Research Technical Completion Report

ARSENIC SPECIATION AND WATER POLLUTION ASSOCIATED WITH MINING IN THE COEUR D'ALENE MINING DISTRICT, IDAHO

By
C.M. Wai
W.M. Mok
Department of Chemistry

Idaho Water Resources Research Institute
University of Idaho
Moscow, Idaho 83843

October, 1985

The research on which this report is based was financed in part by the United States Department of the Interior as authorized by the Water Research and Development Act of 1978 (P.L. 95-467).

Research Technical Completion Report

G903-06

ARSENIC SPECIATION AND WATER POLLUTION ASSOCIATED WITH MINING IN THE COEUR D'ALENE MINING DISTRICT, IDAHO

By

C. M. Wai

W. M. Mok

Department of Chemistry

Submitted to: U.S. Geological Survey
United States Department of the Interior
Washington, D.C. 20242

Idaho Water Resources Research Institute
University of Idaho
Moscow, Idaho 83843

October, 1985

TABLE OF CONTENTS

Page

LIST OF FIGURES

LIST OF TABLES

ABSTRACT

The Coeur d'Alene Mining District is one of the major silver, lead, and zinc producing areas in the United States. The area also encompasses some of the foremost pollution problems in Idaho. The primary problems of environmental concern in this area today are the operating and abandoned tailings piles scattered throughout the district, the huge quantities of mine wastes accumulated along the streams, and the acid mine drainage from existing mines in the district. From previous studies, it is known that mine wastes containing iron sulfide (pyrite) in this area are capable of producing acid waters under oxidizing conditions. The redox status of ground water is an important factor in determining the degree of acid water formation and subsequent leaching of metals from mine tailings and ore bodies in this mining area. A new approach for measurement of the redox status of ground water involving analysis of water samples for concentrations of two arsenic species, As(V) and As(III), has been studied in this project. Based on thermodynamic equilibrium considerations, the apparent redox conditions can be evaluated from measured ratios of As(V)/As(III) in water.

A simple solvent extraction method has been developed for the separation of arsenic species in mine waters using ammonium pyrrolidinedthiocarbamate (APDTC) as a chelating agent. The APDTC extraction method combined with neutron activation technique provides a very sensitive method for determining arsenic species in natural water systems. A detection limit of 0.1 ppb for the arsenic species in natural waters can be easily achieved using this method. This

analytical method for arsenic speciation study is in the process of being published by ANALYTICAL CHEMISTRY.

Ground water samples were collected from a major lead-zinc mine (the Bunker Hill Mine) and from other locations of the Coeur d'Alene Mining District to study the relationships between the arsenic species and other water quality data. The As(V)/As(III) ratios in ground waters collected from the Bunker Hill Mine were found to vary by more than two orders of magnitude indicating a wide range of redox conditions existing in the mine. The quality of ground water in the mine is strongly correlated with the ratio of As(V)/As(III) found in the system. Good quality waters were generally associated with low ratios (<1) of As(V)/As(III). The ratio of the arsenic species and the concentrations of dissolved metals in the mine waters varied considerably with time. During the spring run-off, very high As(V)/As(III) ratios were observed in some poor quality waters presumably due to leaching of oxidized ores and mine wastes in certain locations of the upper levels of the mine. In the late summer, the ratio of As(V)/As(III) decreased as the system became more anaerobic and the water quality showed significant improvement correspondingly. The distribution of the arsenic species appears to be a useful chemical indicator to evaluate the potential of acid water formation and associated metal pollution problems in the ground water systems of this and other similar mining areas.

INTRODUCTION

Coeur d'Alene Mining District

Mining is the main industry in the basin of the South Fork of the Coeur d'Alene River in northern Idaho. This mining district is one of the major silver, lead, and zinc producing areas in the United States. The area also encompasses some of the foremost pollution problems in Idaho (Davis, 1978). Most of the pollution of the Coeur d'Alene River occurred before the construction and operation of mine tailings ponds in 1968 (Mink et al., 1971). The settling ponds have greatly reduced the discharge of suspended solids into the river. In the past decade, state and federal agencies have enforced more stringent water quality standards that include requiring the reduction of dissolved heavy metal concentrations in waste discharges. The primary problems of environmental concern in this area today are the operating and abandoned tailings piles scattered throughout the district, the huge quantities of mine wastes accumulated along the streams, and the acid mine drainage from existing mines in the district.

The major sulfide minerals mined in this area are galena (PbS) and sphalerite (Zns). Other sulfide minerals including pyrite (FeS_2), chalcopyrite ($CuFeS_2$), arsenopyrite (FeAsS), and tetrahedrite ($(Cu,Fe,Zn,Ag)_{12}sb_4S_3$) are often found with the lead and zinc sulfides in the ore. It is known that mine wastes and mill tailings containing iron sulfied (pyrite) are capable of producing acid waters under oxidizing conditions (Appalachian Regional Commission, 1971) (Smith, et al., 1970). For example, Wai et al. have shown that oxidation of pyrite to sulfuric acid and compounds of iron in a single ore body in the upper part of a major lead-zinc mine (Bunker Hill Mine) in this area is a main source responsible for the production of acid water in the mine (Wai et al., 1980). In another study of the ground water quality in the Smelterville Flats, Marcy has suggested that the oxidation reduction environment of the sediments can strongly affect the metal concentrations in the aqueous phase (Marcy, 1979). The sediments of the Smelterville Flats consist primarily of mill tailings deposited by the past decades of mining operations in this area. From these previous studies, it is clear that the redox status of ground water is an important factor in determining the degree of acid water formation and subsequent leaching of metals from mine tailings and ore bodies in the Coeur d'Alene Mining District.

Measurement of Redox Potential Using Arsenic Species

Direct in-situ measurement of Eh of ground water by means of an inert metallic electrode generally is difficult. Spurious and uninterpretable data are commonly acquired due to drift in electrode potential readings as a function of time or as readings that arise from potentials generated by minor redox species in the aqueous phase. An alternative approach for measurement of the redox status of ground water involves analysis of water samples for concentrations of two or more dissolved species of the same element that is present in two different oxidation states. Arsenic, for example, occurs in ground water in the two oxidation states As(III) and AS(V); the relative concentration of these two species may be used to measure the redox potential of ground water systems.

Using published thermodynamic data for arsenic species and the assumption of redox equilibrium, Cherry et al have shown that the apparent redox condition, as pH or Eh, can be computed from measured concentrations of As(III) and As(V) species in water (Cherry, 1979). The redox domain for the arsenic couple is largest at high total dissolved arsenic concentrations, but even at concentrations as low as 1-10 ppb the domain has significant extent. These authors also have suggested that ground water probably is best suited for use of arsenic speciation as a redox indicator.

The concentrations of total arsenic in ground waters and in mine waters generally vary from ppb to ppm levels. A reliable and sensitive method which is capable of measuring As(III) and As(V) at ppb level is needed in order to study the variation of arsenic species in ground water systems. During the past year, we have developed a simple solvent extraction method for the separation of As(III) and As(V) using ammonium pyrrolidinedithiocarbamate (APDC) as a chelating agent. After extraction, the arsenic species can be measured by neutron activation analysis (NAA). This solvent extraction method combined with NAA provides a very sensitive technique for studying chemical speciation of arsenic in natural waters. The details of this analytical method for determining arsenic species in water are given in the next section.

Scope of this Study

This project was designed to study the feasibility of using the arsenic species as a chemical indicator for predicting acid water production and the associated metal pollution problems existing in the ground water systems of the Coeur d'Alene Mining District. The first part of this report describes a solvent extraction method developed from the project for the separation of As(V) and As(III) in ground water samples and the techniques of analyzing the arsenic species. The second part of this report presents the ground water quality data collected from two locations of the mining district and shows the correlations between the ratios of As(V)/As(III) and other water quality parameters found in these waters. The locations of the study area, the Bunker Hill Mine and the Smelterville Flats, are shown in Figures 1 and 2. The Bunker Hill Mine near Kellogg, Idaho, extends to a depth of nearly one mile and includes more than 150 miles of underground workings within a highly faulted block of massive quartzites interbedded with argillites and argillaceous quartzites. Water samples were collected from several selected locations in the upper levels of the mine for this study. The ground water problems of the Smelterville Flats have been previously studied by A.D. Marcy using a network of piezometers (Marcy, 1979). A few of the piesometers installed by the previous study are still in working conditions. Water samples were taken from these piezometers for this study. Some surface water samples were also collected from different locations of the Coeur d'Alene River for this arsenic speciation study. The possibility of using the arsenic speciation data for predicting metal pollution problems in the ground water systems of this mining area is discussed.

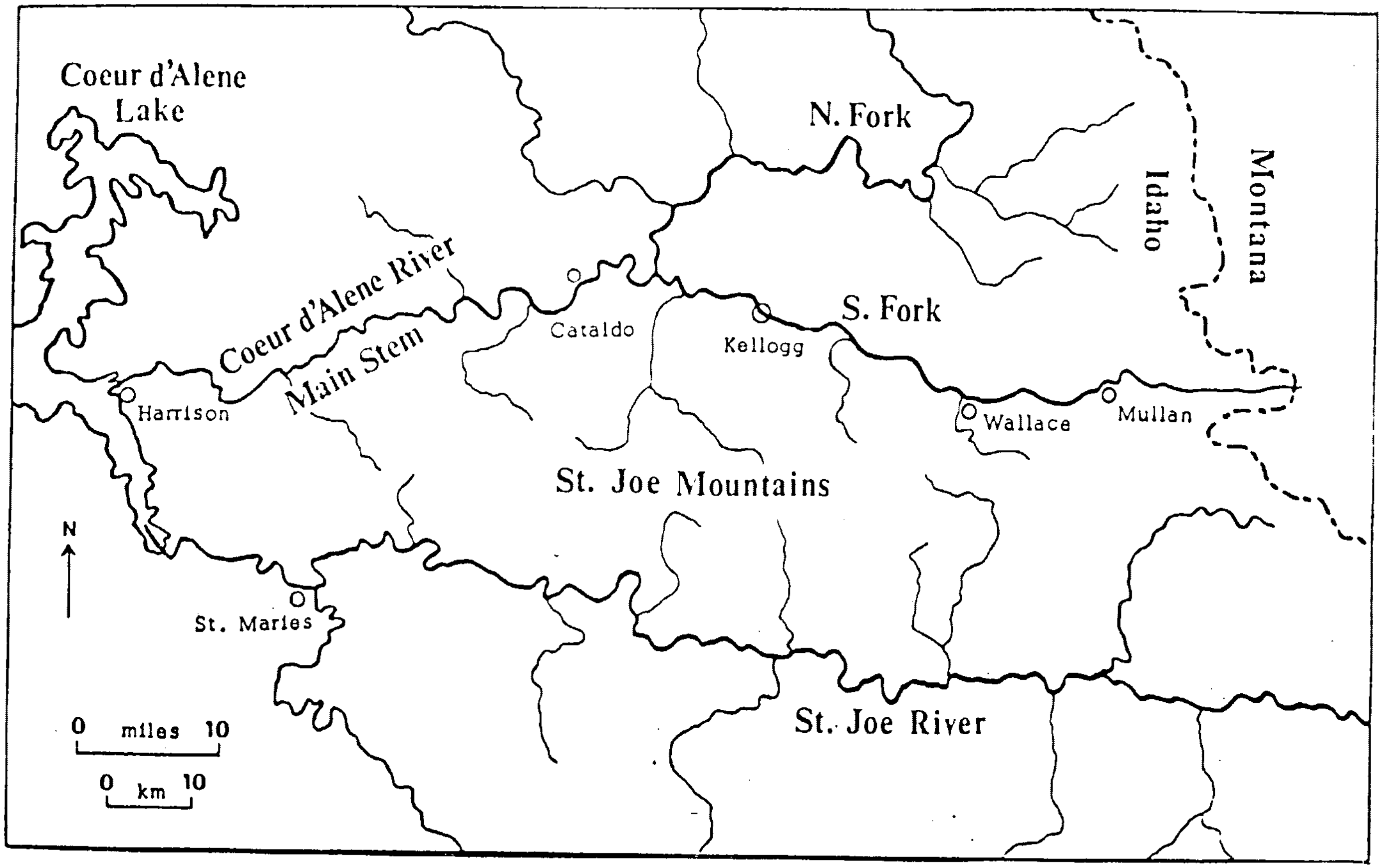


Figure 1. Location of the Coeur d'Alene River Basin in North Idaho.

