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ABSTRACT

SPECIATION AND DETERMINATION OF TRACE LEAD: METHODOLOGY DEVELOPMENT AND ANALYSIS OF NATURAL WATERS USING CHELEX-100 AND GFAAS

by
Xidan Ma

The development of a method for speciation, preconcentration, and determination of lead was successfully conducted using Chelex-100 and graphite furnace atomic absorption spectroscopy (GFAAS). Sorption under static conditions and direct measurements in the bead slurry or after fast elution of lead from beads with HNO_3 solution was used. The effects of buffers, sorption kinetics, filtration criteria, sample concentration, resin particle size and temperature program for the GFAAS were carefully studied. In this study, synthetic aqueous samples containing lead were preconcentrated under static conditions using the ion exchange resin, Chelex-100, and the resin was directly analyzed using GFAAS. The batch preconcentration process was optimized using 250 ml (0.4 ppb Pb) of synthetic lead sample with addition of 0.25g Chelex-100, buffered at pH=5.0 and sorption for 1.5 hours under magnetic stirring. The Chelex-100 resins were separated from the equilibrated solution by filtering under vacuum. Nitric acid (5 ml, 5% v/v) was then used to desorb lead from Chelex-100 resins. Three natural waters, lake, canal and river waters were studied, comparing the Chelex-100 with evaporation methods. The distribution of lead species among suspended solids, colloids or complexes, and ionic form was successfully differentiated with this combination method.

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by
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CHAPTER 1

INTRODUCTION

It is well known that speciation measurements are necessary for studies of the toxicity of metals toward aquatic organisms as well as for understanding the transport and fate of trace metals in streams and ground water.

In fresh waters, trace lead may exist in various physicochemical form, which include hydrated ions of different oxidation states, inorganic and organic complex ions, nonionic dissolved species and colloids. Trace lead is also frequently adsorbed on, occluded in, or included in, inorganic, organic or biological suspended particulate matter. Measurement of the total concentration provides little information on its bioavailability or its interaction with sediments and soil particles. Most studies of the susceptibility of fish to heavy metal poisoning have shown that the free hydrated ions are the most toxic. Ions which are strongly complexed or which are associated with colloidal particles are usually considered to be non-toxic. Therefore, information on the physicochemical forms of trace lead in fresh waters is very useful (1).

The determination of the heavy metals in water using current EPA methods does not provide information on the free metal ions in solution. Using Chelex-100 as absorbent for lead analysis (1) was however proven to be feasible both technically and economically (2), and was suitable for assessing bioavailability. There are several instruments used nowadays in measuring metal concentrations, but for detection limit and economic reasons, GFAAS is usually employed in analyzing trace metals. A number of researchers (3, 4, 5) have

studied Chelex-100 for concentrating different trace metals from waters. However the optimization of the experimental conditions were not reported as to the criteria of pH, equilibrating time, and resin particle size in the preconcentration process, as well as the temperature program for the GFAAS analysis. For example, Buckley et al. (6) reported a four-day equilibrating time for 95% absorption for cadmium, and Angeles et al. (5) claimed that a 8-hour equilibrating time was need for 95% recovery for copper using Chelex-100. Also the methods needed to differentiate the various metal species were not clearly addressed in the literature. *Therefore, the goal of this research is to speciate lead ions using batch ion exchange compared to evaporation as preconcentration, followed by GFAAS to quantify and specify their concentrations.* The sample-loaded ion exchange resin beads were analyzed directly by GFAAS, in slurry form as well as in an eluted solution. This analytical method will measure the concentration of free ions which have greater biological effects, ions bound to colloidal particles, as well as ions held on the suspended solids.

In this work, the use of the chelating resin, Chelex-100, equilibrated with trace metals in a batch process as the preconcentration method, was studied. The purpose of using this resin is to preconcentrate the ions sufficiently so they can be measured. After the preconcentration, the temperature program for the analysis of specific trace metals in GFAAS was initially carried out using a slurry of the resin. Then a direct GFAAS determination of the acid extract of the concentrated sample was conducted. Thereafter, synthetic samples were tested to develop the preconcentration process, and finally samples of lake, canal and river waters were studied using the developed method to

speciate, preconcentrate, and determine the species concentration of lead in the natural waters.

CHAPTER 2

BACKGROUND

2.1 Literature Review

In fresh waters, trace lead may exist in various physicochemical form, which include hydrated ions of different oxidation states, inorganic and organic complex ions, nonionic dissolved species and colloids. Trace lead is also frequently adsorbed on, occluded in, or included in, inorganic, organic or biological suspended particulate matter. Determination of the physical and chemical species in which lead exists in a sample is equally as important as the measurement of the total concentration. It is well established that speciation measurements are necessary for studies of the toxicity of lead toward aquatic organisms as well as for understanding the transport and fate of trace lead in streams and groundwater (1). Measurement of the total concentration provides little information on its bioavailability or its interaction with sediments and soil particles. Most studies of the susceptibility of fish to heavy metal poisoning have shown that the free hydrated ions are the most toxic (7). Ions which are strongly complexed or which are associated with colloidal particles are usually considered to be non-toxic. Therefore, information on the physicochemical forms of trace lead in fresh waters is very useful. In recent years, trace lead speciation, i.e., determination of individual concentrations of various physicochemical forms of trace lead, has become one of the most important problems in water analysis (7, 8, 9).

Two approaches are used in speciation studies. (10). One is the calculation method, in which equilibrium concentrations of various species are calculated with the aid of computers by using pH, the redox potential, equilibrium constants, and measured total concentrations of lead and other constituents interacting with it (e.g., chelating agents). Application of this method is rather restricted because of inaccurate equilibrium constants, lack of equilibrium data especially for interaction with particulate matter, and nonequilibrium conditions which may exist in fresh water. The other one is the experimental one, in which a specific species of lead is determined. In general, it is difficult to directly determine a certain species of lead in fresh waters because of the low concentrations. Many of the lead species exist in natural waters at levels below 1 ppb, therefore, separation and concentration techniques are required prior to determination in speciation studies.

Various separation and concentration techniques proposed to date for speciation studies will be briefly described (11, 12). **Filtration** is widely used for separation and size fractionation of particulate matter in water. For size fractionation, filtration through polycarbonate etched-track membrane filters (nuclepore) of various nominal pore sizes ranging from 12 to 0.015 μm is most recommended using either positive or negative applied pressure. For smaller particles, ultrafiltration is used under higher applied pressures. Ultrafilters consist of a filtration membrane on a porous support with various nominal pore sizes ranging from 14 to 1.1 nm, which correspond to nominal molecular weight cutoffs of 3×10^5 to 500.

The **dialysis** technique, based on diffusion through dialysis membranes of nominal pore sizes ranging from 5 to 1 nm, corresponding to molecular weight cutoffs of 10^4-10^3, is used to separate smaller species from colloidal species in water. In the *in situ* dialysis technique, a dialysis bag filled with purified water is directly immersed in the water body of interest to collect smaller species exclusively. A long time is required to attain the equilibrium. The Donnan effect should also be considered, when nondiallyzable anions are present. In conventional laboratory techniques, purified water is changed periodically or recycled through a chelating resin column to effect nearly perfect separations. In the Donnan dialysis technique, a cation exchange membrane, which is permeable to cations and impermeable to humic substances and anionic complexes, is used to concentrate hydrated lead ions in the water sample into a salt solution.

Gel filtration is based on inclusion and subsequent elution of solutes through a column containing porous polymeric gel (e.g., dextran gel Sephadex) as molecular sieve. It can be used to fractionate humic substances containing trace lead in water according to their molecular size or molecular weight differences, provided to that an appropriate concentration technique is combined with it.

In **Electrodeposition**, species deposited on the mercury or solid cathode include hydrated lead ions and lead complexes which will dissociate in the diffusion layer to liberate lead ions, depending on the deposition potential, the electrode system and other operating conditions. This technique is usually combined with subsequent electrochemical stripping in anodic stripping voltammetry (ASV).

In **Liquid-liquid extraction**, nonpolar organic species (organically associated lead) in water can be extracted with organic solvents such as chloroform and a hexane-butanol mixture.

Other techniques such as **Centrifugation, Flotation, Sorption, Volatilization** are also very useful. Of the available methods for concentrating lead from water, sorption is attractive. Adsorption of lead on ion exchange resins can concentrate it so that the analysis can be carried out with little manipulation of the sample, and thus with less chance of contamination. Conventional cation and anion exchange resins have been used for speciation of heavy metals, but an iminoacetate chelating resin, such as Chelex-100 (Bio-Rad Co.) has been found to be even more suitable for this use (11, 13). There are many published examples of use of this resin for preconcentration and separation of ionic lead from natural waters. Chelex-100 resin binds ionic lead strongly, but since its pore size is only 1.5 nm, large complexes and colloids are not retained on the resin beads. It was shown that solutions of colloidal hydrated ferric oxide and bulky organic dye molecules are quantitatively rejected by the resin (14). This resin, therefore, provides a simple and efficient means to separate the ionic from the colloidal bound or complexed lead ions.

Despite the fact that lead is present in all the natural water samples, species specific determinations of individual lead compounds are not generally possible (15), for the following reasons. (*i*) lead compounds cannot be readily extracted from the sample matrix without disturbing its chemical composition and hence the distribution of lead species. (*ii*) No analytical techniques exist which can directly determine lead forms *in situ* at ultra-trace levels. (*iii*) Many lead compounds are associated with particulate matter in water samples

(16-20) which precludes separation at least of the adsorbed fraction. (*iv*) Frequently, the total lead concentration in samples such as natural waters lies at or below the detection limit of most instrumental methods, and so the desire to speciate at such levels is not easy to satisfy.

As a result of the aforementioned, speciation is often defined on a *functional basis* (such as plant available lead species), or *operationally* (by means of a sequence of specific regents or procedures used to isolate, identify and quantify particular lead phases or forms) (1, 7, 12, 19, 21).

Some instrumental methods are available for analysis. Several workers using techniques such as electrothermal atomic absorption spectrometry (22, 23), anodic stripping votammetry (24), isotope dilution spark source mass spectrometry (25), inductively coupled plasma atomic emission spectrometry (ICP-AES) (26-29) and ICP-MS spectrometry (30-32) have reported the use of ion-exchange preconcentration, normally using column elution, or hydride generation to determine Pb in coastal sea-water and open ocean sea-water reference samples (33-35).

GFAAS is one of the most cost-effective and sensitive techniques for determining trace lead in natural waters, but preconcentration steps are still needed for very trace level samples (13, 16). Recently, direct analysis of solid samples by GFAAS has become more popular (36). Instrumental improvements such as stabilized temperature platform furnaces, and Smith Hieftje, or Zeeman background correction have allowed a significant increase in the achievable accuracy for solid samples, especially if the sample is delivered to the furnace in the form of a stabilized slurry. Powdered solid samples are slurried in dilute

nitric acid with a surfactant added to prevent agglomeration. A small ultrasonic probe, inserted directly into the autosampler cup, is used to agitate the slurry immediately before injection into the graphite furnace, insuring homogeneity. (37, 38). Direct GFAAS for the determination of microelements using fine ion exchange resin beads was first used by Slovak (39). The ion exchanger was separated from the sample water by filtration after the metals were adsorbed. With the addition of a little surfactant, flotation can also be used to rapidly and efficiently separate the ion exchange resin beads from the aqueous phase, and reduce the chance of contamination.

Previous workers have studied the separation, concentration and instrumental analysis methods for determination of trace lead in natural waters in detail. But the optimization of the experimental conditions, the method of using a chelating resin in a batch system to preconcentrate trace lead, followed by direct use of GFAAS to quantify the concentrations of various lead species present, still needs to be further studied.

2.2 Atomic Absorption Methods

2.2.1 Summary of Method

Metals in solution may be readily determined by atomic absorption spectroscopy. The method is simple, rapid, and applicable to a large number of metals in drinking, surface, saline waters, domestic and industrial wastes. While drinking waters free of particulate matter may be analyzed directly, domestic and industrial wastes require processing to solubilize suspended material. Sludges, sediments and other solid type samples may also be analyzed after proper pretreatment.

