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THE BACKGROUND CONCENTRATIONS OF COPPER, LEAD, AND ZINC

IN STREAMS OF THE "NEW LEAD BELT", MISSOURI

BY

NICHOLAS HOWARD TIBBS, 1945

A

THESIS

Submitted to the faculty of

THE UNIVERSITY OF MISSOURI-ROLLA

in partial fulfillment of the requirements for the

Degree of

155394

MASTER OF SCIENCE IN GEOLOGY

Rolla, Missouri

1969

Approved by

_____(advisor)   _____

_____

ABSTRACT

This study was initiated to determine the background concentrations of copper, lead, and zinc in the streams of the Viburnum Trend or New Lead Belt of southeast Missouri. Analytical methods were developed for atomic absorption spectroscopy. These methods initially consisted of coextraction of copper, lead, and zinc using the APDC/MIBK system, and finally of extraction of copper by APDC/MIBK and direct analysis of lead and zinc using the newly developed "Sampling Boat" technique. The data obtained from these analyses were arranged in histograms and critically analyzed. The background concentrations were established to be 4-6 ppb for all three elements. Methods are presented for identifying both short term and long term contamination by using the data distributions. Short term contamination of a factor of 2-3 was determined to occur on the Bee Fork below the St. Joseph Lead Company's Fletcher Mine.

The data distributions were not useful for geochemical prospecting under the studied geological conditions. It is recommended that future studies be initiated in order to establish the degree of long term contamination introduced by the industrialization of this beautiful area.

ACKNOWLEDGMENTS

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I. INTRODUCTION

A. Purpose of Study

The advent of mining activity in the Viburnum Trend or New Lead Belt of southeast Missouri has presented an opportunity for an interesting study in the interdisciplinary area of water geochemistry and inorganic water pollution. The New Lead Belt, predicted to be one of the largest lead deposits in the world, extends from just west of Ellington, Missouri on a due north line to Viburnum, Missouri. At present this area is one of sparse population and relative wilderness, with rugged hills and swift, crystal-clear streams. It was anticipated that the lead mining activity will stimulate a sharp increase in industrial activity in the future in this area. Here then was a potential "before-after" study in pollution.

It was presumed that this intense mining activity in the New Lead Belt could cause significant contamination in the stream waters by the heavy metals - notably copper, lead, and zinc, the primary ore metals.

It was the purpose of this investigation to establish the background concentrations of copper, lead, and zinc in the stream waters of the New Lead Belt in order to enable a subsequent investigation to quantitatively establish the amount of contamination by these metals which may occur as a result of mining, milling, or other industrial activity.

B.   Scope of the Investigation

Following the initiation of this study, it soon became evident that a major portion of this investigation would be the development of sufficiently rapid and sensitive methods for the analysis of copper, lead, and zinc.   The Department of Geology, University of Missouri-Rolla, is equipped with a Perkin-Elmer Model 303 Atomic Absorption Spectrophotometer.   Atomic absorption spectroscopy was chosen as the most expedient method of analysis available, because of its extreme sensitivity and selectivity for the analysis of many elements.   Accordingly, the preliminary portion of this study was devoted to acquiring an understanding of atomic absorption spectroscopy.

Analytical methods were developed that were sensitive, rapid, and routine.   The most effective method of sample concentration was developed to enable atomic absorption analysis.

The background concentrations of copper, lead, and zinc in stream waters of the New Lead Belt area were determined.

The scope of the study was broadened in part because of the beginning of active mining and milling by the Fletcher Mine, St. Joseph Lead Company, six miles east of Bunker, Missouri in Reynolds county.   At this site it was possible to evaluate the level of contamination caused by the mining and milling activity.

Another aspect of this study was related to geochemical prospecting. Sampling of spring waters and ground water from mine faces was done in order to evaluate the possibility of locating ore bodies through geochemical techniques.

C. Previous Work

Little, if any, work has been done on the concentrations of copper, lead, and zinc in the streams of the New Lead Belt area. NAMDARIAN (1967) reported on the concentration of these metals in spring waters of Crawford, Dent, Phelps, and Pulaski counties of Missouri. His work indicated that the concentrations of these metals was very low and that sample concentration would be necessary for atomic absorption analysis.

Analysis of these metals in natural waters by atomic absorption spectroscopy has been reported by other investigators (FISHMAN, 1966; FISHMAN and DOWNS, 1966; TENNY, 1967), but little information about the details of analysis or the concentrations to be expected in the type of water encountered in the New Lead Belt could be gained from their reports.

WIXSON (1968) discussed the use of background data in establishing contamination. He emphasized the New Lead Belt as an ideal model for a pollution study.

DE GEOFFROY, et al. (1967) demonstrated the possibility of using zinc analysés of spring waters for locating shallow stratiform zinc deposits in southwest Wisconsin.

D. Area of Study

1. Location and Accessibility

Plate 1 shows Reynolds and Iron counties and the station locations in these counties. Samples were taken from streams in the Black River basin above Clearwater Lake. This basin is roughly outlined on the north side by Highway 32 in Iron county, and on

the northwest, west, south, and east sides by the Reynolds county boundary.

The highest density of stations was located in the general area of the Viburnum Trend or New Lead Belt. These stations were located in this manner, because these locations appear to have the greatest potential for contamination.

Streams of the area were not all readily accessible because many of the major roads are located on divides. Roads that did provide access were generally poor. The effect of this situation was a lessening of the amount of sampling that was accomplished in one work day.

2. Physiographic and Geologic Setting

The regional age of the area is one of maturity. Stream valleys are well developed, wide, and separated by narrow divides of steep ridges. Streams are swift flowing and clear. Smaller streams may flow completely beneath gravel in the stream beds at times of low flow.

The sedimentary rocks of the area are principally of shallow sea origin. These sediments are chiefly carbonates; they are of Cambrian and Ordovician age. The sediments are deposited noncon-formably on a Precambrian surface of high relief. The Precambrian rocks which outcrop in the area consist of felsites and granites.

The structure of the area is simple. There are few faults. Obvious structure in the sedimentary rocks is lacking with the exception of primary dips peripheral to the Precambrian knobs.

3. Climate

The climate of the area is moderate with mild winters and humid summers. Annual precipitation is 40-44 inches; the annual run-off is 14-16 inches (WIXSON, 1968).

4. Culture

The area is one of sparse population. According to the 1960 census, Iron county had a population of 8,041, and Reynolds county had a population of 5,161. It is the author's personal observation that the general populace show little regard for maintaining the beauty of this area. This is evidenced by much dumping of trash and litter, and direct contamination of streams by livestock and waste matter.

II. PRINCIPLES OF ATOMIC ABSORPTION SPECTROSCOPY

A. Basic Principles

Atomic absorption spectroscopy had been slowly developing since the early publication by WALSH (1955). In the past few years it has enjoyed a spectacular rise in application in almost all fields requiring rapid, accurate chemical analysis of trace elements.

For the geochemist the text by ANGINO and BILLINGS (1967) presents a comprehensive treatment and bibliography on the application of atomic absorption spectroscopy to problems in geology. Perhaps the best treatment of the subject is given by SLAVIN (1968); he presents a complete bibliography. New developments are constantly being reported in the "Atomic Absorption Newsletter", a regular journal published by the Perkin-Elmer Corporation.

The basic atomic absorption spectrophotometer components are a hollow cathode lamp, flame, monochromator, photomultiplier, and readout device.

The hollow cathode lamp emits wavelengths characteristic of the element composing the cathode of the lamp. This beam of light is passed through a flame in which a sample solution is being aspirated at a constant rate. The large majority of atoms in this flame are in the ground state. Atoms which are of the same element as the cathode will absorb energy from the lamp emission. Other elements will not absorb this energy. A monochromator is then used to select the wavelength (i.e., one at which absorption occurs). The amount of absorption is determined by a photomultiplier and read out on either a galvanometer or a chart recorder.

B. Details of the Perkin-Elmer Model 303

The Perkin-Elmer Model 303 Atomic Absorption Spectrophotometer
has several characteristics which greatly enhances its applicability
to ultrasensitive analysis. This instrument utilizes a double beam
system. In this system the beam from the hollow cathode lamp is
mechanically split, one half of the beam passes through the flame,
the other by-passes the flame and the ratio of one beam to the other
is measured. This effectively reduces lamp warmup and drift
effects. The Perkin-Elmer Model 303 utilizes a Bi-0-Ag photomultiplier
which extends the sensitivity of the instrument into the far ultra-
violet (below 2200 $\overset{o}{A}$). The analytical lines for zinc and lead are
in this range.

The Perkin-Elmer Model 303 offers increased capabilities
through the use of electronic scale expansion. Expansions up to
100x are possible with the chart recorder accessory, but in most
applications only 10x is practical because of simultaneous expansion
of background noise.

C. Methods of Increasing Sensitivity by Instrumentation

Many modifications in instrumentation have been attempted in
order to increase sesnitivity. These primarily consist of efforts
to increase the atomic density in the flame.

The use of the Fuwa tube (FUWA, et al., 1964) has been shown
to give sensitive results for many metals. The sensitivity is
increased by passing the beam through a long tube filled with atomic
vapor from a burner. KOIRTYOHANN and FELDMAN (1964) obtained

sensitivities of 5 ppb for copper and 0.5 ppb for zinc. Sensitivity
for lead was worse at 20 ppb.

The heated premix burner has also been investigated. VENGHIATTIS
(1968) presented a comprehensive analysis of this accessory and
reported increased sensitivities for lead at 20 ppb, copper at 8 ppb,
and zinc at 1.5 ppb.

Modifications such as the ones mentioned above were not
practical in this study as they required alteration of the instrument
which was being used for other studies.

Perkin-Elmer has recently developed a new accessory, called the
"Sampling Boat", which greatly increases the detection limits of
lead and zinc. The application of this accessory to this study is
discussed in Chapter VII.

III. METHODS OF SAMPLE CONCENTRATION

A. Necessity of Sample Concentration

A method of analysis for the content of copper, lead, and zinc in the streams of the New Lead Belt had to be developed. No previous information was available on the concentration of these metals in the streams of this area. NAMDARIAN's work (1967) indicated that the expected concentrations for these metals could be quite low, in the range of less than 50 ppb. Water samples were collected and an attempt was made to determine the metal content without previous treatment of the sample except for filtering. Only zinc showed any peaks at the maximum working scale expansion. It was apparent that concentration was necessary for analysis of the water samples.

B. Methods of Concentration

In the analysis of a large number of water samples, the method of concentration must be rapid, simple, and inexpensive.

Methods of concentration can be divided into two major categories:

(1) Physical
   a. Concentration by Evaporation
   b. Freeze-dry concentration

(2) Chemical
   a. Coprecipitation
   b. Ion exchange
   c. Solvent extraction

1. Physical Methods of Concentration

    a. Concentration by Evaporation

        TENNY (1967) used evaporation to concentrate water samples from Lake Michigan. NAMDARIAN (1967) tested evaporation as a concentration method. Tests were performed in both open beakers and retorts. NAMDARIAN found for samples spiked with Ag^{110} and evaporated in open beakers, that only 33.6% of the Ag^{110} was recovered. The best results were for samples spiked with copper and evaporated in retorts with a recovery of 91%. These low recoveries in conjunction with the tedious procedure (sample evaporation took up to 40 hours) made evaporation an unsatisfactory method of concentration.

    b. Freeze-Dry Concentration

        Freeze-dry concentration (BOLTER, personal communication) is accomplished by very rapid freezing of an aqueous sample with dry ice. To samples of low salt content, such as fresh water, a pure carrier salt must be added. The sample is then evaporated under vacuum which takes about 8 hours. BOLTER, et al. (1964) described this method more fully.

    This method of concentration was rejected for two reasons. It required the building of a bulky vacuum system. Contamination by the carrier salt was a possibility, and the high salt content of the final solution could have caused difficulties such as burner clogging and chemical interferences. Time was not a factor. The 8 hours of evaporation could have taken place overnight.

2. Chemical Methods of Concentration

   a. Coprecipitation

   Concentration by coprecipitation is performed by collecting a large volume of water (10 liters), preparing it by acidification to a given pH, adding a carrier, and then raising the pH by adding an appropriate hydroxide. The carrier precipitates taking the trace elements with it. The precipitate is removed and ordinarily the carrier is then taken up with the proper solvent.

   JOYNER and FINDLEY (1966) investigated coprecipitation to determine manganese and iron in sea water. BURRELL (1965) used coprecipitation in conjunction with solvent extraction to determine nickel and cobalt in sea water. Although coprecipitation offers a simple method of concentration, the necessity of using extremely large samples causes inconvenience in the field and prevents rapid analyses in a small laboratory.

   b. Ion Exchange

   In the ion exchange technique concentration is accomplished by trickling a large volume of sample at a controlled rate through an active resin which quantitatively adsorbs selected ions. These ions are then eluted with a selected solvent. Concentration is determined by the ratio of eluent volume to sample volume.

   NAMDARIAN (1967) investigated the use of ion exchange resins. Using the hydrogen form of AG 50 W-X8, 200-400 mesh, he was able to concentrate the zinc in four liters of sample into 25 milliliters of eluent. Recovery was 99.9%. This represents a concentration

factor of 160. Recovery of 100% was attained using 175 milliliters of eluent; this represents a concentration factor of 23. The eluent was 4 M HCl. NAMDARIAN used other eluents with less satisfactory results. Similar experiments with cadmium gave unsatisfactory results; maximum recovery attained was 78%.

Ion exchange does present a rapid means of concentration, provided the proper choice of resin and eluent is made. NAMDARIAN lists several references that indicate a resin would be available which would permit the concentration of copper, lead, and zinc simultaneously. The major drawback would be the necessity of collecting large samples. In addition the concentration factors necessary for this study could be difficult to achieve.

c. Solvent Extraction

Concentration of water samples by solvent extraction - also known as liquid-liquid extraction - is accomplished by first treating the sample chemically with a suitable buffer and chelating agent. Then the element or elements of interest are extracted from the treated sample into a smaller volume of an immiscible organic solvent by agitation of both phases in an extraction vessel. The cation or cations extracted are quantitatively taken up by the solvent. The concentration factor is governed by the ratio of solvent to sample. An additional advantage in atomic absorption spectroscopy is the fact that there is a "solvent effect" which further enhances the concentration factor. This effect will be discussed in Chapter V.

C. Choice of Concentration Method

Solvent extraction was chosen as the method of concentration for the analyses in this investigation for several reasons. Most notably, references in the literature (SPRAGUE and SLAVIN, 1964; WILLIS, 1962; TAKEUCHI, et al., 1966; MULFORD, 1966; PLATTE, 1967) reported on the simplicity and applicability of solvent extraction. Analyses were reported for metals in water in the low ppb range. In addition, chelating agents with a broad spectrum, allowing single step concentration of many elements at the same time, made solvent extraction an appealing method of concentration.

The disadvantages of solvent extraction were not evident. The proper system for simultaneous extraction of copper, lead, and zinc had to be developed. Development of this system soon led to some analytical difficulties.

