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Analysis of trace elements in river and spring waters

Faridoon Andeshire Namdarian

ANALYSIS OF TRACE ELEMENTS IN

RIVER AND SPRING WATERS

BY

FARIDOON ARDESHIRE NAMDARIAN

A

THESIS

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L H Bolter (advisor)   _Burridge_

J K Manuel

ABSTRACT

Methods for the analysis of trace elements in natural fresh waters were investigated.

Preconcentration of the water samples by reducing the volume and by using cation adsorption resins was studied. It was concluded that cation absorption was the more promising procedure.

The methods used for analysis were absorption spectrophotometry, neutron activation analysis, and atomic absorption spectrophotometry. Atomic absorption spectrophotometry was considered the most suitable method for the analysis of trace elements in waters.

Calcium, copper, lead, zinc, and cadmium were determined in a number of Missouri springs and stream water samples.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

Chapter I

INTRODUCTION

A. Introduction

Analysis for trace elements in fresh water has become a major task in recent years. Several scientific disciplines are interested in this type of study.

The geochemist needs a large number of reliable data to establish the range of geochemical background values in determining the rate of weathering, supergene mobility of elements, and geochemical balance between continents and oceans.

The applied geochemist is interested in using high trace element concentrations in ground and surface waters to find new ore deposits.

Probably the most important application of trace element analysis in waters is with regard to pollution problems. Many trace elements, while harmless or even beneficious at "low" concentrations, become toxic at higher levels. Lead, an element of known toxicity, accumulates in bones. The cadmium concentration in water was recently reported as being possibly responsible for high blood pressure in humans.

The "normal" values for trace elements in fresh waters are in a range of less than a part per billion (ppb) to a few ppb. Until a few years ago, no analytical methods were available which permitted reliable analysis of a large number of samples. In recent years, the development of new techniques and instruments, such as neutron activation analysis and atomic absorption

spectrophotometry, has provided the scientist with tools to undertake such studies.

B. Purpose of this thesis.

Relatively little work has been done to apply the recently developed sensitive analytical techniques for the analysis of trace elements in water. It was therefore felt that the most important task with regard to this problem was to compare several methods for their feasibility and to develope procedures to increase the efficiency and sensitivity of these methods.

The analyzed water samples were collected from an area in the vicinity of Rolla, Missouri which is described in Chapter II. Since values for Missouri waters are not abundant the individual results are reported, but it should be kept in mind that the investigation of a specific region was of secondary importance in this thesis. The main emphasis was placed on the investigation of methods.

C. Methods Used

The following three methods were investigated: absorption spectrophotometry, neutron activation analysis, and atomic absorption spectrophotometry. The choice for these three procedures was based on the availability of facilities on the U.M.R. campus.

The sensitivity of absorption spectrophotometry as well as atomic absorption spectrophotometry is in most cases not sufficient to determine trace elements in such low concentrations as present in the fresh water. The cations of interest must therefore be

concentrated from the original sample before analysis. Neutron activation analysis, while much more sensitive, also needs a certain amount of sample preparation as well as concentration if a nuclear reactor with a relatively low neutron flux is used as is the case with the reactor on the Rolla campus. Investigation of methods of sample pre-enrichment was therefore part of this study. The procedures studied for this purpose were reduction of the water volume by evaporation and concentration of cations by ion absorption.

D. Acknowledgements

Dr. Ernst Bolter supervised the thesis. Thanks also goes to Dr. W. R. Carroll of the U.M.R. Chemistry Department and Dr. D. R. Edwards, Director of the University of Missouri at Rolla Reactor Center, and Mr. G. W. Leddicotte, Associate Professor of Nuclear Engineering of the University of Missouri at Columbia.

Dr. Paul Dean Proctor, Dean of the School of Science, University of Missouri at Rolla took great interest in the progress of this thesis.

Chapter II

SAMPLING AREA

The sampling points are located in Phelps, Dent, Crawford, and Pulaski Counties, Missouri (Fig. 1).

The maximum dimensions of the area are bounded by parallels 37° 25' and 38° 05' North latitude and meridians 91° 50' and 91° 55' West longitude (Fig. 2).

The area is drained by the Meramec River and tributaries, including Dry Fork, Little Dry Fork, Crooked Creek, Benton Creek, and others. The drainage basins are separated by long, sinuous divides. Dry Fork, the most important tributary of the Meramec River, drains a region which is underlain predominantly by the Roubidoux sandstone.

The area has many springs which are especially common in the lower courses of the smaller creeks near the contact of the Gasconade with the Roubidoux formation. Sandstones in the Roubidoux are significant aquifers and dolomites of the Gasconade formation contain many caves and other solution openings.

The lowest points in the area range from 648 to 840 feet from sea level and the highest from 1,200 to 1,349 feet. The relief between ridges and valleys ranges from 250 to 596 feet.

The Ordovician rock formations practically cover the largest portion of the area (Figs. 3 and 4). They consist of sandstone, dolomite, and argillaceous dolomite. Cenozoic forms the broad alluvium in the flood plain and terraces.
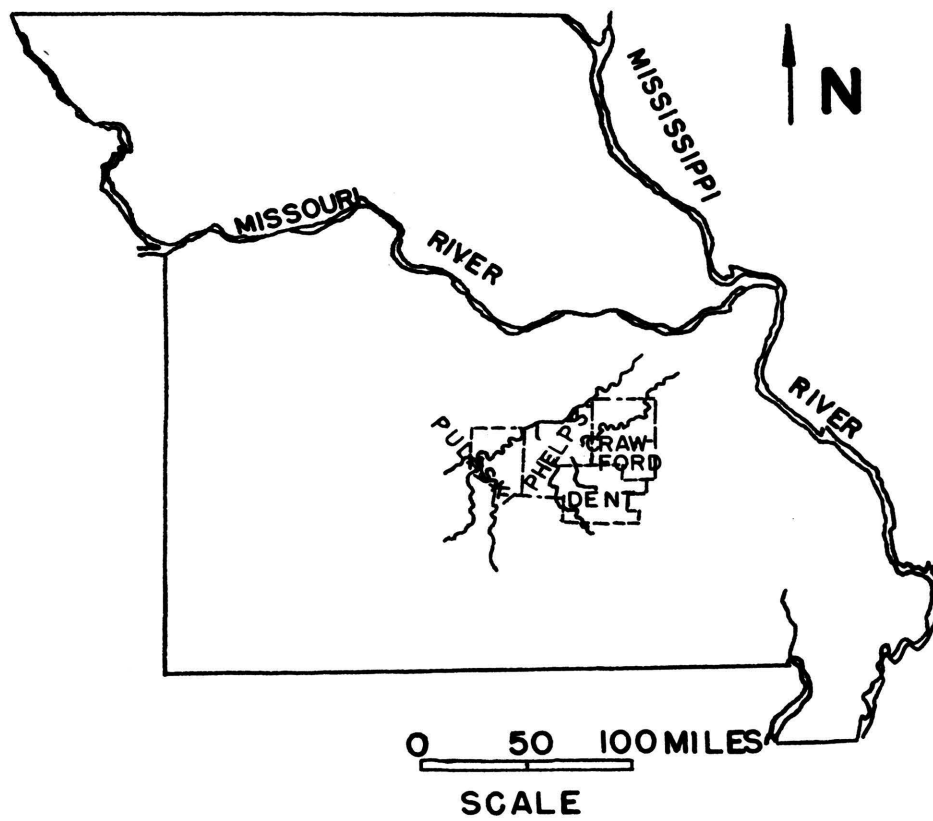
Figure 1. Location of the thesis area.
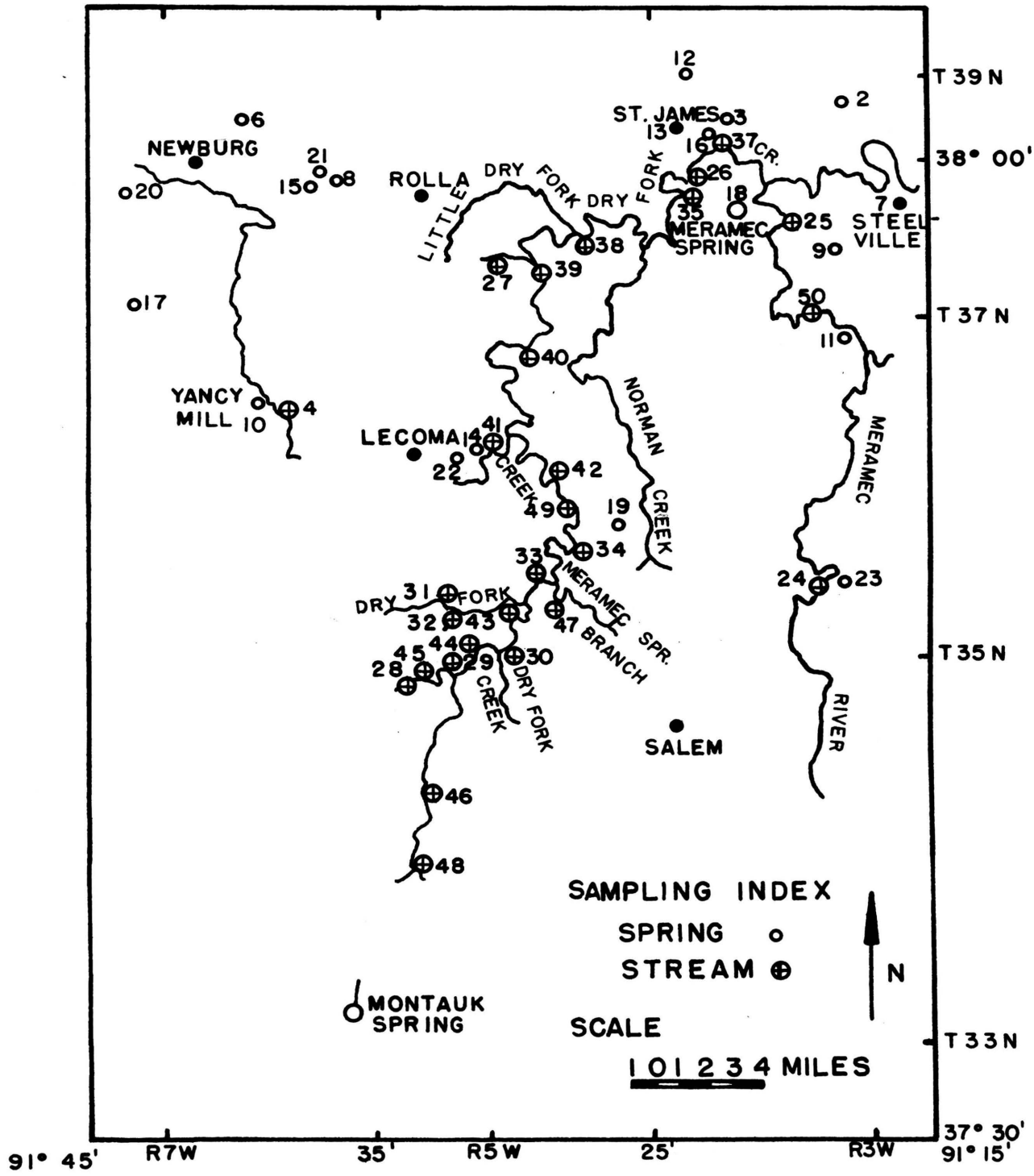
SAMPLING INDEX MAP
FIG. 2

The area contains many small and uneconomical mineral deposits. The main deposits are fire clay and iron ores. The sink structures usually contain the fire clay deposits. Pyrite occurrences are common in the area and limonite is found in the soils of all formations.