There are flame and flameless atomization atomic absorption methods. In direct aspiration atomic absorption spectroscopy a sample is aspirated and atomized in a flame. A light beam from a hollow cathode lamp whose cathode is made of the element to be determined is directed through the flame into a monochromator, and onto a detector that measures the amount of light absorbed. Absorption depends upon the presence of free unexcited ground state atoms in the flame. Since the wavelength of the light beam is characteristic of only the metal being determined, the light energy absorbed by the flame is a measure of the concentration of that metal in the sample. This principle is the basis of atomic absorption spectroscopy.

Although methods have been reported for the analysis of solids by atomic absorption spectroscopy (40) the technique generally is limited to metals in solution or solubilized through some form of sample processing.

1. Preliminary treatment of wastewater and/or industrial effluents is usually necessary because of the complexity and variability of the sample matrix. Suspended material must be subjected to a solubilization process before analysis. This process may vary because of the metals to be determined and the nature of the sample being analyzed. When the breakdown of organic material is necessitated, the process should include a wet digestion with nitric acid.
2. In those instances where complete characterization of a sample is desired, the suspended material must be analyzed separately. This may be accomplished by filtration and acid digestion, with subsequent determination, and the sum of the dissolved plus suspended concentrations will then provide the total concentration

present. The sample should be filtered as soon as possible after collection and the filtrate acidified immediately.

3. The total sample may also be treated with acid without prior filtration to measure what may be termed "total recoverable" concentrations.

When using the furnace technique in conjunction with an atomic absorption spectrophotometer, a representative aliquot of a sample is placed in the graphite tube in the furnace, evaporated to dryness, charred, and atomized. As a greater percentage of available analyte atoms are vaporized and dissociated for absorption in the tube than the flame, the use of small sample volumes or detection of low concentrations of elements is possible. The principle is essentially the same as with direct aspiration atomic absorption except a furnace, rather than a flame, is used to atomize the sample. Radiation from a given excited element is passed through the vapor containing ground state atoms of that element. The intensity of the transmitted radiation decreases in proportion to the amount of the ground state element in the vapor. The metal atoms to be measured are placed in the beam of radiation by increasing the temperature of the furnace thereby causing the injected specimen to be volatilized. A monochromator isolates the characteristic radiation from the hollow cathode lamp and a photosensitive device measures the attenuated transmitted radiation.

When using atomic absorption methods, interference must be considered and eliminated for both direct aspiration and flameless atomization. For direct aspiration, the most troublesome type of interference is usually termed "chemical" and is caused by lack of absorption of atoms bound in molecular combination in the flame. This phenomenon

can occur when the flame is not sufficiently hot to dissociate the molecule, as in the case of phosphate interference with magnesium, or because the dissociated atom is immediately oxidized to a compound that will not dissociate further at the temperature of the flame.

Chemical interference may be eliminated by separating the metal from the interfering material. While complexing agents are primarily employed to increase the sensitivity of the analysis, they may also be used to eliminate or reduce interference.

The presence of high dissolved solids in the sample may result in an interference from non-atomic absorbance such as light scattering, must be eliminated by using background correction. If background correction is not available, a non-atomic absorbing wavelength should be checked. Preferably, high solids type samples should be extracted.

Ionization interference occurs where the flame temperature is sufficiently high to generate the removal of an electron from a neutral atom, giving a positive charged ion. This type of interference can generally be controlled by the addition to both standard and sample solutions, of a large excess of an easily ionized element.

Although quite rare, spectral interference can occur when an absorbing wavelength of an element present in the sample but not being determined falls within the width of the absorption line of the element of interest. The results of the determination will be erroneously high, due to the contribution of the interfering element to the atomic absorption signal. Also, interference can occur when resonant energy from another element in a multi-element lamp or a metal impurity in the lamp cathode falls within the bandpass of the slit setting and that metal is present in the sample. This type of interference may sometimes be reduced by narrowing the slit width.

In flameless atomization, the problem of oxide formation is greatly reduced with furnace procedures, because atomization occurs in an inert atmosphere. The technique, however, is still subject to chemical and matrix interference. The composition of the sample matrix can have a major effect on the analysis. It is those effects which must be determined and taken into consideration in the analysis of each different matrix encountered.

Gases generated in the furnace during atomization may have molecular absorption bands encompassing the analytical wavelength. When this occurs, either the use of background correction or choosing an alternate wavelength outside the absorption band should eliminate this interference. Non-specific broad band absorption interference can also be compensated for with background correction.

Interference from a smoke-producing sample matrix can sometimes be reduced by extending the charring time at a higher temperature or utilizing an ashing cycle in the presence of air. Care must be taken, however, to prevent loss of the analysis element.

Samples containing large amounts of organic materials should be oxidized by conventional acid digestion prior to being placed in the furnace. In this way broad band absorption will be minimized.

From anion interference studies in the graphite furnace it is generally accepted that nitrate is the preferred anion. Therefore nitric acid is preferable for any digestion or solubilization step.

Several methods have been developed for spectral interference caused by matrix products. **The two-line correction method:** The two-line correction procedure requires

the presence of a reference line from the source, this line should lie as close as possible to the analyte line but must not be absorbed by the analyte. If these conditions are met, it is assumed that any decrease in power of the reference line from that observed during calibration arises from absorption or scattering by the matrix products of the sample, this decrease is then used to correct the absorbance of the analyte.

The continuous-source correction method: A deuterium lamp provides a source of continuous radiation throughout the ultraviolet region, the configuration of the chopper is such that radiation from the continuous source and the hollow cathode lamp are passed alternately through the graphite-tube atomizer. The absorbance of the deuterium radiation is then subtracted from that of the analyte beam. The slit width is kept sufficiently wide so that the fraction of the continuous source that is absorbed by the atoms of the sample is negligible. Therefore, the attenuation of its power during passage through the atomized sample reflects only the broad-band absorption or scattering by the sample matrix components. A background correction is thus achieved.

Zeeman background correction method: Application of Zeeman effect to background correction is based upon the differing response of the two types of absorption peaks to polarized radiation. Unpolarized radiation from an ordinary hollow cathode source is passed through a rotating polarizer, which separates the beam into two components, plane-polarized at 90 deg to one another. These beams pass into a tube-type graphite furnace. A permanent magnet surrounds the furnace and splits the energy levels in such a way as to produce the three absorption peaks. The central peak absorbs only that radiation that is plane-polarized with the field. During that part of the cycle when the

source radiation is polarized similarly, absorption of radiation by the analyte takes place. During the other half cycle, no analyte absorption can occur. Broad-band molecular absorption and scattering by the matrix products occur during both half cycles. The data acquisition system is programmed to subtract the absorbances during the perpendicular half cycle, thus giving a background corrected value. Zeeman background correction provides a more accurate correction for background than the methods described earlier do.

Smith-Hieftje background correction method: This method is based upon the self-reversal, or self-absorption, behavior of radiation emitted from hollow cathode lamps when they are operated at high currents. High currents produce large concentrations of nonexcited atoms, which are capable of absorbing the radiation produced from the excited species. An additional effect of the high currents is to significantly broaden the emission band of the excited species. The net effect is to produce a band that has a minimum in its center, which corresponds exactly in wavelength to that of the absorption peak. In order to obtain corrected absorbances, the lamp is programmed to run alternately at low and high currents. The total absorbance is obtained during the low-current operation, and the absorbance due to background is provided by measurements during the second part of the cycle, when radiation at the absorbance peak is at a minimum. The data acquisition system then subtracts the background absorbance from the total to give a corrected value. Recovery of the source when the current is reduced takes place in milliseconds. The measurement cycle can be repeated often enough to give satisfactory signal-to-noise ratios.

The most important parameter for lead analysis by GFAAS is the pyrolysis temperature. Usually, for liquid samples, this temperature is 600°C, while for solid samples the temperature is 800°C. A Pd-modifier may be used to reduce losses of lead due to volatilization during the ashing process.

2.2.2 Definition of Terms

Optimum Concentration Range: A range, defined by limits expressed in concentration, below which scale expansion must be used and above which curve correction should be considered. This range will vary with the sensitivity of the instrument and the operating condition employed.

Sensitivity: The concentration in milligrams of metal per liter that produces an absorption of 1%.

Detection Limit: Detection limits can be expressed as either an instrumental or method parameter. The limiting factor of the former using acid water standards would be the signal to noise ratio and degree of scale expansion used; while the latter would be more affected by the sample matrix and preparation procedure used. The Scientific Apparatus Makers Association (SAMA) has approved the following definition for detection limit: "That concentration of an element which would yield an absorbance equal to twice the standard deviation of a series of measurements of a solution, the concentration of which is distinctly detectable above, but close to blank absorbance measurement." The detection limit value may differ from the optimum detection limit reported by the various instrument manufacturers.

Dissolved Metals: Those constituents (metals) which will pass through a 0.45 μm membrane filter.

Suspended Metals: Those constituents (metals) which are retained by a 0.45 μm membrane filter.

Total Metals: The concentration of metals determined on an unfiltered sample following vigorous digestion, or the sum of the concentrations of metals in both the dissolved and suspended fractions.

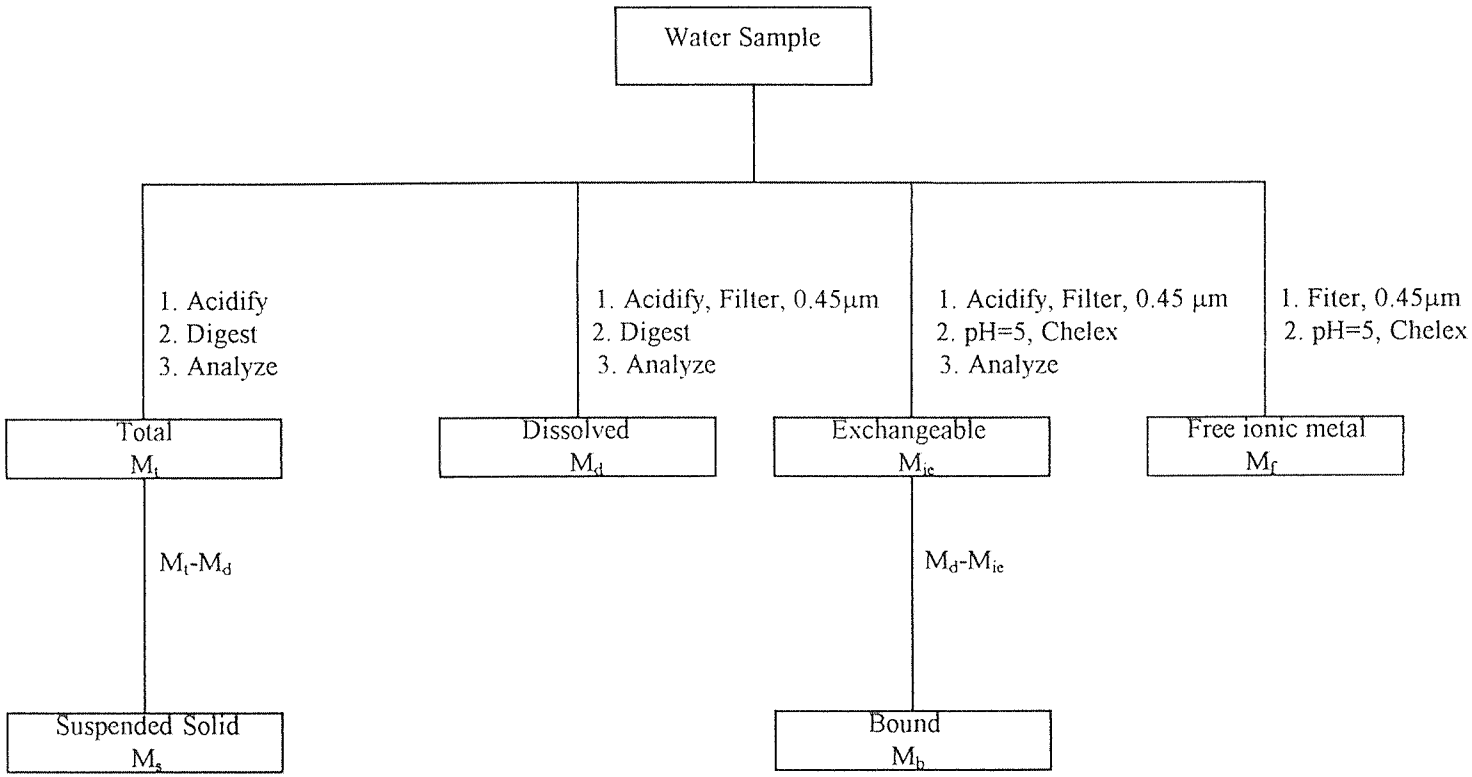
Total Recoverable Metals: The concentration of metal in an unfiltered sample following treatment with hot dilute mineral acid.