IV. CHOICE OF SOLVENT EXTRACTION SYSTEM

A. Previous Work

In atomic absorption spectroscopy, reports of investigations concerning the use of solvent extraction for the analysis of trace elements are frequently encountered. TAKEUCHI, et al. (1966) gave a brief but comprehensive evaluation of many extraction methods. MULFORD (1966) presented a summary of many extraction systems used in atomic absorption spectroscopy. Various specific systems were evaluated in other papers. WILLIS (1962) used the APDC/MIBK system to determine Pb, Hg, Bi, and Ni in urine. BELCHER, et al. (1964) determined silver by extraction as a di-n-butyl salicylate into MIBK. DAGNALL and WEST (1964) extracted lead from aqueous solutions with 8-hydroxyquinoline in chloroform and MIBK. They also used DDTC in ethyl acetate. JOYNER (1965) extracted Fe and Mn from sea water with a DDTC/MIBK system. MANSELL and EMMEL (1965) used the APDC/MIBK system to extract Co, Cr, Mo, Ni, and V from a 25% NaCl brine; they used the oxine/chloroform system to extract Co, Cu, Mo and Ni. SPRAGUE and SLAVIN (1964) used the APDC/MIBK system to determine traces of Cu and Pb in KCl. PLATTE (1967) used the DDTC/MIBK system to analyze industrial waters for Fe^{III}, Cu, Zn, Cd, and Pb.

B. Requirements of the Solvent Extraction System

For many spectroscopic methods of analysis a solvent extraction system must be specific. Chemical pretreatment of a sample is necessary to remove interfering ions. Rigid pH control is often necessary in many systems to obtain selective extractions.

In atomic absorption spectroscopy interferences are negligible because specificity is inherent in the principle. Therefore, an extraction system need not be specific. It is advantageous in multi-elemental analysis to use chelating agents with a broad spectrum.

There are limitations which must be placed on the choice of solvents. ALLAN (1961, p. 469) stated that "...only esters and ketones behave satisfactorily in the flame". Commonly used solvents such as chloroform and carbon tetrachloride give very erratic flames and soon clog the burner. In addition, a solvent must have a low solubility in water to obtain significant concentration factors; solvents such as ethyl acetate which are satisfactory in other respects are severely limited in their application by their relatively high solubility.

C.   Choice of Two Systems

In atomic absorption spectroscopy, one solvent extraction system is outstandingly popular. This is the APDC/MIBK system. The broad spectrum of this system makes it ideal for multi-elemental analysis; the system is not strongly dependent upon pH for many elements. The major drawback of this system was the cost of APDC.

Another system appeared to offer the advantages of the APDC/MIBK system at less cost. This system was the DDTC/MIBK system.

Investigation of these two systems is treated in Chapters V and VI. The primary effort in the experimentation was devoted to the APDC/MIBK because of its apparent popularity. Investigation

of the DDTC/MIBK system was aimed principally at a reduction
in cost.

MIBK was chosen as a solvent because it was reportedly one
of the best solvents for atomic absorption spectroscopy and it
was readily available.

D. Other Extraction Systems

Other systems were not investigated in the laboratory; however,
research in the literature revealed other systems that could be
applied to the analysis of copper, lead, and zinc. TAKEUCHI, et al.
(1966) presented an interesting report of investigations in which
they compared the relative sensitivities of several metal chelates
by atomic absorption spectroscopy. They showed little variation
in sensitivities, but they did report several extraction systems
applicable to copper and lead. Interesting among these systems
was the use of cupferron, dithizone, and 8-hydroxyquinoline in
MIBK. This work illustrated that other extraction systems for the
coextraction of copper, lead, and zinc could have been developed.

Other papers illustrating extraction systems were by GENTRY
and SHERRINGTON (1950) on 8-hydroxyquinoline, and by FURMAN, et al.
(1949) on extraction of cupferrates. ELWELL and GIDLEY (1961)
used dithizone/MIBK to determine cadmium, lead, and zinc. MULFORD
(1966) reported on the extraction of copper using cupferron/MIBK.

V. INVESTIGATION OF THE APDC/MIBK SYSTEM

A. Previous Work With the APDC/MIBK System

The classic work on APDC is the paper by MALISSA and SCHOEFFMANN (1955). As a translation of the German text was unavailable, this paper was of little help in the investigation of the system. SLAVIN (1964) presented a concise summary of the applications of this system. He presented R. L. Pereira's (University of Connecticut) method of synthesis, which was modified after the procedure of MALISSA and SCHOEFFMAN[1]. MULFORD's paper (1966) dealt in detail with the APDC/MIBK system. He listed references, elements which could be extracted, and the ranges of pH at which extractions could be performed.

Specific applications of APDC/MIBK are common in the literature of atomic absorption spectroscopy. SPRAGUE and SLAVIN (1964) determined small amounts of copper and lead in refined KCl solutions using this system. BROOKS, et al. (1967) used APDC/MIBK extraction to determine copper in sea water. WILLIS (1962) demonstrated the applicability of APDC by extracting lead and other heavy metals from urine. An example of the extraordinary degree to which this system has been applied would be FARMER's paper (1967) which demonstrated the analysis of trace iron in Nylon-66 by APDC/MIBK extraction.

With such a formidable array of supporting work, little difficulty was anticipated in the analysis of fresh water. This

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[1]The APDC used in this study was obtained from K&K Laboratories, New York @ $126.00/100 g. It is also available from Fisher Scientific Company under the name of 1-pyrrolidinecarbodithiodic acid, ammonia salt.

was not found to be the case. Several problems which arose are treated in the following sections of this chapter. A final method is proposed (Appendix I).

B. Experimental Difficulties

1. Purity of Distilled Water

Initially, a distillation apparatus was not available for producing the very pure water necessary for this study. The deionized water from the laboratory was known to contain significant amounts of metal (as compared to the expected concentration in the samples). An attempt was made to further purify the deionized water by acidifying two liters with 1.2 ml of glacial acetic acid, adding two grams of APDC and extracting into two 100 ml portions of MIBK. Preparation of standard solutions resulted in failure as the treated deionized water caused a large amount of precipitate to form.

A source of good quality distilled water was finally obtained from Mike Oko, a graduate student in the Metallurgy Department, University of Missouri-Rolla. Oko's water was triple distilled in glass stills; the source of water was the deionized water from the nuclear reactor pool. The present satisfactory supply of water in the laboratory is obtained by single distillation of reactor pool water in a Barnstead still equipped with a vapor scrubber glass column.

2. Effects of Solvent in the Flame

Preliminary work with the APDC/MIBK system outlined another basic problem of analysis. Aspiration of the organic solvent at the fuel-air ratio optimum for aqueous samples gave a white luminous flame which strongly absorbed the energy emission from the hollow cathode lamp. This resulted in a very high peak for the blank in a standard series, and subsequent lesser resolution of the standard peaks. At first, it was thought that the luminous flame was to be tolerated and that the high blank was a result of impure water. However, further information (ALLAN, 1961) quickly demonstrated that reduction of the acetylene flow to the point of a non-luminescent flame resulted in a substantially lower background from the blank. It became necessary to aspire MIBK continuously in order to maintain the flame.

Continuous aspiration of MIBK controlled another problem in the analysis of organic solvents. Lead and zinc were analyzed at 2170 $\overset{o}{A}$ and 2143 $\overset{o}{A}$, respectively. At these wavelengths, there is a strong absorption of the lamp energy emission by the flame; as the fuel to air ratio decreases this absorption decreases. The effect of removing the organic solvent from the flame fuel mixture between samples caused a decrease in absorption and subsequently yielded a higher but erroneous absorption peak.

There was one benefit obtained through the use of organic solvents that must be stressed. Aspiration of an organic solvent can result in up to a five-fold increase in sensitivity over aqueous solutions. This is because of an increase in the amount of solvent

reaching the flame through the premix burner chamber. Without this increase in sensitivity, application of solvent extraction would be less useful for the development of ultrasensitive methods of analysis. It would have been impossible to obtain the concentration factors necessary for analysis in this investigation.

3. Effect of Buffer

MULFORD (1966) presented the pH ranges for presumably complete extraction of the elements which have been determined using the APDC/MIBK system (Table 5.1).

Element	pH
Copper	0.1 - 8
Lead	0.1 - 6
Zinc	2 - 6

Table 5.1. pH ranges for extraction with APDC. (After Mulford, 1966)

A buffer solution was prepared according to instructions by PLATTE (1967), from ammonium acetate and glacial acetic acid (see Appendix I). PLATTE used this buffer to bring the pH of acidified solutions to 2.5[1]. The pH value of the buffer was determined to be 5.5, which is within the range of pH prescribed by MULFORD for the extraction of copper, lead, and zinc. However, the use of this buffer in the determination of standard series ranging from 5-50 ppb of these metals in aqueous solution resulted in erratic values of

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[1]This application of a buffer is questionable. A buffer of pH of 2.5 would be more suitable.

absorbance. It was postulated that this variability might be introduced through incomplete extraction as a result of the pH (e.g. buffer).

To test this hypothesis three series of standards were prepared by extraction with APDC/MIBK, using different buffers. One series was buffered with the previously described buffer. The second series was buffered with a commercially prepared potassium bipthalate buffer with a pH of 4.0. The third series was buffered with a commercially prepared potassium chloride-hydrochloric acid buffer with a pH of 2.0. Results of this experiment are illustrated in Figures 5.1a and 5.1b which show standard curves using each buffer for copper and lead respectively. Ideally the curves should be a
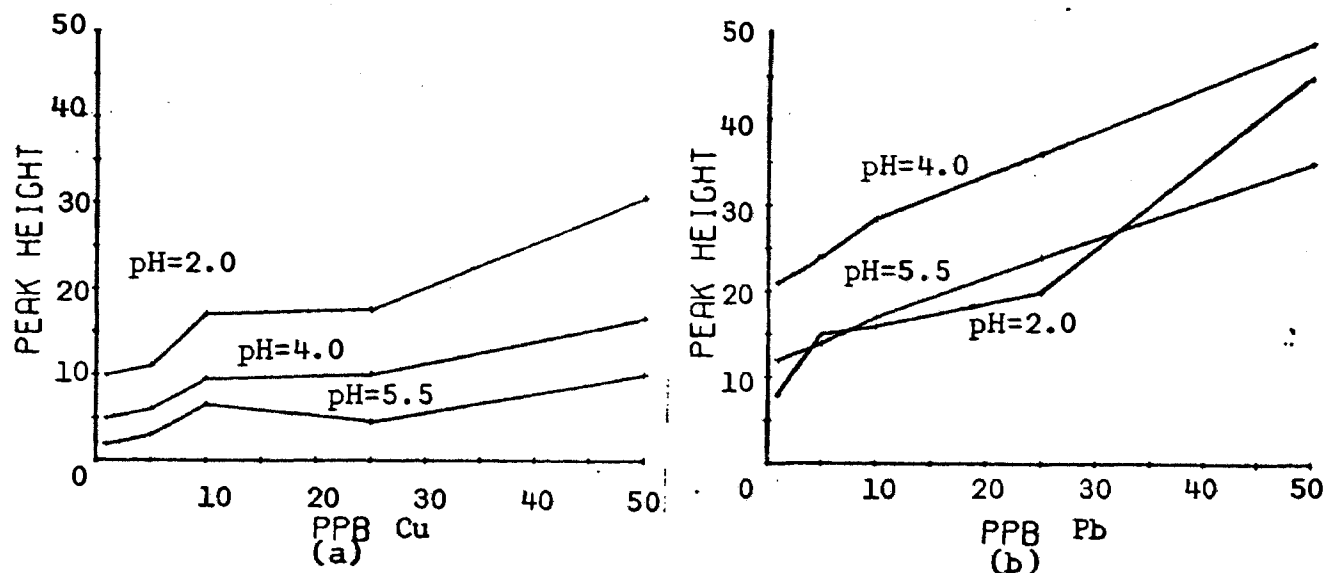
Figure 5.1. Test of buffer effect on APDC/MIBK extraction.
(a) Copper. (b) Lead. The pH is indicated for each curve. Curves are not compensated for blanks.

straight line. The extreme variability of points on the copper

standard curves (Fig. 5.1a) are indicative of the problem previously

encountered with the use of the ammonium acetate-glacial acetic

acid buffer. In this case, all three series for copper yielded

similar curves. This similarity cannot be ascribed to improper

procedure in the preparation of standards because the standards

for lead were prepared in the same procedure, and the curves

prepared from the coextracted lead series yielded dissimilar curves.

As can be seen from Figure 5.1b, the lead series extracted at

pH's of 4.0 and 5.5 resulted in reasonably good standard curves.

The lead series extracted at a pH of 2.0 had a broad variation

from linearity. None of these curves bear any similarity to the

copper standard curves, ruling out procedural errors in the standard

preparation. Zinc (not shown) presented very erratic standard

curves of which the pH of 5.5 series was the best.