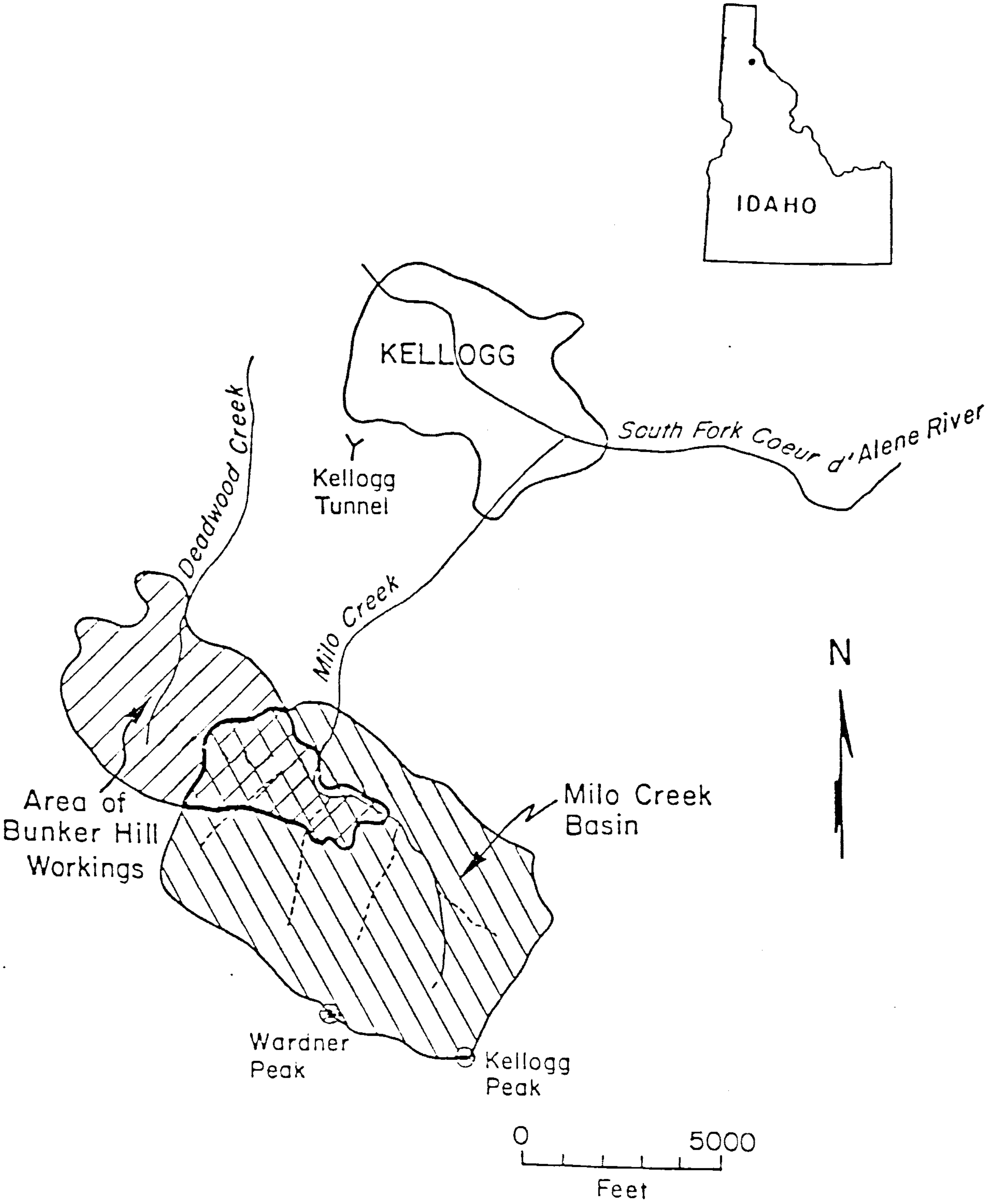
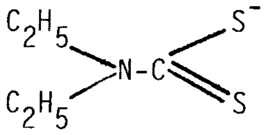


Figure 2. Location of Bunker Hill Mine, Kellogg, Idaho.

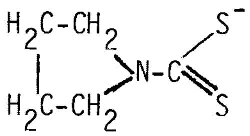
SEPARATION PROCEDURES AND ANALYTICAL TECHNIQUES FOR ARSENIC SPECIATION STUDIES

Extraction of Arsenic(III) and Arsenic(V) from Natural Waters with Dithiocarbamates

The derivatives of dithiocarbamic acid are known to chelate with a large number of metal ions to form complexes which are soluble in organic solvents. Sodium diethyldithiocarbamate (NaDDTC) and ammonium pyrrolidinedithiocarbamate (APDTC) are two of the dithiocarbamate derivatives which have been widely used as chelating agents for preconcentration and separation of trace metals from aqueous solutions (Lo et al., 1983) (Yu et al., 1983).



DDTC



PDTC

One unique feature of this extraction method is that the alkali metals, the alkaline earth metals, the halogens, aluminum, sulfate, and phosphate which do not complex with dithiocarbamates can be simultaneously removed during the extraction. The extraction method, therefore, not only concentrates trace metals but also eliminates interfering matrix species present in natural water systems. As a result, the sensitivity and the accuracy of trace metal analysis can be significantly improved. The efficiency of dithiocarbamate extraction depends on the pH of solution and varies considerably from one metal to another. The effects of pH on the extraction of the following metals-cadmium, cobalt, copper, iron, lead, manganese, nickel, and zinc with a mixture of APDTC and NaDDTC into chloroform are shown in

Figure 3. By careful control of pH of solution, selective extraction of certain metals may be achieved.

Another interesting feature of dithiocarbamate extraction is that the stability of a metal-dithiocarbamate complex depends on the oxidation state of the metal ions involved. For example, both NaDDTC and APDTC form stable complexes with As(III) but not with As(V). Therefore, the former can be separated from the latter by extracting with these chelating agents into an oganic phase under proper conditions. The pH dependence on the extraction of As(III) with APDTC into chloroform is shown in Figure 4. Quantitative extraction of As(III) can be achieved from pH 0.8 to about 5 after several minutes of shaking. Extraction of As(V) with APDTC was found negligible at $pH>1$, but did show a few percent of extraction at $pH\leq1$. Therefore, to separate As(III) from As(V), the extraction should be carried out at $pH>1$. We chose to extract As(III) at pH 1.5 because at this pH the extraction of iron, manganese, titanium, and zinc can also be minimized. The presence of large amounts of these metals in a sample will interfere with the determination of trace quantities of arsenic. The pH dependence curve for the extraction of As(III) with NaDDTC is similar to the one with APDTC shown in Figure 4. However, NaDDTC is unstable at low pH and consequently may result in incomplete extraction of As(III). For this reason, NaDDTC is not recommended in our procedure for the extraction of arsenic.

In highly polluted ground waters, the degree of extraction of As(III) with APDTC may be significantly reduced due to competition caused by other metal ions present in the system. Such interferences can be reduced by the use of EDTA (ethylenediaminetetracetic acid) as

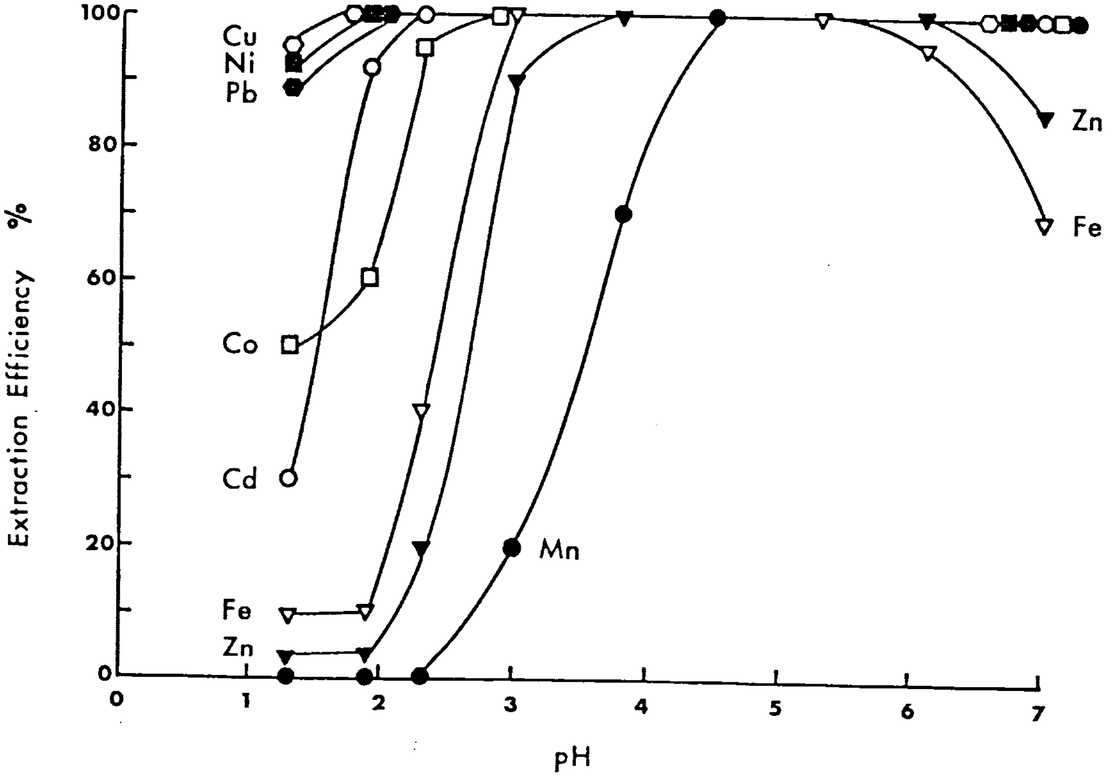


Figure 3. pH dependence of the extraction of Cd, Co, Cu, Fe, Pb, Mn, Ni and Zn with a mixture of APDTC and NaDDTC into chloroform.

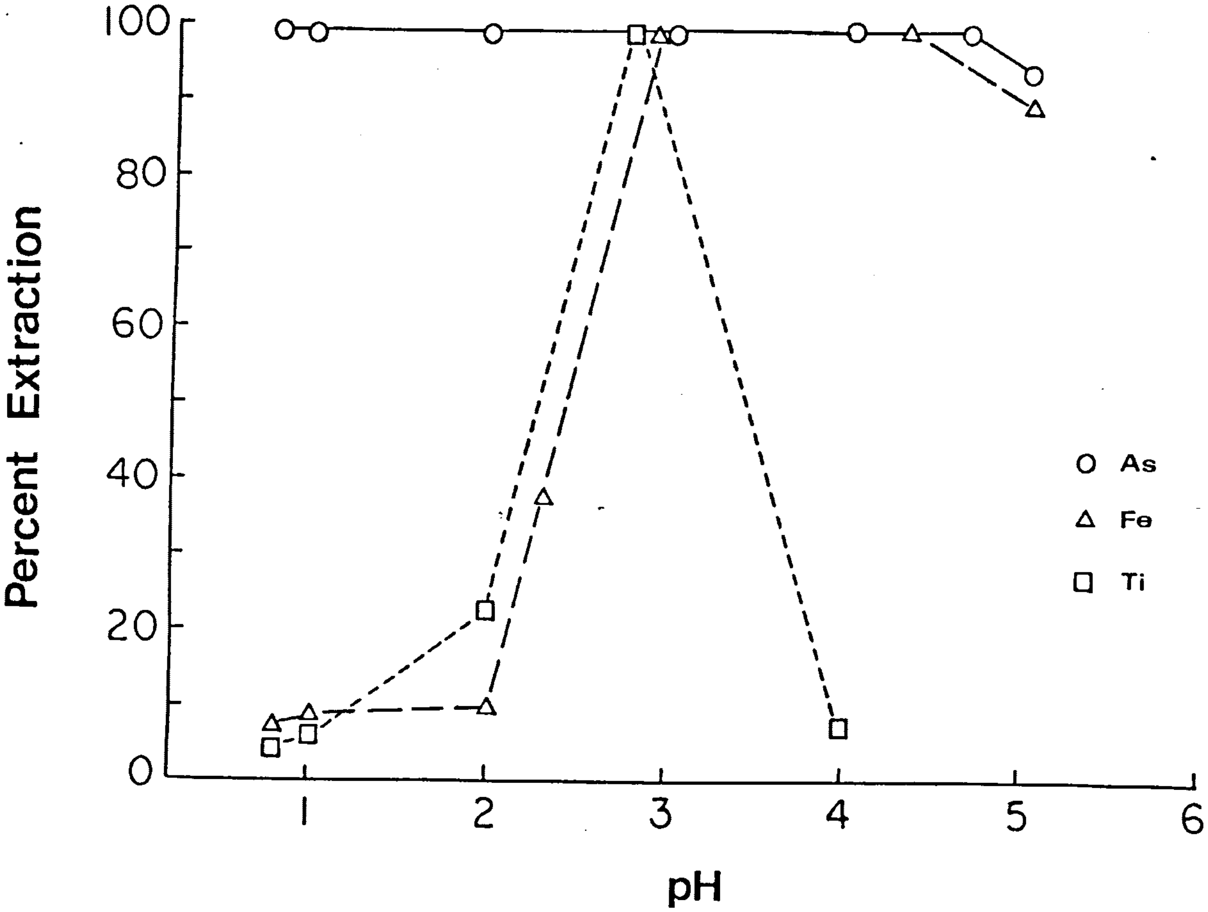


Figure 4. pH dependence of the extraction of As(III) and two other metals, Fe and Ti, with APDTC from aqueous phase into chloroform.

a masking agent. Table I shows the results of APDTC extraction carried out with and without the masking agent (disodium salt of EDTA) in a mine water spiked with ppb levels of arsenic. In the absence of EDTA, arsenic recovery may not be satisfactory, depending upon the water quality. In our experiments, a concentration of about 0.5% EDTA is used to eliminate interferences caused by other concomitant metal ions in complex systems such as acid mine waters.