2.3 Speciation Scheme Based on Physicochemical Separations

By combining a number of physicochemical separation procedures, a scheme can been devised to divide the total metal concentration into operationally defined classes of metal species, as is shown on Figure 1:

From the literature review and GFAAS method description, we can see that previous workers had studied the separation, concentration and instrumental analysis methods of the trace lead in natural waters in detail. But the optimization of the experimental conditions, the method of using batch ion exchange to preconcentrate trace lead, and separate the species, and the analysis of either a slurry or eluted lead sample, followed by GFAAS to quantify the concentrations still need to be further studied.

It can be concluded from the literature review that sorption on a Chelex-100 resin can be used for speciation and preconcentration of lead in natural waters.



M_t: Total metal. M_s: Suspended Solid. M_{ie}: Exchangeable metal.

M_d: Dissolved metal. M_b: Bound metal. M_f : Free Ionic Metal

Figure 1. Speciation scheme

Schemes including sorption under dynamic conditions (in the column) with following elution and GFAAS, ICP-AES, ICP-MS determination were developed. However, dynamic sorption is a time consuming process and elution needs a significant quantity of high purity reagent.

Apparently, lead preconcentration under static condition and direct GFAAS determination in a slurry would allow a reduced time of analysis and save expensive reagents.

CHAPTER 3

EXPERIMENTAL APPROACH

3.1 Experimental Apparatus

3.1.1 Instrumentation

1. Instrument

A Thermo Jarrell Ash atomic absorption spectrometer equipped with furnace atomizer (model 188) and Smith Hieftje background correction was used for the determination of the trace lead samples.

The instrument includes:

A dual channel, double-beam Spetrometer with a grating monochromator, photomultiplier detector, adjustable slits, a wavelength range of 190 to 800 nm, and provisions for interfacing with a strip chart recorder.

Hollow cathode lamp: Single element lamp (lead).

Graphite Furnace: P/N 4090-40, platform tube. (From CPI, Inc.)

2. GFAAS conditions

In all instances, charring and atomization temperature were optimized since the presence of high concentrations of matrix can affect the selection of the optimum temperature. All analyses were done using solid pyrolytic graphite forked platforms inserted in pyrolytically coated graphite tubes. Calibration with aqueous standards was used throughout. Peak area measurements were used for quantitation. Oxygen ashing proved useful in removing organic material prior to atomization and was used routinely. Standard and sample

volumes for analysis were 20 µl by manual injection. Wavelength selection included the use of alternate, less sensitive non-resonance lines when the analyte concentration was sufficiently high. Usually, 217 nm wavelength (sometimes 283.3 nm) was used. Double-beam optics and Smith Hieftje background correction was used. The optimized program for the lead determination is shown in Table 1:

Table 1. Optimized Program for Lead Determination

	Drying	Pyrolysis 1	Pyrolysis 2	Atomization	Cleaning
Temp. (°C)	110	300	490	1800	2550
Ramp (°C/min)	10	20	40	0	
Hold (sec)	5	5	25	4	4
Purge	1	2	3	0	3

3.1.2 Reagents

Ultrapure deionized water: Prepared by passing deionized water through a mixed bed of cation and anion exchange resins (Mill-Q, 18 MΩ). Ultrapure deionized water was used for the preparation of all reagents, calibration standards, and as dilution water.

Hydrochloric acid (1:1): Solution of reagent grade hydrochloric acid (Fisher Chemical, Fisher Scientific) and ultrapure deionized water.

Nitric acid (conc.): Spectrograde acid. (Fisher Chemical, Fisher Scientific)

Hydrogen peroxide: 3% and 30% H_2O_2 are all reagent grade. (Fisher Chemical, Fisher Scientific)

Stock standard lead solution: 1000 mg/l of the lead standard solution. (Inorganic Ventures, Inc.)

Calibration standards: A series of standards of lead was prepared by dilution of the stock standard lead solution to cover the concentration range desired.

Gases: Air is supplied from a compressed air line. Argon is from Matheson gas Products Inc.

Buffers: Buffers for pH=4, 5, 6, 7, 9 were from Thomas Scientific Inc.

Filter paper: 0.2 μm and 0.45 μm were the Whatman cellulose nitrate membrane.

Apparatus: Containers, micropipettes, filter holders and test tubes were made of polypropylene from American Scientific Products Inc. and Becton Dickinson Labware Company.

Chelex-100: Both 100-200 and 200-400 mesh Chelex-100 were Na^+ form, from Bio-Rad Laboratories.

3.1.3 Cleaning Procedures

The plastic beakers, filtration apparatus, pipettes and sampling containers were thoroughly washed with detergent and tap water, rinsed with 1:1 nitric acid, tap water, 1:1 hydrochloric acid, tap water, deionized water, and finally ultrapure deionized water in that order(42).

3.2 Experimental Procedure

3.2.1 Preparation of Standards and Calibration

Calibration standards are prepared by diluting the stock lead solutions at the time of analysis. For best results, calibration standards were prepared each time an analysis was to be made and discarded after use. The blank and calibration standards were prepared using the same type of acids or combination of acids.

1.Calibration Blank

5 ml 5% nitric acid (v/v) with 0.25g Chelex-100 added. The supernatant or Chelex-100 slurry was used as the calibration blank.

2. Calibration Standards

Stock standard solution (100 ppm) was diluted with 5% HNO_3 (v/v) to 200 ppb, then diluted with 5% HNO_3 (v/v) to 10 ppb, 20 ppb, 30 ppb, 40 ppb, 50 ppb, 60 ppb respectively. To 5 ml of each of the standards prepared above 0.25g Chelex-100 was added. The supernatant or the Chelex-100 slurry was used as calibration standard.

The calibration curves are shown as Figure 2.

3.2.2 Preconcentration Procedure

1. Chelex-100 adsorption procedure: A 250 ml synthetic lead sample (0.2 or 0.4 ppb) was prepared in a prewashed polypropylene beaker and 0.25g Chelex-100 was added with 5 ml of buffering solution. The beaker was covered with polypropylene sheet for the sorption process under magnetic stirring for different time intervals. After the sorption process was complete, a vacuum filtering apparatus with polypropylene holder and 0.2 μm

Whatman membrane filter was then used to filter out the Chelex resin. The filtered resin was washed off the filter into a plastic test tube with 5 ml (5% v/v) nitric acid. After hand shaking for 1 minute, a slurry was made. This slurry sample was then ready for determination of lead by GFAAS. For a preconcentration blank, the same procedure was followed except that ultrapure deionized water was used instead of synthetic lead samples.

2. Evaporation procedure: A 250 ml sample (filtered, or unfiltered) was transferred to a polypropylene beaker. The sample was heated on a steam bath until the volume was reduced to about 2 ml, 5% HNO_3 was added to make the final volume up to 5 ml. This evaporated sample was then ready to be determined. This method was called "Evaporation method" in this thesis.

3.2.3 Water Sampling and Storage

For the determination of trace lead, contamination and loss are of prime concern. Dust in the laboratory environment, impurities in reagents and impurities on laboratory apparatus which the sample contacts are all sources of potential contamination. For liquid samples, containers can introduce either positive or negative errors in the measurement of trace lead by (a) contributing contaminants through leaching or surface desorption and (b) by depleting concentrations through adsorption. Thus the collection and treatment of the sample prior to analysis requires particular attention. Since lead may be present at ng/l levels in many types of water, a rigorous cleaning of sample vessels is necessary.

The polyethylene containers were soaked in 1:1 nitric acid for 48 hours, followed by a deionized, ultrapure water rinse and drain drying. Before collection of water samples,

the containers were well rinsed with sample. The sample collected was divided into two groups. One was acidified with concentrated nitric acid to pH below 2, for the determination of total lead concentration. The other was filtered through 0.45 μm Whatman cellulose nitrate membrane filter, for the determination of dissolved lead. Both acidified and unacidified samples were stored at 4 °C, in the dark, for future use.

3.2.4 Speciation of Trace Lead

1. To determine total lead: The sample was acidified with concentrated spectrograde nitric acid to a pH of less than 2 at the time of collection. The sample was not filtered before processing. A volume of sample appropriate for the expected level of lead was taken. A representative aliquot of the well mixed sample (usually 250 ml) was transferred to a prewashed Griffin beaker and 3 ml of concentrated spectrograde nitric acid was added. The beaker was heated on a hot plate and evaporated to near dryness cautiously, making certain that the sample did not boil. The beaker was cooled and another 3 ml portion of concentrated spectrograde nitric acid was added. The beaker was covered with a watch glass and returned to the hot plate. The temperature of the hot plate was increased so that a gentle reflux action occured. Heating was continuted until the digestion was complete. (generally indicated when the digestate was light in color or did not change in appearance with continued refluxing). Again, the sample was evaporated to near dryness and cooled. A small quantity of 1:1 HNO_3 was added and the beaker was warmed to dissolve any precipitate or residue resulting from evaporation. The beaker walls and watch glass were washed with ultrapure water and the sample was filtered to remove silicates and other

insoluble material. The sample was evaporated again nearly to dryness (2 ml), and 5% nitric acid was added to make the final volume up to 5 ml. The sample was then ready to be determined.

2. Total recoverable lead: The entire sample was acidified at the time of collection with concentrated spectrograde HNO_3 (5 ml/l). At the time of analysis a 250 ml aliquot of well mixed sample was transferred to a polypropylene beaker. The sample was heated on a steam bath until the volume reduced to 15-20 ml making certain the samples did not boil. After this treatment the sample was filtered to remove silicates and other insoluble material that could clog the atomizer. The sample was evaporated again, nearly to dryness (2 ml), 5% HNO_3 was added to make the final volume up to 5 ml. This evaporated sample was then ready to be determined.

3. Dissolved lead: For determination of dissolved lead the sample was filtered through a 0.45 μm membrane filter as soon as practical after collection. Prewashed plastic filtering apparatus was used. First 50-100 ml of sample was used to rinse the filter flask and discarded. The required volume (usually 250 ml) of filtrate was collected and acidified with 1:1 spectrograde HNO_3 to a pH below 2. (Normally, 3 ml of 1:1 acid per liter was sufficient to preserve the sample) The sample was evaporated on a steam bath until nearly dry (2 ml), then 5% HNO_3 was added to make the final volume up to 5 ml. The sample was ready to be analysed.

4. Exchangeable lead: To determine the Chelex-100 exchangeable lead, the sample was filtered through a 0.45 μm membrane filter, as described above. 250 ml filtrate was put in a prewashed polypropylene beaker, 0.25g Chelex-100 and 5 ml pH=5 buffering solution

was added. The beaker was then covered with polypropylene sheet for the sorption process under magnetic stirring for 1.5 to 2 hours. After the sorption process was complete, a vacuum filtering apparatus with polypropylene holder and 0.2 μm Whatman membrane filter was then used to filter Chelex resin. The filtered resin was then washed off the filter into a plastic test tube with 5 ml 5% nitric acid. The sample was slurred by hand shaking for 1 minute. This slurry sample was ready for the determination by GFAAS.