Because samples could not always be analysed immediately after

extraction, these same three series were allowed to stand in contact

with the aqueous solutions from which they were extracted for one

day and a repeat determination was made. The results of this

experiment are presented in Figures 5.2a, 5.2b, and 5.2c. The

copper series (Fig. 5.2a) yielded even more erratic curves than

the day before with apparent decomposition of the chelate in the

most acidic series. For lead (Fig. 5.2b) it is evident that the

two least acidic series were stable and that the relative changes

in slope[1] of the standard curves indicate that the pH of 5.5 series

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[1]Absolute slope changes have no significance in the comparison of
these curves as the slope of the curves is dependent on instrument
parameters which may change from day to day.
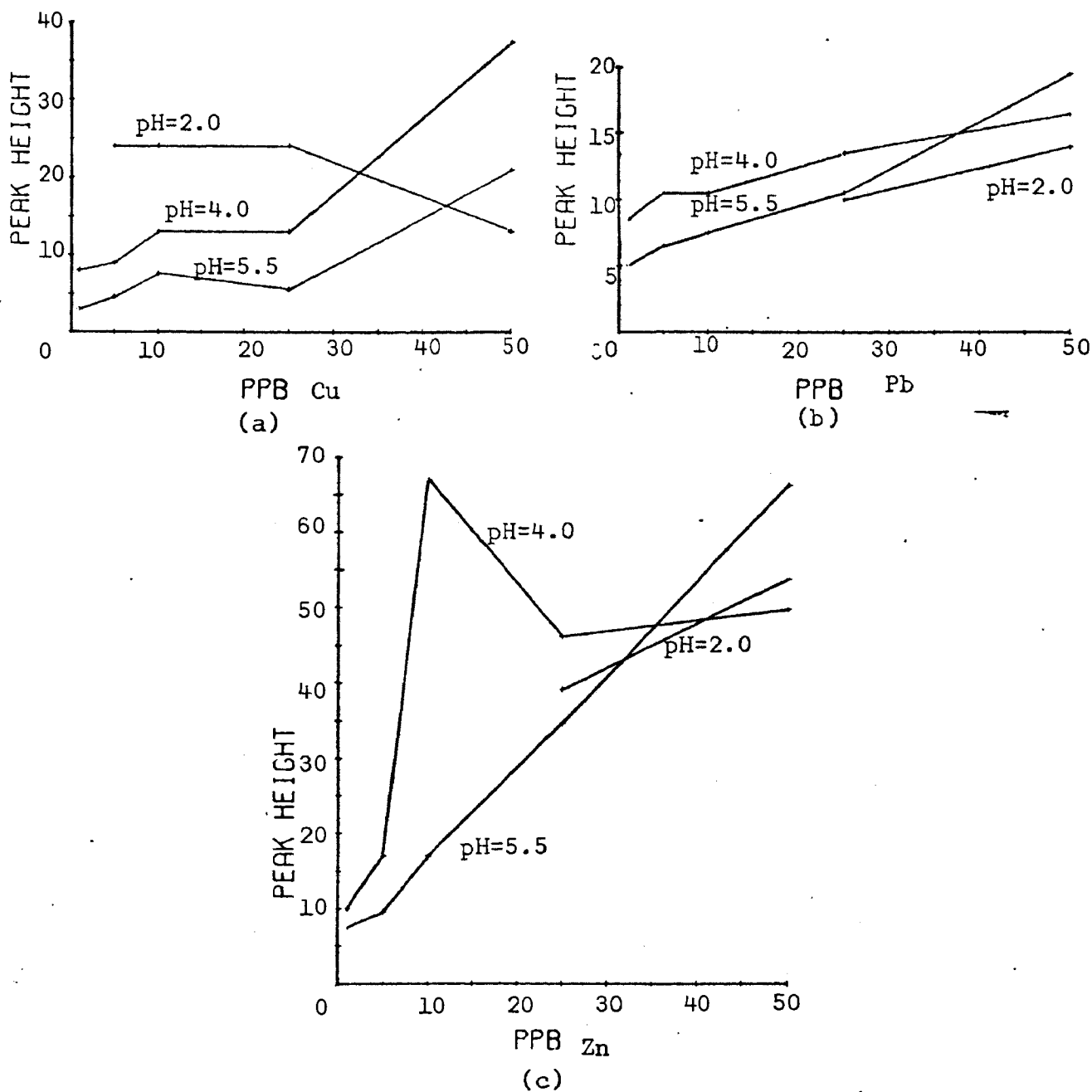
Figure 5.2 Test of time effect on different APDC/MIBK extracts.
(a) Copper. (b) Lead. (c) Zinc. The pH is indicated
for each curve. Curves are not compensated for blanks.
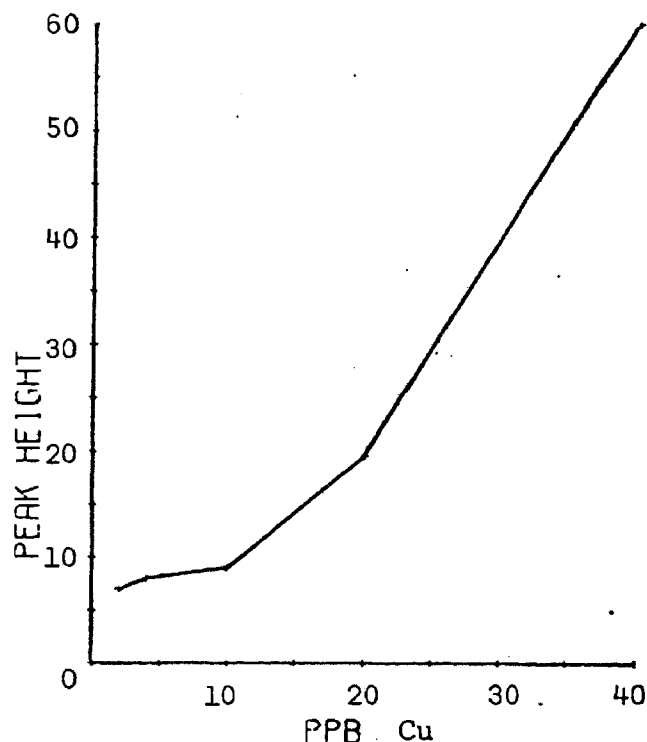
Figure 5.3. Calibration curve for copper extracted by APDC/MIBK
from water acidified with 2N HCl to a pH of 2-3.
The curve is not compensated for the blank.

was the most stable of the three series. One surprising result

of the stability tests was the very good curve for zinc in the pH

of 5.5 series (Fig. 5.2c) as compared to the poor curve obtained

the day before.

Because of the unsatisfactory results of the extraction tests

for copper, it was decided to prepare a standard series for extraction

by acidifying with 2N HCl to a pH range of 2-3. The exponential

curve which resulted (Fig. 5.3) suggested that the extremely small

quantities (on the order of 1-5 micrograms) of copper as the APDC

complex in the MIBK phase were not stable in the presence of acid,

or did not extract efficiently into the MIBK phase.

At this point the decision was made to use the ammonium acetate-glacial acetic acid buffer since it gave the best general results for the coextraction of copper, lead, and zinc.

C.   Recent Developments of the APDC/MIBK System

Development of the "Sampling Boat"[1] accessory (Chapter VII) has eliminated the need to determine lead and zinc by solvent extraction. Consequently, a method for the extraction of copper alone was developed. Because of the broad pH range over which copper reportedly was extractable by APDC/MIBK (MULFORD, 1966), it was decided to attempt to extract copper at the ambient pH of the water sample. This worked very well as is demonstrated by the standard curve in Figure 5.4. An added bonus was the stability of the chelate as is demonstrated by Figure 5.4 which presents a calibration curve determined for the same standards six days later. The procedure for the determination of copper by this method is presented in Appendix II. This method is presently being employed for routine determinations of copper in water at concentrations of less than 50 ppb.

D.   Summary of Coextraction Method by APDC/MIBK

Experience has shown that good analytical curves for all three elements can be obtained by the method outlined in Appendix I. However, for some undetermined reason, one can expect erratic curves, occasionally. This could be the result of a breakdown of the metal chelate by the acid solution, as mentioned before. Inter-elemental

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[1]Trademark, Perkin-Elmer Corporation
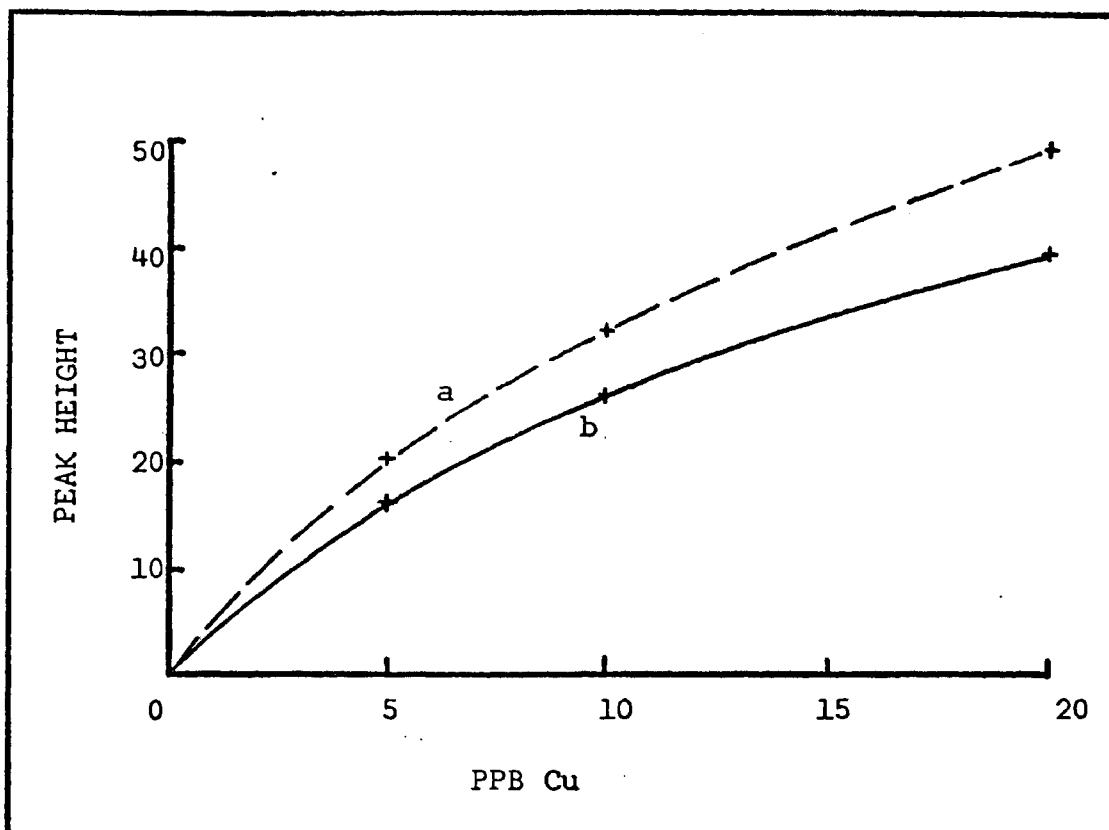
Figure 5.4. Standard calibration curves for copper by APDC/MIBK extraction of water at its natural pH. The stability of the chelate is illustrated by the similarity of (a) the initial calibration curve, and (b) the calibration curve prepared from the same extracts six days later.

interferences can be ruled out as none of the three elements gave

a uniformly superior curve.

Some results of the extraction experiments with APDC/MIBK

were contrary to previously published material. Ranges of pH for

extraction as listed by MULFORD (1966) were not valid in these

experiments. SABINA and SPRAGUE (1964) cited a pH range of extraction

for copper from 3.5 to 8.5 with virtually no difference in absorbance

being measured in the atomic absorption determination. This would

indicate that good calibration curves should have been obtained by

the extraction of copper from acidic solutions. This was not found

to be the case. SABINA and SPRAGUE also gave an optimum pH for lead extraction at about 2.8. This is also contrary to the results of experiments presented here which demonstrated the best results when lead was extracted from solutions at a pH of 4.0 to 5.5.

VI. INVESTIGATION OF THE DDTC/MIBK SYSTEM AND A DISCUSSION OF OTHER SYSTEMS

A. Introduction to the DDTC/MIBK System

Only a brief investigation of this system was performed. PLATTE (1967) presented a method incorporating DDTC (Sodium diethyl-dithiocarbamate) extraction into MIBK. He indicated that ferric iron, zinc, cadmium, copper and lead can be determined at concentrations below 50 ppb. Because of the commercial availability of this compound, a portion of the preliminary experiments in this investigation was performed using the DDTC/MIBK system. This system proved unsatisfactory; the reasons are included in the following discussion.

B. Experimentation with the DDTC/MIBK System

The first difficulty encountered with the commercially available DDTC was the large quantity of fine precipitate which formed upon making up an aqueous solution. Tests have shown that this was not a result of contamination in the water or container. The conclusion can only be drawn that the precipitate was an insoluble residue in the DDTC. With difficulty, it could be removed by filtration; the resulting clear solution seemed to function well in the extraction procedure.

PLATTE (1967) used an ammonium acetate-glacial acetic acid (op. cit.) buffer to adjust acid solutions to a pH of 2.5[1]. Without calculation of the actual pH of the buffer, this buffer was used in the the extraction of copper, lead, and zinc by DDTC/MIBK. This resulted

the
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[1]PLATTE [1]PLATTE indicates an optimum pH range of 2-3 for extraction of
these   these metals.

in good extraction of copper; lead and zinc did not give good

calibration curves. The error in assuming the pH of the buffer

to be 2.5 was recognized and calculations and determinations on

buffered solutions proved an actual buffer pH value of 5.5.

At this point experimentation with the APDC/MIBK system proved

it superior to the DDTC/MIBK system, and the latter system was

abandoned.

VII.   THE "SAMPLING BOAT"[1] TECHNIQUE

In April, 1968, KAHN, et al. of the Perkin-Elmer Corporation described an accessory for the PE 303 Atomic Absorption Spectrophotometer which they called the "Sampling Boat" technique. Detection limits obtained by using only one milliliter of sample were reported to be very low with this technique (Table 7.1). The detection limit reported for zinc of 0.030 ppb made this method particularly appealing for the determination of that metal in this investigation; the detection limit for lead of 1 ppb was not quite as appealing, but it was decided to obtain the accessory and apply it to the analysis of these two metals.

A.   Description of the Technique

Figure 7.1 illustrates the accessory. The basic principle is simple; rather than aspire the sample at a fixed low rate through the premix burner which allows only a small portion of the sample to reach the flame, the sample is placed in a tantalum boat, evaporated to dryness, and placed directly in the flame. The sample is consumed in 1-2 seconds; the result is a high narrow absorption peak as compared to the low broad peak over 15-20 seconds for the former method. It is this short time of consumption for the same amount of sample which gives the remarkable improvement in detection limits.

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[1] Trademark, Perkin-Elmer
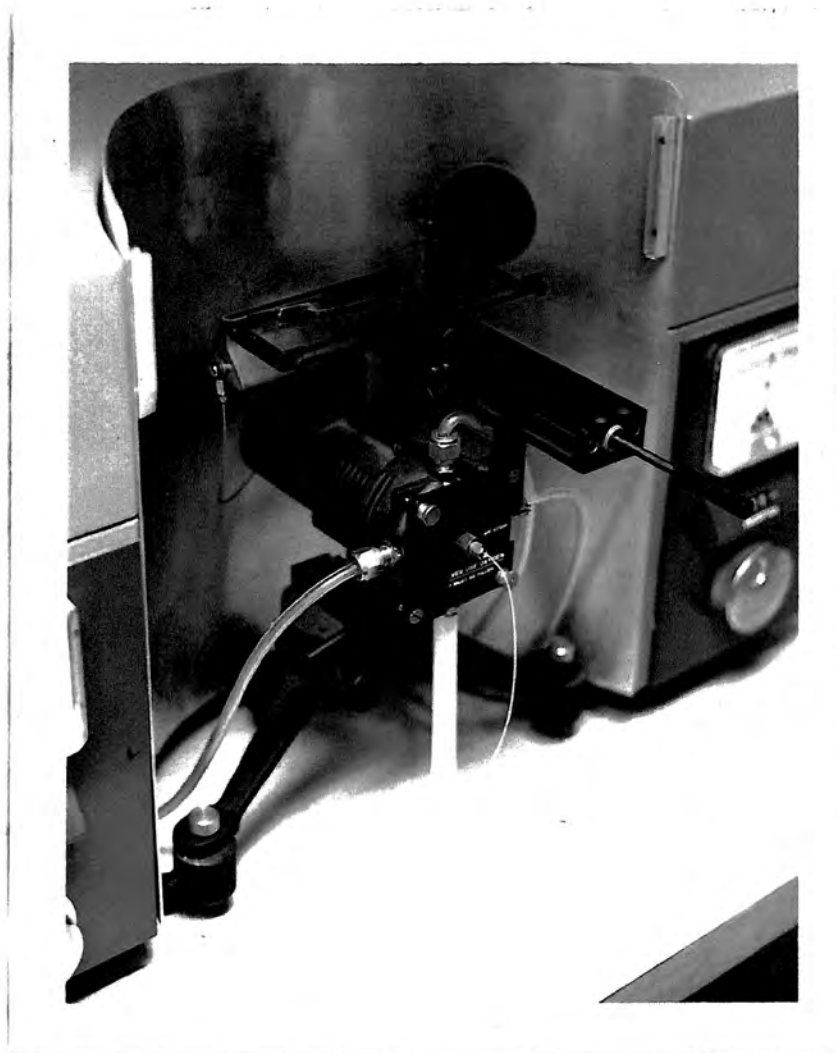
Figure 7.1. "Sampling Boat" accessory.

ELEMENT	BOAT	NEBULIZER	IMPROVEMENT
Arsenic	0.02	0.1	5X
Bismuth	0.003	0.05	16X
Cadmium	0.0001	0.002	20X
Lead	0.001	0.03	30X
Mercury	0.02	0.5	25X
Selenium	0.01	0.1	10X
Silver	0.0001	0.005	50X
Tellurium	0.01	0.3	30X
Thallium	0.001	0.025	25X
Zinc	0.00003	0.002	65X

Table 7.1 The detection limits (ppm) of elements by the "Sampling Boat" and by standard methods with the improvement of the "Boat" over standard methods. (After Kahn, et al., 1968)

The tantalum boat never reaches the temperature of the air-acetylene flame. Only elements which are easily atomized can be determined by this technique. Table 7.1 lists the elements that have been determined by the "Sampling Boat", their detection limits using the "Boat" and the premix burner, and the relative improvement of the "Boat" over the burner.

