APPENDIX E-ANALYTICAL LABORATORY SOPS
2 OF 3

REMEDIAL INVESTIGATION

Stratford Army Engine Plant
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ABSTRACT

The disposal of coal combustion wastes is an environmental concern to the electrical power utilities because high concentrations of potentially toxic water-soluble trace elements, such as arsenic (As), may be released. During the last two years research was conducted to (1) develop a methodology for As speciation in waters and sediments, (2) predict the equilibrium speciation of As in natural waters using geochemical modeling techniques, and (3) determine the chemical speciation of As in fresh water and sediment of a reservoir which receives coal fly ash.

The analytical methodologies have been developed for collection, storage and analysis of freshwater and sediment without significantly altering the speciation of As. Arsenic speciation of water and sediment is simply and reproducibly achieved using hydride generation in conjunction with atomic absorption detection. Very rapid freezing by immersion in liquid nitrogen followed by storage at -80°C is necessary to prevent oxidation of As (III) to As (V) during storage of water samples. Arsenic species are selectively extracted from sediment. At pH 2.3, As (III) is extracted and at pH 11.9 As (V) MMA and DMA are extracted.

The geochemical modeling results indicate the principal controls on distribution of the aqueous species of As are E^H and pH. Under most environmental conditions As is present in the (V) valence state as the $H_2AsO_4^-$ species, while As (III) as the $H_3AsO_3^\circ$ species, is only dominant in low pH and low E^H environments. Sorption of arsenic as As (V) on iron and aluminum oxides could control arsenic concentrations in natural waters.

Field samples were collected from Hyco Reservoir in February and July 1984. The reservoir is apparently contaminated by As discharged from a coal fly ash pond. The majority of As is in the (V) valence state in the water column and ash pond. However, in the interstitial water squeezed from the reservoir sediments, As is equally divided between (V) and (III).

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INTRODUCTION

As the use of coal by industry increases, so will the need to develop more cost effective and environmentally safe methods for disposal of the fly and bottom ash. Currently disposal of this material is achieved by temporary ponding (usually on site) followed by mining and subsequent use as fill material (1). Even though the need for more useful or creative methods for disposal has been recognized, it is likely that these stockpiles will continue to grow. These wastes contain high concentrations of potentially toxic water soluble trace elements and other constituents although they vary in composition (2, 3, 4, 5, 6). Because leachate from these wastes could contaminate local ground and surface waters, the electric power industry has a need to develop reliable methods for the collection, storage and analysis of these elements in order to evaluate the fate of the elements in receiving waters. Arsenic, which is biologically toxic, is one such element present in coal combustion waste. It is the purpose of this effort to identify the predominant inorganic forms of arsenic that would be expected to exist in natural fresh waters and to discuss the effect of such processes as formation of solid phases, adsorption and biological oxidation on the chemical species and concentrations of arsenic in solution.

APPROACH

The distribution of arsenic between its two valence states, distribution among its inorganic solution species, and the relative solution saturation of arsenic minerals were computed using the geochemical model MINTEQ (7) for two arsenic concentrations (0.001 and 0.1 mg L^{-1}) in waters with high and low total dissolved solids. The chemical analyses of the Sacramento and Lower Colorado Rivers which were used to represent low and high total dissolved solids waters respectively are given in Table 1-1. The thermodynamic data for the arsenic species presented by Ball et al. (8) are used in MINTEQ. Arsenic forms few aqueous complexes (Table 1-2) but forms solids with many different metals (9). Although the organic arsenic complexes, methyl arsenate and dimethyl arsenate have been reported in seawater (10), thermodynamic data were not available to represent arsenic organic complexation.

Table 1-1

WATER QUALITY OF LOW AND HIGH DISSOLVED SOLIDS WATERS

($mg\ L^{-1}$)

Components[a]	Low Dissolved Solid[b]	High Dissolved Solid[c]
Na	12.0	124
K	1.4	4.4
Ca	12.2	94
Mg	7.5	30
H_4SiO_4	29.14	22.4
CO_3	74.0	180
Cl	9.9	113
SO_4	7.7	289
H_3BO_3	0.286	0.297
Br	0.006	-
I	0.0018	-
F	0.10	0.2
PO_4	0.210	-
NO_3	0.898	1.0
NO_2	0.019	-
NH_4	0.144	-
Fe(II)	0.015	0.01 (total)
Fe(III)	0.0007	-
Mn	0.0044	0.021
Al	0.005	0.012
Zn	0.00049	-
Cd	0.0001	-
Hg	0.00001	-
Pb	0.00003	0.008
Cu	0.0005	0.0088
Ni	0.0018	0.03
Ag	0.00004	0.001
H_3AsO_4	0.004	-
HS	0.0019	-
Ba	0.021	0.152
Li	-	0.035
Rb	-	0.008
Sr	-	0.802
pe	7.84	7.84
pH	8.01	8.01
T°C	9.5	9.5

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[a] The form of the chemical constituents listed are the MINTEQ model "parent species", i.e., those which are used in all reactions involving that element.

[b] From Nordstrom et al. (43) and Kopp and Kroner (44).

[c] From Table 18G, Livingston (29) except for T, pe and pH.

Table 1-2

AQUEOUS COMPLEXES AND MINERALS FOR ARSENIC IN THE MINTEQ MODEL

Aqueous Species	Log K_r
$H_3AsO_3^o \quad H_2AsO_3^- + H^+$	-9.22
$H_3AsO_3^o \quad HAsO_3^{-2} + 2H^+$	-21.33
$H_3AsO_3^o \quad AsO_3^{-3} + 3H^+$	-34.744
$H_3AsO_3^o + H^+ \quad H_4AsO_3^+$	-0.3050
$H_3AsO_4 \quad H_2AsO_4^- + H^+$	-2.243
$H_3AsO_4^o + F^- \quad HAsO_3F^- + H_2O$	2.832
$H_3AsO_4^o + F^- \quad AsO_3F^{-2} + H^+ + H_2O$	-3.037
$H_3AsO_4^o \quad HAsO_4^{-2} + 2H^+$	-9.00
$H_3AsO_4^o \quad AsO_4^{-3} + 3H^+$	-20.5970
$H_3AsO_3^o + H_2O \quad H_3AsO_4^o + 2H^+ + 2e^-$	-19.444

Minerals

Composition (Name)

AsI_3

As_2O_5

As_4O_6 (Arsenolite)

As_4O_6 (Claudetite)

As_2S_3 (Orpiment)

AsS (Realgar)

$Ni_3(AsO_4)_2 \cdot 8\ H_2O$ (Annabergite)