3.2.5 GFAAS Operation

After samples were prepared, they were analysed by GFAAS. Because differences between the various makes and models of satisfactory atomic absorption spectrophotometers prevent the formulation of detailed instructions applicable to every instrument, we must follow the manufacturer's operating instructions for the particular instrument. The operating procedure for GFAAS is shown below:

(1) The proper lead hollow cathode lamp for the analysis chosen;

(2) Compressed air: 58 psi;

(3) Argon: 58 psi;

(4) Water: 15 GPH;

(5) Atomizer 188 power on;

(6) Smith Hieftje 12 power on;

(7) Printer (microline 320) on;

(8) High voltage is set at 720, and the background current is adjusted to 2.5 mA.

(9)The instrument is aligned and the monochromator is set at the correct wavelength (217 nm). The proper monochromator slit width is set, and the signal energy level is adjusted to match that of background.

The lamp should warm up at least 15 minutes even though operated in a double beam mode. The mode is shown below:

(1) Element : Pb

(2) Optics: AA, DB

(3) Bkgnd: S

(4) Results: Conc.

(5) Statistics: 3

(6) Automizer: CTF

(7) Auto sampler: Off

Peak area: 4.0 sec. STD: normal calibration. 20 μl manual injection.

The Optimized furnace program for lead is shown on Table 1.

CHAPTER 4

RESULTS AND DISCUSSIONS

4.1 Method Development

4.1.1 The Development of Optimized Temperature Program

The development of a temperature program for the determination of the slurry sample was initially carried out with standards containing 0.25 g Chelex, to generate a reproducible temperature program to be used throughout the study. Such an optimized program should offer both maximum atomic absorption and minimum background interference. In this study, the higher sensitivity wavelength for lead at 217 nm instead of 283.3 nm was used. A dual-beam spectrometer with Smith Hieftje background correction and L'vov graphite tube were employed.

Although W. Slavin, N.J. Miller-Ihli, G.R. Garnick (37, 38) reported that using direct GFAAS analysis of plant material slurry sample with Zeeman background collection and omitting pyrolysis step 2 can obtain reasonable results, it is very important for accurate and repeatable analysis to choose suitable pyrolysis temperature. Figure 3 shows the results of the background interference and atomic absorption due to the Chelex-100 slurry injection. It clearly indicates that a high background interference is observed when pyrolysis temperatures below 460°C are used. However it decreases as the pyrolysis temperature is increased, and reaches a minimum at about 520°C. On the other hand, the atomic absorption of lead also decreases as the pyrolysis temperature becomes higher than 480°C. The optimum point where the maximum possible atomic absorption and minimum

background interference are obtained is a pyrolysis temperature of 490°C as indicated in Figure 3. The optimized program is shown in Table 1, and was then used throughout this study.

The use of commonly employed matrix modifiers, $Pd(NO_3)_2$ (5, 41), for high interference samples in GFAAS was also examined. Figure 4, shows the results of using these matrix modifiers in the analysis of a 20 ppb lead standard where the Chelex slurry was injected. The comparison of the supernatant and slurry injections where modifiers were added, to the supernatant injection of the standard where no modifier added, indicates that almost no difference was found using the temperature program shown in Table 1. However, a higher volatilization temperature for lead of about 1000°C rather than 500°C was requred with the addition of modifier. This is an important observation, as the use of expensive matrix modifier may be avoided with the help of proper temperature programming.

4.1.2 The Difference between Supernatant and Slurry Calibration Curves

The matrix effects of the supernatant and slurry injections into GFAAS were also investigated with a series of calibration standards. The results, shown in Figure 2, indicated that the absorption was about 15% lower for slurry than supernatant injection. Therefore, it is important to use the same matrix if possible as the basis for calibration standards. The same conclusion was also reported by Haswell (41) stating that it is important to use matrix-matched standards whatever technique is used.

4.1.3 The Effects of Chelex-100 Slurry Mass and Concentration of HNO_3

To 5 ml 20 ppb 5% nitric acid standard Pb solutions 0.05, 0.10, 0.15, 0.20, 0.25, 0.30g Chelex-100 were added respectively. 20 μl slurry samples were injected into the GFAAS, using the slurry standard calibration curve for the quantification. The results are shown on Table 2.

Table 2. The Effects of Mass of Chelex-100 in the Slurry on Absorption of Pb

Chelex (g)	0.05	0.10	0.15	0.20	0.25	0.30
ppb(Pb)	18.8	18.1	18.2	18.1	17.7	18.6
RSD(%)	2.3	1.8	2.3	2.4	1.4	2.0

Table 2. shows that for same concentration of lead in solution, varying the Chelex-100 mass in the slurry, has little effect on the analysis results.(Average of 3 replicate sample)

Many reports state that the addition of nitric acid improved the results of GFAAS analysis, but the concentration range of nitric acid were not reported. Here , the effects of nitric acid concentration on analysis results were studied. Solutions containing about 20 ppb lead in ultrapure water and 0.25g Chelex-100 were prepared. These were desorbed in 0.5% , 1%, 2%, 3%, 4%, 5% nitric acid solution for 5 minutes, then hand shaking for 1 minute, 20 μl of each were injected to GFAAS. Table 3, shows the results.

Table 3. The Effects of Nitric Acid Concentration

HNO_3%.	0.0	0.5	1.0	2.0	3.0	4.0	5.0
ppb(Pb)	Trace	5.7	21.5	21.5	21.0	19.5	20.5

The results shown in Table 3, indicate that a nitric acid concentration above 1% (v/v) is necessary for the analysis. Below 1% of nitric acid, irregular absorption was found. This phenomena can be attributed to the strong adsorption of cations with Chelex-100 under neutral pH (5-6). To reproduce the injection with such a inhomogeneous slurry in the GFAAS is therefore very difficult. However with the addition of above 1% nitric acid, the strongly adsorbed lead (at pH=5-6) with Chelex-100 was washed out into the acid solution. Reproducible results were then obtained. An examination of the possible undesorbed lead ions from Chelex-100 was also conducted to make sure that all the lead on the resins was washed off with above 1% nitric acid. Results indicated that no detectable metal was left on the Chelex-100 after desorption in 1% nitric acid. Because the Chelex-100 is in basic form, it requires a strong acid solution, 5% (v/v) nitric acid, to ensure the complete washout of absorbed lead. However, the matrix effect still existed for the case of slurry standards

Therefore, the temperature program, matrix problems, effects of slurry mass and nitric acid concentration were carefully studied prior to the preconcentration process. The preconcentration of the sub-ppb lead synthetic samples was then carried out to examine the effects of buffering pH, lead concentration, equilibrating time, and resin particle size on the adsorption of the ionic lead onto Chelex-100 resins (mesh 100-200).

4.1.4 The Effects of pH Buffering and Equilibration Time

250 ml synthetic lead samples (0.4 ppb) were prepared in prewashed polypropylene beakers with addition of 0.25g Chelex-100, (100-200 mesh) and buffered with 5 ml

different pH buffering solutions. The beakers were then covered with polypropylene sheets for the sorption process under magnetic stirring for different time intervals. After finishing the sorption process, the vacuum filtering apparatus with polypropylene holder and 0.2 μm Whatman membrane filter were then used to filter out the Chelex resins. The filtered resin was then washed off the filter into the plastic test tube with 5 ml (5% v/v) nitric acid. These slurry samples were analyzed by GFAAS.

The results shown in Figure 5 indicate that the absorption efficiency is strongly dependent on the buffering pH and the equilibrating time. At pH=9.0, an absorption lower than 30% was obtained, and absorption of 90% was observed with the pH buffered at 4.0. However, the optimum condition was at pH=5 with equilibrating time greater than 1.5 hour, where absorption efficiency was observed to be as high as 98%. Fairly similar results were also obtained when using 200-400 mesh Chelex-100 resin. Buffering pH at 6 and 7 was also studied and it was concluded that lower absorption was observed compared that at pH at 4 and 5.

4.1.5. The Analysis of Tap Water

A 250 ml tap water (Newark, New Jersey) having clear appearance was preconcentrated using both the Chelex-100 and evaporation methods. The results are shown in Figure 6, where almost identical concentration (about 1.3 ppb) for both methods is obtained. This strongly supports the evidence that all the ionic lead is sorbed by the Chelex-100 in such a sample, which contains little particulate or strong complexing agents, compared to EPA method with evaporation in order to increase sensitivity of the analysis. This implies that

Chelex can be a very good resin for measuring and speciating the dissolved ionic lead in natural waters. The free ionic lead is considered to be the major source of trace metal biotoxicity to the living organism in waters (43, 44). Florence (1) also conducted a study for the transport of the metals through biomembrane via the simulation of the biomembrane with thio (sulfur bonds) resins for lead in the river and sea waters. Results indicated that a very comparable amount of lead was absorbed by both the thio resins and Chelex-100, which shows that Chelex-100 is a good chelating resin for the speciation, preconcentration and therefore determination of the bioavailable lead in water.

4.1.6 The Precision and Accuracy of the GFAAS Method

1. Relative standard derivation of GFAAS analysis

20 μl supernatant and Chelex-100 slurry of about 20 ppb standard lead solution (5 ml 5% nitric acid solution with 0.25g Chelex-100 inside) were injected into GFAAS for analysis, using the appropriate calibration curves. The results are shown on Table 4.

Table 4. Concentrations Obtained by GFAAS on 20 ppb Standard Pb Solution

	1	2	3	4	5	6	7	Mean	SD
Super.	21.6	18.6	18.1	19.1	20.2	20.5	17.4	19.4	1.48
Slurry	16.4	21.8	18.0	16.9	18.9	15.2	15.8	17.6	2.25

The relative standard derivation:

RSD=SD/Mean×100%

for supernatant: RSD=1.48/19.4=7.63%

for slurry: RSD=2.25/17.6=12.8%

The experimental data show that using supernatant standard results of GFAAS analysis are more reproducable.

2. Determination of the detection limit

The Scientific Apparatus Makers Association (SAMA) has approved the following definition for detection limit:

The concentration of an element which would yield an absorbance equal to twice the standard deviation of a series of measurements of a solution, the concentration of which is distinctly detectable above, but close to blank absorbance measurement. Or:

$$S_m=X_{bl}+3S_{bl}$$

where:

S_m: Detection limit.

X_{bl}: Blank mean.

S_{bl} : Standard derivation of blank.

To 50 ml ultrapure water buffered with 5 ml pH=5.0 buffer solution, 0.25g Chelex-100 was added, to preconcentrate for 2 hours, then filtered. 5 ml 5% nitric acid was used to wash the resin into test tube. The supernatants were analyzed by GFAAS, using lead supernatant standard calibration curve. Results are shown in Table 5.

Table 5. Lead Concentration in Blank Using Preconcentration on Chelex-100

	1	2	3	4	5	mean	RSD(%)
Pb (μg/l)	0.000	0.010	0.030	0.030	0.000	0.014	107

From the data in Table 5, we can determine the detection limit of the method according to the SAMA definition:

$$S_m=X_{bl}+3S_{bl}=0.014+3\times0.015=0.059\ \mu g/l$$

which is comparable to the value 0.04 μg/l found in the literature (5).

Because the limit of quantitation (LOQ)=$10S_{bl}$=10×0.015=0.15 ppb, the concentration of analytes should be 0.2 ppb or more when using this analysis method.

3. Accuracy of the method

Accuracy determines the closeness of the analytical data to the true value. It is estimated from the recovery of a known standard spiked into the sample. EPA defines the spike recovery as:

$$\%\ Recovery=100\ (X_S-X_u)/K$$

Where:

X_S: Measured value for the spiked sample

X_u: Measured value for the unspiked sample adjusted for dilution of the spike

K: Known value of the spike in the sample

The tap water sample (Newark, New Jersey) was measured using Chelex-100 preconcentration procedure and total recoverable metal procedure 1 ml 40 ppb standard lead solution was spiked into some samples, giving an adjusted concentration of 0.8 ppb standard lead. The results are shown in Table 6.