B. Investigation of the Technique

The principle of the "Sampling Boat" technique is simple; no difficulty was anticipated in its application. As seen in the following discussion, this was not the case. Many basic problems plagued the use of the accessory, limiting its application and reliability.

An immediate observation of the technique is the fact that it measures the total mass of a given metal present in a sample, not its concentration. That is, the quantity measured is micrograms (or nanograms) not micrograms per liter. KAHN, et al. (1968) reported a detection limit for zinc of 0.03 ppb for a one milliliter sample. This represents 0.03 nanograms of zinc. The minimum detectable amount (absolute detection limit) of zinc is 0.03 nanograms regardless of the sample volume. What then is the maximum amount of zinc that can be determined by this technique, i.e. that mass of zinc at which the calibration curve is no longer useable?

In order to determine this, a series of standards ranging from 1 to 20 nanograms were run. Figure 7.2 represents the calibration curve obtained. It can be seen, despite the deviation of individual points, that above 10 nanograms the curve flattens considerably and would be useless for analytical determinations; therefore, 10 nanograms is the maximum analyzable mass of zinc. For a 50 ppb (50 μg/l) solution, 10 nanograms represents a 0.2 milliliter sample, which is an extremely small volume to be quantitatively delivered into the tantalum boat. The difficulty of accurately delivering small volumes was interpreted as the cause of deviation of points in the curve represented in Figure 7.2.

Lead, on the other hand, has a detection limit of 1 ppb for a one milliliter sample. The absolute detection limit for lead is therefore one nanogram. Figure 7.3 is a standard curve ranging from 5 nanograms to 100 nanograms of lead. One milliliter samples were used for this curve. With the exception of the value for 40 nanograms (rejected in plotting the curve) deviation is slight, indicating
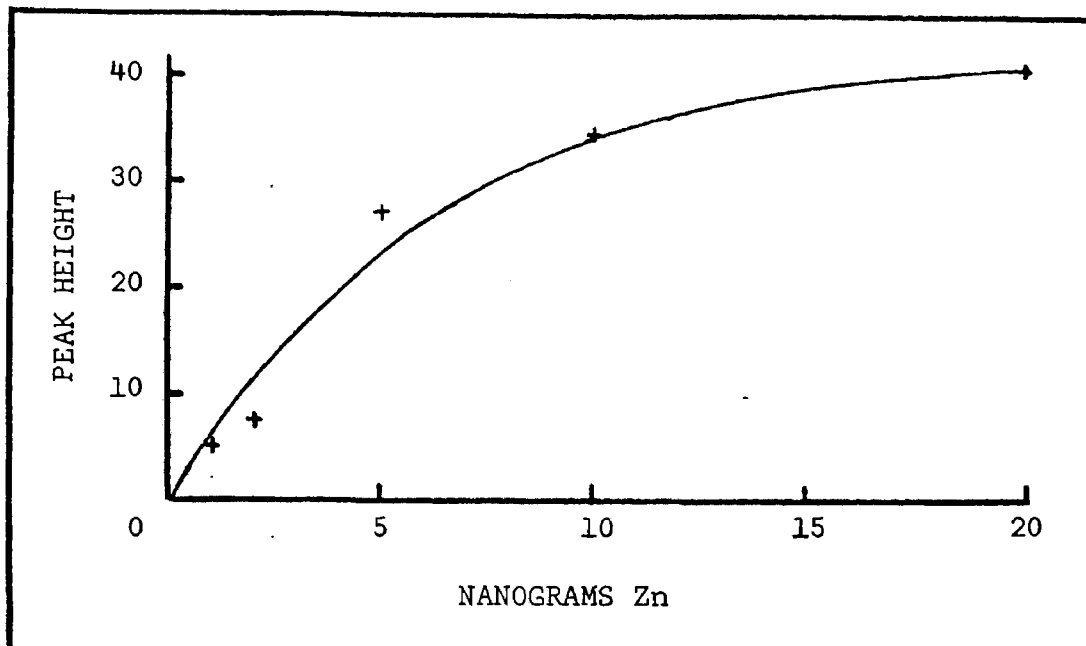
Figure 7.2. Standard calibration curve for zinc using the "Sampling Boat" accessory.
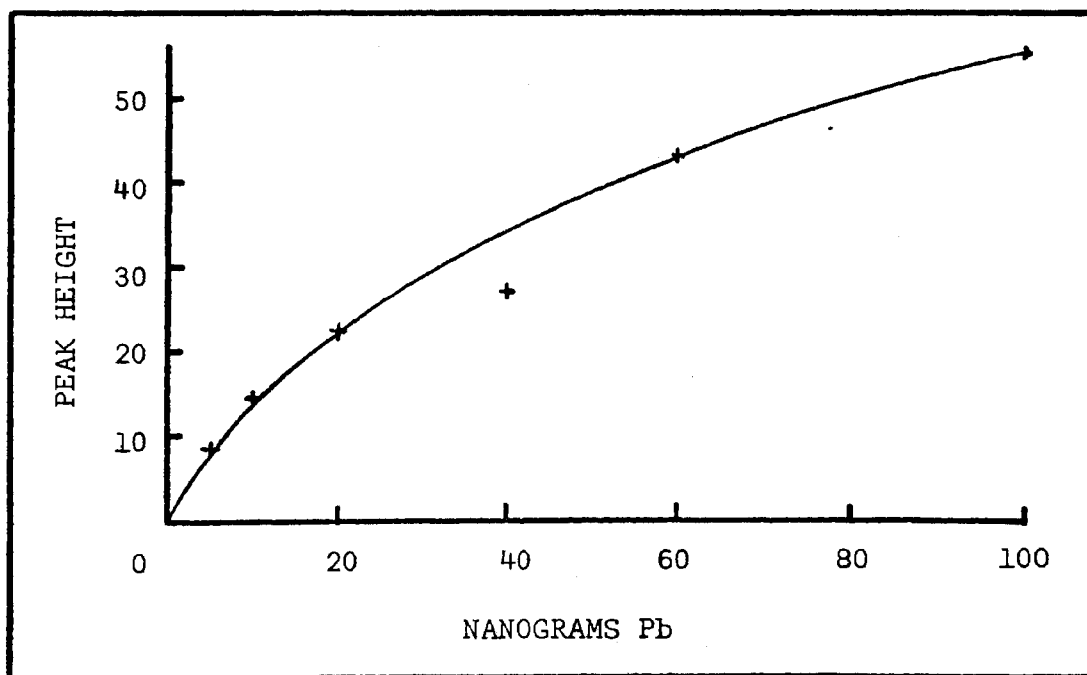
Figure 7.3. Standard calibration curve for lead using the "Sampling Boat" accessory. The 2170 A wavelength was used. Point at 40 ng is rejected in plotting the curve.

sample delivery to the tantalum boats is uniform. As can be seen from Figure 7.3, lead can be analyzed over the entire range up to 100 nanograms.

At this point the methods for determining lead and zinc by the "Sampling Boat" were considered fully developed. The following discussion demonstrates that this is not the case. Appendix 3 gives the methods of analysis.

The preliminary results were encouraging but misleading in many respects. Table 7.2 represents a typical problem with zinc analyses. These values for ten series of standards show an extreme variation. This is a result of contamination of the tantalum boats. The extreme sensitivity of this technique for zinc almost renders it useless without careful precautions. Contamination at the subnanogram and nanogram levels of zinc are not difficult to encounter in the average laboratory[1]. The analysis of zinc demands dust free, clean conditions. Contamination of the boat in storage can be irradicated by placing the boats in the flame as in regular analysis (preferably zinc) until all peaks subside on the recorder (as many as five or more, Fig. 7.4).

Still another problem encountered with the technique was warping of the sample boats. A distorted boat when placed in the flame appears to distort the flame as compared to a nondistorted boat, with subsequent error in the absorption readout. The tantalum boats are cited by Perkin-Elmer as lasting through ten analyses, however this author's experience was that the boat was so distorted after five analyses as to be worthless.

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[1]Conditions in the laboratory at the time of this work were very severe because of construction work in the laboratory.
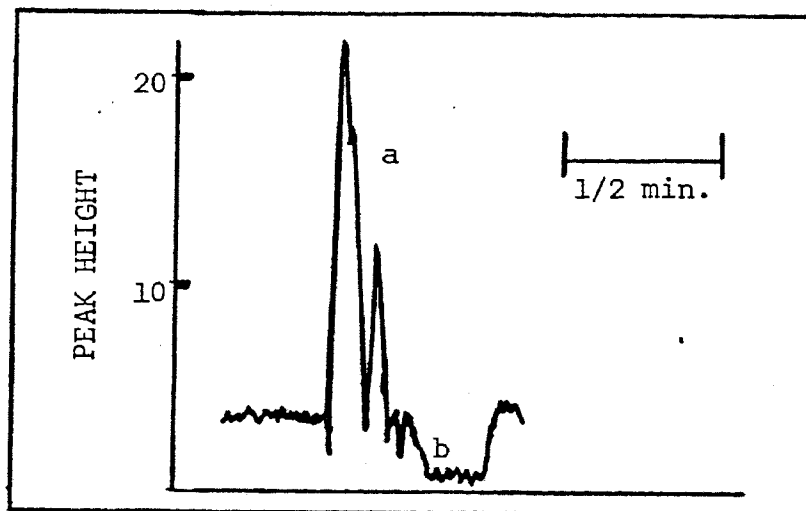
Figure 7.4   Multiple peaks (a) which occur when a contaminated boat is analyzed for zinc at the 2138 A wavelength. Lower base line (b) represents the "desorption" of the boat in the flame.

Run #	0 ng	0.2 ng	0.4 ng	1.0 ng	2.0 ng	4.0 ng
1	12.5	15	17.75	27.5	21.5	30
2	12.5	12.5	25	20	22	29
3	4.5	---	19	28	41.5	45.5
4	13	17.25	14.5	17.5	25	43.5
5	4	---	15	11	34	44
6	5.5	---	22.5	10.5	---	29.5
7	27.25	27	23.25	14.5	21.66	30.5
8	8.66	21.66	19.5	16.75	20	42.5
9	20.5	---	21	37	57	52
10	4	---	---	21	35.5	41.5

Table 7.2   Variability of peak heights for zinc analyses using the "Sampling Boat" accessory under conditions conducive to contamination.

As wavelengths decrease below 2500 Å the flame absorbs increasing amounts of energy from the lamp source. This can be seen in the negative absorption or desorption when a sample boat is placed in the flame (Fig. 7.4). The cause of this is the turbulence above the boat which removes some of the flame from the optical path. The peak height should be measured from the "desorbed" level.

This desorption was annoying. Nothing can be done about it[1] for zinc as there are no wavelengths above 2500 Å suitable for analysis. This is not the case for lead. KAHN, et al. (1968) reported on the use of the 2833 Å analytical wavelength for lead in "Sampling Boat" analysis.

A comparison of the lead hollow cathode lamp (Intensitron[2]) 2170 Å wavelength to the 2833 Å wavelength was made to determine which wavelength was best suited for analysis. The use of the 2833 Å wavelength would be advantageous in reducing the desorption effect of the sample boat in the flame. The tests were performed on standard solutions of lead ranging from 2 to 50 ppm using standard methods. Instrument parameters were not changed other than wavelength. Therefore the greater slope of the curve (Fig. 7.5) determined at 2833 Å represents a greater sensitivity as compared to the curve determined at 2170 Å. Not illustrated by the curves is the fact that the noise (fluctuation) at the 2833 Å wavelength was less than half that at the 2170 Å wavelength. This results in a better detection limit. It can only be concluded that the

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[1]Perkin-Elmer has developed the "Deuterium Compensation Accessory" (KAHN, 1968) to be marketed soon, which can correct this problem.

[2]Trademark, Perkin-Elmer
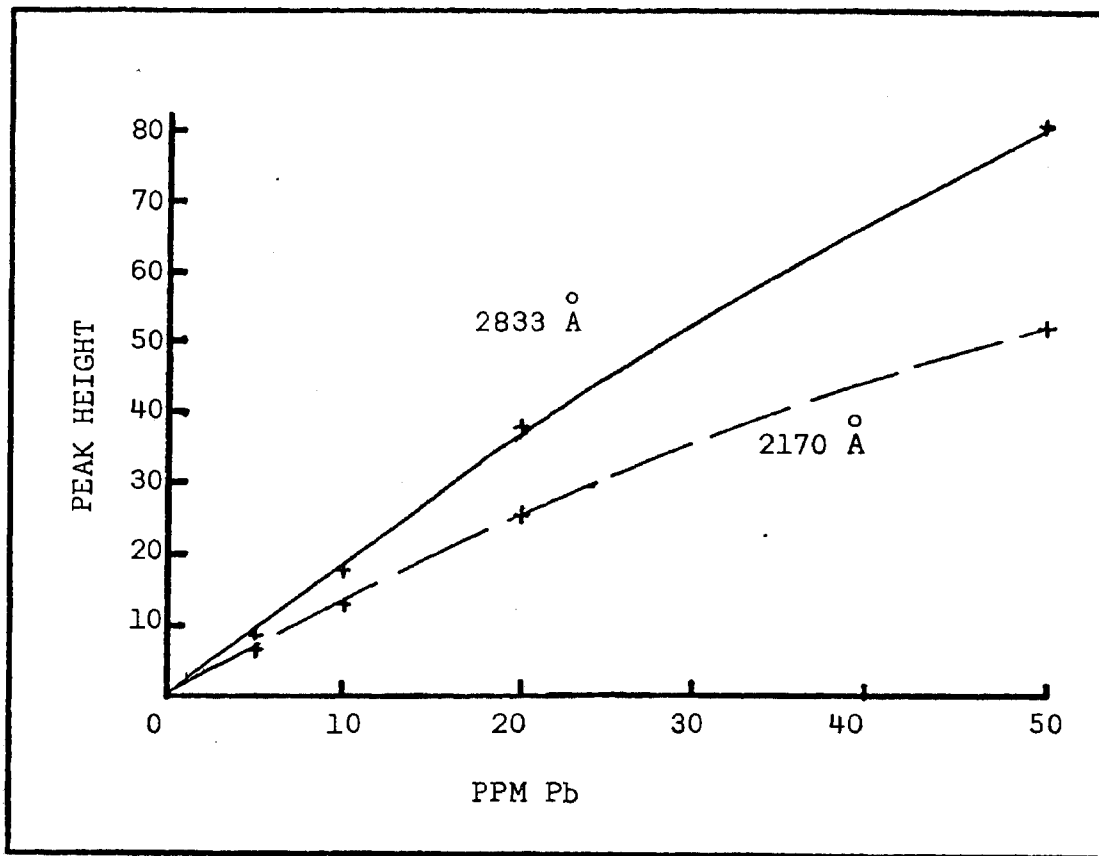
Figure 7.5. Comparison of lead hollow cathode lamp analytical
wavelengths. Instrument parameters: noise suppression
of 3; scale expansion of 3x.

2833 $\overset{\circ}{A}$ wavelength <u>for</u> <u>this</u> <u>particular</u> <u>tube</u> is superior to the

2170 $\overset{\circ}{A}$ wavelength (Appendix 3, modification).