$Ba_3(AsO_4)_2$

$Cu_3(AsCu_4)_2 \cdot 6\ H_2O$

$Fe\ AsO_4 \cdot 2\ H_2O$

$Mn_3(AsO_4)_2 \cdot 8\ H_2O$

Composition

$Pb_3(AsO_4)_2$

$Zn_3AsO_4 \cdot 22.5\ H_2O$

$Ca_3(AsO_4)_2 \cdot 6H_2O$

Sensitivity analyses were performed to establish the effect on the arsenic species distribution of the variables pH, E^H and dissolved sulfide. These variables were chosen for this analysis because: pH is known to vary temporally, E^H data is scarce and may also vary temporally, and dissolved sulfide data is almost nonexistent:

The pH of surface waters varies from as low as 1.7 in some volcanically formed lakes containing free sulfuric acid to 12.0 or more for some closed alkaline lakes rich in Na_2CO_3 (11). Acid drainage from sulfide-bearing deposits or wastes may produce pH values down to 0.8 (12). The usual pH range for open lakes is from slightly less than 6.0 to 9.0. Thus, the range 5 to 9 was chosen to represent the range in pH to include natural waters other than those seriously polluted with acid.

The redox potential (E^H) of oxygenated waters seldom exceed +400 mV although values in surface soils as high as +800 mV have been reported (13). The E^H_{pt} of oxygenated surface waters of lakes usually ranges from 400 to 500 mV (11). Mortimer (14) observed that bacterial production of hydrogen sulfide from sulfate does not occur till the E^H_{pt} is below 100 mV. Therefore, E^H values of 100 and 400 mV were chosen to represent the range of oxygenated natural waters where sulfide production by bacteria is not expected to occur.

Dissolved sulfide concentrations ranging from 1.7 to 10.1 $\mu g\ L^{-1}$ were measured in samples taken from essentially fully oxygenated waters of San Francisco Bay in a recent study (D. D. Vivit, E. A. Jenne and J. W. Ball, unpublished data, 1982). The co-existence of sulfide and oxygen has also been observed in seawater due to the kinetic restraint on sulfide oxidation (15). In less oxygenated shallow estuarine waters, thousand-fold higher sulfide concentrations have been reported (16). In the sensitivity analysis, a hundred-fold range in sulfide concentration from 0.1 $\mu g\ L^{-1}$ to 10 $\mu g\ L^{-1}$ was used to simulate the probable range in sulfide concentration in coastal waters.

The sensitivity analysis was performed by varying the concentration of one constituent (pH, E^H or dissolved sulfide) within the predetermined range while the concentrations of the remaining constituents were held constant; the calculated distributions of aqueous complexes and saturation indices were compared to the base case to determine the relative sensitivities of the distribution to each constituent.

OXIDATION STATE AND EQUILIBRIUM

Arsenic can occur in four oxidation states (-III, 0, III, V) in natural waters, however, arsenic metal (As(0)) occurs only rarely and As(-III) exists only at extremely low E^H values. Therefore, the main oxidation states of arsenic in fresh water are arsenite(III) and arsenate(V). For oxygenated waters only arsenate(V) is predicted to be important based on thermodynamic equilibrium calculations. Arsenite except at very low pH would occur at extremely low concentrations.

The distributions of the arsenic species calculated by MINTEQ assumes that the system is at equilibrium. Even if equilibrium conditions are not met, the resulting calculations can provide boundary conditions toward which the system is proceeding. In most cases assumption of equilibrium or near equilibrium is valid, although redox reactions are frequently not at equilibrium. In some situations, it is possible that the actual distribution of oxidized and reduced species may be quite different from that predicted by thermodynamic equilibrium calculations. The distribution of the redox sensitive elements such as arsenic depends on the past history of the parcel of water and on the rate of the redox reaction. Often the redox reactions are biologically mediated, therefore, approach to equilibrium may depend on the presence of certain biota.

For arsenic, thermodynamic equilibrium between the As(III) and As(V) oxidation states probably does not exist for most natural waters although a quasi steady state distribution between the oxidation states may be achieved. For example, Cherry et al. (17) observed that for deoxygenated waters with an initial As(III)/As(V) ratio of 1, the As(III)/As(V) ratio remained unchanged for as long as 78 days over a pH range of 2 to 10.5. Laboratory studies using these same solutions and redox agents (O_2, H_2S, Fe(III)) common to natural waters indicated that at concentrations of these agents found in natural waters, oxidation or reduction of the arsenic would require months or even years to reach equilibrium. It is therefore probable that in natural waters of low temperature and containing small amounts of redox agents, the chemical oxidation or reduction of arsenic would reach equilibrium only over very long time scales although a quasi steady state may be observed. In contrast, Stauffer et al. (18) observed in hot spring drainages from Yellowstone National Park, that although the total dissolved arsenic was approximately constant, the As(III) to As(V) ratio was strongly bimodal (~50 or <.1) depending on whether S(-II) was dominant. The oxidation of As(III) was observed to proceed rapidly at elevated temperatures (30° to 40°C) once all the S(-II) had been oxidized. In contrast, in the oxygenated but low temperature (<20°C) waters of the Madison river, the As(III)/As(V) ratio remained approximately constant in the flowing river and through the Hibgen Reservoir.

In natural waters, it is possible that oxidation of As(III) to As(V) could occur at rates much faster than those representing abiotic oxidation due to the presence of certain aquatic "bacterioplankton." Schudlark and Johnson (19) using treated and untreated Narragansett Bay water found that, in the absence of bacteria, oxidation proceeded at a slow but constant rate. In the presence of the bacteria, the rate of oxidation was directly proportional to the arsenite concentration at that time and did not depend on the presence of light.

Turner (20) measured the oxidation state of arsenic in ash pond effluents. Although he did report the pH of the solution, he performed only limited measurements of E^H in a DOE flyash pond well. The E^H was reported to have ranged from +35 to +210 mV although particular potentials were not ascribed to any samples. Because of the lack of corresponding pH and E^H values, it is impossible to determine if the solutions in the DOE ash disposal system are in thermodynamic equilibrium with respect to the arsenic oxidation state. The pH of these samples ranged from 6.6 to 7.8. In this pH and E^H range, the dominant oxidation state would range from As(III) at low pH and low E^H to As(V) at the higher pH and E^H measurements resulting in a wide range of values for the As(III)/As(V) total ratio from <<1 to greater than 1 as was reported.