Weathering in the Gasconade formation has produced a large number of caves, galleries, and sinkholes.

HENDRIKS (1954) has studied the geology of the Steelville quadrangle, LEE (1913) has investigated the geology of the Rolla quadrangle, and MUELLER (1951) and YORSTON (1954) have studied the geology of the north and south halves of Meramec Spring Quadrangle respectively.

The names and characteristics of most of the springs are taken from BECKMAN and HINCHEY (1944) who have studied the large springs of Missouri. Some springs, being too small to be recorded by these authors, are described by the names given by the land owners.

Figure 3. GEOLOGIC MAP OF THE AREA

LEGEND

Ojc | ORDOVICIAN Jefferson City Formation

Or | ORDOVICIAN Roubidoux Formation

Og | ORDOVICIAN Gasconade Formation

Cep | CAMBRIAN Eminence & Potosi Formations

Pch | PENNSYLVANIAN Cheltenham Formation

SCALE 1/500,000

5   0   25

Kilometers

AFTER MISSOURI GEOLOGICAL SURVEY

1961

SYS-TEM	SECTION	FORMATION OR GROUP	THICK-NESS IN FEET
PENNSYL-VANIAN		CHEROKEE GROUP	0-200
MISSIS-SIPPIAN		CHESTER GROUP	0-150
		MERAMEC GROUP	0-150
		OSAGE GROUP	0-350
		KINDERHOOK GROUP	0-100
ORDOVICIAN	CANADIAN (ULRICH)	COTTER FORMATION	0-250
		JEFFERSON CITY FORMATION	0-425
		ROUBIDOUX FORMATION	50-275
	OZARKIAN (ULRICH)	GASCONADE FORMATION	60-325
		VAN BUREN FORMATION	50-250
		GUNTER MEMBER	10-75
CAMBRIAN		EMINENCE FORMATION	0-375
		POTOSI FORMATION	0-450
	CAMBRIAN (ULRICH)	DERBY-DOE FORMATION	0-275
		DAVIS FORMATION	0-275
		BONNE TERRE FORMATION	0-400
		LAMOTTE FORMATION	0-400
PRE-CAMBRIAN		PRE-CAMBRIAN	

LEGEND

LIMESTONE
DOLOMITE
SHALE
CHERTY LIMESTONE
CHERTY DOLOMITE
SANDSTONE
GRANITIC ROCKS

Figure 4. Generalized geologic columnar section for the spring region. (After Beckman and Hinchey, Missouri Geological Survey and Water Resources, Rolla, Missouri, 1944)

Chapter III

PREPARATION OF THE SAMPLES

A. Collection and Filtering

The water samples of the springs, Meramec River, and Dry Fork were collected from the area shown on Figure 2. The samples were collected in polyethylene and teflon containers and then transferred to the Geochemistry Laboratory of the University of Missouri at Rolla.

The temperature of the water samples was measured and ranged from 13°C to 20°C, and the pH from 6.4 to 8.2

The samples were collected from active parts of the streams and from the outflow of the springs. The containers were first cleaned and washed with hydrochloric acid in the laboratory and then rinsed with water at the time of collection. From each sampling point one gallon of water was collected.

As soon as the samples were taken to the laboratory, they were filtered with Millipore filters with a pore size of 0.45 microns in order to remove the suspended solids. The process of filtering was very slow and took about 30 to 35 hours per gallon.

B. Concentrating of Samples

The concentration of metals in water is usually too low for direct measurement with the analytical methods and it was therefore necessary to concentrate the metal content in the water. During this process, the loss of cations or contamination of the sample

is a strong possibility. To investigate and compare several
concentration methods became therefore one of the major objectives
of this study.

Two methods of concentration were used in this project:
reducing the volume of the water sample to dryness or near dryness
and concentration of the metals by absorption on a cation exchange
resin.

1. Drying Procedures

The samples were dried in two different ways.

In an Open Beaker

In one set of experiments, 1 ml of distilled
concentrated nitric acid was added to 3-4 liter of sample. The
sample was then reduced in an open glass beaker to a volume of
a few milliliters. At this concentration the sample was usually
in a jelly-like form. The concentrated sample was then transferred
into a small volumetric beaker. The large drying vessel was
washed with distilled nitric acid and water. After adding the
washing solutions to the sample, the sample volume was adjusted
to a specific volume, usually 10 ml, by further drying or diluting.

If the sample was intended for analysis by neutron activation,
this small container was the same 10 ml teflon capsule in which
the sample was subsequently irradiated in the nuclear reactor.

During this drying process, the temperature of the sample
was kept below boiling point in order to avoid loss by splattering.
The process took about 50 hours.

The advantage of this method lies in its simplicity, but it
is obvious that the method has disadvantages which make it

unsuitable for precise analysis. The time needed to reduce a sample to a small volume is too long. During reducing in an open beaker, the sample may become contaminated from the air. Probably the most obvious drawback was the observation that part of the sample dried on the walls of the beaker and could not be brought completely back into solution, even with concentrated nitric acid. Adding 1 ml of concentrated nitric acid to the water sample before drying improved the solubility of the residue, since it was now in the form of a more soluble nitrate, but it did not solve the problem completely.

In order to determine the magnitude of the loss during the drying process, three samples were spiked with about 0.5 mg radioactive Ag^{110}, of known activity, which had been produced in the nuclear reactor at the University of Missouri at Rolla for this purpose. The sample was then concentrated in the described way and the percent recovery of the silver spike was determined by counting the gamma activity. The results are shown in Table 1. The range of recovery for Ag^{110} was 26.0 to 42.0 percent, with an average of 33.6 percent.

In a Retort

In a second set of experiments 3-4 liters of water spiked with 1 ml distilled nitric acid were reduced in glass retorts to a volume of about 30 ml. The volume of the retorts was 2-3 liters. During the drying process, the water was brought to boiling point. The process took about 30 to 40 hours.

After reducing the volume to about 30 ml, the concentrated sample was transferred to a small volumetric glass beaker. The

retort was washed with distilled nitric acid and distilled water
and the washing combined with the concentrated sample. The sample
was then reduced in the small open beaker to 10 ml.

Drying the sample in a retort rather than an open beaker has
the advantage of preventing contamination from the air. It was
obvious that as in the experiments with open beakers, part of the
residue formed during the process could not be removed from the
walls of the retort even by using nitric acid.

In order to determine the losses, samples were spiked with
radioactive Ag^{110}, Sr^{85}, or non-radioactive copper and then
processed in the way described above. The results are given in
the Tables 2, 3, and 4.

The recovery of the spike in retorts is much better than in
an open beaker. Of the silver, 70 to 90 percent was recovered,
while the recovery for Sr^{85} was in the range of 78 to 96.5 percent.

To six samples of 1.5 liters volume each, 10 micrograms of
copper were added and the samples reduced to 10 ml in retorts.
The recovery of the copper was determined with the absorption
spectrophotometer and was in the range of 84 to 96 percent, with
an average of 91 percent (Table 4).

Although concentrating the samples in a retort is a large
improvement compared to the use of open beakers, the results
were not satisfactory. Too large a percentage of cations is lost
and the needed time is much to long for large scale analysis. The
use of cation exchange resins was therefore chosen as an alternative
concentration method.

TABLE 1

Chemical Recovery Experiments

Sample Number	Spike Element	Recovery by Beaker Percent
1	Ag^{110}	32.4
2	Ag^{110}	42.0
3	Ag^{110}	26.0
		33.6%

TABLE 2

Chemical Recovery Experiments

Sample Number	Spike Element	Recovery by Retort Percent
1	Ag^{110}	90.0
2	Ag^{110}	70.0
3	Ag^{110}	85.0
		81.6%

TABLE 3

Chemical Recovery Experiments

Sample Number	Spike Element	Recovery by Retort Percent
1	Sr^{85}	90.0
2	Sr^{85}	96.5
3	Sr^{85}	78.0
		88.10%

TABLE 4

Chemical Recovery Experiments

Sample Number	Spike Element	Recovery by Retort Percent
1	Cu	90.0
2	Cu	92.0
3	Cu	88.0
4	Cu	84.0
5	Cu	95.0
6	Cu	96.0
		91.0%

2. Use of Cation Exchange Resins

Since the method of concentrating the metals by reducing the volume of water was considered unsatisfactory, the possibility of enriching the metals by cation absorption was investigated.

Absorption of ions on organic or inorganic resins and subsequent elution has been widely used in the past for the separation of ions in analytical chemistry. For our purpose, the task was to adsorb the metals efficiently on a resin and then to elute the metals with as small a volume of eluent as possible.

The resin used for adsorption studies was the hydrogen form of AG 50 W - X8, 200 - 400 mesh, a strongly acidic cation exchange resin composed of nuclear sulfonic acid exchange groups attached to a styrene-divinyl benzene polymer lattice. The resin is produced by Bio-Rad and is analytical grade. The adsorption and elution characteristics of zinc and cadmium were investigated to demonstrate the feasibility of this method.

Previous Work

RICHES (1946) used Amberlite IR-100 and CHl to separate Cu, Cd, Ni, Zn and Mn. In 1947 he repeated the experiment with a different size resin and a faster flow rate of the eluent. KRAUS (1952) investigated the use of Dowex-1 to separate Ni, Mn, Co, Cu, Fe and Zn, with 0.005-12 M HCL. CRRIT (1953) used cellulose acetate and a carbon tetrachloride solution of dithizone to concentrate Pb, Zn, Mn, Cd, Co, and Cu. CANNEY (1960) used Amberlite IR-120 resin to determine Cu, Pb, Zn, Co and Ni in barren surface waters.