In summary, the "Sampling Boat" accessory can be valuable in
water analysis. Several conditions must be met. Absolute cleanliness
of the working area and the worker (i.e. dandruff) cannot be
overstressed. Care must be taken in determining a sample aliquot
which will place the analyses in the optimum working range for a
given element (i.e. 0.1 to 10 ng of zinc). If necessary <u>more</u> <u>than</u>
<u>one</u> <u>aliquot</u> may be evaporated in a sample boat in order to place
the quantity of the selected metal in the optimum working range.
For the best results, no distorted boats should be used.

VIII. ANALYSIS OF THE DATA

A. Flow Chart of Sample Treatment

The analytical aspects of this investigation has been thoroughly covered in preceding chapters. However, some elaboration is necessary to illustrate the treatment of a sample from collection through analysis. Appendix IV illustrates this with a flow chart of procedures used at the present time.

B. Establishment of the Background Values

The distribution of all the values for the concentration of copper, lead, and zinc are presented as histograms in Appendix V, Figures A5.1 a-c. The normal parameters of mean and standard deviation are presented with each histogram, but because of the positive skewness of all three distributions, these parameters were relatively meaningless in establishing the background concentration of copper, lead, and zinc.

The distributions are all suggestive of log normal distributions. Treatment of the distributions as log normal would ignore one important aspect of the distributions. More than one contribution to the distributions exist. This is evidenced by the Figures A5.1 a-c, which upon close examination appear to be multi-modal.

One contributing factor is immediately obvious. Sample stations on streams known to contain mining wastes have higher average trace element concentrations than uncontaminated streams. Another contributing factor not immediately obvious is the use of values obtained

through a faulty analysis.   Several high values obtained for zinc
and lead by the "Sampling Boat" technique can be attributed to
analyses performed on specific days during a period of building
construction in the laboratory.

By eliminating those higher values which could be attributed
to the two above mentioned factors, it was observed that the
remaining values for copper, lead, and zinc were almost exclusively
below 20 ppb.

Histograms of the concentration range of 0-20 ppb for each of
the three trace elements are presented in Figures A5.2 a-c.   As
the skewness of these distributions is not as marked as in the
distribution of all values, the normal parameters presented for
these distributions are more useful in evaluating the background
concentrations of copper, lead, and zinc.

As can be seen from Figures A5.2 a-c, the mean calculated
for each of the three trace elements does not correspond to the
range of concentration with the highest frequency.   This range of
concentration with the highest frequency of occurrence is 4-6 ppb
for copper, lead, and zinc.   This is another parameter which could
be useful in establishing the background concentration of these
trace elements in stream waters.

Figure A5.3 is a histogram illustrating the distribution of
pH values determined for stream samples from the study area.   The
lack of skewness of this distribution gives weight to the normal
parameters presented in the figure as a true indication of the
background value of the pH.
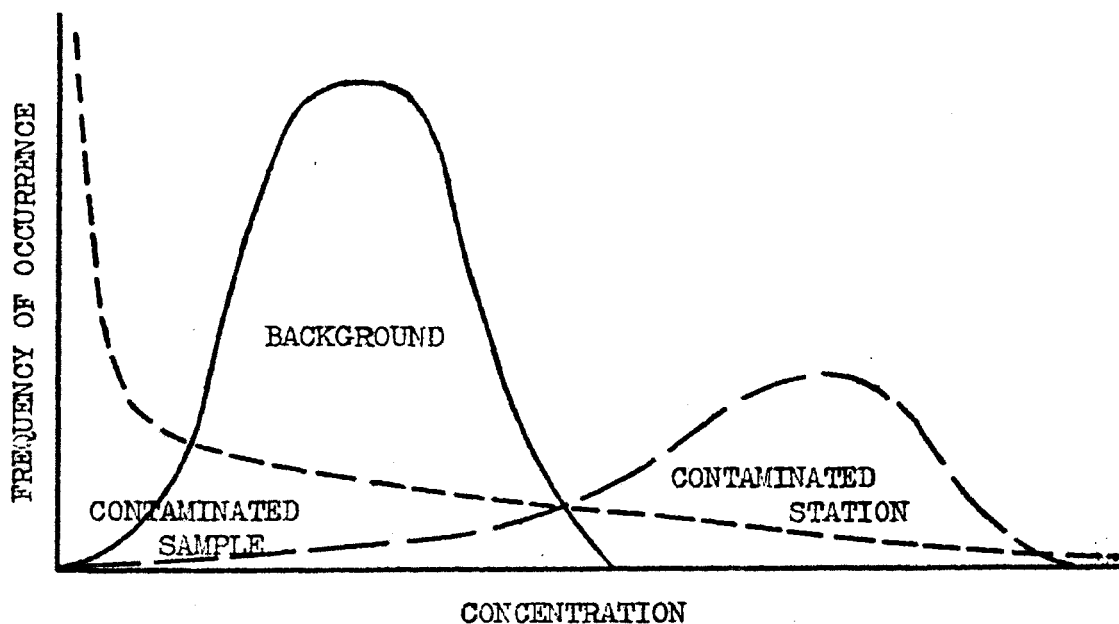
Fig. 8.1. Relative size and shape of distributions affecting the overall distribution of data obtained for trace elements in stream water samples.

C. Interpretation of the Data

It was the author's opinion that the most frequently occurring value was the best parameter for establishing a true background concentration. Although a quantitative proof of the above statement would be difficult with the available data, an intuitive approach was possible which will support this assumption.

Figure 8.1 illustrates three factors which are major contributions to the frequency distribution of trace element concentration as observed in this study. The size and shape of the fields of occurrence of these factors as presented in the figure are only relative; the exact contribution cannot be determined. Other factors probably exist, but they are presumed to be of minor significance as compared to factors presented here.

It was the object of this study to establish the background concentrations. The distribution of background values is illustrated in Figure 8.1, but the distribution is obscured by the other contributing factors. It has been stated that for the distributions obtained in this study, rejection of high values from contaminated stations and faulty analyses left the remainder of the values between 0-20 ppb. Yet, below 20 ppb these distributions still contained values contributed by the above mentioned sources. These included values would be represented in Figure 8.1 by those portions of the contaminated station and contaminated sample distributions which lie within the background distribution.

The argument for the use of the most frequently occurring concentration to establish the background value follows simply from the above presentation. There are contributions from the contaminated sample and contaminated station distributions in the range of the background distribution, which will increase the frequency of occurrence of background values, and possibly cause a shift in the position of the peak of the background distribution. This shift will cause an error in the determination of the true background concentrations. However, this error will be slight in comparison to the error commensurate to the use of normal parameters such as the mean and standard deviation determined from the total distribution, or even from distributions which have had known erroneous data excluded.

As determined by this argument, the background values with the highest frequency of occurrence for copper, lead, and zinc are 4-6 ppb. It would be possible to narrow this interval further by increasing

the number of analyses which would permit a reduction of the interval used in plotting the histograms.

D. Use of the Distributions in Determining Contamination

The data presented here has been used to evaluate the amount of contamination of copper, lead, and zinc from mining activity in the New Lead Belt (WIXSON and BOLTER, 1969; WIXSON, et al., in preparation). In these reports, contamination is determined by the existence of a population of values distinct from the background distribution determined for stations on streams known to be carrying mine wastes. The contaminated station distribution in Figure 8.1 illustrates this type of contamination.

Figure 8.2 illustrates this type of contamination as encountered in the Bee Fork Stream at the Fletcher Mine. The values at station 6 are low and represent the uncontaminated stream. At station FT the mine effluent shows higher values. Station 7, which was Bee Fork below the mine effluent, shows correspondingly high values. At station 8, five miles downstream, copper concentration has returned to normal, lead concentration was nearly normal, but zinc concentration remains high. At station 9, zinc concentration has returned to normal. Hence, this type of contamination is short term; high concentrations of copper, lead, and zinc tend to return to the background level within a short distance from their source. Furthermore, HANDLER (1969) demonstrated that even this short term contamination introduced by the Fletcher mine tailings into the Bee Fork was not at a level of acute toxicity for fish.

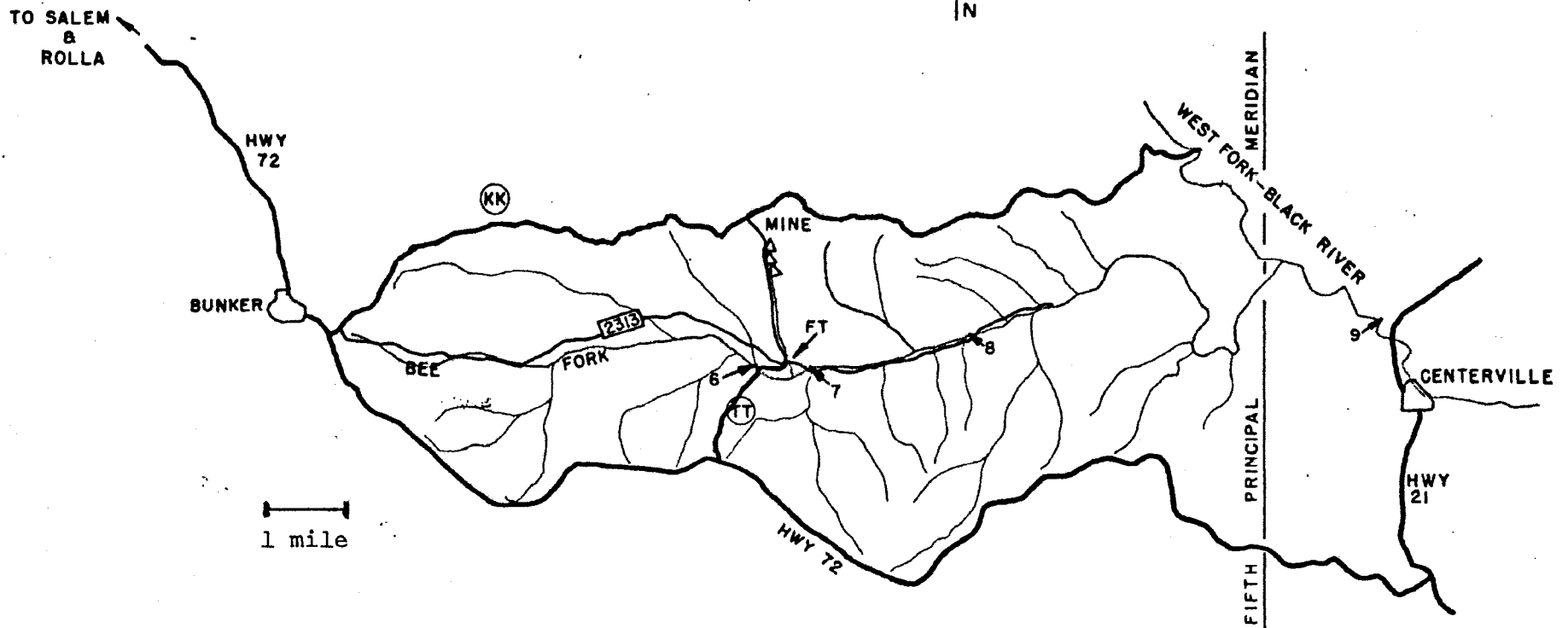| Station Number	Station Number Plate 1	Mean Concentration (ppb)			Station Description
		Cu	Pb	Zn	
6	32-2W-25NE	6.4	5.8	7.3	Bee Fork above mine effluent
FT	32-1W-30NW	30.6	14.4	12.2	Mine effluent
7	32-1W-30N	17.4	15.3	15.9	Bee Fork below mine effluent
8	32-1W-21SE	7.4	91.	14.1	5 miles down stream from station 8
9	32-1E-29N	7.0	---	6.1	West Fork Black River at Centerville

Figure 8.2. Illustration of contamination of copper, lead, and zinc by the Fletcher Mine effluent.

On the other hand, long range effects have not been evaluated, and probably will not be evaluated for several years. The question then arises as to how this long range contamination will manifest itself. It is the author's hypothesis that these long term effects of contamination will be evidenced by a shifting of the maximum frequency peak toward higher concentrations. Evaluation of general contamination in the future may then be made by comparing the distribution of stream water data determined at that time to the distribution of data determined in this investigation.

E. Use of the Distributions in Geochemical Prospecting

The use of spring water samples in geochemical prospecting for zinc ore bodies in southwest Wisconsin was successfully employed by DE GEOFFROY, et al. (1967). These investigators found anomalous values of zinc in spring waters which they postulated had moved through shallow zinc ore bodies in the oxidizing zone.

The application of a similar technique in the New Lead Belt would have been of great value in reducing exploration time and expense. However, analysis of spring waters in the vicinity of the known ore bodies produced no anomalous values for copper, lead, or zinc. In fact, analysis of ground water taken from ore faces in several of the mines of the New Lead Belt did not produce anomalous results, either. It can only be interpreted that the depth of these ore bodies places them well below the zone of oxidation. It is unlikely that spring waters reach these depths, and at the present time a geochemical prospecting method cannot be applied, even to ground waters circulating through the ore body.

IX.   CONCLUSIONS

A.   Analytical Methods

1.   To determine the concentrations of copper, lead, and zinc in the stream waters of the New Lead Belt area by atomic absorption requires some method of concentrating these elements or some method of increasing the absorption signal in the analysis of these elements.

2.   The method for simultaneously concentrating all three elements as developed in this study was a coextraction procedure employing the APDC/MIBK solvent extraction system.   This method was satisfactory for routine work, provided that spiked samples were included in each analysis to test the method.   An effective concentration factor of 100x was obtained with the procedure as outlined in Appendix I.

3.   Several important observations concerning solvent extraction with the APDC/MIBK system were derived from this study.   (a) The ability to extract the small concentrations encountered in this study, and the stability of the metal chelates in the organic phase were influenced by the acidity of the aqueous medium.   In solutions acidified to a pH of 2-3, copper appeared to extract less efficiently as concentrations decreased.   This was contrary to previously reported observations that copper extracts over a pH range of 0.1-8. Deterioration of metal chelates occurred to different degrees in a 24 hour period.   (b) The optimum pH for the extraction of low concentrations of lead was determined to be 4.0-5.5 as compared to a previously reported value of 2.8.   (c) Coextraction with APDC/MIBK

was definitely superior to coextraction with the DDTC/MIBK system.

4. The method outlined in Appendix II for the extraction of copper by APDC/MIBK provides an effective concentration factor of 75x. Several advantages over the coextraction method were obtained through the use of this method. (a) The elimination of a buffer substantially reduces the time required for analysis. (b) This method was more reliable than the coextraction method in the analysis of copper. (c) The copper chelate in the organic phase in contact with the unbuffered aqueous phase was stable for at least one week. This further indicates the role of pH in governing the stability of the chelate. (d) Calibration curves obtained with this method did not indicate a decreasing efficiency of extraction with decreasing concentration as was obtained by extraction of copper from acidified solutions.

5. The "Sampling Boat" technique provided a method of analysis (Appendix III) for lead and zinc that was superior to the coextraction method for these elements. Several factors were important in this technique. (a) Cleanliness is absolutely essential. (b) The correct sample aliquot must be chosen to place the mass of the element being analyzed in the optimum working range. For zinc this optimum range is 0.1-10 nanograms. To analyze lead below 5 ppb in solution, more than one aliquot of sample must be evaporated, in a boat, to increase the sensitivity of analysis. (c) For lead analysis, a test to determine the best analytical wavelength for a given hollow cathode lamp was essential. The 2833 $\overset{\circ}{A}$ wavelength was perferable.