Because only As(III) can be extracted by dithiocarbamates, reduction of As(V) to As(III) is necessary in order to determine total As in water. Sodium thiosulfate, $Na_2S_2O_3$, is an effective reducing agent for As(V). Based on our experiments with spiked As(V) samples, a 0.2% sodium thiosulfate solution at pH 1 provides a satisfactory condition for total reduction of As(V) in natural water samples. Our recommended procedure is to shake the solution for one minute after the addition of thiosulfate followed by a waiting period of five minutes to allow for complete reduction. The difference in As(III) concentrations between two aliquots of a water sample with and without reduction gives the concentration of As(V) in the sample. Another reducing agent tested, potassium iodide, KI, was found less effective than thiosulfate. A mixture of potassium iodide and sodium thiosulfate also did not appear to be better than thiosulfate alone.

The As-PDTC complex in chloroform can be back-extracted into a nitric acid solution for instrumental analysis. To effectively back-extract arsenic, the concentration of nitric acid must be 30% or greater. Incomplete extraction of As may result if the acid concentration is less than 30%. Quantitative recovery of arsenic can be achieved in 10 minutes of shaking with this acid concentration. The

Table I. Effect of EDTA as masking agent on dithiocarbamate extraction of As from mine water

Sample	As(III) added (ng)	As(V) added (ng)	% Recovery of As(III)	% Recovery of As(V)
Mine water without EDTA	500		81.1±1.9	
Mine water with EDTA	400		102.2±1.6	
Mine water with EDTA		400		107.0±1.9

Sample Volume: 50 mL. The results are corrected for the blank As value in sample.

details of the APDTC extraction, the reduction procedure, and the nitric acid back-extraction procedure are given in a manuscript attached in the Appendix. The attached manuscript entitled "Extraction of Arsenic(III) and Arsenic(V) from Natural Waters for Neutron Activation Analysis" has been accepted for publication by Analytical Chemistry and is scheduled to appear in the February, 1986 issue of the journal.

Instrumental Techniques for Analyzing Arsenic in Natural Water Samples

The concentrations of total arsenic in most natural water systems are in the range of 10^{-6} to 10^{-7}g/L (Wedepohl, 1978). In polluted ground waters and mine waters, the total arsenic concentrations may be as high as 10^{-3}g/L. Analytical methods capable of measuring nanogram levels of As(III) and As(V) are necessary for studying the chemistry of arsenic species in aquatic environments. Several analytical techniques such as anodic stripping voltammetry, graphite furnace atomic absorption spectrometry, and neutron activation analysis have the required sensitivity for analyzing such low levels of arsenic under interference-free conditions. However, in real water samples, chemical and spectral interferences from other concomitant elements in the system may place severe restrictions on the detection limits of arsenic using these techniques.

Neutron activation is one of the most sensitive techniques for trace metal analysis. In this technique, the elements to be determined in a sample are made radioactive by irradiating the sample with neutrons, and the radionuclides formed (characterized by their half-lives) give off their characteristic radiations such as gamma rays, which are then identified and measured. The activity or number of counts of detected gamma rays of a particular energy is directly proportional to the disintegration rate of the radionuclide, which in turn is directly proportional to the amount of its parent isotope in the sample. Thus, measurement of the radionuclide gamma rays provides a measure of the total concentration of the parent element. In actual neutron activation analysis, a comparative method is used to quantify the concentration of an element. In the comparative method an element x in a sample and a known amount of the same element x as a standard are irradiated together, and both sample and standard are counted under exactly the same conditions by the same radiation detector. The weight of x in the sample can be calculated from the following equation:

$$\frac{\text{weight of element x in sample}}{\text{weight of element x in standard}} = \frac{\text{activity of x in sample}}{\text{activity of x in standard}}$$

The activities of x in the sample and in the standard should be corrected for decay using the radioactive decay law. Under interference-free conditions, neutron activation analysis can easily detect nanogram levels of arsenic in a sample with good accuracy. We chose this technique to analyze arsenic because of its high sensitivity, and the facilities for neutron activation analysis, including a large volume coaxial ORTECT Ge(Li) detector, a 4096-channel pulse height analyzer, and software for data processing, are available in our laboratory. A 1-MW TRIGA reactor is also conveniently located at the Nuclear Radiation Center of Washington State University (which is about eight miles away from our campus) for sample irradiation. The radioisotope ^{76}As produced from the thermal neutron capture process ^{75}As(n,γ)^{76}As, has a half-life of 26.4 hours and emits a gamma ray of 559 keV which can be used for its identification and quantification.

Detailed descriptions of the neutron activation procedures for determination of arsenic in water samples are given in the manuscript attached in the Appendix. The absolute detection limit of arsenic under our experimental conditions is estimated to be 1 nanogram (10^{-9} gram). The extraction procedure can easily provide a concentration factor of 10. The proposed extraction method, combined with neutron activation analysis, should be able to detect arsenic in natural waters at the 10^{-1} μg/L level (0.1 ppb level) with a reasonable accuracy.

The proposed method for arsenic extraction and neutron activation analysis has been applied to the analysis of two standard reference materials to test the accuracy of our analytical procedure. These standard reference materials are: (1) U.S. NBS Standard River Water SRM 1643a and (2) Standard Seawater NASS-1 from the National Research Council of Canada. The certified values of arsenic in these reference materials are 76±7 μg/L for SRM 1643a and 1.65±0.19 μg/L for NASS-1. Because the certified values do not specify the oxidation state of As, our analysis of these reference materials followed the procedure for total arsenic determination described above. The results of our analysis are given in Table II. Our results agree well with the certified values indicating that our method for total arsenic determination is reasonably accurate.

The accuracy of this extraction method for differentiating As(III) and As(V) species in water could not be thoroughly evaluated because no standard waters containing known amounts of the two arsenic species were available. However, we have tested the accuracy of our method for arsenic speciation using natural waters spiked with known amounts of AS(III) and As(V). Satisfactory recoveries (>90%) of both spiked

Table II. Arsenic in standard reference materials

Reference Material	Certified As Value	As Value Obtained By This Study[a]
SRM 1643a	76±7 μg/L	73±2 μg/L[b]
NASS-1	1.65±0.19 μg/L	1.55±0.05 μg/L

a. Triplicate analyses.

b. Spiked in a water sample collected from the Bunker Hill Mine.

species were observed in most cases as shown in Table III. These results suggest that our extraction method is also reasonably reliable for arsenic speciation studies.

Arsenic(III)/Arsenic(V) Ratios in Natural Water Systems

Arsenic is ubiquitous. The average value of arsenic in soils probably lies in the range of 5-10 ppm. Williams and Whetstone determined arsenic colorimetrically in various soils of the United States (Williams et al., 1940). Their results showed that about 30% of the soils contained less than 5 ppm As, about 50% contained 5 to 10 ppm, and about 20% contained more than 10 ppm. Rain water contains about 1 ppb As. The average As for surface seawater is about 2 ppb. Water samples collected from the Columbia River near Hanford showed an average value of 1.63 ppb As with a range of 0.87 - 4.87 ppb (Silker, 1964). Arsenic in ground waters generally varied from several tenth ppb to several ppb. The U.S. Public Health Service (USPHS) sets 50 ppb as the maximal permissible concentration of arsenic in drinking water.

Little information is available regarding arsenic species in the aquatic environment of the Coeur d'Alene Mining District. Arsenic can exist in natural water systems in different forms depending on the pE and pH of solution. Figure 5 shows the pE-pH diagram of As-H_2O system at 25^0 with 50 μg/L of total arsenic. In slightly acidic or neutral solutions, the higher oxzidation species, As(V), is in the form of H_2AsO_4- and the lower oxidation species, As(III), is in the form of H_3AsO_3 (Cherry, et al., 1979). In theory, knowing the relative concentrations of the two arsenic species and the pH of solution, one can calculate pE of the system by the following equation:

Table III. Recovery of spiked As(III) and As(V) from different natural water systems

Sample	As(III) added(ng)	As(V) added(ng)	% Recovery of As(III)	%Recovery of As(V)	%Recovery of Total As
River water (50 mL)	400		91.8±4.6		
	800	400	104.0±2.1		100.2±2.1
	400	400	107.4±2.5		99.1±2.5
	400	800	103.5±2.5		96.0±2.1
Seawater (100 mL)	400	400	72.4±2.0		88.5±1.8
	800	800	71.4±1.4		98.3±1.8
Mine water (A)		400		93.2±2.6	
Mine water (B)	400		86.5±1.6		
Mine water (C)	400		94.7±1.9		
Mine water (D)	400		107.2±1.5		

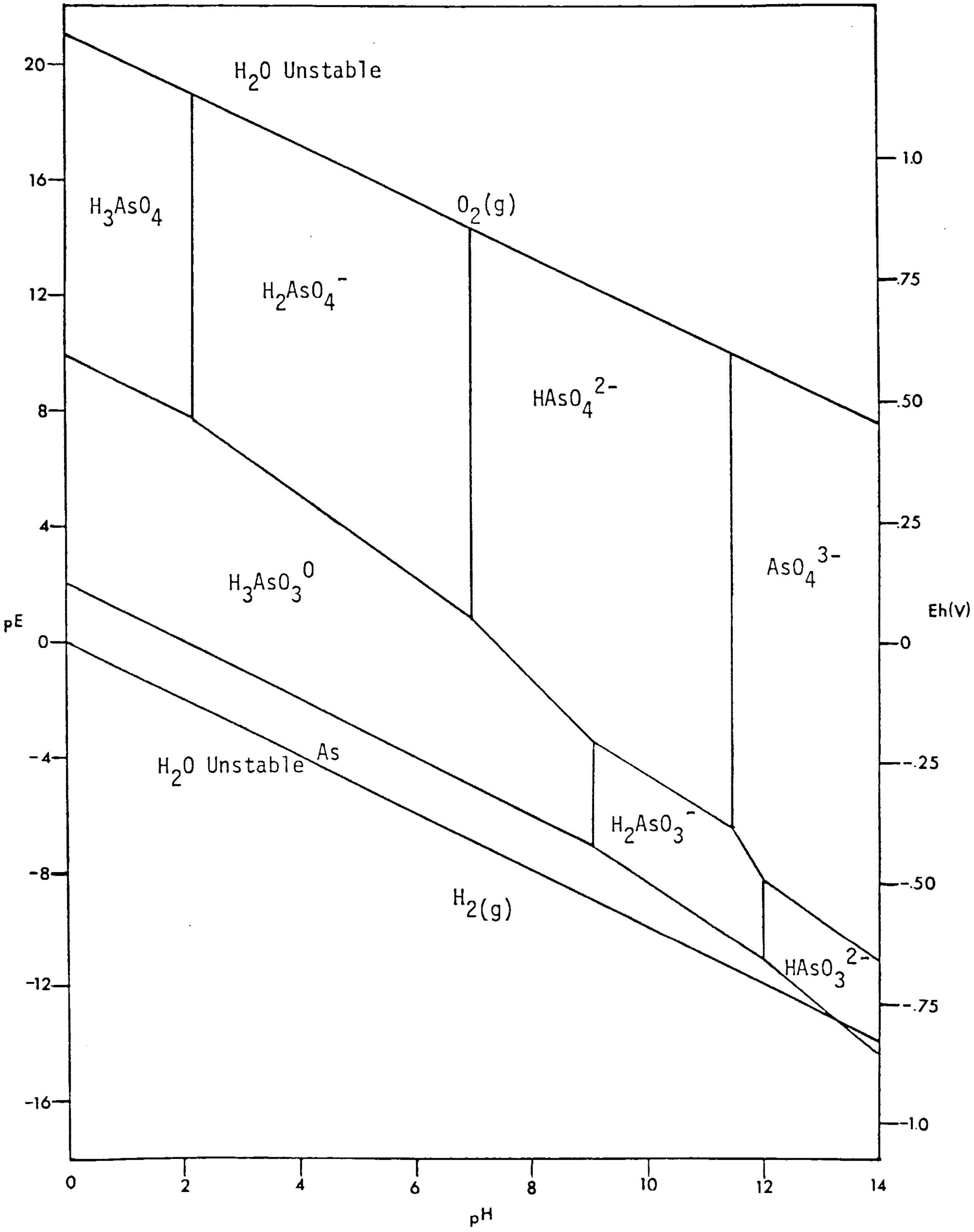


Figure 5. pE-pH diagram for the As-H_2O system at 25°C with total As species of 50 µg/L.

$$pE = 11 - 1.5\ pH - 0.5\ \log[H_3AsO_3]/H_2AsO_4^-] \qquad (1)$$

Equation (1) was obtained from the following equilibrium involving both of the arsenic species expected to exist in slightly acidic and neutral waters.

$$H_3AsO_3 + H_2O = H_2ASO_4^- + 3\ H^+ + 2\ e^- \qquad (3)$$

The thermodynamic redox potential Eh is related to pE by the expression

$$pE = (F/2.303RT)\ Eh \qquad (2)$$

where F is the Faraday's constant, R is the ideal gas constant, T is temperature in kelvin, and Eh is expressed in volts.