Table 6. Lead Concentration in Newark Tap Water

	1	2	3	mean	SD	(%)
Ev. tap	1.28	1.32	1.31	1.30	0.02	2
Ev.tap+sp.	2.02	1.96	2.00	1.99	0.03	2
Ch. tap	1.25	1.19	1.22	1.22	0.03	2
Ch.tap+sp.	1.94	1.97	2.04	1.98	0.05	3

The spike recovery of using EPA method for total dissolved lead with evaporation for preconcentration is:

$$\% \text{ Recovery}=100\ (X_S-X_u)/K=100(1.99-1.30)/0.8=86.3$$

The spike recovery of Chelex-100 preconcentration method is:

$$\% \text{ Recovery}=100\ (X_S-X_u)/K=100(1.98-1.22)/0.8=95.0$$

The results indicate that both evaporation and Chelex preconcentration method are accurate, but the Chelex preconcentration produces a better spike recovery than evaporation method.

4.1.7 Lead Sorption on Chelex-100 from Water Containing Chelating Reagents

Chelating reagents present in water can compete with Chelex for Pb ion. Therefore investigation of Pb distribution between the resin, and EDTA or humic acid was studied. Figure 7. shows that a 1 ppb (50 ml) synthetic lead water solution is preconcentrated to 10 ppb (5 ml) using Chelex-100 (0.25 g) with addition of EDTA and humic acid. The results showed that this preconcentration process was practically not affected by the humic acid (>0.0125%) where no iron existed, but was strongly inhibited by the presence of EDTA (0.0014 M). However Florence (1) reported that lead on an iron-humic acid colloid are

not absorbed by Chelex-100. The issue of humic acid was also studied by Haraldsson et al. (45), it was reported that Pb-humic acid complexes can be absorbed by DEAE-650 (200-400 mesh, Merck), which can therefore be used to speciate Pb-humic acid complexes from ionic lead before Chelex-100 preconcentration. The addition of 5 ml (30%) hydrogen peroxide into the EDTA contained lead solution did not destroy this strong EDTA-Pb complex. This strong chelated complex if analyzed by the current EPA methods will be treated as free ionic form of Pb. However if analyzed by Chelex-100 method, the chelated lead would not be detected and no free ionic lead in the water would be shown. So for water containing strong complexing agents the Chelex exchangeable lead is quite different from dissolved lead by EPA method (figure 1).

4.2 Determination of Trace Lead in Natural Water

After the study of Chelex-100 resins, a series of speciation, preconcentration and determination experments on lead in natural waters were conducted. Results show that it is very promising for the application of this methodology in speciation and determination of trace lead in waters.

4.2.1 Analysis of Trace Lead in Newark Lake Water

A sample of Newark lake water with little suspended solid was collected and analyzed. Results are shown in Figure 8. There is about 2.4 ppb total lead (Figure 8(a)) in the lake water. However after acidification and filtering out the suspended solids with a 0.45 μm filter, the lead concentration in solution is decreased to about 2.2 ppb (Figure 8(b)). This

is the total recoverable lead as defined in the EPA method. Further investigation by using Chelex-100 clearly indicates that the concentration of ionic and recoverable colloidal lead in the lake water is about 1.7 ppb (Figure 8(c)). The difference in the latter two cases is 0.5 ppb which is considered to be the unrecoverable colloidal lead (Figure 8(b)), which is strongly bound to colloidal particles or chelated. This portion of the lead may not be readily available to the biosystems in the lake water. Another study was conducted by the addition of a strong oxidizing reagent (5 ml, 30% hydrogen peroxide) to the above Chelex-100 preconcentration process to examine its effect on the recovery of lead. Results shows that a increase (15%) in the recovery of lead was obtained (figure 8(d)). This increase in the lead concentration strongly supports the above observation that there is colloidal or chelated lead present. The dissolved lead in the lake water was also studied using the EPA and Chelex-100 method. The samples were filtered before acidification or pH adjusted by buffer solution. Results show that the dissolved lead determined by both methods are nearly identical. Further oxidation using 30% hydrogen peroxide did not affect the observation. This also indicates that there is almost no colloidal or chelated lead in the filtered water and all the dissolved lead was exchangeable, or free ionic form. Finally, as can be seen from Figure 8(e), the total colloidal and or complexed lead concentration in the lake water is obtained.

4.2.2. The Analysis of Delaware Raritan Canal Water

Figure 10 shows the determination of lead in Delaware Raritan Canal. The total lead concentration is about 1.3 ppb (Figure 9(a)), and the total recoverable lead is about 1.1

ppb (Figure 9(b)). However, in the case of preconcentration with Chelex-100, there is about 0.9 ppb of lead measured (Figure 9(c)). The difference between EPA total recoverable (Figure 9(b)) and Chelex-100 method (Figure 9(c)) is 0.2 ppb. This can be attributed to the colloidal or strongly chelated lead which inhibit the absorption of lead onto the Chelex-100 resins. Further oxidation with 30% hydrogen peroxide does make up the difference (Figure 9(d)), as the strong oxidizing agent destroys the organic chelating agents. In the case of measuring dissolved lead in the canal water, the current EPA method, Chelex-100 preconcentration, and Chelex-100 with hydrogen peroxide oxidation were tested. Results show that there is almost no difference for lead concentration found by these methods. Figure 8(e) and 9(e) clearly show no colloidal lead is obvious after filtering with 0.45 μm filter paper (EPA method) in the measurement of dissolved lead. However the colloidal lead did exist in the measurement of recoverable lead. This means that the filtering process in the determination of the dissolved lead under natural pH (about 5.3 for natural waters) has removed almost all the particles which strongly retain the lead. Again the strong bound colloidal lead which would not be released by H_2O_2 was considered to be not bioavailable to the aquatic organisms (1).

4.2.3 Analysis of Trace Lead in Passaic River Water

Finally, Passaic river water, containing some suspended solid, from Newark, New Jersey was analyzed using EPA and Chelex-100 preconcentration methods. The total lead was obtained by the rigorous digestion method mentioned before. Figure 10 shows the speciation and concentrations of lead in Passaic River Water. The total lead concentration

is about 10.5 ppb (Figure 10(a)). The total recoverable lead is about 8.7 ppb (Figure 10(b)). About 2 ppb lead was unrecoverable. However after sorption with Chelex-100, from acidified then buffered at pH=5, about 7.0 ppb of lead was found (Figure 10(c)). The difference between EPA total recoverable (Figure 10(b)) and Chelex-100 method (Figure 10(c)) is 1.7 ppb. This can be attributed to the more colloidal or strongly chelated lead which inhibit the adsorption of lead onto the Chelex-100 resins. For measuring dissolved lead in the river water, the current EPA method and Chelex-100 preconcentration methods were tested. Results show that there are almost no difference for lead concentration among these methods. All the lead concentrations measured about 0.4 ppb. Figure 8(e), 9(e) and 10(e) clearly show no colloidal lead after filtering with 0.45 μm filter paper (EPA method) in the measurement of dissolved lead can be found. All the dissolved lead in natural waters were Chelex resin exchangeable. However, the colloidal lead did exist in the recoverable measurement. This means that the filtering process in the determination of the dissolved lead under natural pH (about 5.3 for natural waters) has removed almost all the particles which strongly retain the lead. However, the missing colloidal lead was considered to be not bioavailable to the aquatic organisms (Florence, 1982). After extensive study of the differentiation of the lead species in natural waters, we have found that the speciation of lead in natural waters can be achieved by using a combination of the Chelex-100 and EPA evaporation methods. The important species, ionic lead, which accounts most of the biotoxicity to the living organisms in natural waters can easily determined by using the Chelex-100 preconcentration method. This method

was also confirmed by Florence (1982) to reasonably simulate the bioavailability of ionic lead in waters

4.3 Speciation of Trace Lead in Natural Waters

The trace lead in natural waters can be speciated into operationally defined classes as shown in Figure 1. We can see that unfiltered water samples acidified and digested are analyzed for Total Lead. Figure 8, 9, 10 (a) show the total lead in Newark Lake, Delaware Raritan Canal and Passaic River Waters. When the water samples were acidified then filtered through 0.45 μm filter paper, and analyzed by EPA evaporation method the Recoverable Lead was measured. Figure 8, 9, 10 (b) show the dissolved lead in the three water samples. The difference between (a) and (b) is lead in the Suspended Solids. (as shown in figure 1. $M_s=M_t - M_d$). Acidified water samples, filtered through 0.45 μm filter paper, and adjusted pH to 5.0, are extracted with Chelex-100 resin to measure the Chelex-100 Exchangeable Lead or the total of the Ionic and Recoverable Colloidal Lead. Figure 8, 9, 10 (c) show the Chelex-100 exchangeable lead. The difference between (b) and (c) is strongly Bound Lead or Unrecoverable Colloidal Lead. (as shown in figure 1. $M_b=M_d-M_{ie}$)

Water samples without acidification, are filtered through 0.45 μm filter paper then analyzed by evaporation and Chelex-100 extraction methods to measure the Free Ionic Lead as shown in Figure 8, 9 (e), (f) and 10 (d), (e). The difference between 8, 9 (b) and (f), 10(b) and (e) is the Total Colloidal Lead.

As stated above, the trace lead in natural waters was speciated according to the operationally defined classes. The proposed analytical method gives not only the concentrations of total lead, but especially the free ionic lead, which is the most toxic.

From the analytical data of the three samples, we can see that the difference between EPA determination of dissolved Pb and developed procedure for exchangeble lead was insignificant for all three natural water samples. Howerer when strong oxiding agents are present, results would be different.

CHAPTER 5

CONCLUSION

The differentiation of lead species is a very important task in identifying the real amount of toxic lead available to the organisms in natural waters. Although a number of speciation methods have been reported, to date no literature had reported a straightforward method for speciating of trace lead in waters. In this work, studies of the speciation, preconcentration, and determination of lead in water samples were conducted. The ion chelating resin, Chelex-100, was employed with GFAAS to develop a methodology which is important for the determination of the trace lead available to the aquatic organisms in waters. Chelex-100 was chosen for use in this study not only because of its chelating ability and stability, but also because it binds lead from water in a manner similar to biomembranes. Finally, three natural waters, lake, canal and river water were examined to determine different species of lead in them. Several important conclusions were drawn from this work.

(1) An innovative method for ionic lead speciation, preconcentration, and determination in natural waters was developed. The ion chelating resin, Chelex-100 was used to extract lead from natural water. The sorption took place under static conditions. The resin was analyzed as a slurry for lead, directly by GFAAS without elution.

(2) Practically complete sorption of lead can be achieved in water samples buffered at pH=5, in 1.5 hours by 0.25g of Chelex-100 (100-200 mesh).

(3) In contrast to EPA method, strongly chelated complexes of lead (such as with EDTA) are not sorbed by Chelex-100, but weak complexes with humic acid are mostly sorbed by the Chelex-100 resin. The strong complexes are detected by the EPA method.

(4) A GFAAS temperature program for lead analysis is optimized with the pyrolysis temperature at 490°C, which produces a minimum background interference and maximum lead absorption.

(5) The above program is proven to offer the identical result in analyzing the slurried standard with and without Pd matrix modifier. Therefore, the matrix modifier is not necessary when using this program, which would save the expenditure for the expensive Pd modifier.

(6) A 15% absorption difference between the injections of the supernatant and slurry standards are found. Therefore, it is always important to use a matrix-matched calibration as the basis for analysis.

(7) The proposed analysis method is reproducible and accurate, the detection limit of the preconcentration process with GFAAS is found to be 0.059 μg/l.