B.   Results from the Data

1.   The total data distributions contain contributions from three factors.   These factors are the true distribution of the background values, the distribution of contaminated samples, and the distribution from contaminated stations.   As the number of contaminated stations was low and the number of contaminated samples was presumably low, the most frequently occurring concentration corresponds to the peak of the true background distribution.

2.   Based on the most frequently occurring concentration as the best parameter for evaluating the background, the background concentrations for copper, lead, and zinc was 4-6 ppb for all three elements.

3.   Short term contamination of a factor of 2-3 can be demonstrated for Bee Fork Stream below the Fletcher Mine.   These concentrations were not found to be acutely toxic; they soon returned to normal downstream from the mine effluent.

4.   The data distributions will be useful in determining long term contamination of copper, lead, and zinc.   This long term contamination will be evidenced by a shifting of the most frequently occurring concentration to higher concentration values and may be identified through comparison of distributions of data obtained in the future to the distributions presented in this dissertation.

5.   The large deposits of lead in the area were not evidenced by the analytical results.   Use of the data distributions for geo-chemical prospecting does not appear to be possible.

C. Recommendations for Future Research

1. The determination of successively smaller amounts of metals in water is becoming increasingly important. Future development and refinement of the methods as presented in this report, coupled with improved instrumentation, will result in improved detection limits in the analysis of ultra-trace concentrations of copper, lead, and zinc.

2. Refinement of the presently reported background concentrations is possible by increasing the number of analyses and plotting histograms with narrower intervals.

3. Investigation of the chemistry which controls the concentration of the trace metals in stream waters is recommended in order to determine the reason for the rapid return to the background concentrations in areas subjected to short term contamination. Understanding of this chemistry would be valuable in controlling and preventing contamination.

4. The true purpose and value of this dissertation can only be fully realized through a subsequent duplicate study in the future. Such a study will be necessary to evaluate the effect of industrialization in the New Lead Belt on the concentrations of copper, lead, and zinc in the streams of this beautiful area.

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APPENDIX I

Method of Analysis for Trace Amounts of Copper, Lead, and Zinc by
  Coextraction with APDC/MIBK and Atomic Absorption Spectroscopy

A. Introduction

   The method provides for the coextraction of copper, lead, and

zinc from aqueous solutions buffered to a pH of 5.5. The method is

fast and simple, but subject to occasional unknown error. It

provides a concentration factor of 20, which times a "solvent effect"

of approximately five yields an effective concentration factor of

100. A check of the extraction for each metal is provided in the

procedure. Less than 0.25 ppb of zinc and less than 0.5 ppb of

copper and lead can be easily detected. The method as presented

here allows for determinations up to 30 ppb with higher concentrations

being determined by dilutions. The method can be extended to

higher concentration by modifying the standards to correspond

to the higher concentrations. The determinations are made by

direct comparison to a standard curve. Figure Al.1 presents a

calibration curve for zinc.

B. Equipment

   1. Reagents

      10,000 ppm stock solution of copper, lead, and zinc

      5% APDC
         Dissolve 5g of APDC per 100 ml of distilled water.
         If a precipitate appears, filter on coarse filter
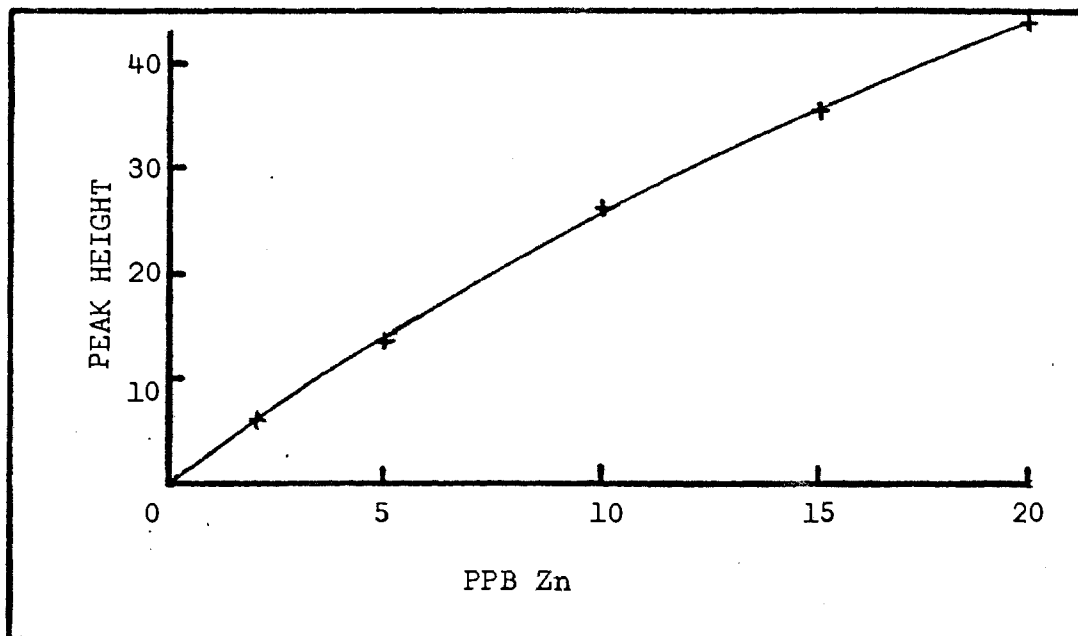   paper. Prepare 10 ml per sample plus 200 ml.

Figure A1.1. Standard calibration curve for zinc coextracted with
copper and lead by APDC/MIBK from water buffered to
a pH of 5.5

MIBK

> Allow enough in one container for all samples, 10 ml
> per sample plus 500 ml. Different batches of MIBK
> may give significantly different backgrounds at
> these concentrations.

Buffer, pH=5.5

> Dissolve 62.5 g of ammonium acetate in about 400 ml
> of distilled water, add exactly 17.5 ml glacial acetic
> acid, and dilute to 500 ml. Purify by adding 20 ml
> of 5% APDC and extracting with two 50 ml portions of
> MIBK in a large seperatory funnel. The required
> volume for analysis is 20 ml per sample plus 50 ml.

2. Glassware

All glassware should be cleaned by the following procedure:

> 1. Rinse with 1:3 nitric acid.
> 2. Rinse with 5% EDTA (optional).
> 3. Rinse three times with distilled water.

250 ml volumetric flasks
> 1 for each sample and standard plus 2

100 ml volumetric flask - 1

500 ml volumetric flask - 1

50 ml volumetric flask - 1

2000 ml separatory funnel - 1

Pipets

1/2 ml - 3	5 ml - 2
1 ml - 1	10 ml - 1
2 ml - 1	15 ml - 1
3 ml - 1	

Automatic pipets
10 ml - 2
20 ml - 1

50 ml graduated cylinder - 1

Beakers as needed

C. Preparation of Standards

1. Take 1/2 ml of each of the 10,000 ppm stock solutions and dilute to 100 ml in the same volumetric flask.

    1/2 ml x 10,000 ug/ml / 100 ml = 50 ppm Cu,Pb,Zn

2. Take 5 ml of the 50 ppm solution and dilute to 500 ml in a volumetric flask.

    5 ml x 50 ug/ml / 500 ml = 0.5 ppm Cu,Pb,Zn

3. Standard series

    (a) Blank, place 250 ml of distilled water in a volumetric flask.

    (b) 2 ppb, place 1 ml 0.5 ppm solution in a 250 ml volumetric flask and dilute to volume.

       1 ml x 0.5 ug/ml / 250 ml = 0.002 ug/ml

    (c) 6 ppb, place 3 ml 0.5 ppm solution in a 250 ml volumetric flask and dilute to volume.

    (d) 10 ppb, place 5 ml 0.5 ppm solution in a 250 ml volumetric flask and dilute to volume.

(e) 20 ppb, place 10 ml 0.5 ppm solution in a 250 ml volumetric flask and dilute to volume.

(f) 30 ppb, place 15 ml 0.5 ppm solution in a 250 ml volumetric flask and dilute to volume.

D. Preparation of Samples

Samples should be filtered.[1]

Pour samples into 250 ml volumetric flasks to mark. Repeat at least two samples and spike the repeated samples with 2 ml of 0.5 ppm solution. The spiked samples should give determinations that are 4 ppb higher than their unspiked counterparts for each of the metals.

E. Analytical Procedure

1. Using a volumetric flask pour exactly 50 ml from each sample.

2. Using the 20 ml automatic pipet, add 20 ml of buffer to each flask.

3. Using a 10 ml automatic pipet, add 10 ml of MIBK to each flask.

4. Using a 10 ml automatic pipet add 10 ml of 5% APDC to each flask.

5. Cap and then shake each flask exactly 2 minutes.

6. Allow the organic and aqueous phases to separate.

7. Slowly add distilled water to each flask until the organic phase is brought up into the narrow neck of the flask.

8. Analyze for each metal in the organic phase according to the standard methods of atomic absorption spectroscopy with these exceptions:

(a) The fuel flow must be reduced while aspirating MIBK until the flame is not luminous.

(b) Because MIBK has a faster aspiration rate than water, the aspiration rate of the nebulizer must be reduced to obtain maximum absorption.

----

[1] Samples of low turbidity which are being analyzed immediately after collection do not have to be filtered before analysis.

(c) To maintain the flame, MIBK must be aspirated at all times when a sample is not being aspirated.

9. Calibration curves are prepared for each of the three metals by plotting absorbance or peak height (chart readout) versus concentration. Determination of the metal content of the unknown samples is made by plotting the absorbance or peak height of the unknown sample on the calibration curve prepared from the standards and reading the corresponding concentration. Absorbance or peak height of the blank of the standard series should be subtracted from both the standards and the samples. If the absorbance or peak height of an unknown sample lies above the standard series, a 1 ml aliquot of the organic extract should be diluted with 1 ml of MIBK and then analyzed. Only half of the signal of the blank should be subtracted from the signal obtained from the unknown sample. The determination is then made from the standard curve and the resulting concentration is multiplied by two.

APPENDIX II

Method of Analysis for Trace Amounts of Copper by Solvent Extraction
with APDC/MIBK and Atomic Absorption Analysis

A. Introduction

The method provides for the extraction of copper by APDC/MIBK
at the pH of the water sample. The pH ranges from 6.8 to 8.0. The
method is fast, simple and accurate. It provides a concentration
factor of 15, which times a "solvent effect" of approximately five
yields an effective concentration factor of 75. The method also
provides for a check of the analytical accuracy. Less than 0.5 ppb
in the aqueous sample can be readily detected; determinations up
to 30 ppb can be made directly with higher concentrations being
determined by dilution of the organic phase. Determinations are
made by direct comparison to a standard curve. Figure 5.4
represents a typical calibration curve.

B. Equipment

    1. Reagents

        10,000 ppm stock copper solution

        2% APDC
            Dissolve 2 g APDC per 100 ml distilled water. If a
            precipitate appears, filter on coarse filter paper.
            Prepare 10 ml per sample plus 150 ml.

        MIBK
            Allow enough in one container for all samples, 5 ml
            per sample plus 300 ml. Different batches of MIBK
            may give significantly different background values
            at these concentrations.

2. Glassware

All glassware should be cleaned by the following procedure:

    1. Rinse with 1:3 nitric acid.
    2. Rinse with 5% EDTA (optional).
    3. Rinse three times with distilled water.

100 ml volumetric flasks
    One for each sample and standard plus five

500 ml volumetric flask - 1

25 ml volumetric flask - 1

Pipets

1 ml - 3	5 ml - 1
2 ml - 1	10 ml - 1
3 ml - 1	15 ml - 1

Automatic pipets

    5 ml - 1
    10 ml - 1

Beakers as needed

C. Preparation of Standards

1. Take 1 ml of the 10,000 ppm stock solution and dilute to 100 ml in a volumetric flask.

    1 ml x 10,000 ug/ml / 100 ml = 100 ppm

2. Take 1 ml of the 100 ppm solution and dilute to 500 ml in a volumetric flask.

    1 ml x 100 ug/ml / 500 ml = 0.2 ppm

3. Standard series

(a) Blank, place 100 ml of distilled water in a volumetric flask.

(b) 2 ppb, place 1 ml of 0.2 ppm solution in a 100 ml volumetric flask and dilute to volume.

    1 ml x 0.2 ug/ml / 100 ml = 0.002 ug/ml

(c) 6 ppb, place 3 ml of 0.2 ppm solution in a 100 ml volumetric flask and dilute to volume.

(d) 10 ppb, place 5 ml of 0.2 ppm solution in a 100 ml volumetric flask and dilute to volume.

(e) 20 ppb, place 10 ml of 0.2 ppm solution in a 100 ml volumetric flask and dilute to volume.

(f) 30 ppb, place 15 ml of 0.2 ppm solution in a 100 ml volumetric flask and dilute to volume.

D. Preparation of Samples

Samples should be filtered.[1]

> Pour samples into 100 ml volumetric flasks to mark. Repeat at least two samples and spike the repeated samples with 2 ml of 0.2 ppm solution. The spiked samples should give determinations that are 4 ppb higher than their unspiked counterparts.

E. Analytical Procedure

1. Using a volumetric flask pour exactly 25 ml from each sample.

2. Using the 5 ml automatic pipet, add 5 ml of MIBK to each flask.

3. Using the 10 ml automatic pipet, add 10 ml of 2% APDC to each flask.

4. Cap and then shake each flask exactly 2 minutes.

5. Allow the organic and aqueous phases to separate.

6. Slowly add distilled water to each flask until the organic phase is brought up into the narrow neck of the flask.

7. Analyze the organic phase for copper according to the standard method of atomic absorption spectroscopy with these exceptions:

(a) The fuel flow must be reduced while aspirating MIBK until the flame is not luminous.

---

[1] Samples of low turbidity which are being analyzed immediately after collection do not have to be filtered before analysis.

(b) Because MIBK has a faster aspiration rate than water, the aspiration rate of the nebulizer must be reduced to obtain maximum absorption.

(c) To maintain the flame, MIBK must be aspirated at all times when a sample is not being aspirated.

8. A calibration curve is prepared from the standards by plotting absorbance or peak height (chart readout) versus concentration. The concentration of copper in the unknown sample is determined by plotting the absorbance or peak height on the standard curve and reading the corresponding concentration. Absorbance or peak height of the blank of the standard series should be subtracted from both the standards and the samples. If the absorbance or peak height of an unknown sample lies above the standard curve, a 1 ml aliquot of the organic extract should be diluted with 1 ml of MIBK and then analyzed. Only half of the signal of the blank should be subtracted from the unknown sample. The determination is then made from the standard curve and the resulting concentration is multiplied by two.

APPENDIX III

Method of Analysis for Trace Amounts of Lead and Zinc Utilizing the "Sampling Boat" Technique

A. Introduction

The method provides for the direct analysis of lead and zinc in stream water without prior treatment other than filtration. For zinc a 0.5 ml sample is used providing ready detection of 0.1 ppb; for lead a 2.0 ml sample allows the detection of 0.5 ppb. The method is rapid and accurate, but much care must be exercised in maintaining standards of cleanliness which will prevent contamination. Figures 7.2 and 7.3 represent typical calibration curves.