Cherry et al. have shown that in the absence of known redox agents, the ratio of As(III)/As(V) in water samples at different pH does not change appreciably for approximately 3 weeks during storage (Cherry et al., 1979). This slow conversion is important because it allows time for sample collection and preparation for analysis to be accomplished prior to the occurrence of any significant change of the As(III)/As(V) ratio in the system. However, in the presence of redox agents common to natural waters, such as H_2S, Fe(III), and O_2, oxidation and reduction of As(III) and As(V) would take place at various rates. Reduction of As(V) by H_2S and oxidation of As(III) by Fe(III) were observed by Cherry et al. to occur at slow but significant rates over time periods of tens of hours (Cherry, et al., 1979). Oxidation of As(III) by oxygen was found to proceed at a much slower rate. Based on these observations, it appears that the use of the As(III) and As(V) pair as an indicator of redox level would be most appropriate for ground water because ground water commonly has slow flow rates.

The relative amounts of As(III) and As(V) in some natural water samples collected recently from this area and analyzed by our method are given in Table IV. For surface waters, either from the river or from the sea, the As(V) concentration is appreciably larger than that of As(III). This high As(V) content is caused, at least in part, by the highly oxidized environment. Several competing processes can modify the concentrations of the arsenic species in natural water systems: oxidation of arsenite to arsenate or the reverse reaction due to redox agents, precipitation and adsorption reactions, dissolution of solid material (especially organic matter), diffusion of arsenic from and into the sediments, and the advection due to the compaction flow. The kinetics of the arsenite-arsenate transformation in the ocean or river waters are still not well understood. Both bacterial and marine phytoplankton can reduce arsenate to arsenite, and the reverse reaction is known to be catalyzed by a number of bacteria (Johnson, 1972) (Osborne et al., 1976). As shown in Table IV, high content of As(III) is notable for water samples coming from a deep well in Joel, Idaho; indicating a reduced environment for the ground water. Water samples collected from the Bunker Hill Mine showed different As(V)/As(III) ratios indicating varied redox environment in the mine. The As(V)/As(III) ratio may provide a basis for obtaining an indication of redox status for the ground water system in this mine.

Table IV. Selective determination of As(III) and As(V) in various types of waters

Sample	As(III) found (ng/mL)	As(V)found (ng/mL)	Total As found (ng/mL)
Snake River water	0.7±0.1	3.0±0.1	3.7±0.1
Seawater from Tacoma, Washington	<0.04	1.9±0.1	1.9±0.1
Well later from Joel, Idaho	0.6±0.1	0.5±0.1	1.1±0.1
Mine water*(A)	1.9±0.2	12.0±1.3	13.9±1.3
Mine water*(B)	2.4±0.1	1.5±0.2	3.8±0.2
Mine water*(C)	6.2±0.3	74.2±1.9	80.3±1.9

*From the Bunker Hill Mine, Kellogg, Idaho

ARSENIC SPECIES IN THE GROUND WATER SYSTEMS OF THE COEUR D'ALENE MINING DISTRICT

The Bunker Hill Mine

The Bunker Hill Mine has been in operation since 1885. The mine is over a mile in depth, and is developed on 31 levels about 200 feet apart. Some of the levels include nearly two miles of drifts. The mine is currently not in production; it is being operated on a care and maintenance basis in which the dewatering pumps, ventilation systems, and major hoists are being operated and maintained. The Kellogg Tunnel on 9 level is the main haulage portal. All water from the mine discharges through the Kellogg Tunnel, and is treated and released into the south fork of the Coeur d'Alene River. Water entering the mine above 9 level drains through a maze of stopes, ore chutes and manways to 9 level. Water entering the mine below 9 level is pumped up to 9 level. Mine workings are currently flooded below 27.5 level.

The quality of the water discharging from the Bunker Hill Mine is poor and represents the mixing of both good and poor quality discharges. The total mine discharge has a pH which averages 2.8 and a zinc concentration which averages 116 mg/L (Riley, 1985). Ten locations in the upper part of the mine were selected for this study initially. Two of the locations were drill holes with visible rusty metal pipes. Erratic arsenic speciation data were obtained from these two locations probably due to the leaching and interactions of the water with the metal surfaces. These two locations were abandoned later in this study. Descriptions of the eight sampling sites and sources of water at each site are given in Table V.

Table V. Descriptions of sampling sites in the Bunker Hill Mine

Site	Mine Level	Water Produced From
New East Reed Flume (NER)	5	Drill holes, rock bolts, fractures
Williams Weir (WW)	5	Drill holes, rock bolts, fractures, ore chutes, stopes, faults
Reed Tunnel Flume (RT)	5	Fractures, rock bolts, ore chute
Reed Tunnel Pump Back (RPB)	5	Fractures, rock bolts, ore chutes, shallow ground water, surface water
Becker Weir (BW)	5	Fractures, bolt holes, ore chutes, stopes, ground water
Bailey Ore Chute (BOC)	9	Faults, fractures
Cherry Ditch Weir (CW)	9	Represent total of gravity drainage above 9 level, including Stanley Ore Chute
Kellogg Tunnel Flume (KT)	9	Total mine discharge

Arsenic species and other water quality data obtained from the eight sampling sites in the mine are given in Tables VI-X. The New East Reed Flume and the Williams Weir belong to one flow system in the mine. The Reed Tunnel Flume, The Reed Tunnel Pump Back, and the Becker Weir belong to another flow system at 5 level of the mine. The Cherry Ditch Weir represents the total of gravity drainage above 9 level. The water quality data in relation to arsenic species observed from these locations are described separately in the following sections:

(1) The Williams Weir system contains some very good quality water in the mine. The New East Reed Flume is a tributary to the Williams Weir. The quality of water at this sampling site is good, with low levels of arsenic, iron, and zinc. The As(V)/As(III) ratio was found low, ranging from 0.6-0.3, indicating a rather reduced environment. Water from some drill holes nearby flows into the New East Reed Flume. Rusty metal pipes were visible from these drill holes and higher As levels were found in these waters. Water from the New East Reed Flume might be affected by these contaminated waters. The water at the Williams Weir drains primarily from colluvium, fractures, faults, rock bolt holes, and exploration drill holes. The concentrations of total arsenic, zinc, and iron in Williams Weir are higher than those in New East Reed Flume. The AS(V)/As(III) ratio remains low (0.2-0.5) at Williams Weir.

(2) The Becker Weir system drains the portion of the 5 level that is west of the Williams Weir system. The Reed Tunnel and the Reed Pump Back are tributary to the Becker Weir. The water at the Reed Tunnel Flume comes from colluvium, fractures, and a fault. It is the best quality source tributary to the Becker Weir. The total arsenic, zinc,

Table VI. pH values and concentrations of arsenic species, Ca, Mg, Zn, Mn, Fe, Cd and Cu in mine waters from the Bunker Hill Mine, Kellogg, Idaho

LOCATION : BUNKER HILL MINE

DATE OF SAMPLING : 5-1-85

SAMPLE	PH	TOTAL AS	AS(III)	AS(V)	AS(V)/AS(III)
NERF	5.8	3.2±0.2	2.0±0.1	1.2±0.2	0.6
WW	3.5	6.3±0.2	6.3±0.2	N.D.	
RTF	5.6	0.1	0.1	N.D.	
RPB	5.4	0.2	0.2	N.D.	
BW	2.9	463.7±0.6	35.3±2.1	428.4±2.2	12.1
BOC	3.9	8.1±0.7	3.0±0.4	5.1±0.8	1.7
CW	2.8	793.0±38.2	25.7±1.8	767.3±38.3	29.9
KT	2.9	11.4±0.9	N.D.	11.4±0.9	

ARSENIC CONCENTRATIONS ARE REPORTED IN : NG/ML

< INDICATES THAT THE RESULT IS LESS THAN THE GIVEN VALUE

N.D.: NOT DETECTABLE, <0.1 NG/ML

LOCATION : BUNKER HILL MINE

DATE OF SAMPLING : 5-1-85

SAMPLE	CA	MG	ZN	MN	FE	CD	CU
NERF	9.78	1.19	<0.05	0.46	0.87	<0.01	<0.02
WW	12.67	15.14	66.08	14.24	16.33	0.19	*0.03
RTF	8.96	6.63	1.69	0.37	0.09	<0.01	<0.02
RPB	8.19	5.76	1.58	0.34	*0.05	<0.01	<0.02
BW	30.16	65.33	646.8	77.69	811.0	1.56	0.69
BOC	2.92	0.90	0.25	0.93	7.68	<0.01	<0.02
CW	42.10	81.98	506.6	82.79	523.9	1.04	1.17
KT	104.7	117.9	110.0	45.21	47.22	0.25	0.25

RESULTS ARE REPORTED IN : MG/L

< INDICATES THAT THE RESULT IS LESS THAN THE GIVEN VALUE

* INDICATES THE RESULT IS WITHIN 2.5X THE DETECTION LIMIT AND SHOULD BE INTERPRETED ACCORDINGLY

Table VII. pH values and concentrations of arsenic species, Ca, Mg, Zn, Mn, Fe, Cd and Cu in mine waters from the Bunker Hill Mine, Kellogg, Idaho

LOCATION : BUNKER HILL MINE

DATE OF SAMPLING : 5-21-85

SAMPLE	PH	TOTAL AS	AS(III)	AS(V)	AS(V)/AS(III)
WW	3.6	4.9±0.2	3.9±0.2	1.0±0.2	0.2
RTF	5.5	0.1	0.1	N.D.	<0.1
RPB	5.3	0.15	0.1	0.05	0.5
BW	2.9	249.0±3.5	20.4±1.1	228.6±3.7	11.2
BOC	3.9	8.5±0.3	6.0±0.3	2.5±0.4	0.4
CW	2.7	1336.1±38.5	42.3±1.5	1293.8±38.5	30.6
KT	2.7	47.7±1.6	3.8±0.3	43.9±1.7	11.6

ARSENIC CONCENTRATIONS ARE REPORTED IN : NG/ML

< INDICATES THAT THE RESULT IS LESS THAN THE GIVEN VALUE

N.D.: NOT DETECTABLE, <0.1 NG/ML

LOCATION : BUNKER HILL MINE

DATE OF SAMPLING : 5-21-85

SAMPLE	CA	MG	ZN	MN	FE	CD	CU
WW	11.03	12.04	44.00	10.93	10.73	0.11	<0.02
RTF	8.34	6.26	1.39	0.29	0.05	<0.01	<0.02
RPB	7.06	5.45	1.40	0.38	*0.04	<0.01	<0.02
BW	22.31	51.21	380.4	56.08	494.1	0.84	0.30
BOC	3.38	0.87	0.26	0.92	7.10	<0.01	<0.02
CW	48.67	94.02	660.3	95.24	678.9	1.48	1.88
KT	73.03	90.00	151.8	52.46	101.9	0.37	0.47

RESULTS ARE REPORTED IN : MG/L

< INDICATES THAT THE RESULT IS LESS THAN THE GIVEN VALUE

* INDICATES THE RESULT IS WITHIN 2.5X THE DETECTION LIMIT AND SHOULD BE INTERPRETED ACCORDINGLY

Table VIII. pH values and concentrations of arsenic species, Ca, Mg, Zn, Mn, Fe, Cd and Cu in mine waters from the Bunker Hill Mine, Kellogg, Idaho

LOCATION : BUNKER HILL MINE

DATE OF SAMPLING : 6-6-85

SAMPLE	PH	TOTAL AS	AS(III)	AS(V)	AS(V)/AS(III)
NERF	5.8	3.1±0.2	2.1±0.2	1.0±0.3	0.5
WW	3.5	6.1±0.2	4.9±0.3	1.2±0.4	0.2
RTF	5.6	0.3±0.1	0.2±0.1	N.D.	<0.1
RPB	5.4	0.1	0.1	N.D.	<0.1
BW	2.9	222.6±2.4	18.3±0.6	204.4±2.5	11.1
BOC	3.9	3.3±0.2	1.8±0.1	1.5±0.2	0.8
CW	2.8	827.9±5.8	27.2±0.6	800.7±5.8	29.4
KT	2.9	18.5±0.4	2.0±0.2	16.5±0.4	8.3