INORGANIC AQUEOUS COMPLEXES

Using the thermodynamic data from Table 1-1 for As(III) and As(V), an E^H-pH diagram indicating the predominant aqueous species, was constructed (Figure 1.1). The absence of any arsenic complexes, other than the weak fluoride ones, means that the main factors controlling the distribution of arsenic in natural waters is the E^H and pH of the system (21, 22) and that there should be no difference between the inorganic species distributions for the high and low dissolved solid waters. As illustrated in Figure 1, equilibrium calculations indicated that arsenite will be dominant only at low pH and low E^H, whereas arsenate will be dominant at all other E^H and pH values used. These results were confirmed by the simulation analysis (Appendix A). At pH=5 for both the low dissolved solids and high dissolved solids water at E^H=100, the arsenic was represented almost 100% by $H_3AsO_3^o$ and at E^H=400 almost 100% by $H_2AsO_4^-$. At pH=7.5 and 9 for both E^H values, arsenate dominated with the most abundant species being $HAsO_4^{-2}$, representing about 85% of the total arsenic.

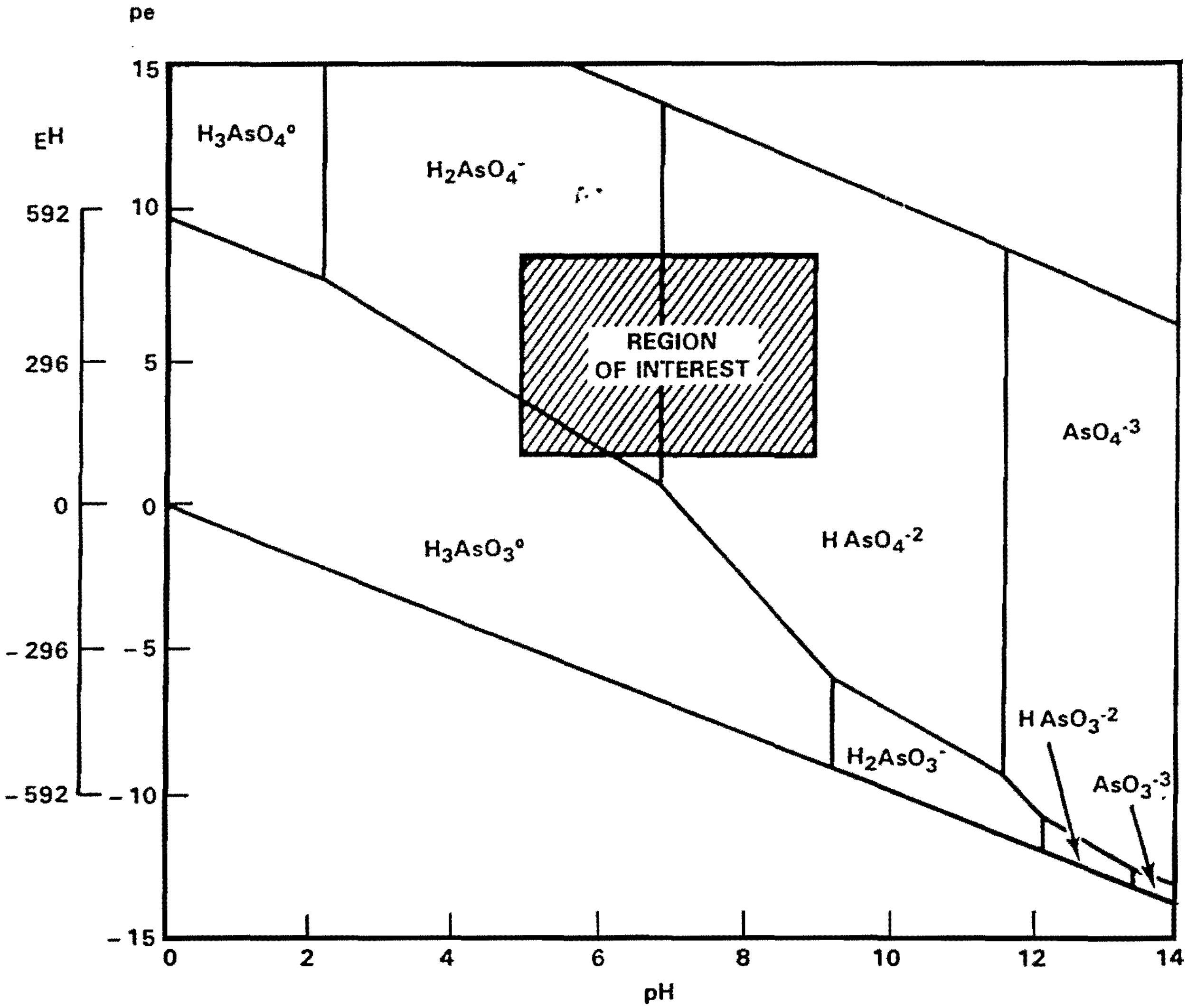

Figure 1-1. E^H-pH Diagram for Arsenic Aqueous Species

The only other aqueous species of arsenic in the MINTEQ model were the two arsenate fluoride species $HAsO_3F^-$ and AsO_3F^{-2} both of which constituted an insignificant fraction of the total arsenic. Only at a fluoride concentration of 1.58 mg L^{-1} would the fluoride species constitute 10% of the total As(V).

In contrast to the slow reaction rates commonly found for oxidation/reduction reactions, the establishment of hydrolysis is usually very fast especially if the hydrolysis species are simple. Thus assuming a measured distribution of the redox equilibria, the actual aqueous species in solution can be accurately predicted from the pH.

Turner et al. (23) computed the equilibrium distribution for trace elements including arsenic in fresh and seawater. The approach used was to approximate the complexation of the trace elements by a series of linear equations for each element or each oxidation state which are then solved simultaneously. The dominant oxidation state predicted for oxygenated (pe = 12.4) seawater at pH 8.2 was As(V) with the dominant aqueous species (98%) being $HAsO_4^{2-}$. This agrees with the pe-pH diagram. The As(V) oxidation state was also computed to be the dominant valence state for arsenic in oxidized (pe = 14.6) freshwater at pH 6 and the dominant aqueous species (89%) was $H_2AsO_4^-$ which agrees with the pe-pH diagram and the MINTEQ speciation calculations. Because of the lack of important aqueous arsenic complexes with the inorganic constituent of the water, the speciation changes between the sea and freshwater were due solely to the change in pH.

SOLUBILITY CONTROLS ON ARSENIC

The stability diagram (Figure 1-1) for arsenic indicates the predominant aqueous species that would occur at specific pH and E^H values. A second very important aspect of the arsenic geochemical modeling is to identify any solid phases which could possibly exert, under some environmental conditions, a solubility control on dissolved arsenic concentration. Although there are over 160 arsenic containing minerals known in nature (9), thermodynamic data and kinetic data exist for only a few. Holm et al. (24) stated that most of these solids are slow in nucleation and growth. This lack of pertinent thermodynamic and kinetic data makes it impossible to be certain whether some of the more complex arsenate solids for which the thermodynamic data do not exist may exert a more effective control on dissolved arsenic than some of the solid phases considered. Even with this limitation, the saturation indices (SI) calculated can be used to suggest solid phases that may be formed and that could limit dissolved arsenic concentration.