Using 1 gallon of original sample and 2 M HCl as eluent, he achieved an enrichment factor of 38. FRITZ (1961) used 0.1 and 1 M HF as eluent for large numbers of metal ions. In this investigation Dowex 50W - X8, 100 to 200 mesh resins were used. FRITZ (1962) used the same resins, but with 0.3 M HBr as eluent. In 1963 he used Dowex 50W - XB to separate Bi, Fe, Cd, Cu, Mn and Ni using various mixtures of aqueous acetone and HCl for elution. STRELOW (1963) also used Bio-Rad AG 50W - X8 for cation exchange equilibrium distribution. Nitric acid and sulfuric acid were used for elution with a concentration range of 0.1 N to 4.0 N. Except for the work done by CARRIT (1953) and CANNEY (1960), the previous studies were concerned with the separation of elements, not their concentration. Nevertheless, these determinations were a valuable help in selecting promising eluents for the work.

Since CARRIT (1953) used cellulose acetate which was considered inferior to modern resins, his study was of little value to this project. The work of CANNEY (1960) indicated that HCl would be a promising eluent.

Method

About 1 to 2.5 gm of resin was used to prepare adsorption columns in 100 ml burettes with a 1.2 cm diameter. Both top and bottom of the resin column were plucked with glass wool to keep the resin in place.

Before using the column, the following procedure was used to prepare the resin:

1) The column was washed with 50 ml of demineralized water.

2) The column was washed again with 20 ml of 10% ammonium citrate.

3) 30 ml 3 M HCl was passed through to convert the resin to the hydrogen form.

4) The free acid was then washed out with demineralized water, until the elution produced no AgCl in an $AgNO_3$ solution.

After preparation of the adsorption column, Zn or Cd was adsorbed from aqueous solutions. The aqueous metal containing solutions had been brought to a pH of 6.5 to 7.5. After adsorption of the cation, it was eluted at a certain flow rate with the selected eluent. The eluted solution was separated during elution into individual fractions and the metal content in every fraction determined with an atomic absorption spectrophotometer.

In different experiments, Zn was eluted with a mixture of equal parts of 85 percent acetone and 2.1 M HCl (Tables 5 and 6), with equal parts of 1 M EDTA and 6 M HCl (Tables 7 and 8), with 2 M HCl (Table 9, Figure 5) and with 4 M HCl (Table 10, Figure 6).

In five different experiments, cadmium was eluted with 150-250 ml volumes of 2-6 M HCl and also the acetone - HCl mixture used for Zn. The percent recovery was then determined (Table 11).

The adsorption of both zinc and cadmium at the resin was in all cases 100 percent if the pH of the water sample was adjusted to pH 6.5 - 7.5.

The results from elution were not in all cases satisfactory. It is easy to remove more than 50 percent of the adsorbed metal with about 50 ml eluent, but the last few percent of the adsorbed metal needs a relatively large volume of eluent, which decreases the

concentration factor (Figures 5 and 6).

Cadmium

In the experiments for cadmium elution, 150-250 ml of different eluents stripped off only between 70 and 80 percent of the Cd from the column (Table 2). It is obvious that elution with HCl or an acetone HCl mixture as used in these experiments is not satisfactory.

Zinc

The use of 85 percent acetone - 2.1 M HCl mixture resulted in an incomplete recovery (Tables 5 and 6). When the stripping was done with a 0.1 M EDTA (Disodium ethylenediamine tetraacetate) -6 M HCl mixture too much eluent was needed for 100 percent recovery (Tables 7 and 8).

Elution with 4 M HCl (Table 10, Figure 6) gave better results than elution with 2 M HCl (Table 9, Figure 5). Zinc was completely removed from the column with 175 ml of eluent. If four litres of natural water would be used for concentration on the resin, an elution with 175 ml of 4 M HCl would represent an enrichment of zinc by almost a factor of 23. This would be enough to determine zinc in natural water by atomic absorption spectrophotometry.

C. Comparison of Concentration Procedures

It can already be seen from the results outlined above, that concentrating metals by cation absorption is by far the most promising among the investigated methods. Using about one gallon of water for the concentration by absorption takes a few hours, while 1-2 days are needed to reduce the same volume to achieve the desired concentration

of metals. Also, by using analytical grade adsorption resins, the possibility of contamination of the sample can be greatly reduced. The greatest advantage in using adsorption resins, however, lies in the fact that a 100 percent recovery can be achieved. This was demonstrated in the experiments described above. To show this point even more clearly, unspiked samples from 3 springs were divided into 3,000 ml portions each and concentrated by the described 3 procedures (in a beaker, in a retort, and by cation adsorption using 2 M HCl as an eluent). Then zinc was determined in the concentrated samples with the atomic absorption spectrophotometer and the zinc concentration in the spring waters was calculated. The results are shown in Table 12. Assuming that the values determined by cation exchange concentration are correct, then only 10 to 15 percent of the zinc was found using concentration in an open beaker. Using a retort, the results were better, but the yield was still only between 68 and 77 percent compared to the cation adsorption procedure. The yields achieved in this experiment are even lower than the above described results of the experiments with spiked water, in which other cations (Ag, Sr, Cu) had been used.

TABLE 5

Elution of Zinc

Fractions (ml)	Eluent	Percent Recovery
20	(85% Acetone + 2.1 HCl)	58.58
20	"	4.60
20	"	.27
20	"	0
20	"	0
50	"	0
50	"	0
200		63.45%

DETAILS:

Amount adsorbed..........10 μg

Amount of resin..........1 gm

Flow rate................1/2 ml/minute

Absorption..............100%

Recovery................63.45% with 200 ml eluent

TABLE 6

Elution of Zinc

Fractions (ml)	Eluent	Percent Recovery
25	(85% Acetone + 2.1 HCl)	69.11
25	"	8.00
25	"	5.12
25	"	5.12
25	"	4.85
25	"	3.49
50	"	0
50	"	0
250		95.70%

DETAILS:

Amount adsorbed..........10 μg

Amount of resin..........2.5 gm

Flow rate................1/2 ml/minute

Absorption...............100%

Recovery.................95.7% with 150 ml eluent

TABLE 7

Elution of Zinc

Fractions (ml)	Eluent	Percent Recovery
10	(1:1 0.1 M EDTA + 6 M HCl)	19.6
10	"	14.8
10	"	21.2
20	"	16.0
20	"	7.0
30	"	13.4
50	"	8.0
50	"	2.6
50	"	0
250		102.6%

DETAILS:

Amount adsorbed..........5 μg

Amount of resin..........1 gm

Flow rate................1/2 ml/minute

Absorption...............100%

Recovery.................102.6% with 200 ml eluent

TABLE 8

Elution of Zinc

Fractions (ml)	Eluent	Percent Recovery
10	(1:1 0.1 M EDTA + 6 M HCl)	72.40
10	"	14.80
10	"	1.60
20	"	1.32
20	"	1.32
30	"	0.44
50	"	2.40
50	"	0
200		94.28%

DETAILS:

Amount adsorbed..........5 μg

Amount of resin..........2.5 gm

Flow rate...............1 ml/ minute

Absorption...............100%

Recovery.................94.28% with 150 ml eluent

TABLE 9

Elution of Zinc

Fractions (ml)	Eluent	Percent Recovery
20	2 M HCl	78.5
20	"	7.5
20	"	2.7
20	"	2.6
20	"	1.2
20	"	1.0
20	"	0.9
20	"	0.8
20	"	0.9
20	"	0.1
240		96.2%

DETAILS:

    Amount adsorbed..........10 μg

    Amount of resin..........column of 1.2 x 12 cm

    Flow rate................1 ml/minute

    Absorption...............100%

    Recovery.................96.2% with 240 ml eluent
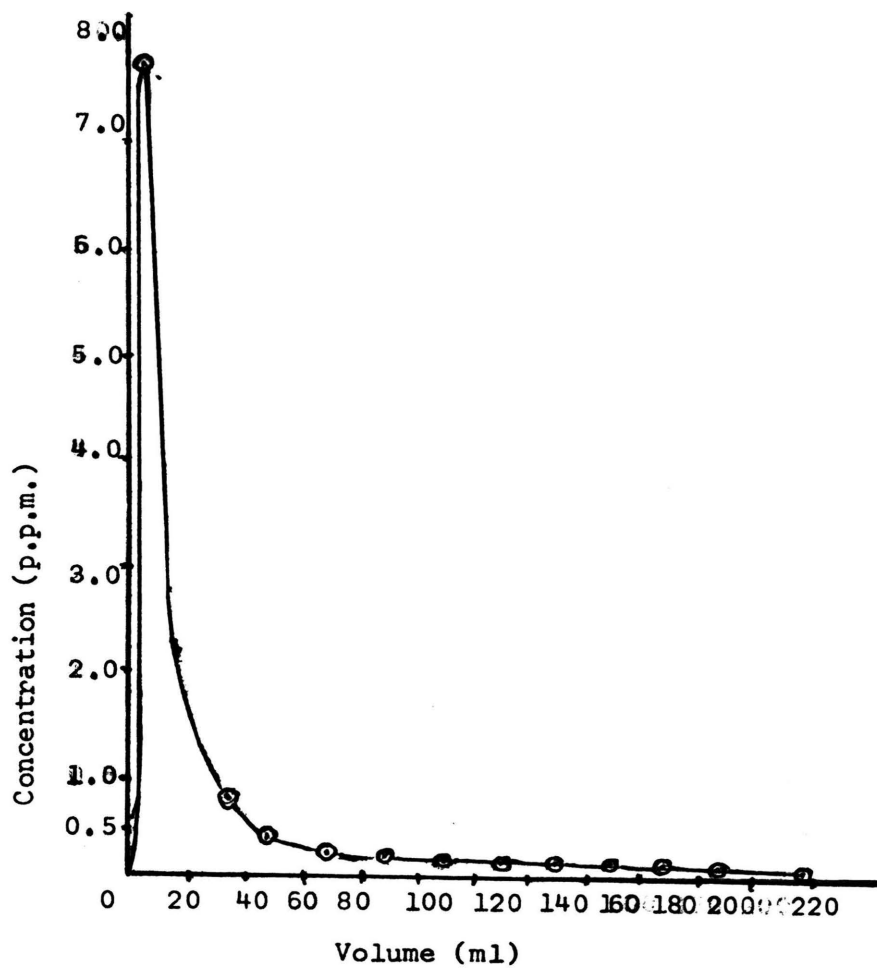
Figure 5.   Elution of zinc with 2 M HCl.