ARSENIC CONCENTRATIONS ARE REPORTED IN : NG/ML

< INDICATES THAT THE RESULT IS LESS THAN THE GIVEN VALUE

N.D.: NOT DETECTABLE, <0.1 NG/ML

LOCATION : BUNKER HILL MINE

DATE OF SAMPLING : 6-6-85

SAMPLE	CA	MG	ZN	MN	FE	CD	CU
NERF	10.13	1.30	*0.05	0.61	0.94	<0.01	<0.02
WW	10.84	10.47	34.50	9.60	9.58	0.10	*0.02
RTF	8.13	5.86	1.34	0.28	*0.05	<0.01	<0.02
RPB	6.99	5.26	1.26	0.27	*0.05	<0.01	<0.02
BW	21.08	47.54	306.1	53.09	416.4	0.64	0.24
BOC	3.20	0.92	0.28	0.94	7.22	*0.020	<0.02
CW	45.97	89.53	573.8	87.93	572.0	1.32	1.69
KT	99.52	107.0	143.7	55.78	79.90	0.34	0.40

RESULTS ARE REPORTED IN : MG/L

< INDICATES THAT THE RESULT IS LESS THAN THE GIVEN VALUE

* INDICATES THE RESULT IS WITHIN 2.5X THE DETECTION LIMIT
AND SHOULD BE INTERPRETED ACCORDINGLY

Table IX. pH values and concentrations of arsenic species, Ca, Mg, Zn, Mn, Fe, Cd and Cu in mine waters from the Bunker Hill Mine, Kellogg, Idaho

LOCATION : BUNKER HILL MINE

DATE OF SAMPLING : 6-25-85

SAMPLE	PH	TOTAL AS	AS(III)	AS(V)	AS(V)/AS(III)
NERF	5.9	3.3±0.2	2.6±0.2	0.7±0.3	0.3
WW	3.5	1.5±0.1	0.5±0.1	1.0±0.1	2.0
RTF	5.4	0.3±0.1	0.1	N.D.	
RPB	5.4	0.1	0.1	N.D.	
BOC	3.6	7.3±0.3	6.1±0.3	1.2±0.4	0.2
CW	2.7	519.4±5.0	31.3±0.8	488.1±5.1	15.6
KT	2.7	5.1±0.3	1.9±0.2	3.2±0.4	1.7

ARSENIC CONCENTRATIONS ARE REPORTED IN : NG/ML

< INDICATES THAT THE RESULT IS LESS THAN THE GIVEN VALUE

N.D.: NOT DETECTABLE, <0.1 NG/ML

LOCATION : BUNKER HILL MINE

DATE OF SAMPLING : 6-25-85

SAMPLE	CA	MG	ZN	MN	FE	CD	CU
NERF	10.00	1.21	*0.06	0.61	0.90	<0.01	<0.02
WW	10.87	9.24	30.94	8.12	8.19	0.04	<0.02
RTF	7.70	5.36	1.31	0.29	*0.03	<0.01	<0.02
RPB	6.63	4.65	1.20	0.25	0.17	<0.01	<0.02
BOC	2.90	0.87	0.33	0.96	7.15	<0.01	<0.02
CW	40.39	81.16	468.4	75.20	384.4	0.92	1.13
KT	106.8	120.5	102.6	64.50	56.92	0.18	0.27

RESULTS ARE REPORTED IN : MG/L

< INDICATES THAT THE RESULT IS LESS THAN THE GIVEN VALUE

* INDICATES THE RESULT IS WITHIN 2.5X THE DETECTION LIMIT AND SHOULD BE INTERPRETED ACCORDINGLY

Table X. pH values and concentrations of arsenic species, Ca, Mg, Zn, Mn, Fe, Cd and Cu in mine waters from the Bunker Hill Mine, Kellogg, Idaho

LOCATION : BUNKER HILL MINE

DATE OF SAMPLING : 7-30-85

SAMPLE	PH	TOTAL AS	AS(III)	AS(V)	AS(V)/AS(III)
NERF	6.4	1.9±0.2	1.2±0.2	0.7±0.3	0.6
WW	3.8	6.5±0.3	4.4±0.3	2.1±0.4	0.5
RTF	5.8	0.5±0.2	N.D.	0.5±0.2	
RPB	5.7	0.1	0.1	N.D.	
BW	3.0	106.7±1.9	15.5±0.9	91.2±2.1	6.0
BOC	3.6	3.4±0.2	3.0±0.2	0.4±0.2	0.1
CW	2.8	143.9±1.9	15.9±0.8	128.0±2.1	8.1
KT	---	2.8±0.2	1.0±0.2	1.8±0.3	1.8

ARSENIC CONCENTRATIONS ARE REPORTED IN : NG/ML

< INDICATES THAT THE RESULT IS LESS THAN THE GIVEN VALUE

N.D.: NOT DETECTABLE, <0.1 NG/ML

LOCATION : BUNKER HILL MINE

DATE OF SAMPLING : 7-30-85

SAMPLE	CA	MG	ZN	MN	FE	CD	CU
NERF	10.08	1.18	<0.05	0.52	0.60	<0.01	<0.02
WW	9.68	8.27	25.6	7.04	5.40	*0.02	<0.02
RTF	9.96	6.21	2.03	0.58	*0.04	<0.01	<0.02
RPB	9.04	5.83	1.85	0.51	<0.03	<0.01	<0.02
BW	23.37	53.0	294.5	54.96	364.7	0.48	0.17
BOC	3.08	1.03	0.60	1.09	8.13	<0.01	<0.02
CW	38.40	80.77	352.9	73.94	284.6	0.82	0.86
KT	110.2	148.9	121.3	73.74	51.01	0.21	0.27

RESULTS ARE REPORTED IN : MG/L

< INDICATES THAT THE RESULT IS LESS THAN THE GIVEN VALUE

* INDICATES THE RESULT IS WITHIN 2.5X THE DETECTION LIMIT AND SHOULD BE INTERPRETED ACCORDINGLY

and iron contents of the water from the Reed Tunnel Flume are low and the As(V)/As(III) ratio is small. The Reed Pump Back picks up water flowing out of the Reed Tunnel and discharges it at the Becker Weir. It also collects surface runoff and shallow ground water. The quality of water at the Reed Pump Back is also very good and the As(V)/As(III) ratio in the water is low (0.1-0.5). Some poor quality water from the old workings flows into the Becker Weir, so that the total arsenic, zinc, and iron contents in the water of this sampling site are very high. The As(V)/As(III) ratio in Becker Weir is more than an order of magnitude greater than those observed at the Reed Tunnel or Reed Pump Back. The variations of As(V)/As(III) ratio and the total arsenic, zinc, and iron contents of the water collected from May 1 to July 30 of 1985 in Becker Weir are shown in Figure 6. The As(V)/As(III) ratio shows a positive correlation with the zinc, iron, and total arsenic contents in the water. The ratio of As(V)/As(III) was found high in the late spring and decreased in the summer. It appears that in the spring run-off, leaching of the oxidized ores and mine wastes would probably result in poor-quality water in some locations of the mine. After the system is flooded with water over a period of time, the ground water becomes anaerobic. When this occurs, the As(V)/As(III) ratio begins to decrease and the water quality shows improvement.

(3) The Bailey Ore Chute represents the good-quality water on 9 level of the mine. The As(V)/As(III) ratio found in this location is again low (0.1-0.8). The total arsenic, zinc, and iron contents of the water are also low.

(4) The water sampled at the Cherry Weir is a composite of all gravity drainages from the eastern portion of the mine. It includes

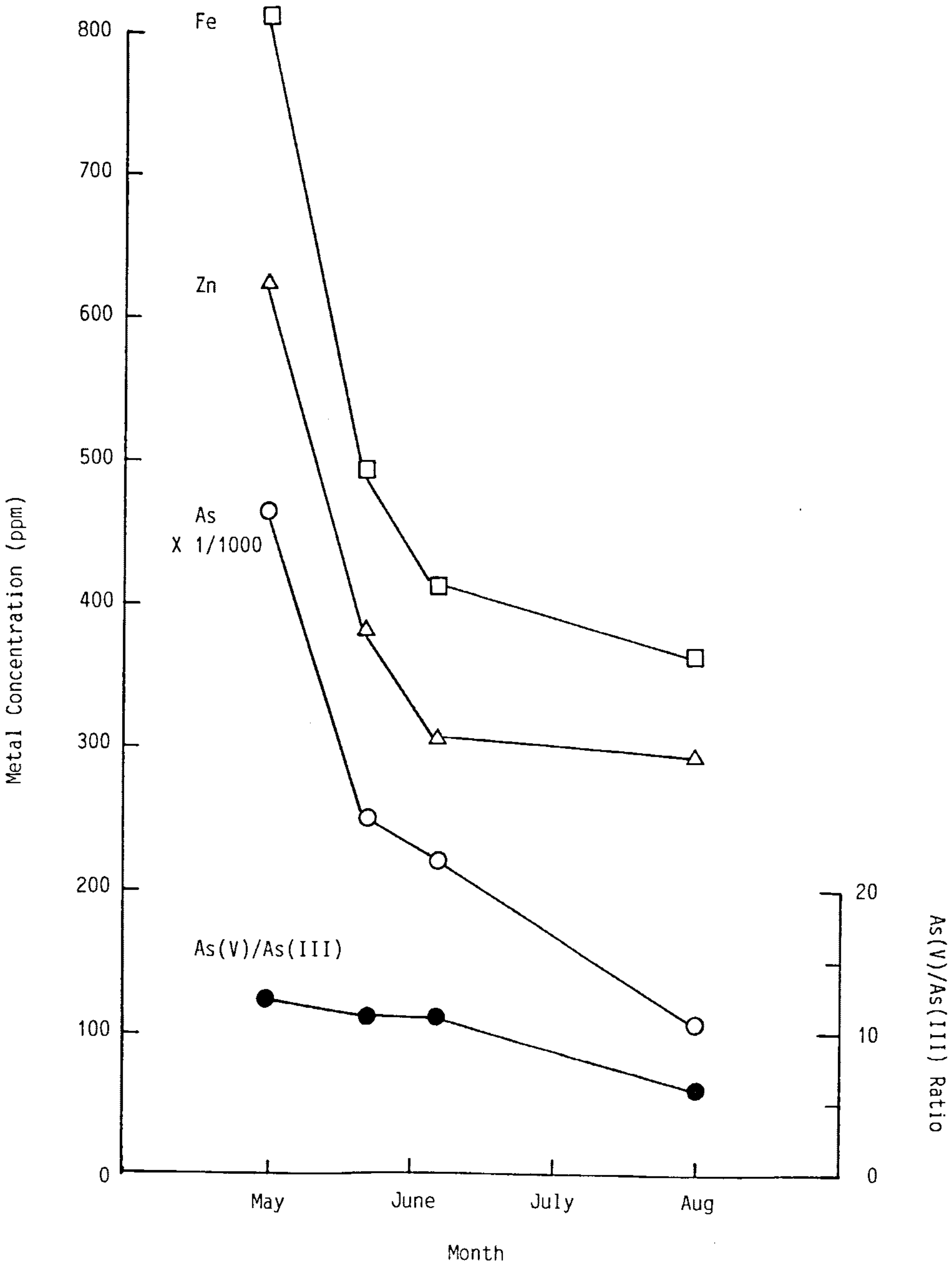


Figure 6. The variations of As(V)/As(III) ratio and the total arsenic, zinc, and iron contents of the water collected from May 1 to July 30 of 1985 in Becker Weir.

very poor-quality water from the Flood-Stanly Ore Body. The variations of As(V)/As(III) ratio and the concentrations of total arsenic, zinc, and iron from May 1 to July 30 of 1985 are shown in Figure 7. In the late spring, the ratio of As(V)/As(III) was over 30 when the total arsenic was above 1,300 ppb and the zinc and iron concentrations were above 650 ppm. In the late summer, the As(V)/As(III) ratio decreased to about 8 with the total arsenic less than 150 ppb, and the zinc and iron contents were about 350 ppm or less. The As(V)/As(III) ratio shows a strong correlation with the quality of water at this site. Measurements of the Eh of the water at this site with a standard platinum electrode during the sampling period showed values fluctuating from 445 to 510 millivolts with no obvious trend. The As(V)/As(III) ratio appears to be a much more sensitive and reliable indicator for the observed water quality in comparison with the electric potential measurement.

(5) Kellogg Tunnel. All of the water from the Bunker Hill Mine discharges via the Kellogg Tunnel. The water is piped from the portal to a water treatment plant where the water is treated and released into the South Fork of the Coeur d'Alene River. The quality of the discharge from the Kellogg Tunnel is very sensitive to the operation of the low level pumps in the mine. The As(V)/As(III) ratio remains high (1.8-11.8), the zinc and the iron contents in the water generally exceed 100 ppm and 50 ppm, respectively.

Other Locations of the Coeur d'Alene Mining District.