The 15 arsenic containing solid phases included in the MINTEQ thermodynamic data base are listed in Table 1-1. All of these solid phases were calculated to be undersaturated in both the high and low dissolved solid waters except for orpiment (As_2S_3) and $Ba_3(AsO_4)_2$. Orpiment has been observed in deposits from hot springs (25) and also as a weathering product of arsenic-rich ores (26). The geochemical model calculated that orpiment would be in equilibrium or oversaturated at the lower E^H = (100 mV), low pH (5) and high sulfide (10 µg L^{-1}) for the low dissolved solids water and at low E^H, low pH and both sulfide concentrations (0.1 and 10 µg L^{-1}) for the high dissolved solids water. Thus, orpiment may be a solubility control for arsenic under conditions of low pH, low E^H and high sulfide concentrations, if there are no significant kinetic inhibitions to its precipitation.

One other solid, $Ba_3(AsO_4)_2$, was calculated to be oversaturated in both waters at all E^H, sulfide and arsenic levels used at the intermediate (7) and high (9) pH values, and was oversaturated at the high E^H and arsenic concentrations for the high dissolved solids water at pH 5. Simulations with pH 9, high dissolved arsenic (0.01 µg L^{-1}) and high TDS water resulted in calculations of an oversaturation of 12 orders of magnitude. Wagemann (22) suggested that at barium ion concentrations typical for freshwaters, $Ba_3(AsO_4)_2$ would hold total dissolved arsenic concentrations at rather low levels. A cursory review of x-ray diffraction and mineralogical references (27) shows no evidence for the geologic occurrence of this solid phase.

The same thermodynamic data (28) had been used previously (E. A. Jenne, unpublished data, 1979) for $Ba_3(AsO_4)_2$ and resulted in calculated oversaturation in the leachates of fly ash and in geothermal waters of Yellowstone National Park. We, therefore, assume that there is a major error in the thermodynamic data of Chukhlantsev (28). If $Ba_3(AsO_4)_2$ does serve as an effective solubility control, it would have a significant effect on the barium concentration in solution. Table 3 gives the barium concentration in solution in equilibrium with $Ba_3(AsO_4)_2$. These barium concentrations are many orders of magnitude less than the average river concentration of 54 mg L^{-1} (29) and would make barium undetectable by conventional analytical methods even in waters with very low arsenic concentrations, which further suggests that Chukhlantsev's thermodynamic data (28) is erroneous.

Table 1-3

THE CONCENTRATIONS OF BARIUM COMPUTED TO BE IN EQUILIBRIUM WITH SOLID $Ba_3(AsO_4)_2$, USING THE THERMODYNAMIC DATA OF CHUKHLANTSEV (28)

pH	As (mg L^{-1}) 0.001	0.01
7.5	1.5×10^{-6}	7.0×10^{-8}
9.0	1.4×10^{-7}	6.3×10^{-9}

SORPTION

Although it is unlikely that solubility controls exist for arsenic, Stauffer et al., (18) suggested that arsenic concentrations may be controlled by sorption. Iron and aluminum amphoric solids appear to preferentially sorb arsenic (30; 31; 33). When the aluminum and iron were removed from the soils, sorption was eliminated or appreciably reduced (30). The amount of sorption on the iron and aluminum depends on the oxidation state of the arsenic, and the composition and pH of the solution. Arsenic is predominantly absorbed as the V oxidation state (34; 35) although some sorption of As(III) has been found (36). The sorption of As(V) appears to be influenced by pH with a drop in sorption occurring at pH's above 7.5 (35; 37; 38) although sorption remained approximately constant over the range from pH 3 to 7.5 (35; 37; 39). Sorption of As(III) was constant over a pH range of 4 to 10 (35, 36, 31). The relationship between sorption and pH indicates that the chemical species most likely being sorbed is $H_2AsO_4^-$ for As(V) and $H_3AsO_3^\circ$ for As(III). Although arsenate is the most strongly adsorbed, methylarsonic acid and dimethylarsenic acid are also absorbed, although less strongly, and all three follow Langmuir isotherms (24). Arsenic(V) and phosphate displace each other from sorption sites (40; 41), therefore, sorption of arsenic will be less in soils with high phosphate concentrations. Chloride, nitrate and sulfate had little effect on the adsorption of arsenic (42). Based on the data, it is very likely that sorption exerts a control on arsenic concentrations in natural waters.

CONCLUSIONS

- The principal controls on distribution of the aqueous species of arsenic are E^H and pH.

- For most environmental conditions the arsenate, As(V), as the $H_2AsO_4^-$ species, is dominant.

- Arsenate, As(III), as the $H_3AsO_3^o$ species, is only dominant in low pH and low E^H environments.

- Orpiment (As_2S_3) appears to be a potential limiting-controlling mineral for arsenic in low pH, low E^H and high sulfide environments.

- Arsenic will be highly mobile regardless of its oxidation state.

- The available thermodynamic data for $Ba_3(AsO_4)_2$ must be erroneus or else the kinetic inhibitions to its precipitation are enormous considering there is no evidence for its geologic occurrence or gross oversaturation computed with Chukhlantsev's thermodynamic data.

- Sorption of arsenic as As(V) on iron and aluminum oxides could control arsenic concentrations in natural waters.

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Section 2

DETERMINATION OF ARSENIC SPECIES IN LIMNOLOGICAL SAMPLES BY HYDRIDE GENERATION ATOMIC ABSORPTION SPECTROSCOPY

INTRODUCTION

This section describes the analytical methods used to determine the arsenic species in waters and sediments. Also, sample storage tests were conducted to select methods of storing and shipping environmental samples that would minimize changes in speciation. Based on results of previous studies we selected hydride generation coupled with atomic absorption spectroscopy as the method of quantification of arsenic. In this technique arsenate, arsenite, methylarsonic acid, and dimethylarsinic acid are volatilized from solution at a specific pH after reduction to the corresponding arsines with sodium borohydride (1). The volatilized arsines are then swept onto a liquid nitrogen cooled chromatographic trap, which upon warming, allows for a separation of species based on boiling points. The released arsines are swept by helium carrier gas into a quartz cuvette burner cell (2), where they are decomposed to atomic arsenic. Arsenic concentrations are determined by atomic absorption spectroscopy. Strictly speaking, this technique does not determine the species of inorganic arsenic but rather the valence states of arsenate (V) and arsenite (III). The actual species of inorganic arsenic are assumed to be those predicted by the geochemical equilibrium model described in Section 1 of this report.

EXPERIMENTAL SECTION

Apparatus

The apparatus needed for the volatilization, separation and quantitation of arsenic species is shown schematically in Figure 2-1-a. Briefly, it consists of a reaction vessel, in which arsenic compounds are reduced to volatile arsines, a liquid nitrogen cooled gas chromatographic trap, and a H_2 flame atomic absorption detector.