TABLE 10

Elution of Zinc

Fractions (ml)	Eluent	Percent Recovery
25	4 M HCl	99.90
25	"	0.65
10	"	0.20
25	"	0.05
25	"	0
25	"	0
225		100.80%

DETAILS:

Amount adsorbed..........10 μg

Amount of resin.........column of 1.2 x 12 cm

Flow rate...............1 ml/minute

Absorption..............100%

Recovery...............99.9% with 25 ml eluent
100.8% with 175 ml eluent
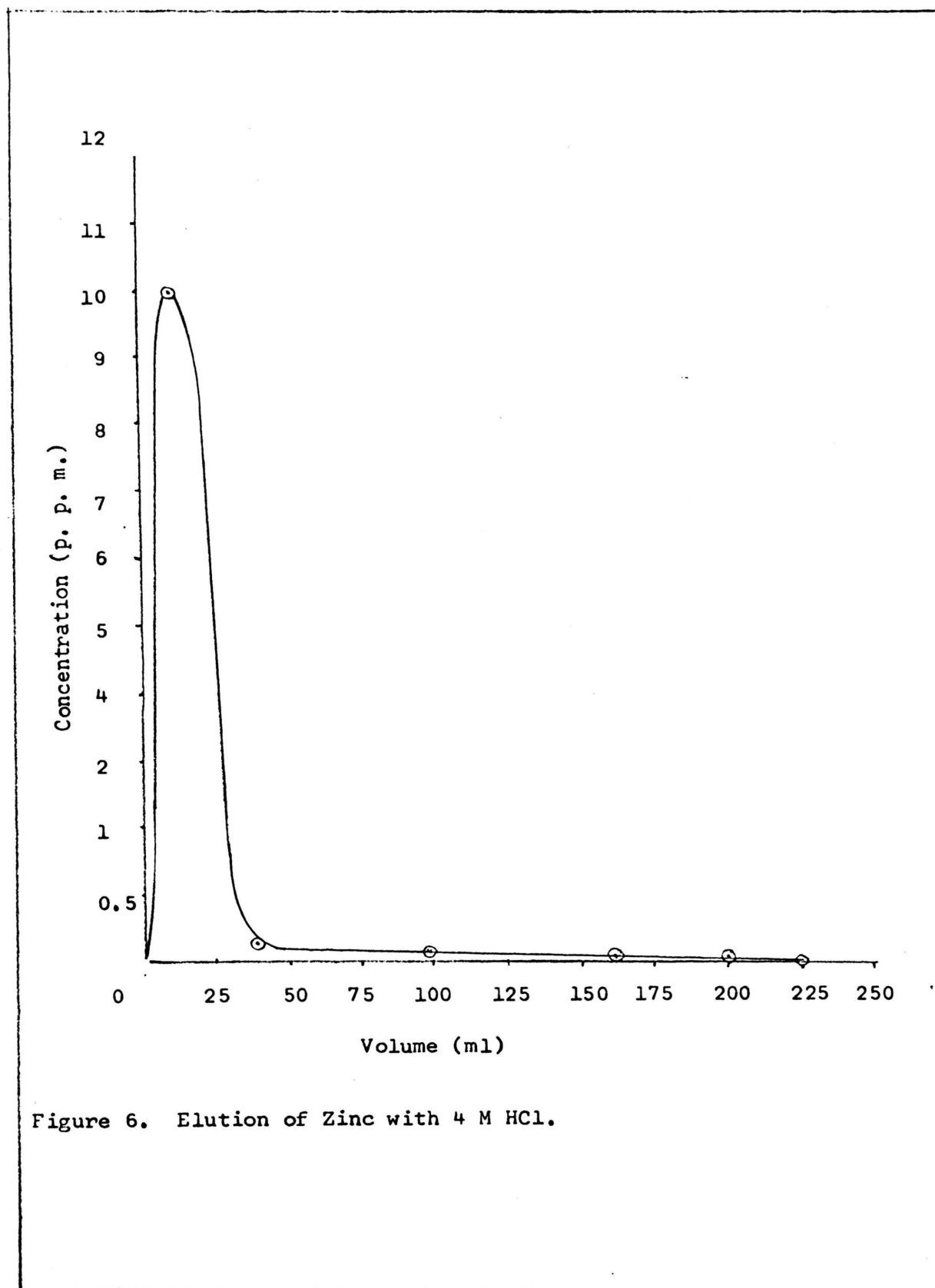
Figure 6. Elution of Zinc with 4 M HCl.

TABLE 11

Elution of Cadmium

Total Volume (ml)	Eluent	Percent Recovery
250	2 M HCl	70.0
200	3 M HCl	71.4
150	4 M HCl	72.6
200	6 M HCl	73.2
200	(85% acetone - 2.1 M HCl)	78.0

DETAILS:

Amount adsorbed..........5 μg

Amount of resin..........2.5 gm

Flow rate...............1 ml/minute

Absorption...............100%

TABLE 12

Comparison of Concentration Methods for the Zinc Determination.
Zinc Concentration in Three Springs

Sample	By Beaker (ppb)	By Retort (ppb)	By Cation Exchange (ppb)
Meramec Spring	8.0	53	78
Brook Spring	8.4	50	70
Lake Spring	9.0	49	64

Chapter IV

ANALYTICAL METHODS

For analysis of trace elements in water, three methods were
investigated: absorption spectrophotometry, neutron activation
analysis, and atomic absorption spectrophotometry. These procedures
were selected because they were the only ones for which the
necessary equipment was available on the U.M.R. campus.

Availability as well as performance of the needed equipment
influenced the course of this project to a great extent. For
instance, neutron activation analysis is an excellent tool to
determine very low trace concentrations, if the neutron flux in
the nuclear reactor is high (10^{12} - 10^{14} $n/cm^2 \cdot sec$). However, the
reactor on the U.M.R. campus produced only a flux of about
10^{10} $n/cm^2 \cdot sec$ at the time of this investigation. The question
was therefore not how useful is neutron activation for the analysis
of trace elements in water, but how much work can be done by using
a reactor with such a low neutron flux.

The possibility of investigating the use of the atomic absorption
spectrophotometer, a very promising method for trace element analysis,
was limited because the available instrument was acquired and
installed by the Department of Geological Engineering and Geology
at a very late stage of this project. The time available for the
use of this instrument was therefore very limited. Also, a very
limited number of element emission lamps were available.

A. Absorption Spectrophotometry

From previous investigations in the Department of Geology and from literature research it was concluded that the only heavy metal in fresh waters which might be determined by this method was copper and only copper analyses were therefore performed with this method.

1) Theory of Absorption Spectrophotometry

The use of light absorption in quantitative analysis is based upon the laws of Lambert and Beer, which relate the proportion of light absorbed to the length of the light path in the absorbing medium and to the concentration of the absorbing species. The two laws of light absorption are usually combined in the derived equation

$$\frac{P}{P_o} = 10^{-abc}$$

or, taking logarithms

$$Log_{10} \frac{P_o}{P} = abc$$

Symbols:

Po = incident radiant power

P = transmitted radiant power

a = absorptivity (specific extinction)

b = internal cell length

c = concentration (grams/liter)

Absorbance is therefore proportional to concentration for any given substance at a particular wave length. However, Beer's Law relating concentration and absorption may appear not to hold for a given system, if the absorbing molecules are modified by changes in the medium or by an increase in concentration. This makes calibration under

precisely controlled conditions, such as exist for the test measurements, essential. Instruments are normally calibrated in absorbance and percentage transmissions units. The former are more generally used in plotting absorption and calibration curves, since they simplify mathematical calculations.

A spectrophotometric method may depend upon the natural absorption of the ion, group or molecular species of interest. More frequently in inorganic trace analysis it is necessary to convert the substance to another chemical form or complex (e.g. with an organic reagent). For instance, for the copper analysis the copper 2-2' biquinoline complex is most frequently used.

2) Method

The Beckman Model B Spectrophotometer was used for analysis. The determination of copper was done by utilizing the copper 2-2' biquinoline complex according to a method described by CHENG KUANG LU (1953) and GUEST (1953). Before analysis, the spring and stream water samples were concentrated by a factor of ten by reducing the water in open beakers on an electric hot plate.

The procedure for analysis is the modification of CHENG and GUEST'S as follows:

1) 5 ml of concentrated water sample was placed in a 60 ml separatory funnel.

2) 1 ml of solution containing 50 mg of hydroxylamine hydro-chloride was added and mixed.

3) The pH was adjusted to pH 5-6 with NH_4OH

4) 10 ml of copper buffer solution consisting of sodium acetate,

hydroxylamine hydrochloride and sodium tartrate was added.

5) Exactly 4 ml of 0.02% 2-2' biquinoline was added.

6) The solution was vigorously shaken for one minute and then let stand for five minutes.

7) The aqueous part of the solution was drained.

8) Eight drops of distilled water was added to wash the organic compound. The water was then drained.

9) The solution was then centrifuged for one minute to pull down all suspended particles or trapped air.

10) The spectrophotometer wave length was adjusted to 546 mμ.

11) The copper compound was drained in a quartz cell for measurement.

12) A blank solution prepared in the same way was placed into the instrument, and slit and dark control of the spectrophotometer were adjusted to zero absorption.

13) The absorption of standards prepared exactly as the unknown samples was measured and a standard curve plotted.

14) Absorption of the water samples was measured.

15) The copper concentrations in the unknown samples were determined by comparing the absorption values with the standard curve and by correcting for the pre-enrichment of the water sample.

3) Previous Work

GUEST (1953) used 2-2' biquinolene for detection of copper in metallurgical analysis. His recommendations for pH 4.4-7.5 and period of shaking were observed. The analytical range is reported as being between 0.001-10.0 percent.

HOSTE, et. al (1953) used cuproine for the analysis of water (Isomyl alcohol containing 0.01% cuproine). The sensitivity of this method is 0.02 μg/ml. HOSTE (1950) demonstrated that 2-2' biquinolene as a reagent for copper is specific. SMITH AND McCURDY (1952) have used 2,9 - Dimethyl -1, 10 phenanthroline for determination of copper instead of the 2-2' biquinolene reagent. NORWITZ and GORDON (1965) used a solution of neo-cuproine (0.1% in ethanol) and chloroform for copper analysis. CHENG (1953) used 2-2' biquinolene at a pH of 4-5. HASHMI, et. al (1966) claims that formic acid hydrazide reacts with Au, Cu, Co and Ni in acid medium and gives a definite color. The blue color of the copper compound remains for more than six hours.

4) Results

The results for 30 spring and stream samples are given in Table 13. A standard curve is shown in Figure 7. By concentrating the water samples by a factor of 10, the sensitivity of this method is about 1 ppb. This compares quite well with atomic absorption spectrophotometry, a method which will be described later. But the work necessary to produce the copper biquinolene complex for absorption spectrophotometry makes this method cumbersome and time consuming compared with atomic absorption spectrophotometry.