Ground waters and surface waters were also collected from other locations of the Coeur d'Alene Mining District for this arsenic speciation study. Ground water samples were collected from several

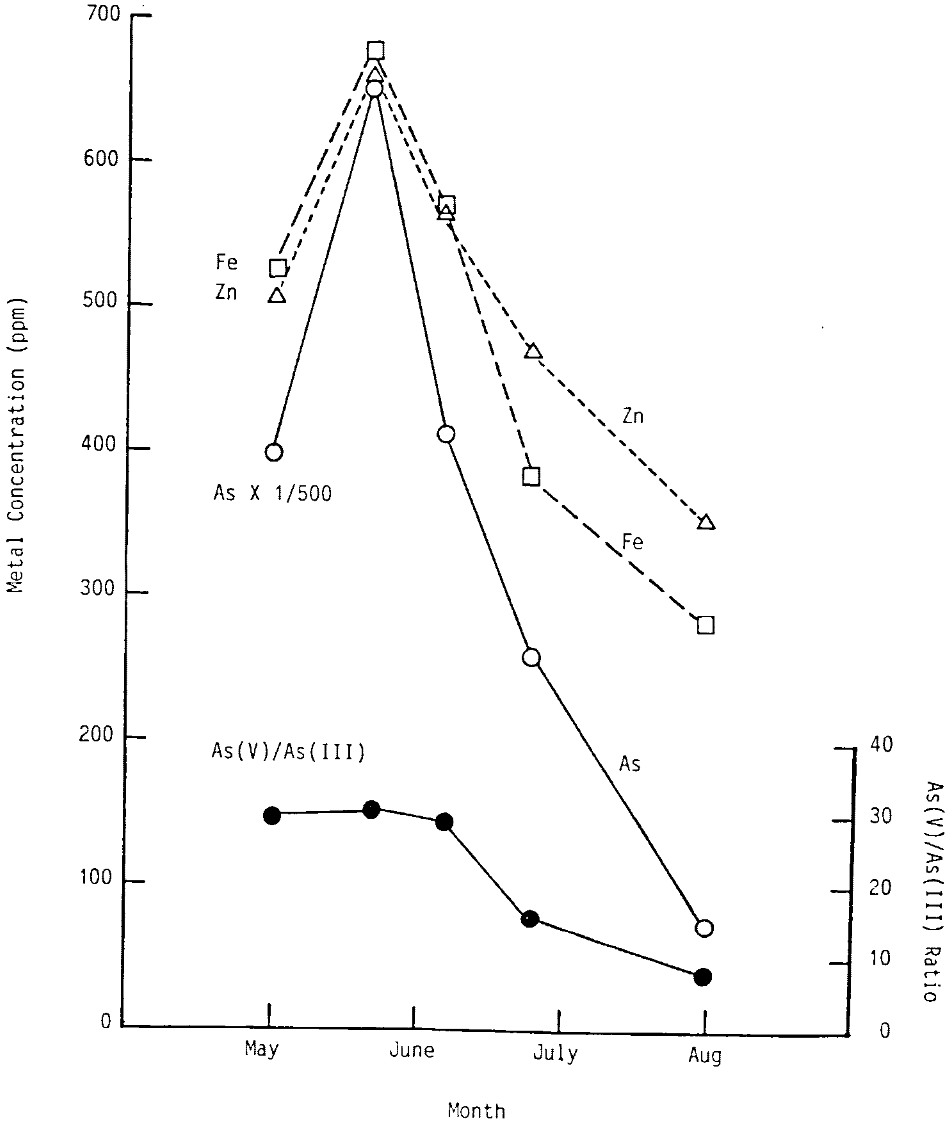


Figure 7. The variations of As(V)/As(III) ratio and the concentrations of total arsenic, zinc, and iron of the water collected from May 1 to July 30 of 1985 in Cherry Weir.

piezometers installed seven years ago by Dale Marcy of this chemistry department in the Smelterville Flats (Marcy, 1979). The piezometers were made of polyvinyl chloride pipes 20 feet long and 3/4 inch diameter. Unfortunately, some of the existing piezometers were contaminated with dirts and dried up later in the summer. Two of the piezometers near the airport runway were still suitable for this study. The distribution of the arsenic species and the concentrations of some metals in the waters collected from these piezometers are given in Table XI.

According to Marcy's study conducted seven years ago, these two locations in the Smelterville Flats showed good water quality. Our results agree with this previous findings. The As(V)/As(III) ratios in these ground waters were found to be low, indicating a rather reduced environment. Marcy also indicated in his study that the ground water quality in the Smelterville Flats varied considerably from one location to another. However, we were not able to sample other locations because most of the piezometers installed by Macy are no longer existing. We did collect surface waters at several different locations along the Coeur d'Alene River. The results are given in Table XII.

The surface waters collected from the Coeur d'Alene River showed unusually low As(V)/As(III) ratios compared with the water collected from the Snake River near Lewiston, Idaho. It is known that As(III) in an aqueous solution can be oxidized slowly to As(V) when the solution is exposed to air. In natural waters, the conversion of As(III) to As(V) has been shown to depend on biological activities which may be lacking in the Coeur d'Alene River (Johnson, 1972) (Osborne et al., 1976). It is possible that the arsenic species ratio may provide a measure of the

Table XI. Arsenic species and other metals found in ground waters collected from two locations of the Smeltersville Flats

Site	Date	Total As	As(V)/ As(III)	Fe	Zn	Mn	Cu	Cd	Ca
Y1	5/23	1.9±0.1	0.5	0.5	5.2	4.9	.02	.01	50.7
	6/7	2.7±0.2	0.4	1.7	5.8	4.9	.02	.01	62.6
	7/31	1.7±0.1	0.3	0.8	18.7	3.3	.02	.01	65.1
Y2	5/23	1.2±0.1	0.3	0.2	17.7	27.9	.02	.01	61.6
	6/7	0.8±0.1	0.4	0.1	23.8	14.7	.02	.01	68.7
	7/31	1.3±0.1	0.3	0.4	18.8	17.0	.02	.01	72.2

Total As concentration in ppb.
Other metal concentrations in ppm.

Table XII. Arsenic species found in surface waters at different locations of the Coeur d'Alene River

Sample Location	pH	Total As	As(III)	As(V)	As(V)/ As(III)	Zn	Fe	Mn
[a1]SFSVBN(1)	6.9	2.44±0.07	1.47±0.06	0.97±0.09	0.66	3.04	0.04	2.23
[a2]SFSVBS(2)	7.2	1.79±0.05	1.57±0.05	0.22±0.07	0.14	2.32	N.D.	0.74
[b]MEDL(1)	7.4	2.63±0.08	1.93±0.07	0.70±0.11	0.36	0.27	0.13	0.03
MEDL(2)	7.2	1.50±0.05	1.16±0.04	0.34±0.06	0.29	0.01	N.D.	0.04
[c]CAVL(1)	7.0	0.86±0.05	0.65±0.05	0.21±0.07	0.32	0.12	0.08	0.01
CAVL(2)	7.3	0.71±0.04	0.41±0.03	0.30±0.05	0.73	0.04	1.14	0.50
[d]SFBAB(1)	7.4	2.41±0.08	1.89±0.07	0.52±0.01	0.28	1.60	0.04	0.33
SFBAB(2)	7.3	2.87±0.06	2.22±0.05	0.65±0.08	0.29	1.65	0.01	0.19
[e1]CDACW(1)	6.9	0.41±0.05	0.18±0.03	0.23±0.06	1.28	0.90	0.02	0.86
[e2]CDACE(2)	7.3	0.44±0.03	0.27±0.03	0.17±0.04	0.63	0.85	N.D.	0.16

(1) Date of sampling: 10-2-85
(2) Date of sampling: 11-1-85
a1 South Fork at the Smelterville exit bridge from I-90, north side of bridge
a2 South Fork at the Smelterville exit bridge from I-90, south side of bridge
b Medicine Lake beside Highway 3
c Cave Lake beside Highway 3
d South Fork at the Bunker Avenue bridge
e1 Coeur d'Alene River (main stream) at the Cataldo Bridge, west side, close to the North Fork
e2 Coeur d'Alene River (main stream) at the Cataldo Bridge, east side
Arsenic concentrations are reported in: ng/mL
Metal (Zn, Fe, Mn) concentrations are reported in: mg/L
N.D.: not detectable, <0.003 mg/L of Fe.

biological activities of a natural water system. Further research is definitely needed to understand the factors controlling the inter-conversion of As(V) and As(III) species in various natural water systems.

SUMMARY

An analytical method for determining the arsenic species, As(V) and As(III), in natural waters is described in this report. The proposed extraction procedure, combined with neutron activation analysis, enables us to determine the arsenic species in natural waters at 0.1 ppb level. The arsenic speciation technique has been applied to the ground water systems of a major lead-zinc mine (the Bunker Hill Mine) in northern Idaho. The observed ratios of As(V)/As(III) in the ground waters collected from various location of the mine varied by two orders of magnitude. The As(V)/As(III) ratios were found to correlate strongly with the quality of the mine waters studied. Good-quality waters were generally associated with low As(V)/As(III) ratios. Poor-quality mine waters always showed high As(V)/As(III) ratios indicating oxidized conditions of the recharge sources or the sampling locations. A seasonal variation of As(V)/As(III) ratio was also observed in the ground water systems of the mine. During the spring run-off, high As(V)/As(III) ratios were observed in some mine waters, presumably caused by leaching of oxidized ores and mine wastes in certain locations of the upper part of the mine. The concentrations of dissolved metals such as zinc and iron in these mine waters were also high. In the late summer, the ratio of As(V)/As(III) decreased as the system became more anaerobic after being flooded with water over a period of time. Associated with the lowering in As(V)/As(III) ratio, the concentrations of dissolved metals in the mine waters were significantly reduced. The ratio of the arsenic species appears to be a suitable chemical indicator for evaluating the acid water formation and associated metal leaching problems existing in this and other similar mining areas. In comparison with the Eh measurements obtained from the mine waters using a Pt electrode, the arsenic speciation method appears to be a much more sensitive technique for evaluating the redox status of the ground water systems. The total arsenic content and the As(V)/As(III) ratio in ground and surface waters collected from other locations of this area are also given. Factors controlling the reversible conversion of As(V) and As(III) and the kinetics of such conversion in natural water systems are largely unknown. Further research along this direction is needed in order to understand the usefulness of the arsenic speciation technique as a chemical indicator for water pollution studies.

REFERENCES

Appalachian Regional Commission, "Acid mine drainage in Appalachia", Washington, D.C., U.S. Govt. Printing Office, House Document 91-180, Publication No. 35-4320, 1, p. 58. 3, p. 17, 1969.

Cherry, J.A., A. U. Shaikh, D.E. Tallman, and R.V. Nicholson, "Arsenic species as an indicator of redox conditions in groundwater", J. Hydrology, 43, 373-92 (1979).

Davis, H.T., "Idaho's environment", Environ. Sci. Technol. 12, 276-283 (1978).

Johnson, D.L., "Bacterial reduction of arsenate in sea water", Nature, 240, 44 (1972).

Lo, J.M., J. C. Yu, F.I. Hutchison, and C.M. Wai, "Solvent extraction of dithiocarbamate complexes and back-extraction with mercury (II) for determination of trace metals in water by atomic absorption sectrometry", Anal. Chem. 54, 2536-39 (1983).

Marcy, A.D., "The chemistry of unconfined mine wastes", M.S. Thesis, Dept. of Chemistry, University of Idaho (1979).

Mink, L.H., R.E. Williams, and A.T. Wallace, "Effects of industrial and domestic effluents on the water quality of the Coeur d'Alene River Basin", Idaho Bureau of Mines and Geology, Pamphlet 149 (1971) 30 p.

Osborne, F.H. and H.L. Ehrlick, "Oxidation of arsenite by a soil isolate of alcaligenes", J. Appl. Bacteriol. 41, 295 (1976).

Riley, J.A., "Acid water implications for mine abandonment, Coeur d'Alene Mining District, Idaho", M.S. Thesis, Dept. of Geology, Univ. Idaho (1985).

Silker, W.B., "Variations in elemental concentrations in the Columbia River", Limnol. Oceanog. 9, 540 (1964).

Smith, E.E. and K.S. Shumate, "Sulfide to sulfate reaction mechanism", Washington, D.C., U.S. Govt. Printing Office, Document 14010FPS02/70, 1970.

Wai, C.M., D.E. Reece, B.D. Trexler, D.R. Ralston, and R.E. Williams, "Production of acid water in a lead-zinc mine, Coeur d'Alene, Idaho", Environ. Geol. 3, 159-62 (1980).

Wedepohl, K.H., "Handbook of geochemistry", Vol. II/3, Springer Verlag, N.Y., 1978.

Williams, K.T. and R.R. Whetstone, "Arsenic distribiton in soils and its presence in certain plants", U.S. Dept. Agr., Tech. Bull. 732 (1940).

REFERENCES (Continued)

Yu, J.C. and C.M. Wai, "Extraction of gold and mercury in seawater with bismuth diethydithiocarbamate for quantitation by neutron activation analysis", Anal. Chem. Acta <u>154</u>, 307-312 (1983).