Reaction Vessel. The reaction vessel is made by grafting a side-arm inlet onto a 30-ml "Midget Impinger" (Ace Glass #7532-20), as illustrated in Figure 2-1-b. The 8-mm diameter side arm may then be sealed with a silicone rubber-stopper type septum (Ace Glass #9096-32) to allow the air-free injection of sodium borohydride. The standard impinger assembly is replaced with a 4-way Teflon stopcock impinger (Laboratory Data control #700542) to allow rapid and convenient switching of the helium from the purge to the analysis mode of operation.

GC Trap. The low temperature GC trap is constructed from a 6 mm o.d. borosilicate glass U-tube about 30-cm long with a 2-cm radius of bend (or similar dimensions to fit into a tall widemouth Dewar flask. Before packing the trap, it is silanized to reduce the number of active adsorption sites on the glass. This is accomplished using a standard glass silanizing compound such as Sylon-Ct® (Supelco Inc.). The column is half-packed with 15% OV-3 on Chromasorb® WAW-DMCS (45-60 mesh). A finer mesh size should not be used, as the restriction of the gas flow is sufficient to overpressurize the system. After packing, the ends of the trap are plugged with silanized glass wool.

The entire trap assembly is then preconditioned as follows: The input side of the trap (non-packed side) is connected via silicone rubber tubing to helium at a flow rate of 40 ml·min^{-1} and the whole assembly is placed into an oven at 175°C for 2 hours. After this time, two 25-µl aliquots of GC column conditioner (Silyl-8®, Supelco Inc.) are injected by syringe through the silicone tubing into the glass tubing. The column is then left in the oven with helium flowing through it for 24 hours. This process, which further neutralizes active adsorption sites and purges the system of foreign volatiles, may be repeated whenever analate peaks are observed to show broadening.

Once the column is conditioned, it is evenly wrapped with about 1.8 m of nichrome wire (22 gauge) the ends of which are affixed to crimp on electrical contacts. The wire-wrapped column is then coated about 2-mm thick all over with silicone rubber caulking compound and allowed to dry overnight. The silicone rubber provides an insulating layer which enhances peak separation by providing a longer temperature ramp time.

The unpacked side of the column is connected via silicone rubber tubing to the output from the reaction vessel. The output side of the trap is connected by a nichrome-wire wrapped piece of 6-mm diameter borosilicate tubing to the input of the flame atomizer. It is very important that the system be heated everywhere (~80°C) from the trap to the atomizer to avoid the condensation of water. Such condensation can interfere with the determination of dimethylarsine. All glass-to-glass connections in the system are made with silicone rubber sleeves.

Atomizer. The eluted arsines are detected by flame atomic absorption, using a special atomizer designed by Andreae (2). This consists of a quartz cross tube as shown in Figure 2-1-c. Air is admitted into one of the 6-mm o.d. side tubes (optimal flows are given in Table 2-1), while a mixture of hydrogen and the carrier gas from the trap is admitted into the other. This configuration is superior to that in which the carrier gas is mixed with the air (Andreae, personal communication 1983) due to the reduction of flame noise and possible extinguishing of the flame by microexplosions when H_2 is generated in the reaction vessel. To light the flame, all of the gases are turned on, and a flame brought to the ends of the quartz cuvette. At this point a flame will be burning out of the ends of the tube. After allowing the quartz tube to heat up (~5 minutes) a flat metal spatula is put smoothly first over one end of the tube, and then the other. An invisible air/hydrogen flame should now be burning in the center of the cuvette. This may be checked by placing a mirror near the tube ends and checking for water condensation. Note that the flame must be burning only inside the cuvette for precise, noise-free operation of the detector.

Table 2-1

OPTIMAL FLOWS AND PRESSURES FOR GASES
IN THE HYDRIDE GENERATION SYSTEM

Gas	Flow rate $ml \cdot min^{-1}$	Pressure $lb \cdot in^{-2}$
He	150	10
H_2	350	20
Air	180	20

Precision and sensitivity are affected by the gas flow rates and these must be individually optimized for each system, using the figures in Table 2-1 as an initial guide. We have observed that as the O_2/H_2 ratio goes up, the sensitivity increases and the precision decreases. As this system is inherently very sensitive, adjustments are made to maximize precision.