B. Neutron Activation Analysis

The analysis of trace elements by neutron activation analysis during this study was limited by the fact that the training reactor at the U.M.R. campus at the time of this study had a neutron flux of only 10^{10} n/sec cm^2. Since the concentration of metals in fresh

TABLE 13

Values Obtained for the Copper Content of Springs
and Streams Water Samples by Absorption Spectrophotometer

Name	Sample Number	Concentration (mg/l)
Montauk Spring	1	8.8
Lake Spring	14	16.0
Brook Spring	16	17.0
Haacke-Owned Spring (a)	3	4.9
Dry Fork	26	17.1
Meramec River	50	4.0
Miller-Owned Spring (a)	13	4.5
Moore-Owned Spring	11	10.5
Meramec River	1-1	11.0
Joe Smith-Owned Spring (a)	9	4.5
Indian Spring	7	8.6
Flag Spring	12	14.5
Mint Spring	23	<1.0
Meramec River	24	5.3
Elm Spring	2	12.3
Meramec River	25	6.5
Piney Creek	4	8.6
Yancy Mill Spring	10	4.4
Boiling Spring	5	7.2
Martin Spring	21	3.5
Rock Spring	6	1.35
Carrol Spring (a)	8	2.2

TABLE 13
(continued)

Name	Sample Number	Concentration (ml/l)
Wilkins Spring	17	4.0
Callahan Spring	15	4.5
Roulfs Spring	20	3.5
Meramec Spring	18	4.9
Bubbling Spring	22	8.4
Brown Spring	19	5.3
Dry Fork	27	10.0
Dry Fork	48	4.8

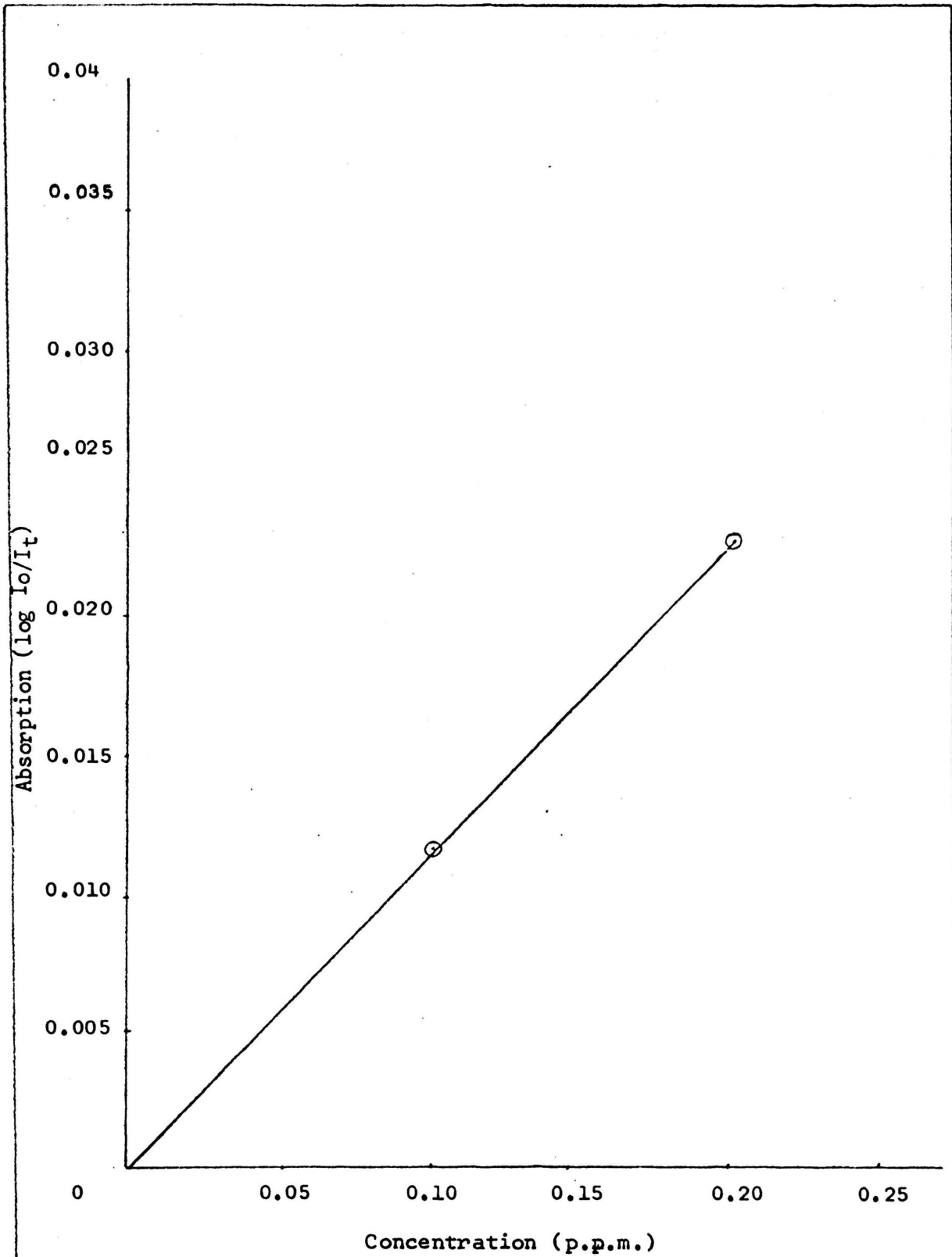(a) Name of spring as given by owner.

Figure 7.   Standard curve for Copper by Absorption Spectrophotometry.

waters is in the low ppb range, it could be expected that such a low neutron flux would produce a measurable amount of radioactive isotopes only for a very limited number of elements.

1) Theory of Neutron Activation

The basic principle of activation analysis is that a stable isotope, when bombarded with neutrons (or charged particles) can undergo a nuclear transformation to a radioactive nuclide.

After the radio nuclide is formed and its emanations have been characterized by radiation detection equipment, qualitative and quantitative inferences can be made of the elemental composition of the original sample before irradiation.

The reactions occurring during activation of a sample are described in a number of books and publications, e.g. by ROSS (1964) and CALI (1964).

Stable isotopes can undergo a variety of nuclear transformations. The reaction used in this study, which is generally the most extensively used in activation analysis, is the neutron-gamma (n, γ) reaction. This is illustrated by the following expression

$$_{29}Cu^{63} + {_{0}}n' \longrightarrow {_{29}}Cu^{64} + {_{0}}\gamma^{0}$$
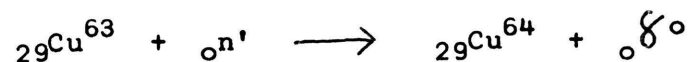
which is usually more simply expressed by the expression

$$Cu^{63} (n, \gamma)Cu^{64}$$
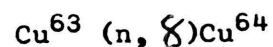
Activation analysis of an element and sensitivity of the method are influenced by a number of factors, all of which must be taken into consideration when this method of analysis is planned.

a) Cross Section

The cross section of an isotope is the probability with which the isotope is undergoing a nuclear process. The cross section has the dimensions of an area and is usually given in "barr (1 barn = 10^{-24} cm^2).

b) Half-life

The half-life of the produced radioactive isotope is given by the formula

$$t_{1/2} = \frac{\ln 2}{\lambda} = \frac{0.69315}{\lambda}$$

where λ is the characteristic decay constant. The half-life of an isotope is most favorable for activation analysis, if it is just long enough to permit the necessary work for analysis, such as radiochemical separations and counting. If the half-life is too long, the number of decays in a given time is too small for accurat counting.

c) Percent Abundance

Most natural elements have several stable isotopes, which are present in nature in a specific ratio. Since in most cases only one of the isotopes is suitable for activation analysis, its percent abundance must be considered.

d) Neutron Flux

The neutron flux with which an isotope is bombarded is measured in neutrons/cm^2 sec. Without going into the details of how to calculate the neutron flux and its effects, it can be stated that the number of produced radioactive isotopes increases with increasing neutron flux. Most nuclear reactors have a neutron flux of 10^{12} - 10^{14} $n \cdot cm^{-2} \cdot sec^{-1}$. The U.M.R. reactor with a flux of abo

10^{10} n·cm^{-2}·sec^{-1} is well below this figure.

e) Activation Time

Initially, the produced radioactivity is dependent on the duration of activation. After a certain time, which depends on the half-life of the produced isotope, a saturation point is reached, i.e. the number of newly produced radio isotopes is equal to the number of decaying isotopes. Activation past this saturation point does therefore not increase the sensitivity of the method.

2) Method of Activation Analysis

The U.M.R. reactor is a swimming pool type. The sample is therefore immersed in water during the activation. This demands that the sample be sealed watertight in a container. In this study, teflon capsules with a 10 ml volume were used.

Monitors

Since the neutron flux is not the same in all reactor positions, produced radioactivities in different samples and standards can be compared with each other only by using "monitors". A monitor is a known amount of element (not the one analyzed for) present in or very close to the sample. Sometimes an "internal monitor" can be used. This is an element present in the sample at a known concentration. In most cases, an external monitor must be activated in the same position as the sample.

After activation of each monitor its activity is determined. This permits the calculations of a correction factor for the sample and standard activities.

Counting

After activation of the sample, the activity of the isotope of interest must be counted. The activity can be gamma or beta rays. In this study, no beta ray counting was attempted. In almost all cases, the isotope of interest must be separated by a radiochemical procedure from the rest of the sample, since its spectrum is obscured and overlapped by the activity of other cations.

Radiochemical Separation

It would be impossible to separate a trace amount of an element, i.e. 1 microgram, from the rest of the sample. Therefore, a "carrier" must be added to the sample before the radiochemical separation. A "carrier" is a certain amount of the element of interest but in non-radioactive form. The amount of the carrier must be large enough to permit a convenient chemical separation (usually in the range of 20-100 mg). Since all isotopes behave chemically the same way, the radioactive isotope is separated from the sample together with the carrier. Since the amount of carrier added before the separation procedure is known and the amount of carrier present after the separation can be measured, the amount of element lost during the separation can be determined. This "yield" factor must then be used to calculate the correct amount of activity of the isotope of interest.

Since the "yield" of the separation is determined, the separation procedure can be designed with emphasis on clean separation without much regard for partial losses during the separation.

During this study, attempts were made to determine silver, copper, arsenic, zinc and cobalt. Silver was separated as AgCl,

copper, arsenic, and zinc as sulphides and cobalt as a cobaltinitrite complex $K_3[CO(NO_2)_6]$. No silver, arsenic, zinc, or cobalt activities were found. Besides copper-radiation, the only other activity detected was from Na^{24}, which produced by far most of the activity but was of no interest in this project. The study was therefore limited to the determination of copper. As a final separation procedure for copper the following generalized method was used:

Copper was precipitated as sulphide. The sulphide was then redissolved in dilute HNO_3 and copper reprecipitated with salicylaldoxime. The copper salicylaldoxime precipitate was then washed and dried at 70°C and the 0.51 MeV peak of the copper spectrum counted in 400 channel gamma ray spectrometer (Model RIDL 34-12B) at the U.M.R. reactor.

