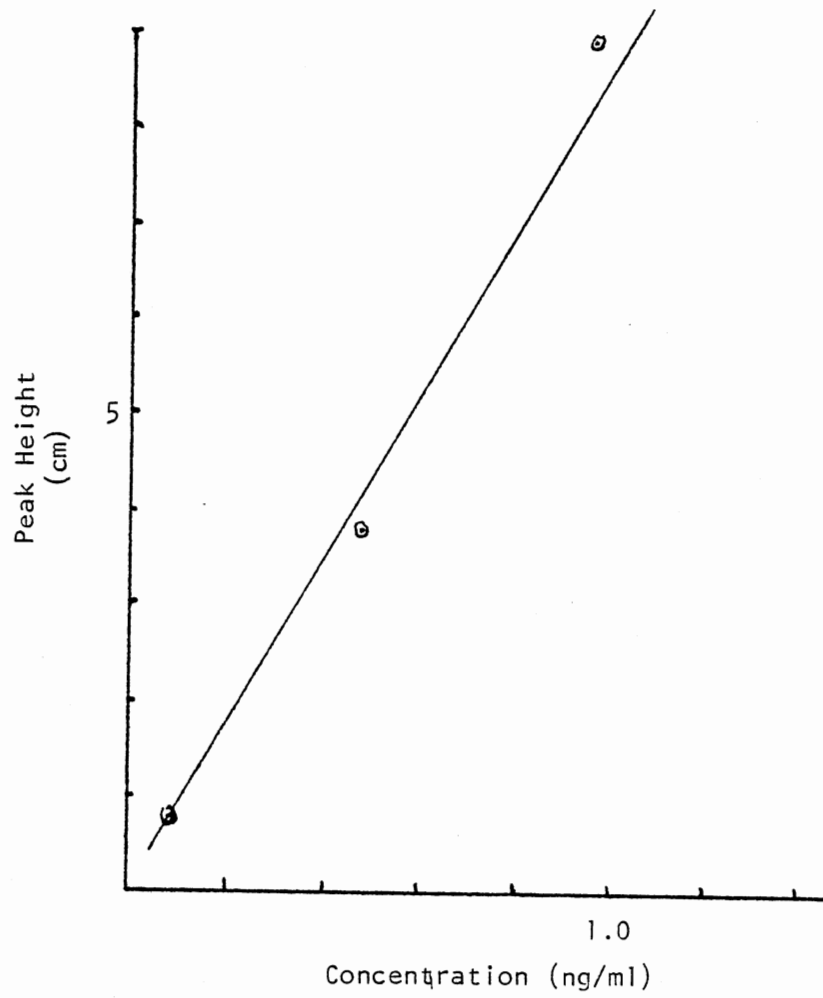


Figure 23. Standard Curve for Zinc (Samples 5-6)