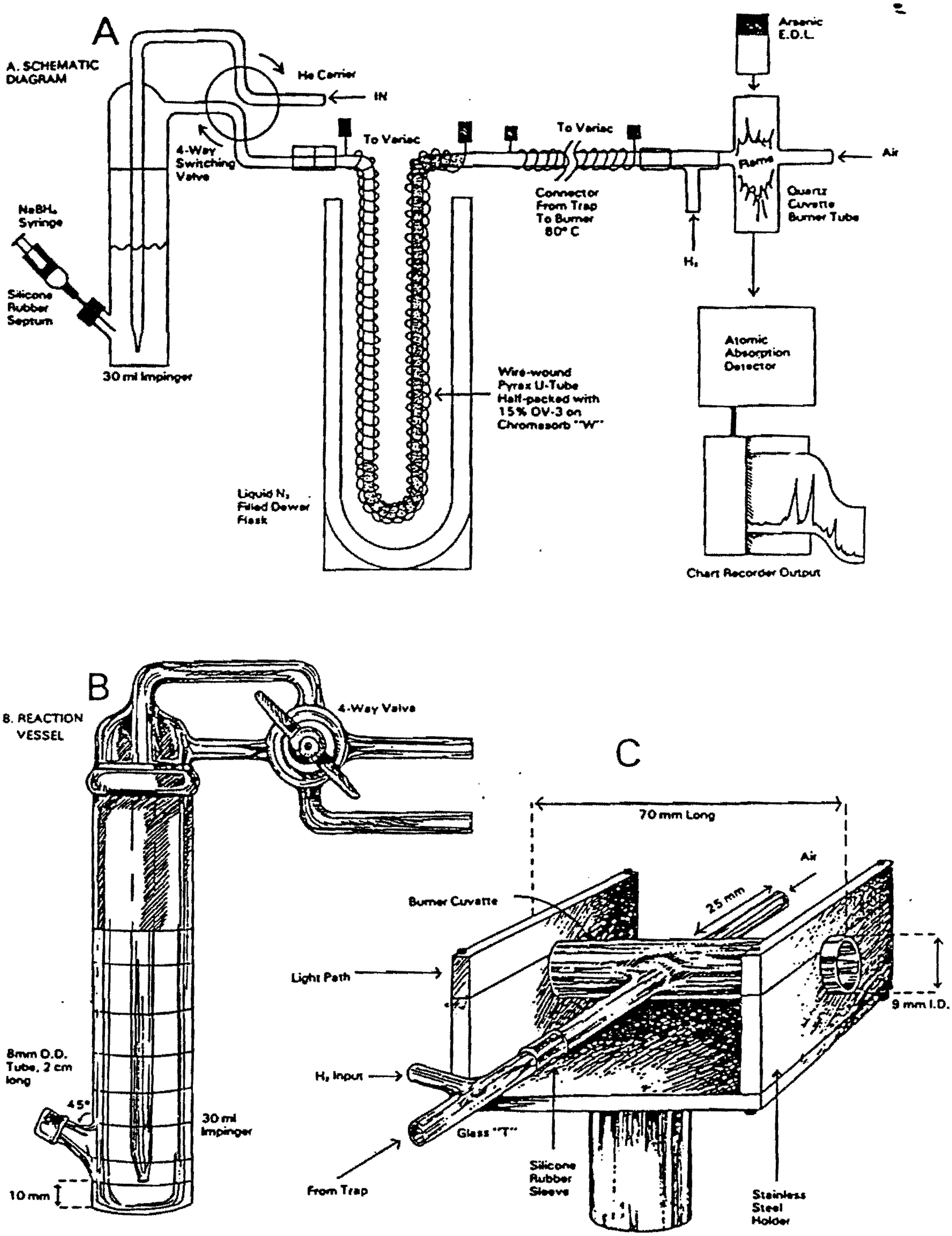


Figure 2-1. Arsenic Speciation Apparatus: (a) Schematic Diagram, (b) Reaction Vessel, (c) Quartz Cuvette Burner Tube.

Detector. Any atomic absorption unit may serve as a detector, once a bracket has been built to hold the quartz cuvette burner in the wave path. This work has been done using a Perkin-Elmer Model 5000® spectrophotometer with electrodeless discharge arsenic lamp. An analytical wavelength of 197.3 nm and slit width of 0.7 nm (low) are used throughout. This wavelength has been shown to have a longer linear range, though about half the sensitivity of the 193.7 nm line (2). Background correction is not used as it increases the system noise and has never been found necessary on the types of sample discussed in this paper.

Standards and Reagents

Arsenite (As(III)) Standards. A 1000 $mg \cdot l^{-1}$ stock solution is made up by the dissolution of 1.73 grams of reagent grade $NaAsO_2$ in 1.0-liter deionized water containing 0.1% ascorbic acid. This solution is kept refrigerated in an amber bottle. A 1.0 $mg \cdot l^{-1}$ working stock solution is made by dilution with 0.1% ascorbic acid solution and stored as above. Under these conditions this solution has been found stable for at least one year.

Further dilutions of As(III) for analysis, or of samples to be analyzed for As(III), are made in filtered Dungeness River water. It has been observed both here and elsewhere (Andreae 1983) that deionized water can have an oxidizing potential that causes a diminished As(III) response at low levels (1 $\mu g \cdot l^{-1}$ and less). Dilute As(III) standards are prepared daily.

Arsenate (As(V)) Standards. To prepare a 1000 $mg \cdot l^{-1}$ stock solution, 4.16 g of reagent grade $Na_2HASO_4 \cdot 7H_2O$ are dissolved in 1.0 liter of deionized water. Working standards are prepared by serial dilution with deionized water and prepared monthly.

Monomethylarsonate (MMA) Standards. To prepare a stock solution of 1000 $mg \cdot l^{-1}$, 3.90 g of $CH_3AsO(ONa)_2 \cdot 6H_2O$ is dissolved in 1.0 liter of deionized water. Working standards are prepared by serial dilution with deionized water. Dilute standards are prepared weekly.

Dimethylarsinate (DMA) Standards. To prepare a stock solution of 1000$mg \cdot l^{-1}$, 2.86 g of reagent grade $(CH_3)_2AsO_2Na \cdot 3H_2O$ (cacodylic acid, sodium salt) is dissolved in 1.0 liter deionized water. Dilute standards are handled as for MMA.

6M Hydrochloric Acid. Equal volumes of reagent grade concentrated HCl and deionized water are combined to give a solution approximately 6M in HCl.

Tris Buffer. 394 g of Tris·HCl (tris (hydroxymethyl) aminomethane hydrochloride) and 2.5 g of reagent grade NaOH are dissolved in deionized water to make 1.0 liter. This solution is 2.5 M in tris and 2.475 M in HCl, giving a pH of about 6.2 when diluted 50-fold with deionized water.

Sodium Borohydride Solution. Four grams of >98% $NaBH_4$ (previously analyzed and found to be low in arsenic) are dissolved in 100 ml of 0.02 M NaOH solution. This solution is stable 8-10 hours when kept covered at room temperature. It is prepared daily.

Phosphoric Acid Leaching Solution. To prepare 1.0 liter of 0.10 M phosphoric acid solution, 6.8 ml of reagent grade 85% H_3PO_4 are dissolved in deionized water.

Trisodium Phosphate Leaching Solution. To prepare 1.0 liter of 0.10 M trisodium phosphate solution, 6.8 ml of 85% H_3PO_4 and 12 g of reagent grade NaOH are dissolved in deionized water.

Acid Digestion Mixture. With constant stirring, 200 ml of concentrated reagent grade H_2SO_4 are slowly added to 800 ml concentrated HNO_3.

METHODS

Total Arsenic Determination

An aqueous sample (5-30 ml) is placed into the reaction vessel and 1.0 ml of 6M HCl is added. The 4-way valve is put in place and turned to begin purging the vessel. The G.C. trap is lowered into a Dewar flask containing liquid nitrogen (LN_2) and the flask topped off with LN_2 to a constant level. A 2.0-ml aliquot of $NaBH_4$ solution is then introduced through the silicone rubber septum with a disposable 3-ml hypodermic syringe and the timer turned on. The $NaBH_4$ is slowly added over a period of about 1 minute, being careful that the H_2 liberated by the reduction of water does not overpressurize the system or foam the contents out of the reaction vessel.

After purging the vessel for 8 minutes, the stopcock is turned to pass helium directly to the G.C. trap. In rapid order, the LN_2 flask is removed, the trap heating coil is turned on, and the chart recorder is turned on. The arsines are eluted in the order: AsH_3, CH_3AsH_2, $(CH_3)_2AsH$ according to their increasing boiling points given in Table 2.2 (1).