3) Results and Discussion of Activation Analysis

Other than the activity of Na^{24}, only the activity of Cu^{64} was found. It was concluded that the U.M.R. reactor had not enough neutron flux intensity to be useful for the analysis of other trace elements in water. Since activation analysis of copper proved to be more difficult and time consuming than the other two investigated methods, no attempt was made to analyze copper quantitatively. Figures 8 and 9 show the half-life determination of the copper peak at 0.51 MeV. The measured half-life of 12.8 hours agrees well with 12.9 hours value given in the literature for Cu^{64}. The measured sample consisted of 3.5 liters of water reduced to a volume of about 5 ml. The copper activity 15 hours after the irradiation was about 1,000 cpm at the 0.51 MeV peak.
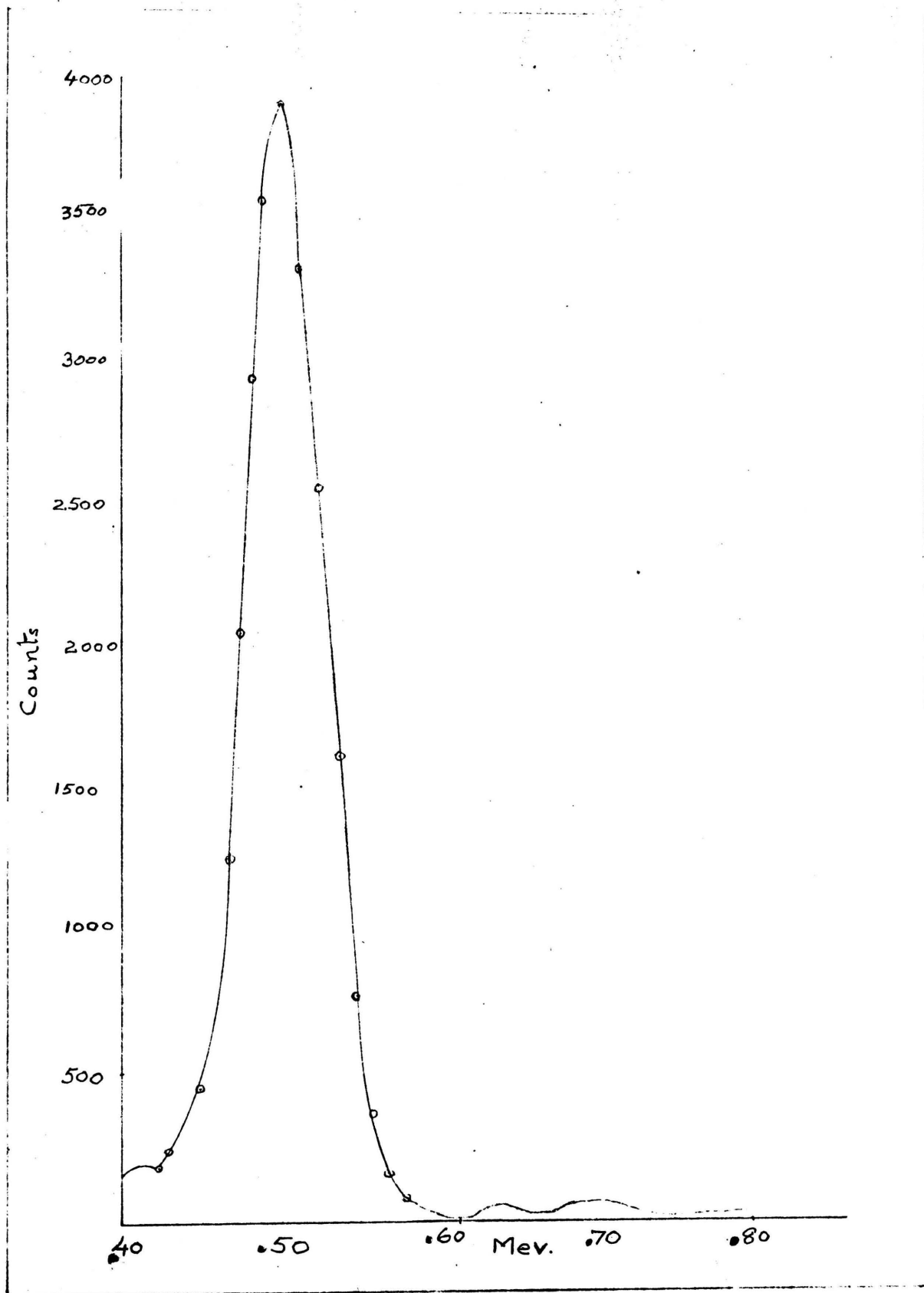
Figure 8. Half-life Determination of Cu^{64}.
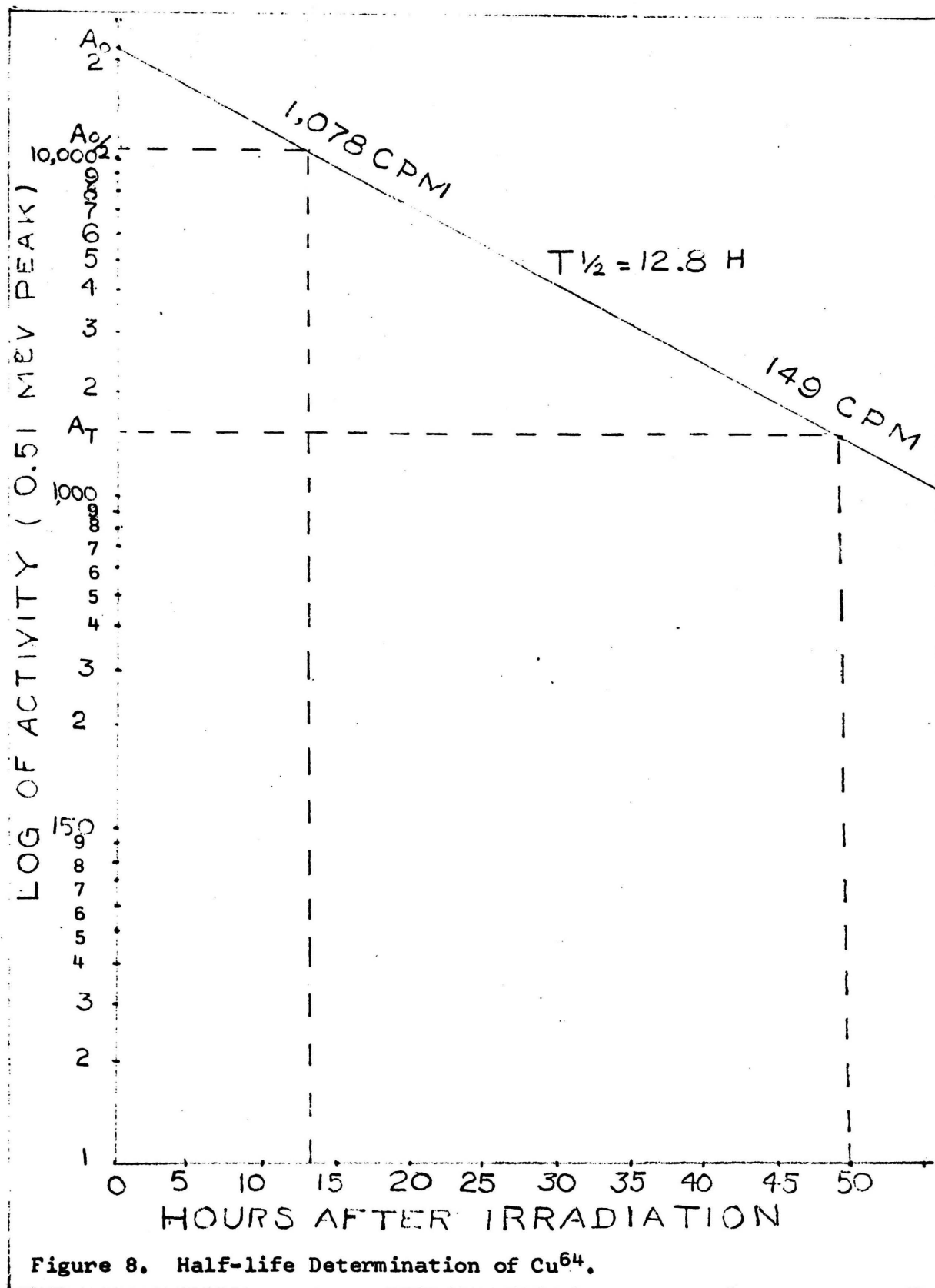
Figure 9.   Gamma ray spectrum for Cu^{64}.

Previous Work

TUREKIAN (1966) determined Ag and Co in streams by neutron activation analysis, using a freeze-dry method for the preparation of the samples and a reactor with a high neutron flux for activation.

C. Atomic Absorption Spectrophotometry

Atomic absorption spectrophotometry has become an important analytical method for trace element analysis only during the last few years. Its sensitivity for metallic elements is surpassed only by neutron activation analysis. It is, compared to other methods, very simple and therefore permits the analysis of many samples in a short time. Since the sample has to be in liquid form, the method is especially suitable for water analysis.

1) Theory and Method

In atomic absorption spectrophotometry, the element of interest is merely dissociated from its chemical bounds and placed into an unexcited, unionized "ground state". It is then capable of absorbing radiation at discrete lines of narrow band width, the same lines as would be emitted if the element were excited.

In practice, the sample, which must be in a liquid state, is brought into a flame (usually an air-acetylene flame) where the ion of interest is converted into the atomic "ground" state. At the same time, radiation from a cathode made of the same element as analyzed is passed through the flame. The radiation from the cathode is then absorbed by the atomar element in the flame. The amount of absorbed radiation is proportional to the amount of element present in the flame. Except for a few multielement

cathodes available, a specific cathode is needed for every element (e.g. a copper cathode for copper analysis). An excellent introduction into the instrumentation of atomic absorption spectrophotometry is given by KAHN (1966).

The instrument used in this project was the Perkin-Elmer Model 303. A number of spring and stream samples were analyzed for calcium, lead, zinc, cadimum and copper (Tables 15 and 16). The number of analyzed elements is limited, since only a few element cathodes were available.

Calcium was determined directly in filtered samples. Lead, zinc, cadmium, and copper were determined in samples which had been concentrated by a factor of 100 by reducing the sample in retorts and beakers. The limit of detection for these elements, as given in the literature (KAHN, 1966) is shown in Table 14.

TABLE 14

Relative Detection Limits by Atomic Absorption Spectrophotometry

Element	ppb
Ca	10
Cd	10
Cu	10
Pb	50
Zn	5

2) Previous Work

ALLAN (1961) has shown that the sensitivity is increased several times if the metal is present in an organic solvent instead

of water.

PLATTE (1965) has used the atomic absorption spectrophotometer Model 303 to determine Fe, Cu, Mn and Zn in water samples using an organic extraction technique to concentrate the water.

3) Results

Standard curves for the analyzed elements are shown in Figures 10 through 13. The results of the calcium, cadmium, copper, zinc and lead analysis are reported in Tables 15 and 16.