APPENDIX

Anal. Chem., Feb., 1986. In Press.

Extraction of Arsenic(III) and Arsenic(V) from Natural Waters for Neutron Activation Analysis

W. M. Mok, N. K. Shah, and C. M. Wai*

Department of Chemistry
University of Idaho
Moscow, Idaho 83843

ABSTRACT

Quantification and speciation of arsenic(III) and arsenic(V) in natural waters can be achieved by extracting the former species with pyrrolidinedithiocarbamate at pH 1-1.5 into chloroform followed by a nitric acid back-extraction for neutron activation analysis. Besides eliminating interferences from matrix species in natural waters, the two-step extraction procedure also provides a large preconcentration factor for arsenic. Detection of 10^{-2} µg/L of arsenic can be achieved using this extraction method and NAA. Applications of this method to arsenic speciation studies in natural water systems are discussed.

Because of its toxicity and possible carcinogenicity, arsenic is one of the most widely measured trace metals in many environmental monitoring programs. Arsenic generally occurs in the oxidation states As(III) and As(V) in natural water systems. Information on the distribution of the two oxidation states of arsenic in water is important for some environmental studies. For example, the ratio of the two oxidation states of arsenic may be used as an indicator of redox conditions of natural water systems [1]. Biologically, As(III) is considered more toxic than As(V) [2]. The concentrations of total arsenic in most natural water systems are in the range of 10^{-6} - 10^{-7} g/L [3]. Analytical methods capable of measuring nanogram levels of As(III) and As(V) are necessary for studying the chemistry of arsenic species in aquatic environments.

Neutron activation is one of the most sensitive techniques for arsenic analysis. Under interference-free conditions, neutron activation analysis (NAA) can easily detect nanogram levels of arsenic in a sample with good accuracy. However, in real samples, spectral interferences from other elements such as Na and Br can greatly limit the sensitivity of arsenic determination by NAA. Radiochemical separations involving anion-exchange and precipitation procedures have been used to isolate $^{76}\mathrm{As}(t_{\frac{1}{2}} = 26.4\ \mathrm{h})$ and to eliminate matrix interferences from irradiated water samples for quantification of arsenic [4]. Radiochemical separation applied to water samples after neutron irradiation for arsenic determination has several drawbacks. First, the oxidation states of arsenic in the original sample cannot be distinguished. Second, a large concentration factor cannot be obtained because the amount of sample allowed in each irradiation is limited. Preconcentration and separation of metals from water samples by solvent extraction prior to neutron irradiation have been applied to several systems [5,6]. Extraction before neutron irradiation can avoid the aforementioned drawbacks and also has the advantage of minimizing radiation exposure for the analyst. This paper describes an extraction method for separation and preconcentration of As(III) and As(V) from natural waters prior to NAA. The proposed method, which is simple and sensitive, is suitable for measuring low levels of arsenic species in natural water systems.

Experimental Section

Reagents. A stock solution of 1000 µg/mL As(III) was prepared by dissolving 0.1320 g of arsenic trioxide (Allied Chemicals) in 2 mL of 1 M NaOH. After addition of 25 mL of water, the solution was acidified with 4 mL of 1 M HCl and diluted to 100 mL with deionized water. A stock solution of As(V) (1000 µg/mL) was prepared by dissolving 0.4163 g of sodium arsenate (J. T. Baker Co.) with 0.5 mL of concentrated H_2SO_4 and diluting to 100 mL with deionized water. Ammonium pyrrolidinedithiocarbamate (APDTC) and sodium diethyldithiocarbamate (NaDDTC) were purchased from the Fisher Scientific Co. Chloroform used in the extraction was Baker analyzed reagent. Nitric acid used in the experiments was of Ultrex grade, also from Baker Chemical Co. Deionized water was obtained by treatment of distilled water through an ion exchange column (Barnstead Ultrapure Water Purification Cartridge) and a 0.2 µm filter assembly (Pall Corp. Ultipor DFA). All containers were washed with 2% Liqui-Nox detergent (Alconox, Inc.) solution and then soaked in 10% HNO_3 for at least 24 hours. After soaking, they were rinsed with deionized water and stored in a class 100 clean hood equipped with a vertical laminar flow HEPA filter (CCI).

Natural seawater (surface) was collected from the coastal waters near the Seattle area using a 15 L polyethylene bottle and filtered through a 0.45 µm Millipore membrane filter before use. A river water sample was taken from the Snake River near Lewiston, Idaho. Ground water was obtained from a local well near Joel, Idaho. Mine waters were from the Bunker Hill Mine in the Coeur d'Alene Mining District, Idaho. A synthetic seawater was prepared according to the procedure published in the literature [7].

Extraction Procedures. The extraction solution was prepared by dissolving 5 g of APDTC in 100 mL of deionized water. The solution was always prepared fresh prior to use, filtered to remove the insoluble material, and shaken with chloroform for 1 min to remove bromine and other impurities. A 12% EDTA solution was also prepared fresh and was used as a masking agent for the extraction. All water samples analyzed were saturated with chloroform before extraction.

To extract As(III), normally a 100 mL sample was poured into an Erlenmeyer flask equipped with a ground stopper. The water sample was adjusted to pH 1.5 before 2 mL of the extraction solution, 4 mL of the EDTA solution, and 10 mL of chloroform were added. The mixture was shaken vigorously on a mechanical wrist action shaker (Burrell Model 75) for 10 min and then was allowed to sit for 10 min for phase separation. The organic phase was removed from the flask and washed a couple of times with small amounts of deionized water to remove Na and other impurities. Exactly 8 mL of the organic phase was then transferred to a flask and 2 mL of 50% HNO_3 were added to back-extract As. The mixture was shaken again for 10 min on the mechanical shaker. After phase separation, 1 mL of the acid solution was transferred into a polyethylene vial for neutron irradiation.

To determine As(V), a second aliquot of the water sample was placed in an Erlenmeyer flask and adjusted to pH 1.0 with HNO_3. Reduction of As(V) to As(III) was achieved by the addition of 1 mL of a 25% sodium thiosulfate solution followed by 1 min of shaking. After a waiting period of 5 min, 2 mL of the extraction solution, 4 mL of the EDTA solution, and 10 mL of chloroform were added to the flask and the total As(III) was extracted by the procedure described in the previous section. The difference in As concentrations between the two aliquots represents the amount of As(V) in the original water sample. A procedure blank made of 100 mL of deionized water and run through the same extraction procedure was run with each set of experiments. No detectable amount of As was found in any of the blanks.

Sample Irradiation and Counting. The details of sample sealing procedure for neutron irradiation are given elsewhere [5,6]. Standards were made of 1 mL solutions containing proper concentrations of As, heat sealed in the same kind of polyethylene vials as the samples. All samples and standards were normally irradiated for 2 hours in a 1-MW TRIGA reactor at a steady neutron flux of 6×10^{12} n/cm^2 sec., followed by one day of cooling. Before counting, samples and standards were transferred into new 2/5 dram polyethylene vials using disposable syringes. This sample transfer step is necessary in order to avoid interferences of ^{24}Na and other radioactivities produced in the plastic material of the irradiated vials. Each sample was counted for 2×10^3 seconds in a large volume coaxial ORTEC Ge(Li) detector with a resolution of about 2.3 keV at the 1332-keV γ from ^{60}Co. The 559 keV γ from ^{76}As was used to determine the arsenic concentrations in samples.

Results and Discussion

One advantage of using dithiocarbamic acid derivatives to extract trace metals from natural waters is that interfering matrix species including the alkali metals, the alkaline earth metals, and the halogens can be effectively eliminated during extraction. This is particularly useful for NAA because ^{24}Na ($t_{\frac{1}{2}}$ = 15 h) and ^{82}Br ($t_{\frac{1}{2}}$ = 36 h) are generally two of the major interfering isotopes produced from thermal neutron capture of ^{23}Na and ^{81}Br which are ubiquitous in natural waters. The high neutron capture cross sections of sodium and bromine would result in high intensity γ peaks which tend to mask small peaks from trace metals in γ spectrometry and limit their determination. In the case of As, the most intensive γ peak of ^{76}As at 559 keV is also close to the 554 keV γ-ray emitted by ^{82}Br. Therefore, elimination of Na and Br is essential in order to detect low levels of As in natural water samples. Recently, metal-dithiocarbamate complexes such as $Bi(DDTC)_3$ and $Pb(DDTC)_2$ have also been used to extract trace metals from natural waters for NAA [5,8]. One reason for using these metal-DDTC complexes is because both Bi and Pb do not produce radioisotopes that would cause interference in γ spectrometry. Selective extraction of metals may be achieved using these metal-dithiocarbamate complexes if the extraction constants of the metals being extracted are greater than that of Bi or Pb. The extraction constant of As(III)-DDTC complex is probably much lower than that of Pb(II), because $Pb(DDTC)_2$ was not able to extract As(III) according to our experiments. The extraction constant of $Bi(DDTC)_3$ is many orders of magnitude greater than $Pb(DDTC)_2$, and hence it is not expected to extract As(III) from aqueous solution [9,10]. Selective extraction of certain metals can also be done by adjusting pH of solutions as the extraction efficiencies of many metal-dithiocarbamate complexes depend strongly on acidity.

The effects of pH on the extraction of As(III) in deionized water with APDTC are shown in Figure 1. Quantitative extraction of As(III) was observed over a wide range from pH 0.6 to about 6. Above pH 6, the efficiency of extraction of As(III) begins to decrease very rapidly. The extraction curves for Cu(II), Fe(II), Mn(II), and Zn(II) with APDTC from pH 0.7 to 9 are also shown in Figure 1. The extraction efficiencies for Fe, Mn, and Zn are very low ($\leq$10%) at pH<2. Because these metals may be present in polluted waters at high concentrations, extraction at pH<2 would significantly reduce their extraction efficiencies. Another factor which should be considered is the possibility of extracting As(V) in acid solution. According to the literature, As(V) cannot be extracted by APDTC even at low pH. However, in our experiments, a small fraction (2-6%) of As(V) was always found in the organic phase with APDTC extraction at pH≤1. To avoid the extraction of As(V) and to reduce Fe, Mn, and Zn, a pH value of 1.5 was finally chosen for the extraction of As(III) in our procedure. The pH dependence curve for As(III) with NaDDTC extraction is similar to the one with APDTC shown in Figure 1. One problem with using NaDDTC at low pH is that it is unstable in acid solution and consequently may result in incomplete extraction of As(III). Indeed, partial extraction of As(III) with NaDDTC was frequently observed at pH<2, especially if shaking was not carried out immediately after the addition of the chelating agent. For this reason, NaDDTC is not recommended as an extracting agent for As(III) in our procedure.

In complex natural water systems, the degree of extraction of As(III) with dithiocarbamate may be significantly reduced due to competition caused by other metal ions present in the system. However, such interferences can be reduced by the use of EDTA as a masking agent [11]. Table I shows the results of APDTC extraction carried out with and without the masking agent in a mine water spiked with ppb levels of As. In the absence of EDTA, the percentage of As recovery may not be satisfactory depending upon the water quality. In our experiments, a concentration of about 0.5% EDTA is used to eliminate interferences caused by other concomitant metal ions in complex systems such as natural seawaters and acid mine waters.

Sodium thiosulfate is an effective reducing agent for As(V). The reduction of As(V) to As(III) with thiosulfate in acid solution is fast; only several minutes are necessary to complete the reduction at pH 1. The efficiency of the reduction process appeared to decrease at higher pH. Addition of potassium iodide to thiosulfate did not seem to enhance the efficiency of reduction. This observation is different from Kamada's report which indicated that treatment of potassium iodide was essential for the reduction of As(V) [11]. Based on our experiments with spiked As(V) samples, a 0.2% sodium thiosulfate solution at pH 1 provides a satisfactory condition for total reduction of As(V) in natural water samples. Our recommended procedure is to shake the solution for 1 min after the addition of thiosulfate followed by a waiting period of 5 min to allow for complete reduction. The difference in As(III) concentrations between two aliquots of a water sample with and without reduction gives the concentration of As(V) in the sample.

The organic bound As in chloroform can be back-extracted into a nitric acid solution for NAA. With a 50% HNO_3 solution, back-extraction of As can be achieved within 10 min of shaking. Incomplete extraction of As may result if the acid concentration is less than 30%. The Ultrex grade HNO_3 blank did not show any detectable amount of As under our irradiation and counting conditions. Technical grade HNO_3 should be avoided because it may contain traces of As. After irradiation, the acid solution containing ^{76}As can be transferred to a new polyethylene vial using a disposable syringe for γ counting.