Table 2-2

REDUCTION PRODUCTS AND THEIR BOILING POINTS OF VARIOUS AQUEOUS ARSENIC SPECIES

Aqueous form	Reduction product	B.P., °C
As(III), arsenous acid, $HAsO_2$	AsH_3	-55
As(V), arsenic acid, H_3AsO_4	AsH_3	-55
MMA, $CH_3AsO(OH)_2$	CH_3AsH_2	2
DMA, $(CH_3)_2AsO(OH)$	$(CH_3)_2AsH$	35.6

Arsenic (III) Determination

The same procedure as above is used to determine arsenite, except that the initial pH is buffered at about 5 to 7 rather than <1, so as to isolate the arsenous acid by its pKa (1). This is accomplished by the addition of 1.0 ml of Tris buffer to a 5- to 30-ml aliquot of unacidified sample. (If the sample is acidic or basic, it must be neutralized first, or the buffer will be exhausted.) For the As(III) procedure, 1.0 ml of $NaBH_4$ is added in a single short (~10 seconds) injection, as the rapid evolution of H_2 does not occur at this pH.

Small, irreproducible quantities of organic arsines may be released at this pH and should be ignored. The separation of arsenite, however, is quite reproducible and essentially 100% complete. As(V) is calculated by subtracting the As(III) determined in this step from the total inorganic arsenic determined on an aliquot of the same sample previously.

SEDIMENTS

Total Inorganic Arsenic

A 1.00-g aliquot of freeze-dried and homogenized sediment is placed into a 100-ml snap-cap volumetric flask. Five milliliters of deionized water is added to form a slurry and then 7 ml of the acid digestion mixture is added. After 5 minutes, the caps are replaced and the flasks heated at 80 to 90°C for 2 hours. Upon cooling the samples are diluted to the mark with deionized water, shaken, and allowed to settle overnight. An appropriate-sized aliquot of the supernatant liquid (25-100 μl) is added to 20 ml of deionized water and run as for total arsenic.

Leachable Arsenite

An aliquot (~1-2 g) of fresh or freshly thawed wet homogeneous sediment is weighed to the nearest 10 mg directly into a 40-ml acid-cleaned Oak Ridge type centrifuge tube. To this is added 25 ml of 0.10 M H_3PO_4 solution and the tubes are agitated with the lids on. Periodic agitation is maintained for 18 to 24 hours, at which time the tubes are centrifuged for 30 minutes at 2500 RPM. Twenty milliliter aliquots of the supernatant liquid are removed by pipetting into cleaned polyethylene vials and saved in the refrigerator until analysis. Analysis should be accomplished within the next couple days.

For analysis, an appropriate-sized aliquot (10-100 μl) is added to 20 ml of well-characterized filtered river water (or other nonoxidizing/nonreducing water). Enough 1.0 M NaOH solution is added to approximately neturalize the H_3PO_4 (1/3 the volume of the sample aliquot), and then 1.0 ml of Tris buffer is added. The sample is then analyzed as for As(III).

Leachable Arsenate, MMA and DMA

An aliquot (~1-2 g) of wet sediment is weighed into a centrifuge tube, as above. To this are added 25 ml of 0.1 M Na_3PO_4 solution, and the tubes agitated periodically for 18 to 24 hours. After centrifugation the supernatant liquid (dark brown due to released humic materials) is analyzed as for total arsenic using an appropriate-sized aliquot in 20 ml of deionized water. The total inorganic arsenic in this case should be only As(V), as As(III) is observed to not be released at this pH. No pre-neutralization of the sample is necessary as the HCl added is well in excess of the sample alkalinity.

Interstitial Water Analysis

Interstitial water samples may be treated just as ordinary water, except that as they are quite high in arsenic, usually an aliquot of 100 to 1000 μl diluted in deionized water or river water is appropriate in most cases.

Storage Experiments

Storage experiments designed to preserve the original arsenic speciation of samples were carried out for a wide variety of conditions. For water samples, 30-ml and 60-ml polyethylene bottles precleaned in 1 M HCl were used.

Conditions of temperature ranging from 20°C to -196°C were assessed, as well as preservation with HCl and ascorbic acid. Storage tests were carried out over a period of one month for water samples.

The stability of the As(III)/As(V) ratio in interstitial water at room temperature, in the presence of air was carried out over a 24-hour period to determine the feasibility of the field collection of interstitial water.

Because of the time-consuming nature of sediment analysis, a two-point storage test was carried out with triplicate samples analyzed for two sediments at two temperatures (0°C and -18°C). Mud samples were stored in polyethylene vials and analyzed at time zero and one month.

RESULTS AND DISCUSSION

Data Output

Using the procedures outlined above, and a mixed standard containing As(V), MMA, and DMA, standard curves were prepared for each of the arsines generated. A typical chromatogram from this procedure is illustrated in Figure 2.2. Under the conditions described in this paper, the elution times for the various arsines are as follows: AsH_3, 24 ± 2 s; CH_3AsH_2, 53 ± 2 s and $(CH_3)_2AsH$, 66 ± 2 s. Notice that the peaks are broadened and that the sensitivity decreases as the boiling point of the compound increases. The small amount of signal after the DMA peak is probably a higher boiling impurity in the DMA, or some DMA that is lagging in the system during elution. We had previously noted much larger, multiple peaks in this region when water was allowed to condense between the trap and the detector. Such peaks were effectively eliminated and the DMA peak sharpened with the addition of the heating coil between the trap and the detector.

The typical standard curves in Figure 2.3 are prepared from the mean of two determinations at each concentration. Arsenic peak-height response appears to be linear to at least 600 mau (milliabsorbance units), which is the full scale setting used on our chart recorder. Andreae (3) shows that arsenic response is extremely non-linear above this for the peak height mode, and recommends the use of peak area integration to increase the linear range. We have chosen to simply use a small enough sample aliquot to remain within 600 mau.