TABLE 15

Zinc, Lead, Copper and Cadmium Content of Springs and Stream Waters (By Atomic Absorption Spectrophotometry)

Name	Sample Number	Pb ppb	Zn ppb	Cd ppb	Cu ppb
Yancy Mill Spring	10	6.9	50.0	11.2	3.60
Wilkins Spring	17	7.0	3.6	13.6	3.64
Rock Spring	6	5.0	6.6	11.8	3.64
Boiling Spring	5	6.9	3.3	12.1	2.85
Meramec River	24	6.8	50.2	11.8	3.20
Meramec Spring	18	5.7	4.1	10.4	3.70
Brown Spring	19	5.7	3.8	11.2	2.90
Carrol Spring	8	14.2	5.2	8.1	3.60
Moore-owned Spring	11	7.0	51.3	13.1	4.10
Elm Spring	2	5.9	4.4	13.1	2.85
Piney Creek	4	5.2	5.5	11.8	2.20
Dry Fork	27	9.0	4.1	10.6	3.30
Roulfs Spring	20	5.0	30.0	10.6	3.10
Bubbling Spring	22	7.5	51.1	10.0	3.10
Gollahon Spring	15	6.7	51.0	11.8	2.85

TABLE 16

Calcium Content of Springs and Streams (By Atomic
Absorption Spectrophotometry)

Name	Sample Number	Concentration ppm
Montauk Spring	1	18.40
Elm Spring	2	18.30
Haacke-owned Spring	3	4.50
Piney Creek	4	21.50
Boiling Spring	5	11.00
Rock Spring	6	10.00
Indian Spring	7	18.50
Carrol Spring	8	3.50
Joe Smith-Owned Spring	9	18.30
Yancy Mill Spring	10	18.60
Moore-owned Spring	11	21.60
Flag Spring	12	9.75
Miller-owned Spring	13	14.40
Lake Spring	14	31.11
Gollahan Spring	15	12.60
Brook Spring	16	26.70
Wilkins Spring	17	21.75
Meramec Spring	18	26.60
Brown Spring	19	7.00
Roulfs Spring	20	12.55
Martin Spring	21	13.60
Bubbling Spring	22	14.75
Mint Spring	23	15.00

TABLE 16
(continued)

| Name	Sample Number	Concentration ppm
Meramec River	24	16.30
Meramec River	25	15.80
Dry Creek	26	12.75
Dry Fork	27	16.50
Dry Fork	28	6.40
Dry Fork	29	2.00
Dry Fork	30	2.00
Dry Fork	31	1.48
Dry Fork	32	1.50
Dry Fork	33	1.50
Dry Fork	34	8.80
Dry Fork	35	9.50
Dry Fork	36	8.75
Dry Fork	37	18.50
Dry Fork	38	18.20
Dry Fork	39	13.30
Dry Fork	40	10.40
Dry Fork	41	24.75
Dry Fork	42	6.60
Dry Fork	43	5.20
Dry Fork	44	2.75
Dry Fork	45	5.40
Dry Fork	46	1.50
Dry Fork	47	17.80
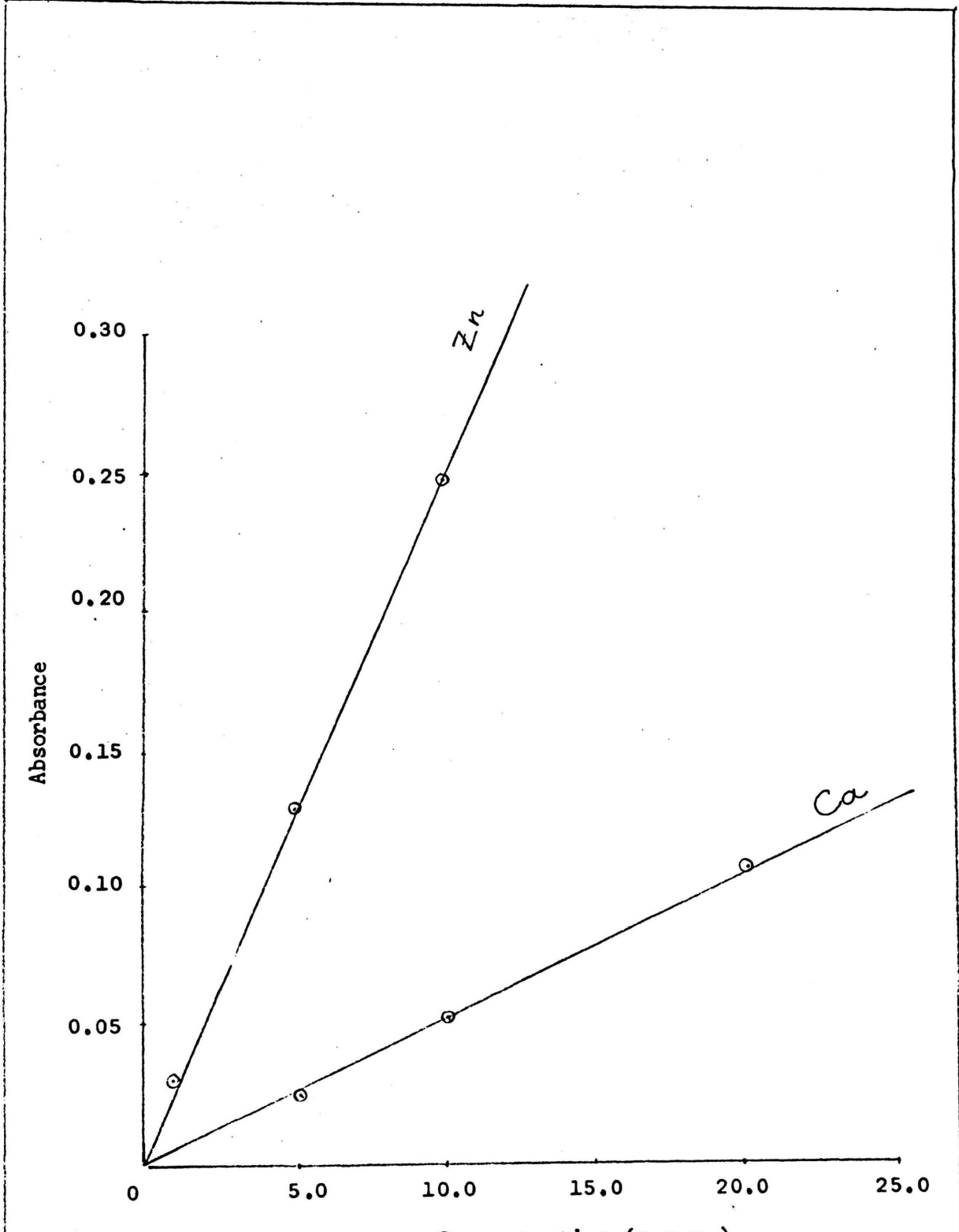
Figure 10. Standard curves for calcium and zinc (Atomic absorption spectrophotometry).
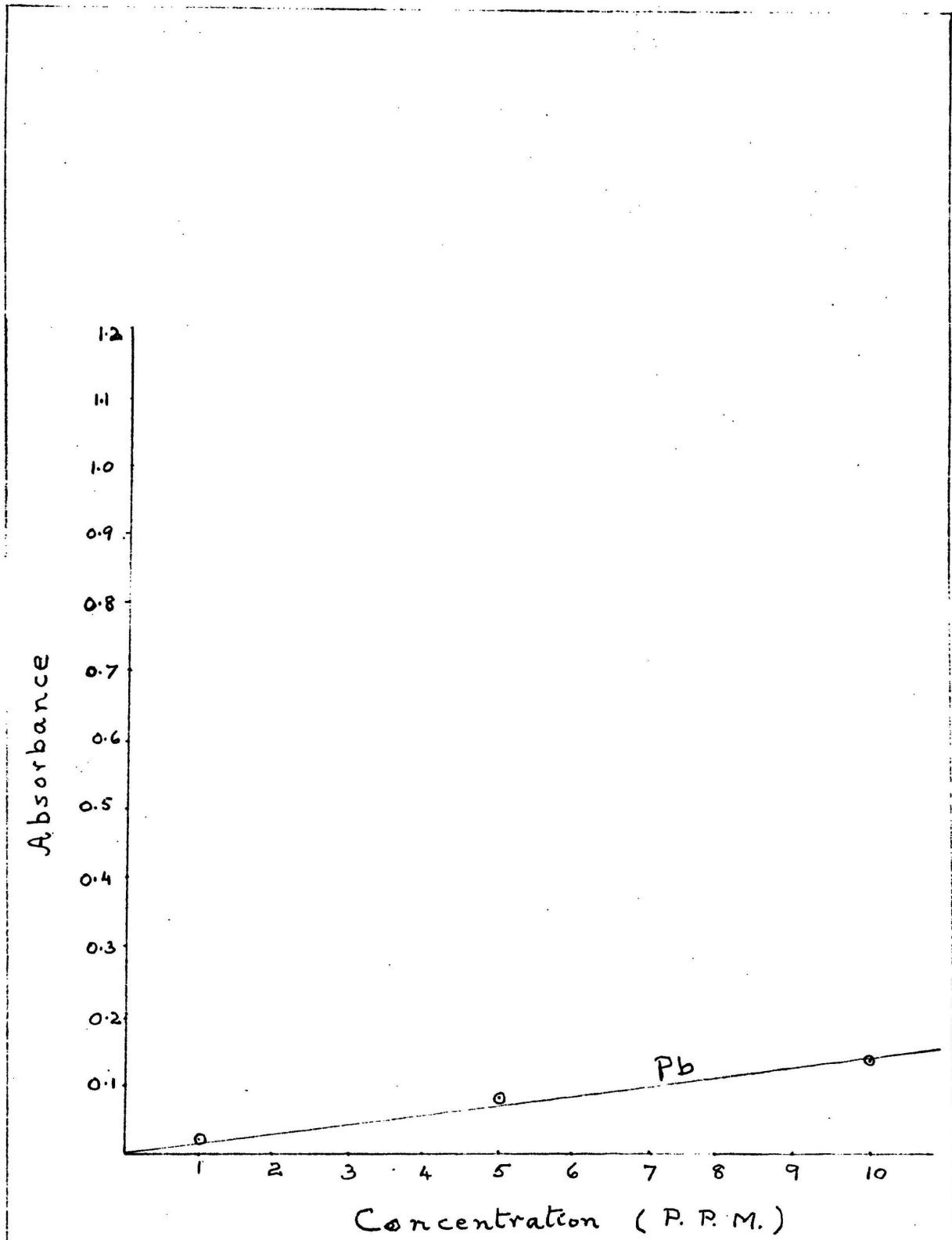
Figure 11. Standard curve for lead (Atomic absorption spectro-
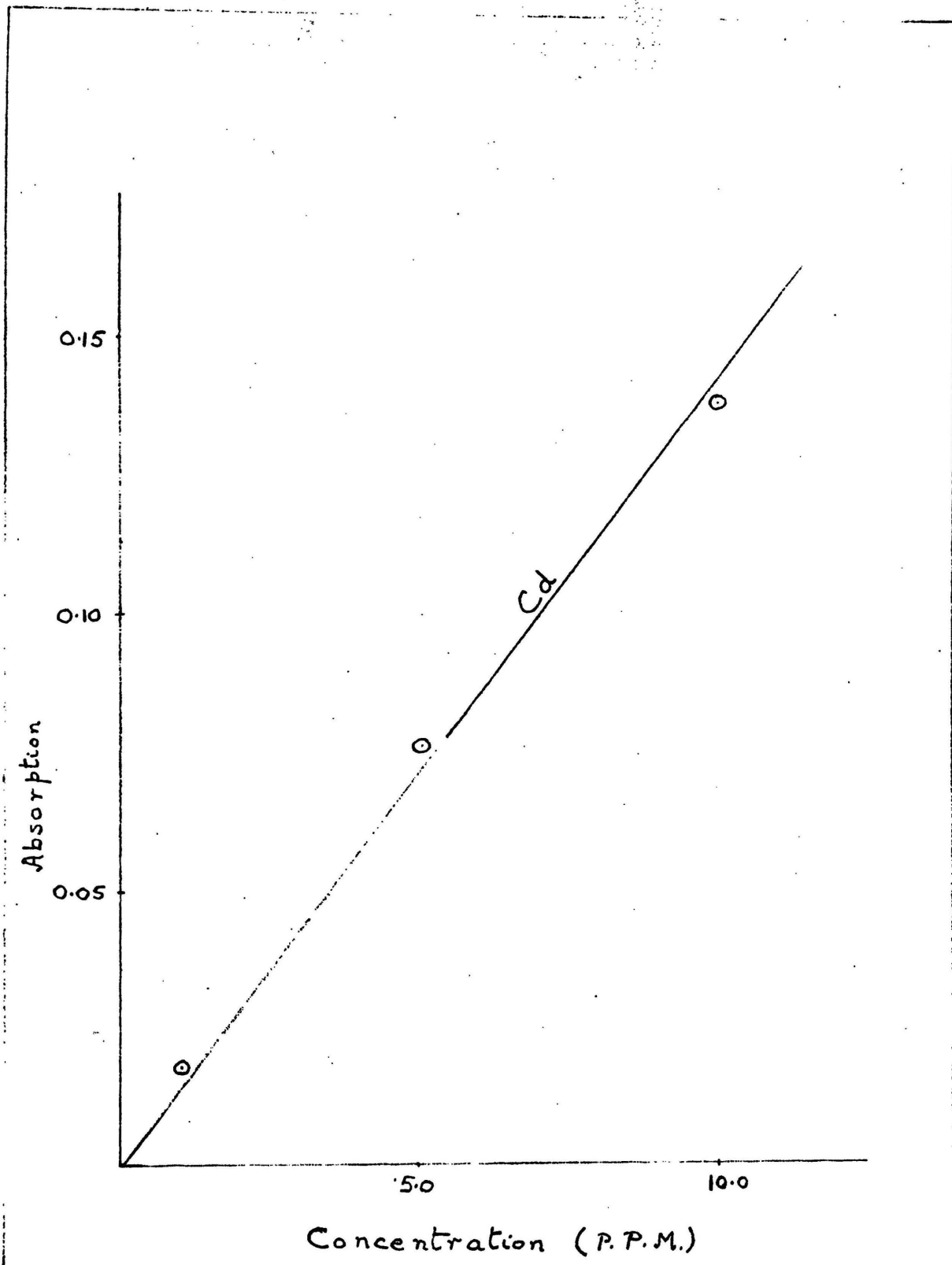photometry).