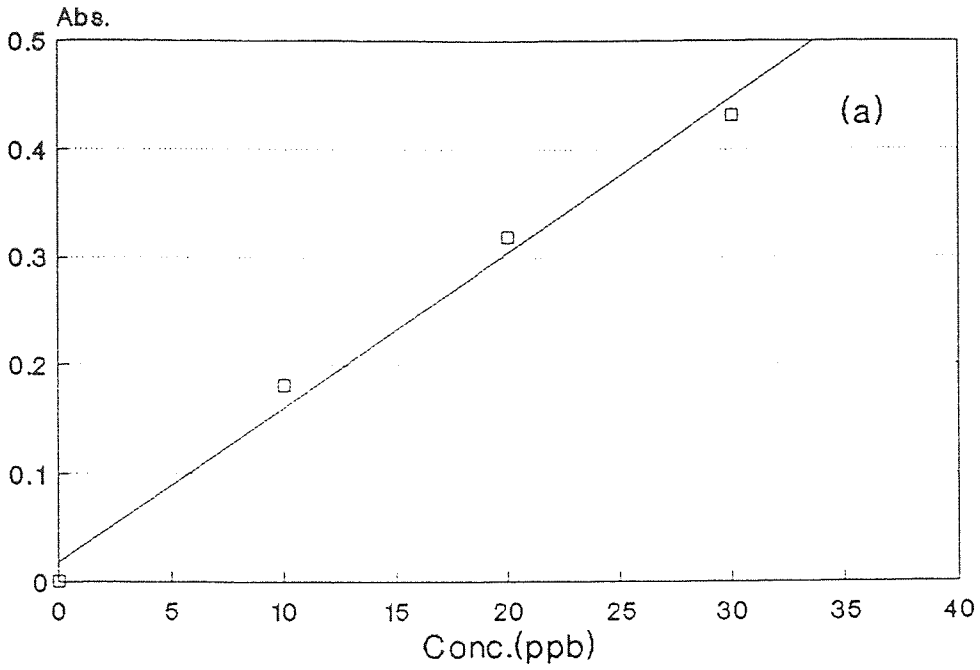
(8) The study of Newark tap water using Chelex and evaporation method clearly indicates that free ionic lead is the only species of lead existing in the tap water.

(9) Determination of the species of lead in lake, canal and river waters shows that the EPA and proposed Chelex-100 preconcentration methods give different results. The difference is attributed to the missing colloidal lead which can not be extracted by Chelex-100 resin.

(10) Combination of the EPA method with proposed Chelex preconcentration method can speciate lead forms in natural waters.

APPENDIX I

LIST OF FIGURES



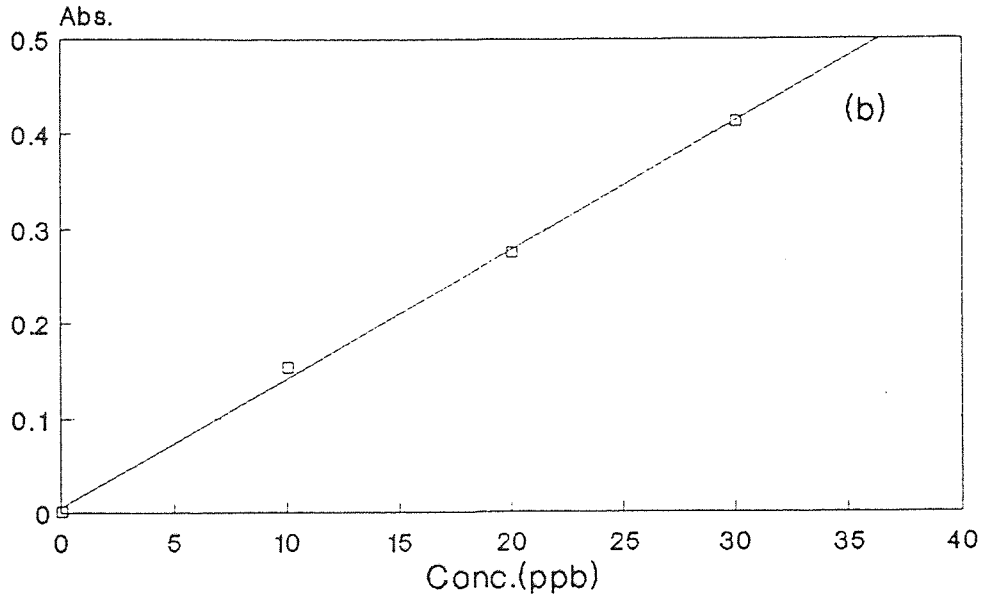


Figure 2. Lead Absorption in Supernatant Solution Containing 5% HNO3 (a) and in Chelex-100 Slurry in 5% HNO3 (b)

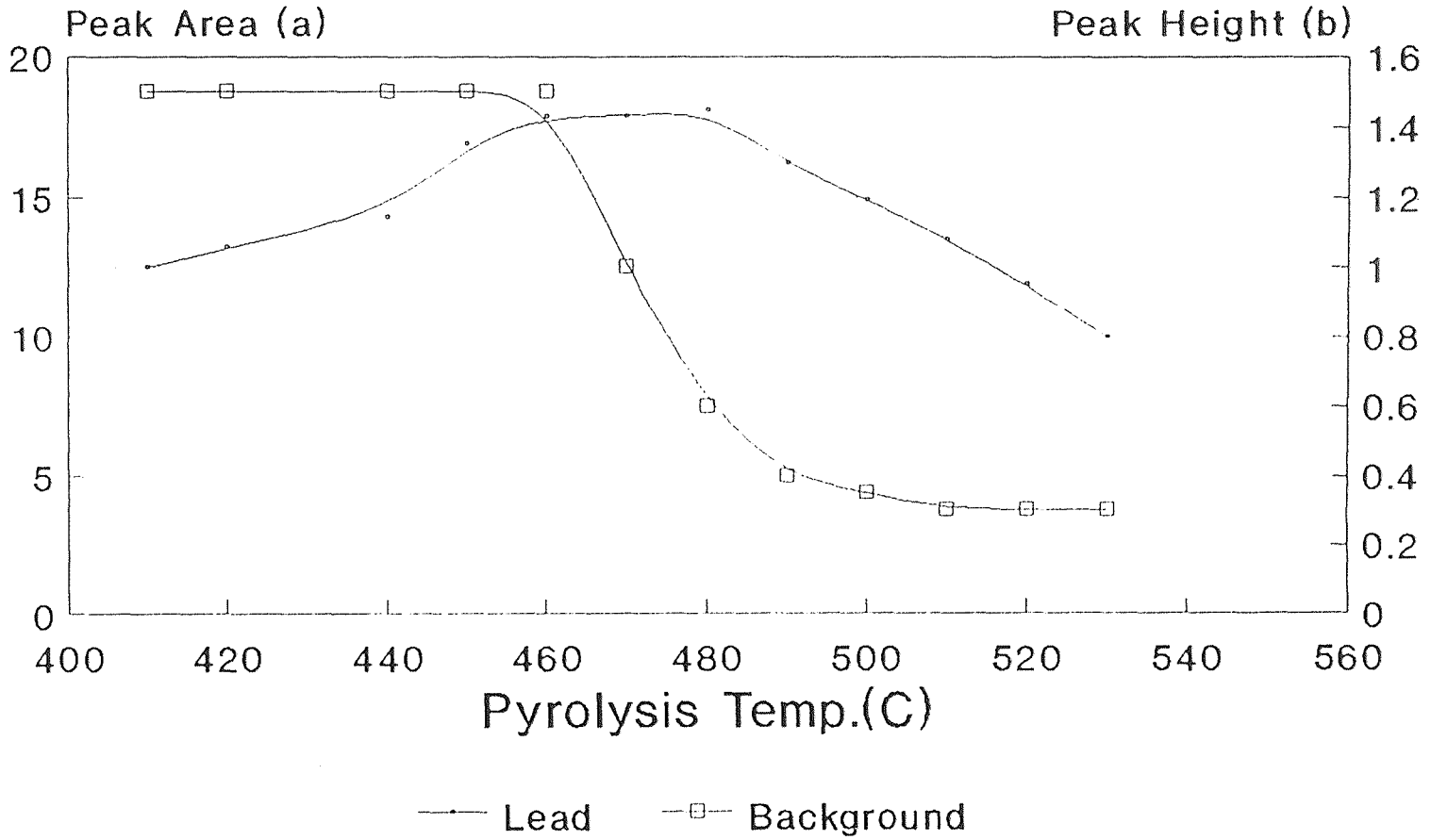


Figure 3. Effect of Pyrolysis temperatur
on the Absorption of Pb and Smith
Hieftje Background in Slurry