The proposed extraction method not only eliminates interferences for NAA but also provides a large preconcentration factor for As. In the APDTC extraction step, the aqueous to organic phase ratio is normally kept no more than 20:1. A concentration factor of 20 can be obtained in the first step of the proposed extraction. Another concentration factor of 5 or more can also be obtained in the acid back-extraction step. Therefore, a total concentration factor of 100 or more can be achieved from the proposed two-step extraction procedure. The absolute detection limit of As under our experimental conditions and based on three standard deviations of the background under the 559 keV peak is estimated to be 1 ng. With a preconcentration factor of 100, this method should be able to detect As in natural waters at the 10^{-2} µg/L level. The proposed extraction procedure combined with NAA is likely to be one of the most sensitive methods for determining low levels of As in natural water systems. The extraction method can also be combined with graphite furnace atomic absorption spectrometry (GFAAS) for As determination in natural waters. However, because concentrated HNO_3 is not a preferred matrix for GFAAS, dilution of the acid solution from the back-extraction process is necessary in order to reduce matrix interference for As determination. This would result in a smaller preconcentration factor for As. In general, NAA is relatively free from chemical interferences because the γ rays emitted from a nucleus are independent of the chemical environment of the atom. If spectral interference can be eliminated, NAA is likely to be the most reliable technique for trace element determination in environmental samples.

The proposed method for As extraction and NAA has been applied to the analysis of NBS Standard River Water (SRM 1643a) which is certified to contain 76±7 ng/g of As. Because the certified value does not specify the oxidation state of As, our analysis of this standard reference material followed the procedure for total As determination described in the experimental section. Using synthetic seawater as diluent and based on five replicate analyses, the average arsenic content in SRM 1643a determined by this extraction method and NAA was 82.0±2.3 µg/L. The average coefficient of variation for the series of replicates was ±2.8%. In another case, a mine water sample was spiked with

SRM 1643a and the total recovered As was found to correspond to 73±2 µg/L in the reference material. These experimental values agree well with the certified value given by NBS. In addition to SRM 1643a, we have also tested the accuracy of our method by analyzing a seawater reference material (NASS-1) obtained from the Marine Analytical Chemistry Standards Program, National Research Council of Canada. The total As in NASS-1 which has been determined by two different techniques (anodic stripping voltammetry and hydride generation atomic absorption spectrometry) is certified to be 1.65±0.19 µg/L according to the Marine Analytical Chemistry Standards Program. Using our extraction method and NAA, the total As in NASS-1 was found to be 1.55±0.05 µg/L based on triplicate analyses of 100 mL aliquots of the seawater reference material. The agreement is again good, indicating that our method for total As determination is reasonably accurate. The accuracy of this extraction method for differentiating As^{3+} and As^{5+} species in water could not be thoroughly evaluated because no standard waters containing known amounts of the two As species were available. However, from our experiments of natural waters spiked with known amounts of As^{3+} and As^{5+}, satisfactory recoveries (>90%) of both arsenic species were observed in most cases as shown in Table II. The results were corrected for the blank arsenic values.

In the case of natural seawater, a low recovery of spiked arsenic(III) (~72%) was observed. The seawater presumably contained species capable of oxidizing As^{3+} to As^{5+}, since the recovery of total As was found satisfactory in this experiment. There have been reports in the literature indicating that when sodium arsenite was added to natural seawater it could be oxidized to arsenate [12]. This effect was found more pronounced at low As concentrations [13]. The results observed in our experiments with spiked seawater appear to be consistent with these reports.

The results of selective determination of As^{3+} and As^{5+} in various types of natural waters using the proposed extraction method and NAA are presented in Table III. For surface waters, either from the river or from the sea, the As^{5+} concentration is appreciably larger than that of As^{3+}. This high As^{5+} content is caused, at least in part, by the high oxidized environment. The average total arsenic for surface seawater is reported to be 2 μg/L [3]. Several competing processes can modify the concentrations of the arsenic species in natural waters: oxidization of arsenite to arsenate or the reverse reaction, precipitation and adsorption reactions, dissolution of solid material (especially organic matter), diffusion of arsenic from and into the sediments, and the advection due to the compaction flow. The kinetics of the arsenite-arsenate transformation in the ocean or river waters are still not well understood. Both bacterial and marine phytoplankton can reduce arsenate to arsenite, and the reverse reaction is known to be catalyzed by a number of bacteria [14,15]. On the other hand, high content of arsenic(III) is notable for water samples coming from a deep well indicating a reduced environment for the ground water. Underground waters collected from a major lead-zinc mine in northern Idaho show varied As(III)/As(V) ratios as shown in Table III. It is interesting to note that a lower As(III)/As(V) ratio appears to correlate with a higher total arsenic content in the water. This seems to suggest that leaching of arsenic and perhaps other metals may be related to the redox environment of the ground water system. With the assumption of redox equilibrium, the arsenic ratio may provide a basis for obtaining an indication of redox status for natural waters according to the Nernst equation. Investigations are currently in progress to follow the ratio of As(III)/As(V) as a chemical indicator to evaluate the redox status and quality of groundwaters in a galena-sphaleride mine in Idaho.

Literature Cited

1. Cherry, J. A.; Shaikh, A. U.; Tallman, D. E.; Nicholson, R. V.; J. Hydrology, 1979, 43, 373.
2. Arsenic-Medical and Biological Effects of Environmental Pollutants, National Academy of Sciences, 1977.
3. Wedepohl, K. H; "Handbook of Geochemistry," Vol. II/3, Springer Verlag, N.Y., 1978, Ch. 33.
4. Lenvick, K.; Steinnes, E.; Pappas, A. C.; Anal. Chim. Acta, 1978, 97, 295.
5. Yu, J. C.; Wai, C. M.; Anal. Chem., 1984, 56, 1689.
6. Mok, W. M.; Wai, C. M.; Anal. Chem., 1984, 56, 2623.
7. Lo, J. M.; Yu, J. C.; Hutchison, F. I.; Wai, C. M.; Anal. Chem., 1982, 54, 2536.
8. Shen, L. H.; Yeh, S. J.; Lo, J. M.; Anal. Chem., 1980, 52, 1882.
9. Wyttenbach, A; Bajo, S.; Anal. Chem., 1975, 47, 2.
10. Yeh, S. J.; Lo, J. M.; Shen, L. H.; Anal. Chem., 1980, 52, 528.
11. Kamada, T.; Talanta, 1976, 23, 835.
12. Johnson, D. L.; Pilson, M. E.; Anal. Chim. Acta, 1972, 58, 289.
13. Johnson, D. L.; Pilson, M. E.; Environ. Lett., 1975, 8, 157.
14. Johnson, D. L.; Nature, 1972, 240, 44.
15. Osborne, F. H.; Ehrlick, H. L.; J. Appl. Bacteriol., 1976, 41, 295.

Credit

This work was supported in part by the Idaho Water Resources Research Institute with funding from the U. S. Geological Survey. Neutron irradiations were performed at the Washington State University Nuclear Radiation Center under the Reactor Sharing Program supported by DOE.

Table I. Effect of EDTA as masking agent on dithiocarbamate extraction of As from mine water.

Sample	As(III) added (ng)	As(V) added (ng)	% Recovery of As(III)	% Recovery of As(V)
Mine water without EDTA	500		81.1±1.9	
Mine water with EDTA	400		102.2±1.6	
Mine water with EDTA		400		107.0±1.9

Sample Volume: 50 mL. The results are corrected for the blank As value in sample.

Table II. Recovery of spiked As(III) and As(V) from different natural water systems.

Sample	As(III) added (ng)	As(V) added (ng)	% Recovery of As(III)	% Recovery of As(V)	% Recovery of total As
River water (50 mL)	400		91.8±4.6		
	800	400	104.0±2.1		100.2±2.1
	400	400	107.4±2.5		99.1±2.5
	400	800	103.5±2.5		96.0±2.1
Seawater (100 mL)	400	400	72.4±2.0		88.5±1.8
	800	800	71.4±1.4		98.3±1.4
Mine water (A)		400		93.2±2.6	
Mine water (B)	400		86.5±1.6		
Mine water (C)	400		94.7±1.9		
Mine water (D)	400		107.2±1.5		

Table III. Selective determination of As(III) and As(V) in various types of waters.

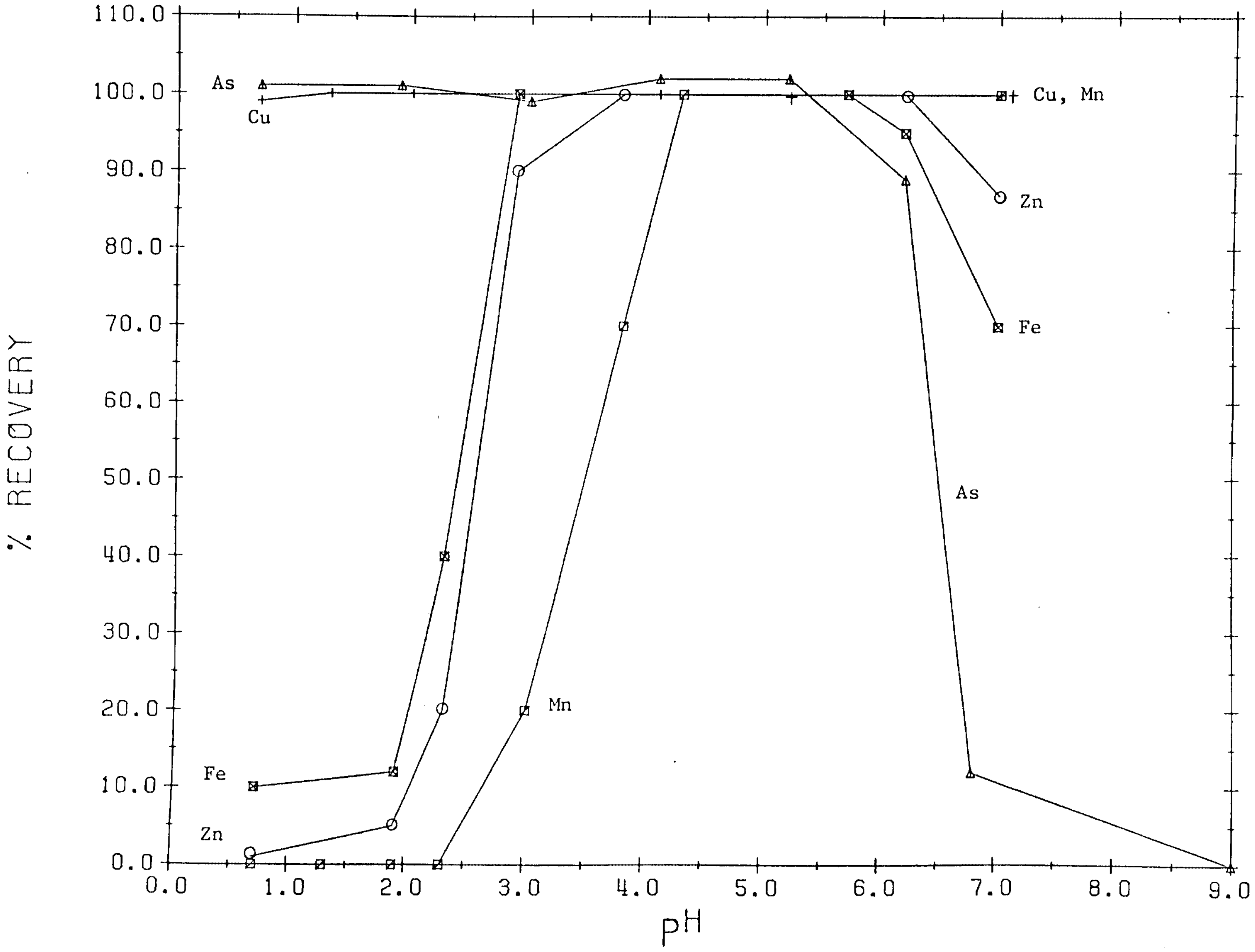
Sample	As(III) found (ng/mL)	As(V) found (ng/mL)	Total As found (ng/mL)
Snake River water	0.7±0.1	3.0±0.1	3.7±0.1
Seawater from Tacoma, Washington	<0.04	1.9±0.1	1.9±0.1
Well water from Joel, Idaho	0.6±0.1	0.5±0.1	1.1±0.1
Mine water* (A)	1.9±0.2	12.0±1.3	13.9±1.3
Mine water* (B)	2.4±0.1	1.5±0.2	3.8±0.2
Mine water* (C)	6.2±0.3	74.2±1.9	80.3±1.9

* From the Bunker Hill Mine, Kellogg, Idaho.

Figure Captions

Figure 1. pH dependence of the extraction of As(III) and other metals, Cu(II), Fe(II), Mn(II), and Zn(II), with APDTC from aqueous phase into chloroform. As(V) is not extractable at pH>1 as discussed in the text.

Figure 1


% RECOVERY
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0.0
pH
0.0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
As
Cu
Cu, Mn
Zn
Fe
As
Mn
Fe
Zn

Brief

This two-step extraction process involving pyrrolidinedithiocarbamate and nitric acid eliminates matrix interferences and concentrates As(III) and As(V) from natural waters for neutron activation analysis.