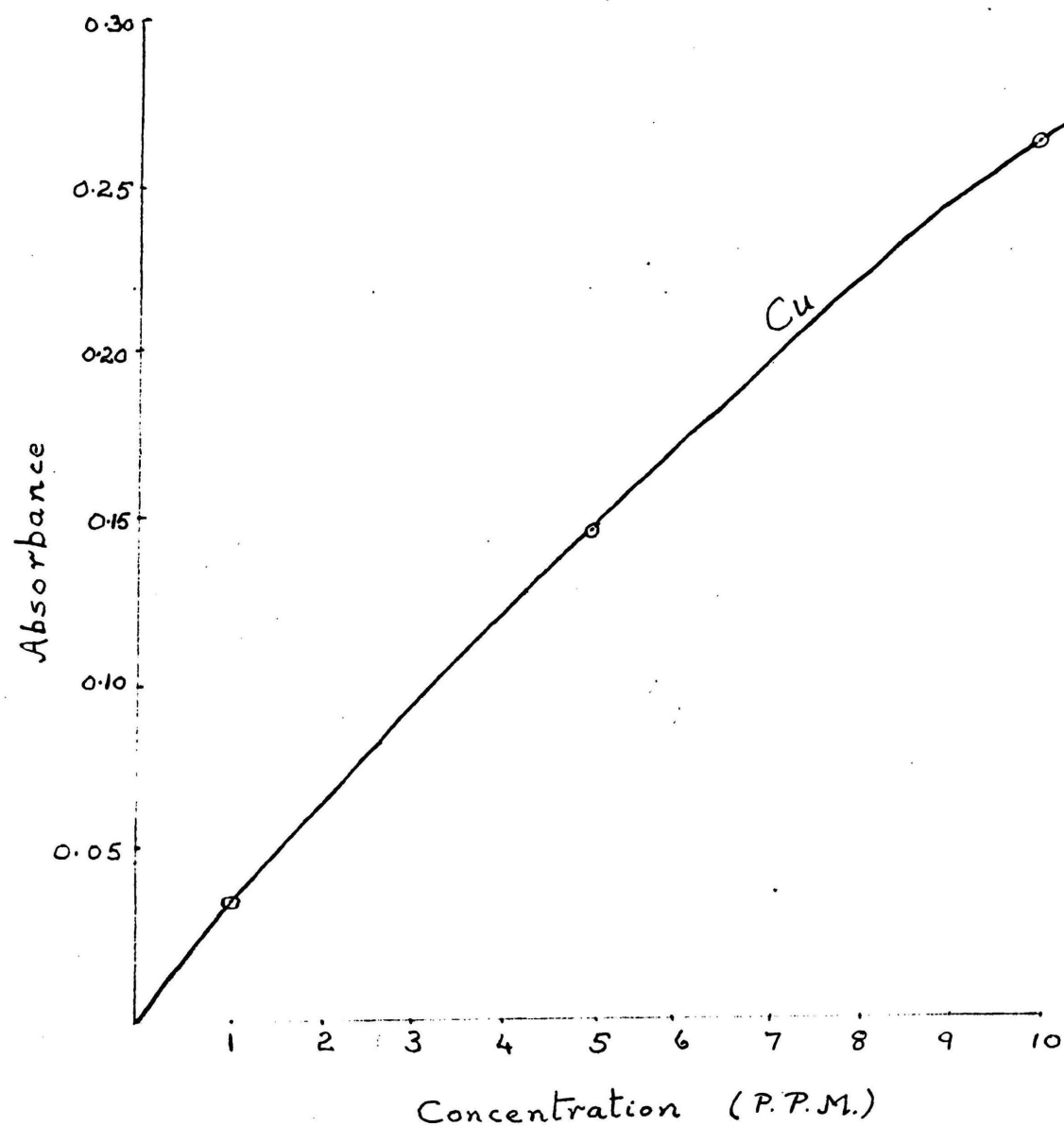**Figure 12.** Standard curve for cadmium (Atomic absorption spectrophotometry)

Figure 13. Standard curve for copper (Atomic absorption
spectrophotometry).

Chapter V

SUMMARY AND CONCLUSIONS

In order to determine trace elements in spring and stream waters, the sample in most cases must be concentrated before the actual analysis, since the available instruments are not sensitive enough for direct determination. The concentration methods investigated in this thesis include reducing the volume of water samples by drying in open beakers and closed retorts and by adsorption of the cations on a cation resin. It could be demonstrated, that reducing the volume of the samples by drying processes is not a feasible technique. In addition to the possibility of contamination and the long time needed for this procedure, the recovery of the cations of interest was in all cases much less than 100 percent, resulting in values which are to low.

Concentrating the cations at an adsorption resin is by far the most promising method. It can be done in a short time and the possibility of contamination from the air is greatly reduced. A recovery of 100 percent is possible. More work needs to be done to study the elution behaviour of elements other than zinc.

The investigated analytical procedures were absorption spectrophotometry, neutron activation analysis and atomic absorption spectrophotometry.

Adsorption spectrophotometry was considered useful only for the analysis of copper. The time needed to complete the copper analysis makes the procedure with this method less desirable than by atomic absorption spectrophotometry.

The possibilities for neutron activation analysis were greatly reduced by the low neutron flux of the U.M.R. reactor. Only the radiation from copper and sodium isotopes were detected. A neutron flux of about 10^{10} $n \cdot cm^{-2} \cdot sec^{-1}$ was obviously not sufficient for the analysis of other trace elements present in the low ppb range.

Analysis by atomic absorption spectrophotometry was by far the best method. In many cases the sample still must be concentrated, since the sensitivity of the instrument is not always sufficient. But no chemical preparation of the sample is necessary and a large number of samples can be analyzed in a short time.

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    M.S. thesis.

VITA

Faridoon A. Namdarian was born on March 31, 1933 in Yezd, Iran. He received his primary and secondary education from Markar and Kaykhosrove School, Yezd, Iran during the years 1950-51 and 1953-54 respectively.

In June, 1957 he received his Bachelor of Science degree in Geology from Teheran University, Iran. He was enrolled for Traffic Control in 1955-56 and graduated in June, 1957.

He was appointed as a teacher in Hayat High School, Sheraz, Iran in September, 1957. In April, 1958 he was appointed as the Airport Manager for Shiraz Civil Airport, Iran.

He was enrolled in Woolwich Polytechnic, London, England, in June, 1961 and received an ordinary level certificate of Pure and Applied Mathematics in June, 1963 and enrolled in Acton Technical College in September 1963 from which he received an Advanced Certificate of Pure and Applied Mathematics in January, 1964.

In February, 1965 he was enrolled in the graduate school of the University of Missouri at Rolla for work toward the Master's degree in Economic Geology (Geochemistry).

The writer married Dr. Dolly Namdarian (formerly Irani) in 1961 and has two children. She was a great help in this work and was looking forward to its conclusion. She passed away in 1966, before his graduation.