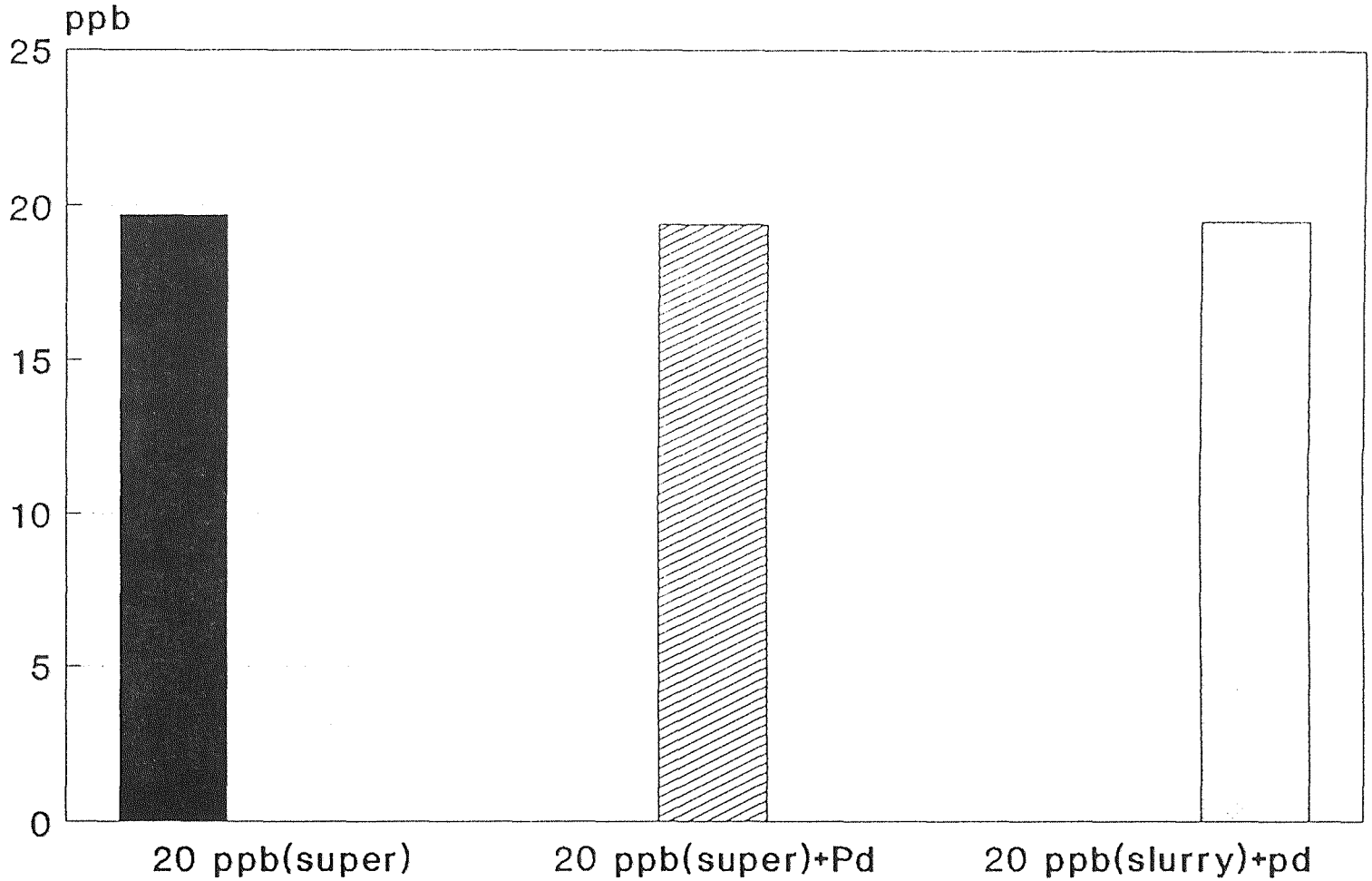


Figure 4. Comparison of Lead Sample with and without Pd Modifier at 217 nm

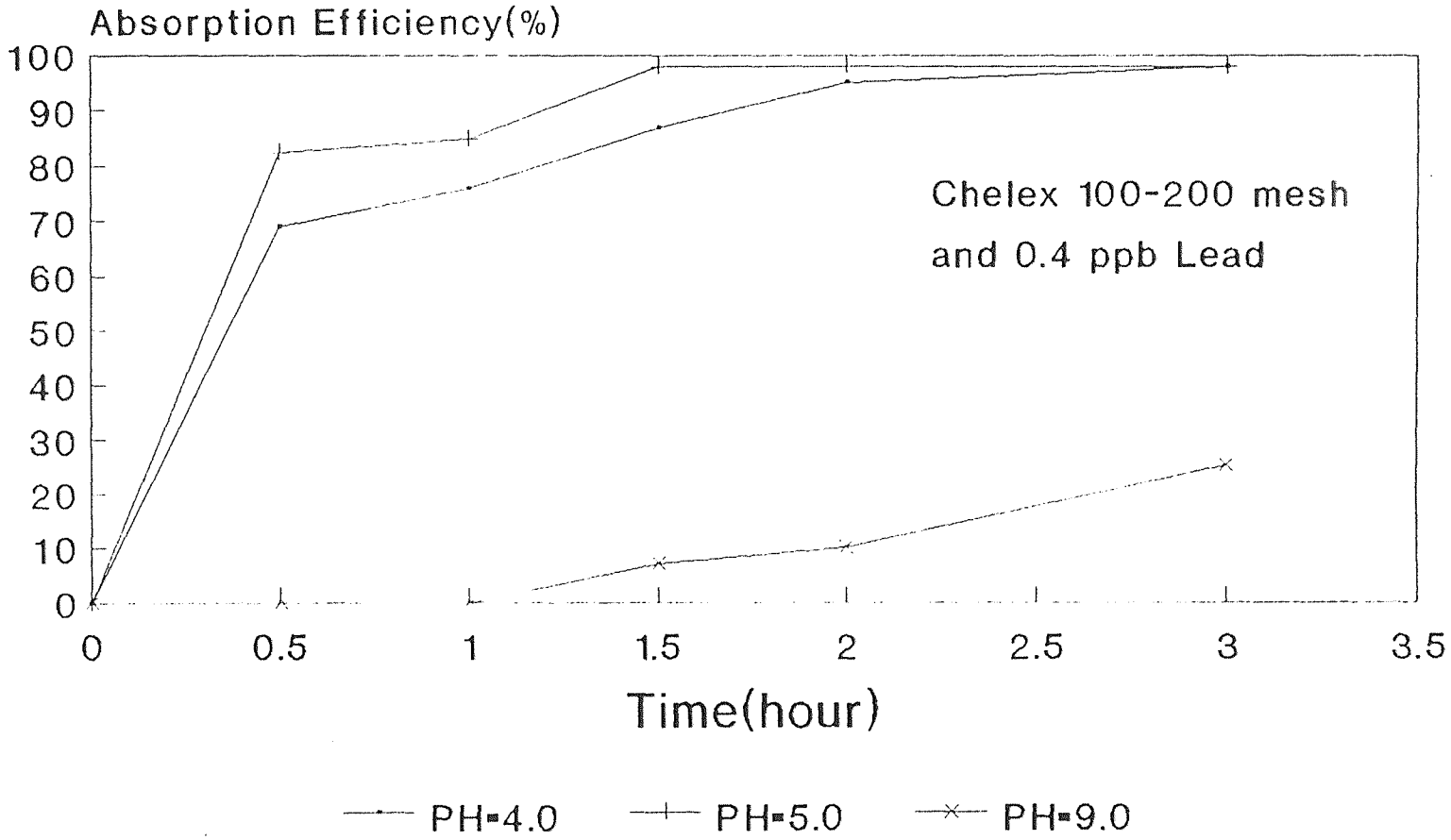


Figure 5. Time Effect on the Absorption of Lead in Aqueous Solution Using Chelex Resin