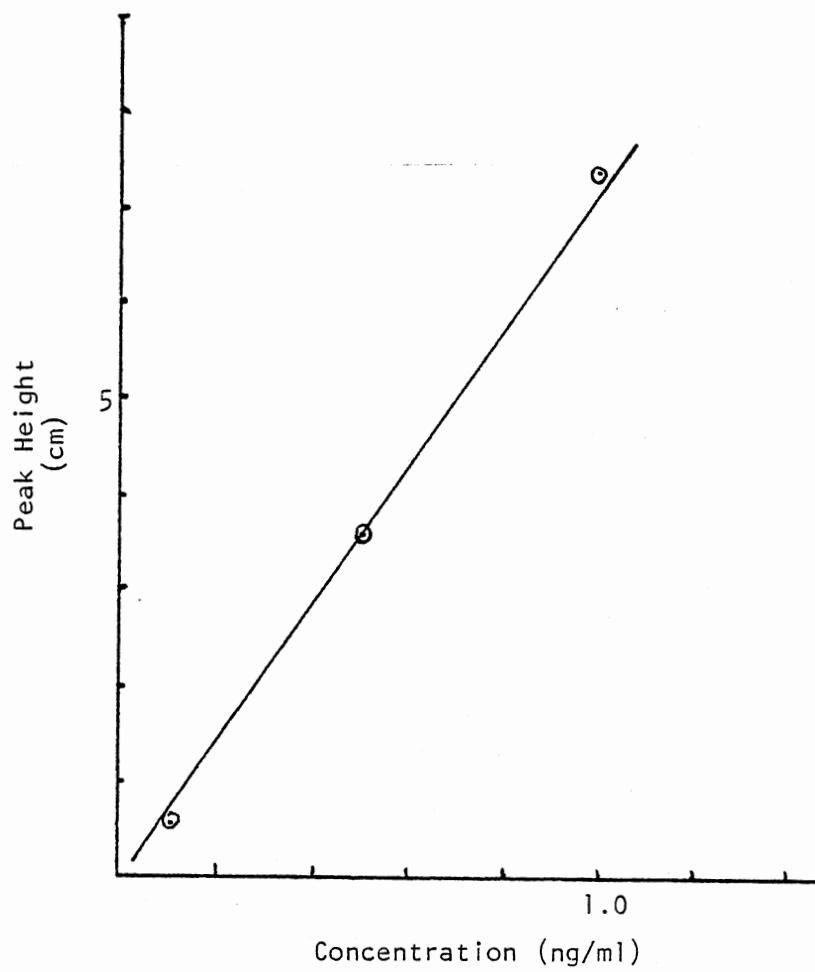


Figure 24. Standard Curve for Zinc (Samples 7-10)

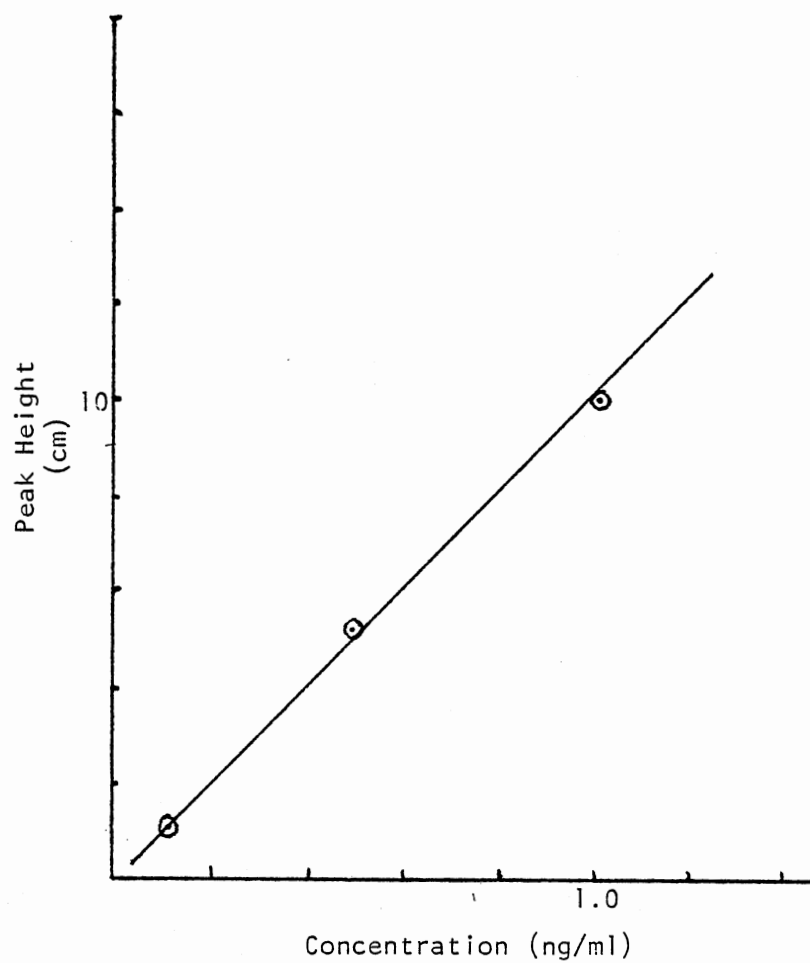


Figure 25. Standard Curve for Zinc (Samples 11-12)

2  
VITA

Austin Ketcher

Candidate for the Degree of

Doctor of Education

Thesis: CONCENTRATIONS OF SELECTED METALLIC ELEMENTS IN THE UPPER  
ILLINOIS RIVER

Major Field: Higher Education

Biographical:

Personal Data: Born at Pensacola, Oklahoma, October 7, 1929, the son of Robert L. and Marvie Ellen Ketcher.

Education: Graduated from Haskell Institute, Lawrence, Kansas, in 1946; received the Bachelor of Science in Education degree from Northeastern Oklahoma State University, Tahlequah, Oklahoma, in 1952; did graduate work at Northeastern State College during the summers of 1954-57; awarded the Master of Science degree by Oklahoma State University in 1958; attended National Science Foundation summer institutes, Kansas State University, 1961; Ohio State University, 1962; Oklahoma Baptist University, 1963; and Texas A&M, 1969; completed requirements for the degree of Doctor of Education at Oklahoma State University in July, 1982.

Professional Experience: Entered the teaching profession in 1948 in the rural schools of Adair County and continued in this capacity until 1951 and 1952 through 1955; taught science in Stilwell, Oklahoma, 1955-1956; taught chemistry, physics and biology in Broken Arrow, Oklahoma, 1956-1957; taught science and mathematics at Stilwell High School, 1958-1965; employed as Chemistry Professor at Northeastern State University, 1965 to present.