B. Equipment

1. Sample boats

   One for each sample and standard plus two. Do not use distorted boats. The boats should be cleaned if suspected to be contaminated by placing them in the flame as in the zinc analysis until the chart tracing does not display peaks.

2. Reagents

   10,000 ppm stock solutions of lead and zinc

3. Glassware

   Volumetric flasks

   > 100 ml - 10
   > 500 ml - 1

   Pipets

   > 1/2 ml - 1   5 ml - 1
   > 1 ml - 3   10 ml - 1
   > 2 ml - 1   15 ml - 1
   > 3 ml - 1

   Beakers as needed

C. Preparation of Standards

    1. Take 1 ml of each of the 10,000 ppm stock solutions and dilute to 100 ml in the same volumetric flask.

        1 ml x 10,000 ug/ml / 100 ml = 100 ppm Pb,Zn

    2. Take 1 ml of the 100 ppm solution and dilute to 500 ml in a volumetric flask.

        1 ml x 100 ug/ml / 500 ml = 0.2 ppm PB,Zn

    3. Standard series

        (a) Blank, use distilled water.

        (b) 2 ppb, place 1 ml of 0.2 ppm solution in a 100 ml volumetric flask and dilute to volume.

            1 ml x 0.2 ug/ml / 100 ml = 0.002 ug/ml

        (c) 6 ppb, place 3 ml of 0.2 ppm solution in a 100 ml volumetric flask and dilute to volume.

        (d) 10 ppb, place 5 ml of 0.2 ppm solution in a 100 ml volumetric flask and dilute to volume.

        (e) 20 ppb, place 10 ml of 0.2 ppm solution in a 100 ml volumetric flask and dilute to volume.

        (f) 30 ppb, place 15 ml of 0.2 ppm solution in a 100 ml volumetric flask and dilute to volume.

D. Preparation of Samples

Samples must be filtered as particulate matter may give high determinations.

At least two samples should be spiked by placing 2 ml of 0.2 ppm solution in a 100 ml volumetric and filling to volume with the sample being spiked. Spiked samples should give determinations 4 ppb higher for lead and zinc than their corresponding unspiked samples.

E. Analytical Procedure

Zinc

1. Clean boats are placed in a heated sand bath. Care must be taken not to handle boats more than 1/2 inch from either end. Good, clean latex gloves are preferable.

2. Into each boat place 0.5 ml of each standard and each sample. Care must be taken in recording the position of each boat and its contents in order to avoid errors.

3. The contents of the boats are allowed to evaporate to dryness.

4. The boats are analyzed using the "Sampling Boat" accessory and atomic absorption. See Notes at end.

5. A calibration curve is prepared by plotting peak heights obtained from the standards versus their concentrations. The concentration of the unknown sample is determined by plotting its peak height on this curve and obtaining the corresponding concentration. The peak height of the blank should be subtracted from the peak heights of the standards only.

Lead

1. Same as zinc analysis Step 1.

2. Successively evaporate four 1/2 ml aliquots of each standard and each sample in the boats. Extreme caution must be taken in this step to avoid confusion of samples.

3. Same as zinc analysis Step 4. See Notes at end, also Modification of Lead Procedure.

4. Same as zinc analysis Step 5.

F. Notes on Atomic Absorption and the "Sampling Boat" Accessory

1. Care must be taken to align the accessory so that the boats are directly above the triple slot burner. With reasonable care, this can be done visually.

2. Do not use distorted boats.

3. Experimentation with scale expansion and noise suppression is necessary to obtain the optimum signals.

4. If "desorption" occurs, measure the peak height from the "desorbed" level.

G. Modification of Lead Procedure

The Standard Methods Handbook recommends the use of the lead
2170 A line for analysis. For each individual lamp, tests
should be made to determine whether the 2833 Å or the 2170 Å
line is superior in lead analysis. The 2833 A line is preferable
as it greatly reduces "desorption".

APPENDIX IV ·

Flow Chart of Sample Treatment

A. Introduction

The following flow chart presents the treatment of a sample
from collection at the sample site through analysis in the
laboratory. The purpose of the flow chart is to enable a sub-
sequent investigation to duplicate the present investigation.
Use of the flow chart in conjunction with Appendices I-III and
Plate 1 will enable such duplication.

Flow Chart of Sample Treatment

FIELD

COLLECTION OF 1 LITER SAMPLE

DETERMINATION OF TEMPERATURE TO $\pm 0.1^{\circ}$C

DETERMINATION OF pH TO ± 0.03 pH UNITS

LABORATORY

FILTRATION THROUGH 0.45u MILLIPORE FILTER
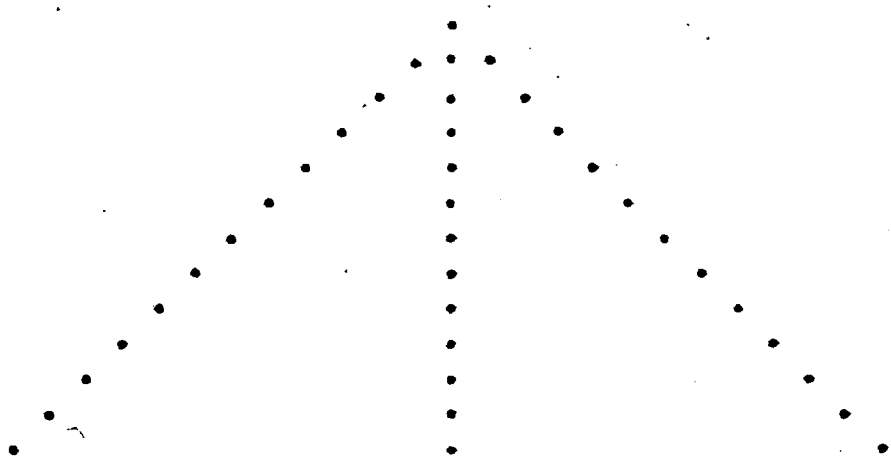
COPPER DETERMINATION   LEAD AND ZINC   OTHER ANALYSES
APPENDIX 2   DETERMINATION
                             APPENDIX 3

APPENDIX V

Distribution of the Data

A. Introduction

   In Figures A5.1a-c the distributions of copper, lead, and
zinc for streams in the New Lead Belt are presented. The normal·
parameters are included. Figures A5.2a-c are included to illustrate
the effect on the distributions of removing known anomalous values.
Figure A5.3 is included to illustrate the total distribution of pH
of the stream waters. These distributions should be used to
evaluate future contamination by direct comparison of the
distribution of data obtained at that time to these distributions.
Contamination will be evidenced by the occurrence of a second peak
in the distribution at high values of concentration, or by the
shifting of the peak representing the most frequently occurring
value towards higher concentrations.
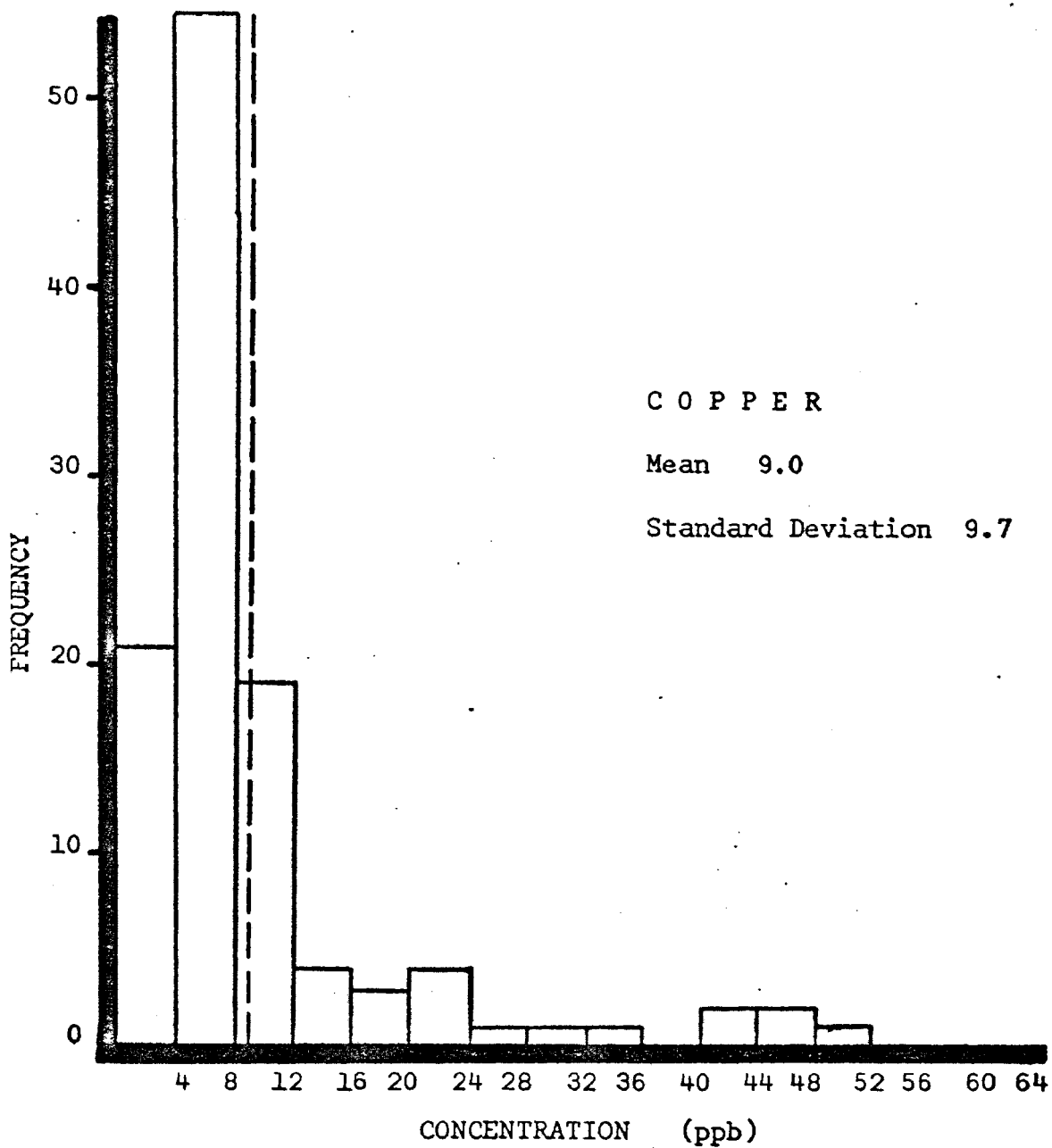
Fig. A5.1a.   The total distribution of data on copper content of streams in the New Lead Belt.
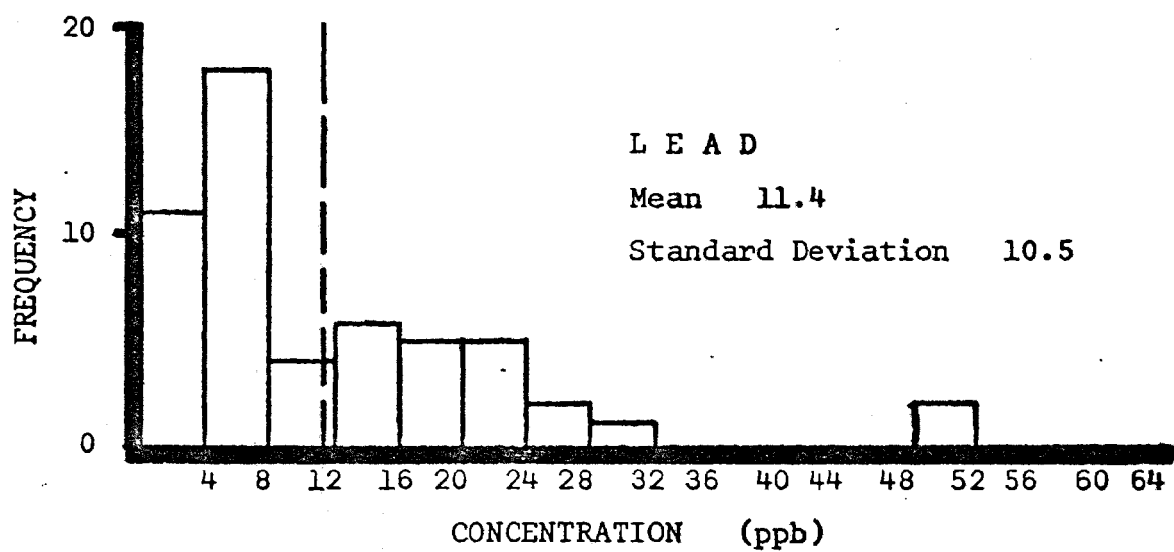
Fig. A5.1b. The total distribution of data on lead content of streams in the New Lead Belt.
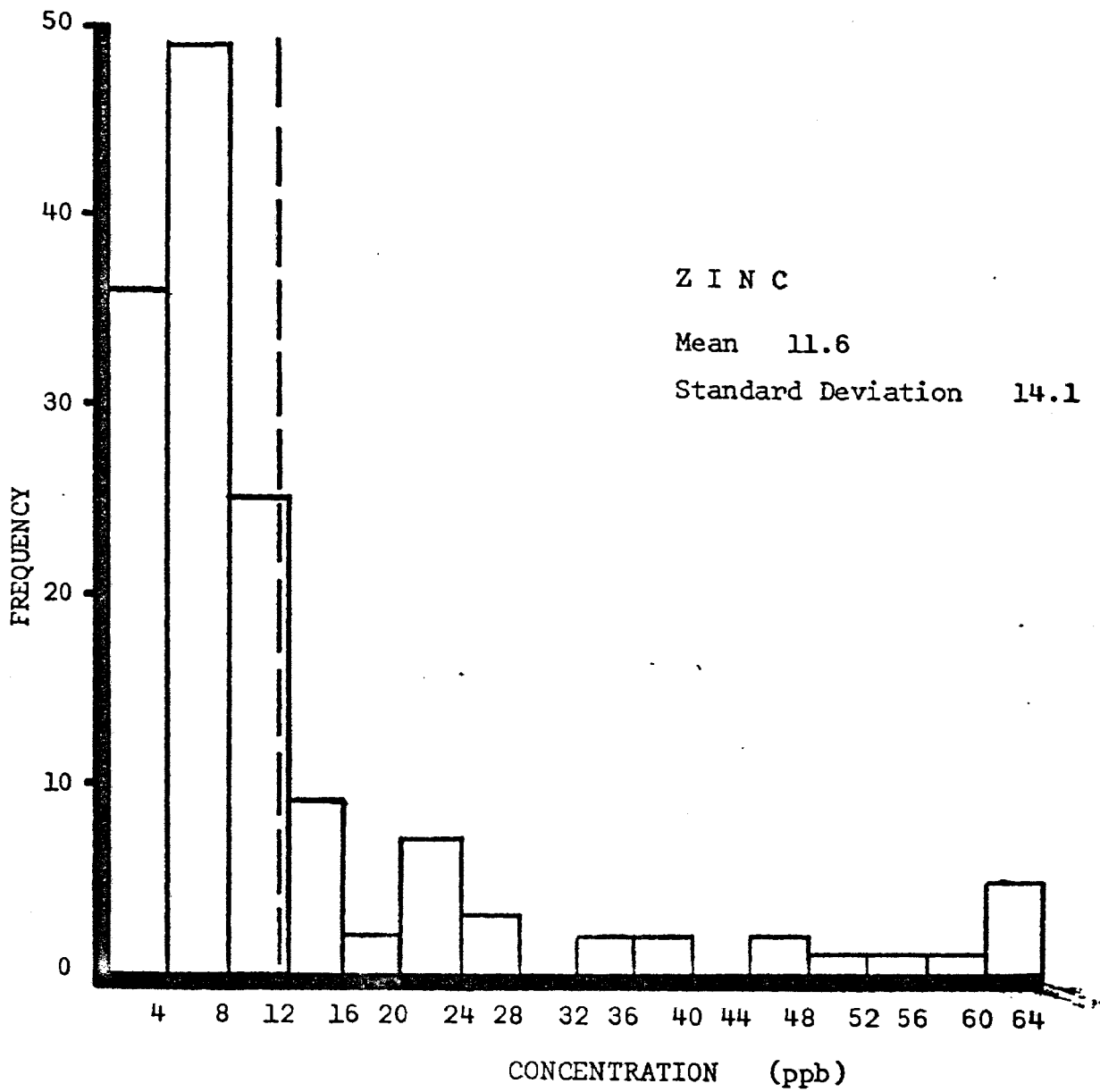
Fig. A5.1c. The total distribution of data on zinc content of streams in the New Lead Belt.
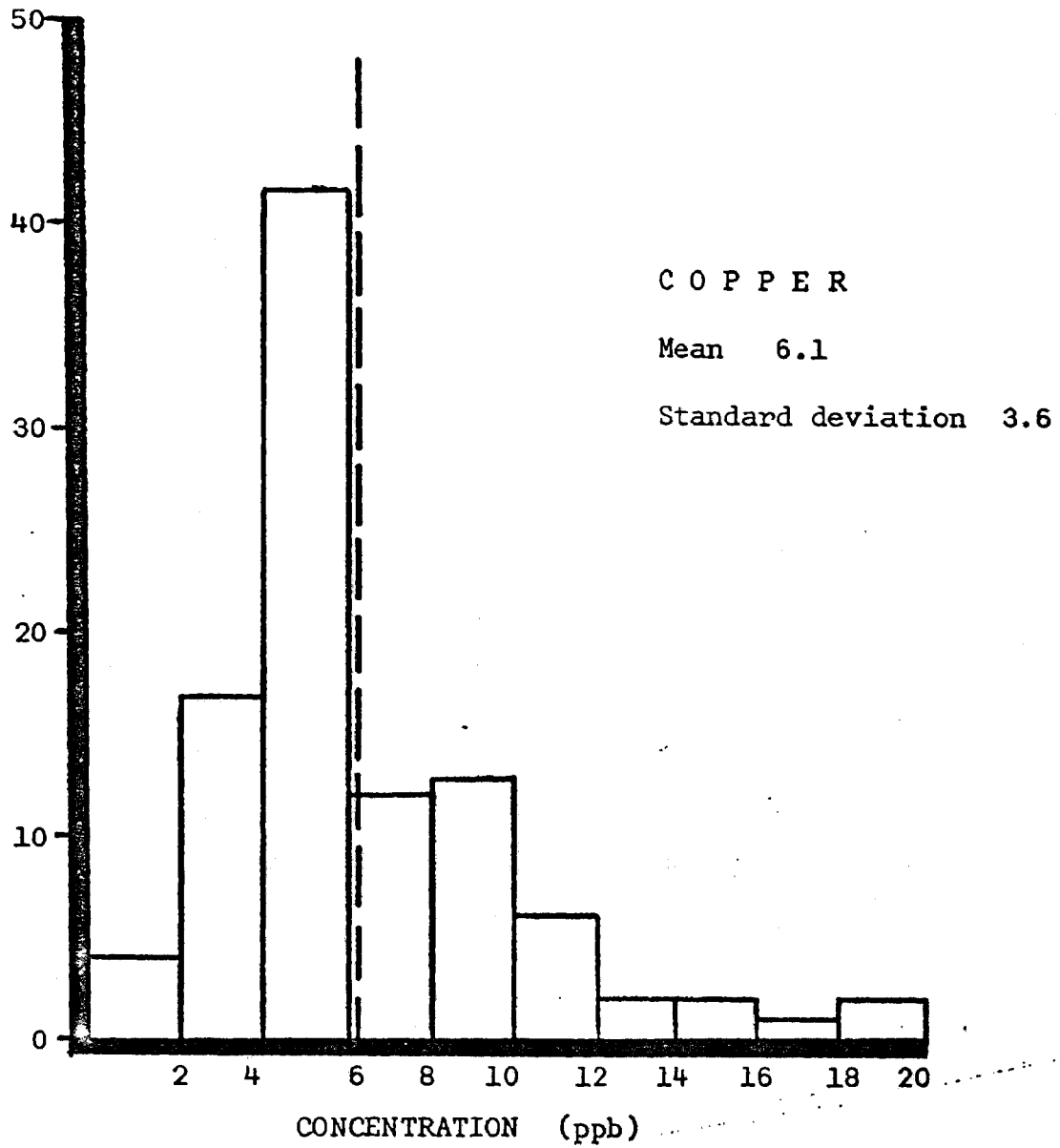
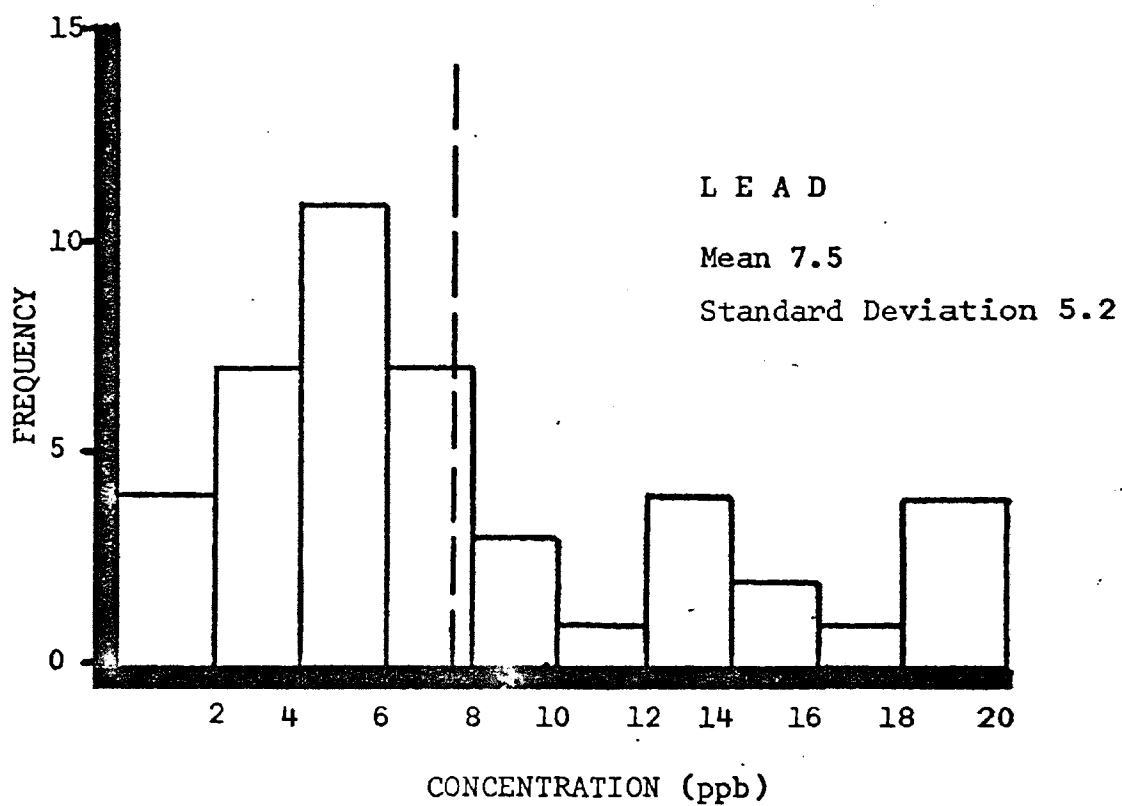Fig. A5.2a. The distribution of data for copper concentrations over the range of 0-20 ppb.