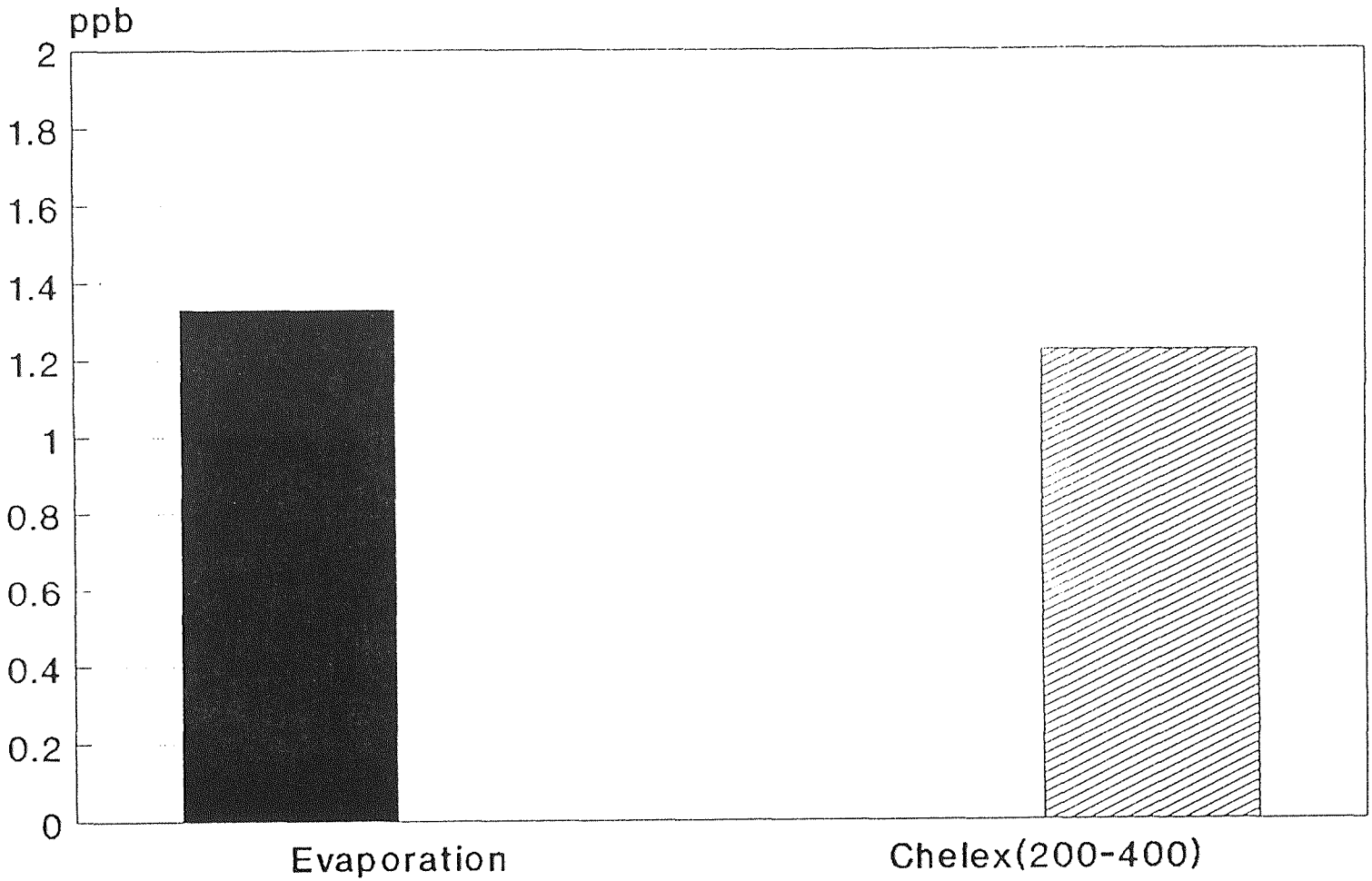


Figure 6. Pb Concentration in Newark Tap Water

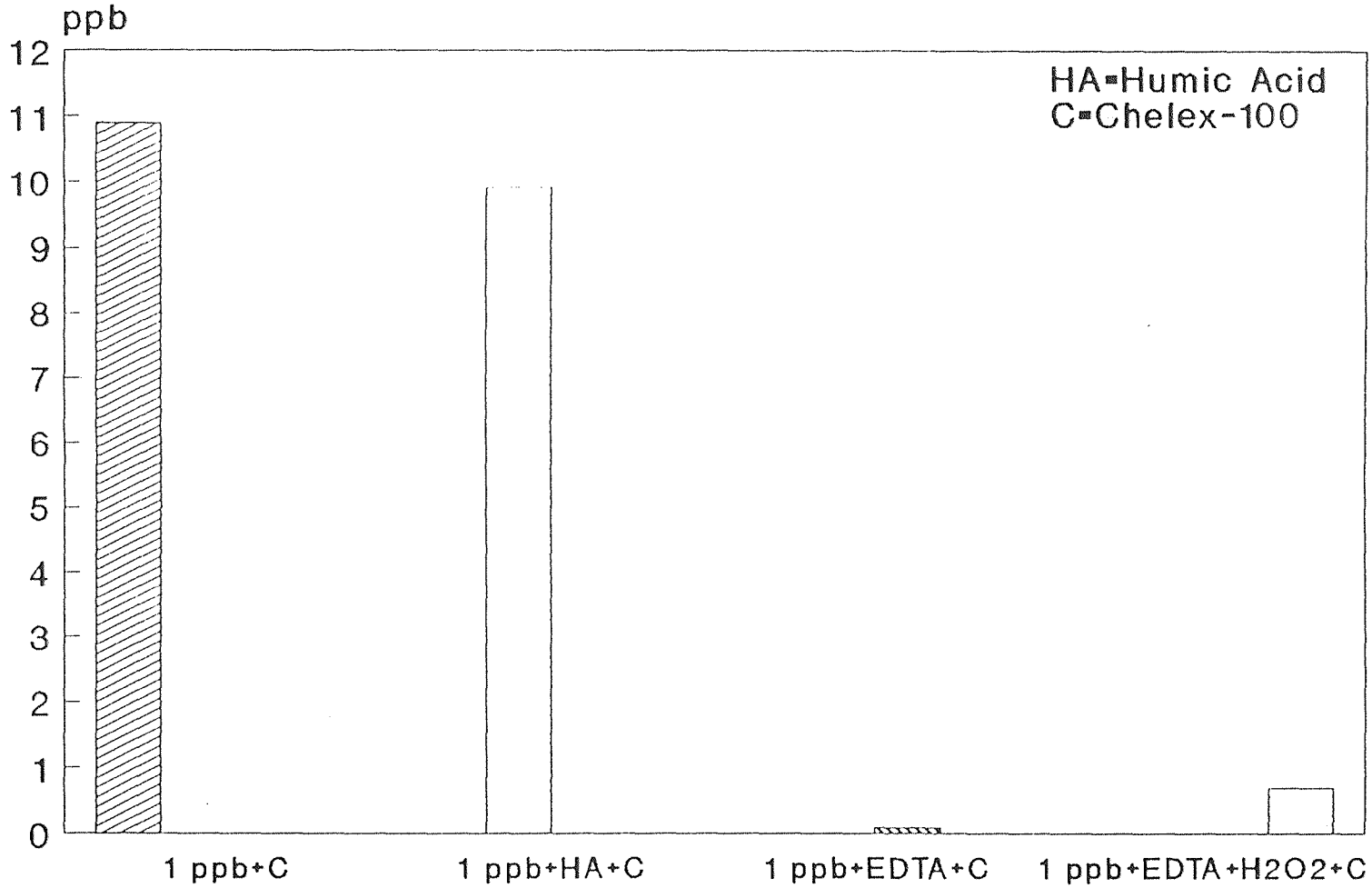


Figure 7. Lead Absorption Using Chelex with added EDTA and Humic Acid

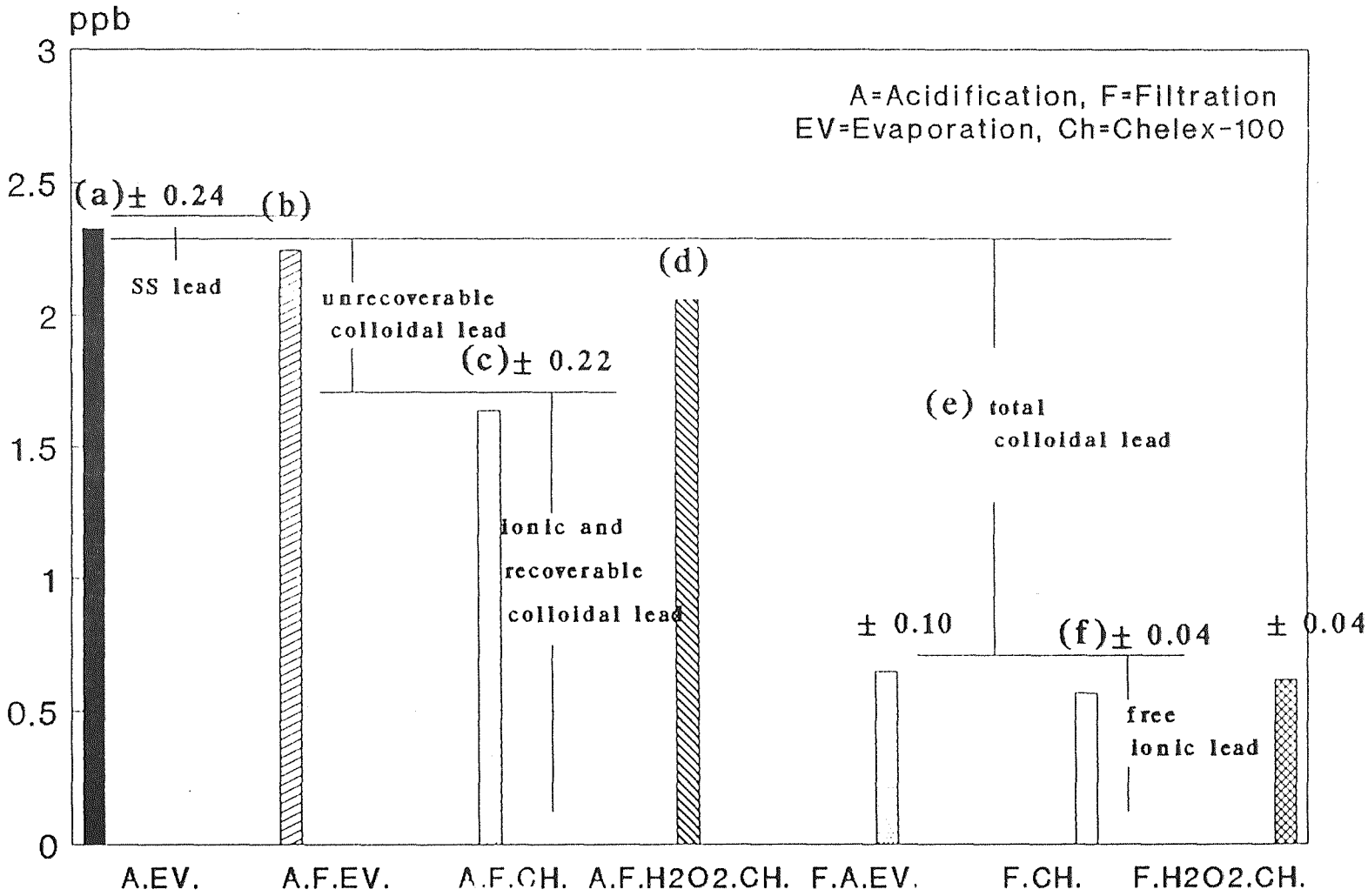


Figure 8. Lead Concentration in Newark Lake Water

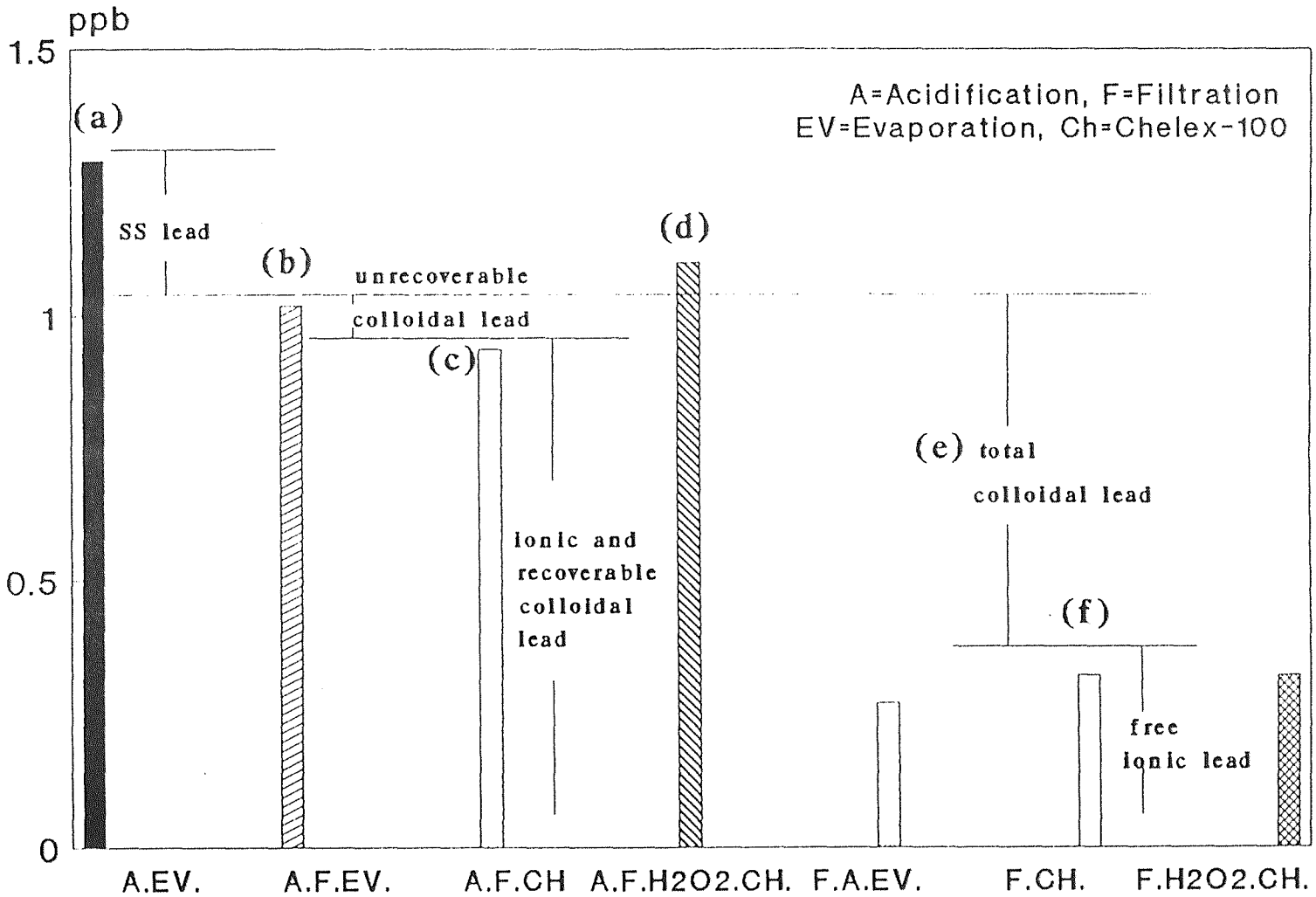


Figure 9. Lead Concentration in Delaware Raritan Canal

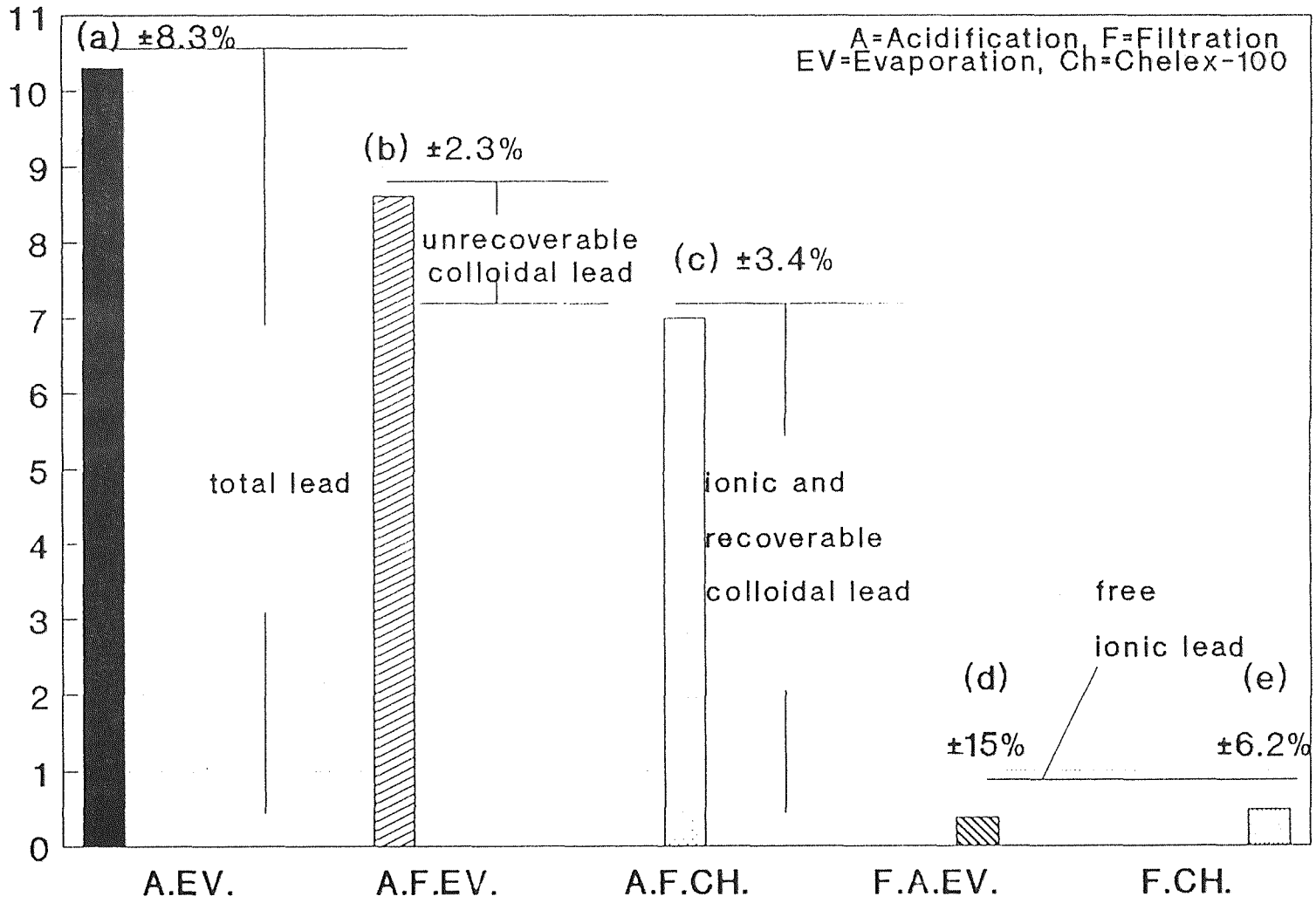


Figure 10. Lead Concentration in Passaic River Water

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