Fig. A5.2b. The distribution of data for lead concentration over the range of 0-20 ppb.
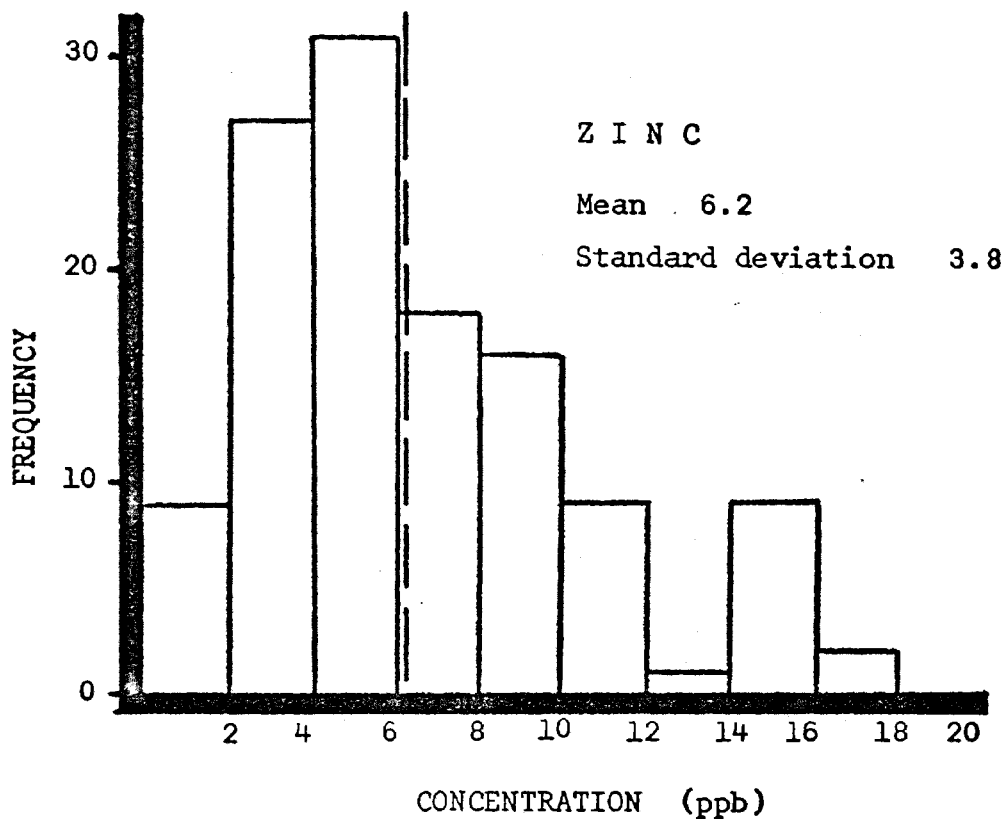
Fig. A5.2c. The distribution of data for zinc concentration over the range of 0-20 ppb.
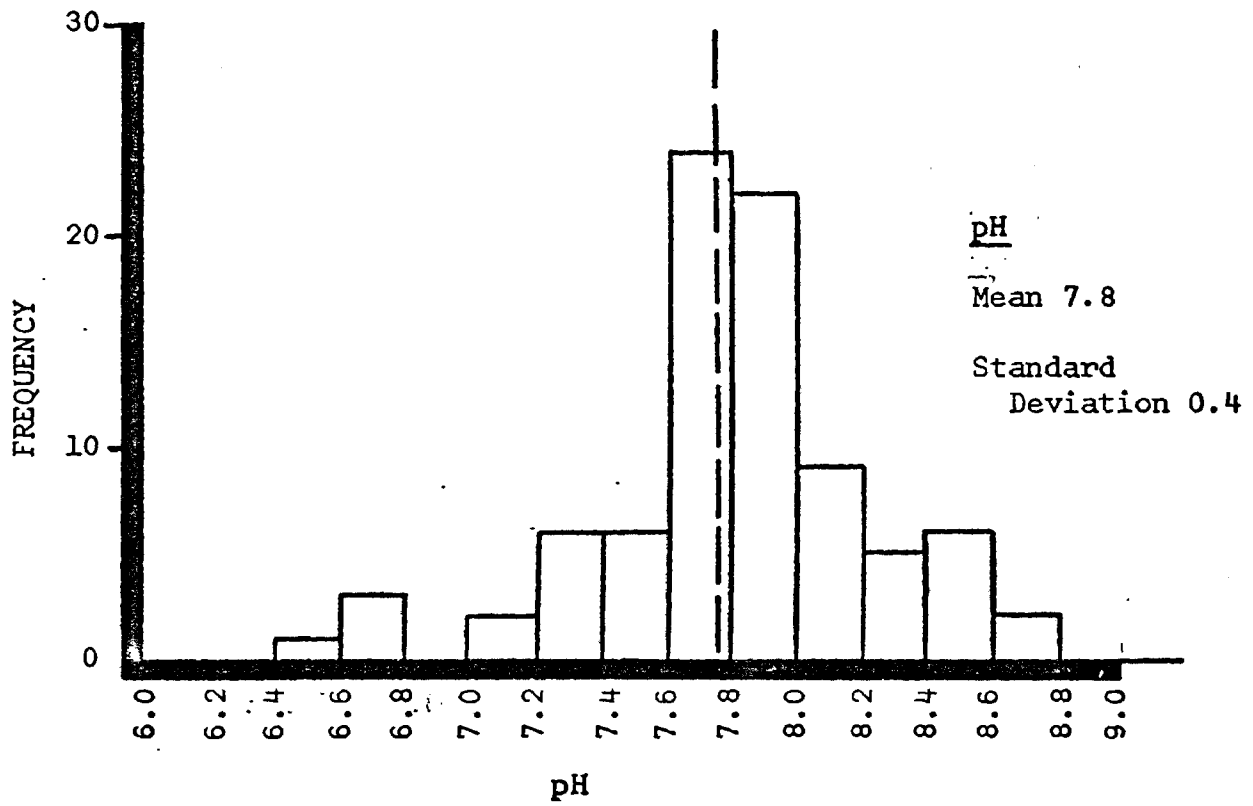
Fig. A5.3. The distribution of data on the pH of stream waters of the New Lead Belt.

APPENDIX VI

List of Abbreviations

APDC - Ammonium pyrrolidine dithiocarbamate

DDTC - Sodium diethyl dithiocarbamate

MIBK - Methyl isobutyl ketone

MnAK - Methyl n-amyl ketone

ppb - Parts per billion; microgram per liter

ppm - Parts per million; milligrams per liter

VITA

Nicholas Howard Tibbs, son of John and Betty Tibbs, was born a United States citizen on May 31, 1945 in Windsor, England. He received his primary and secondary education in Poplar Bluff, Missouri, and while in high school was elected to the National Honor Society. He entered the University of Missouri, School of Mines and Metallurgy in September 1962 and received the degree of Bachelor of Science in Geology from the University of Missouri-Rolla (formerly the School of Mines and Metallurgy) in June, 1966. As an undergraduate, he was elected to the honorary fraternity of Phi Kappa Phi.

In the summer of 1966, the author studied the electron microprobe at the Geology Department, University of Minnesota under a fellowship granted by the Materials Analysis Corporation.

The author served as a Graduate Teaching Assistant at the University of Missouri-Rolla from September 1966 to June 1967. He has served as Research Assistant under his advisor, Dr. Ernst Bolter, on USDI Grant #B-021-Mo from July, 1967 to the present time.

On June 1, 1968, Nicholas Tibbs married Mary Susan Prost. They reside in Rolla, Missouri at the present time.