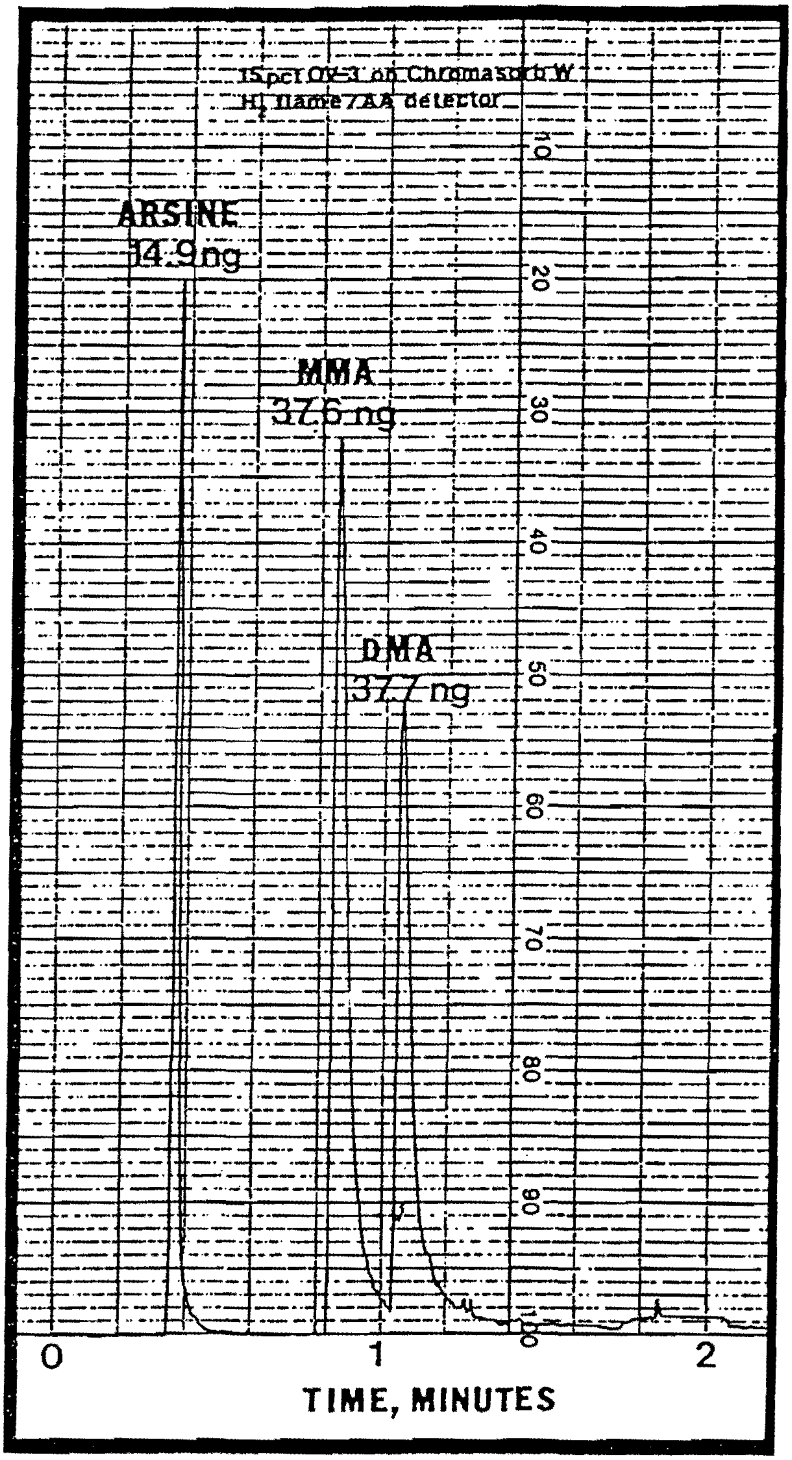


Figure 2-2. Typical chromatogram of arsenic hydride species. Vertical axis absorbance, horizontal axis time.

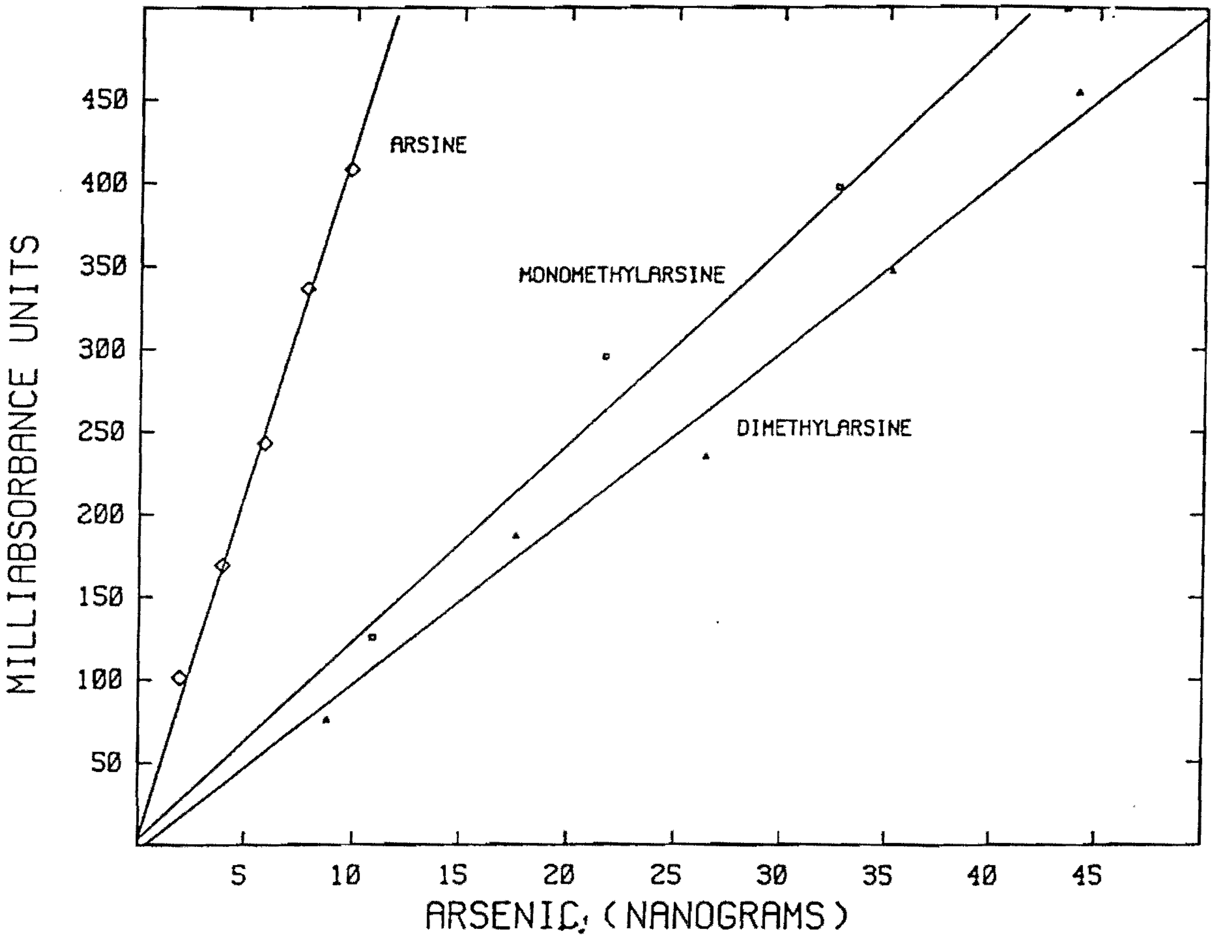


Figure 2-3. Standard curves, absorbance versus concentration for arsenic hydride species, atomic absorption detector.

As arsenic response is quite sensitive to the H_2/O_2 ratio in the flame, it is necessary to restandardize the instrument whenever it is set up. Usually, however, the response is quite constant and stable over the entire day.

Precision, Accuracy and Detection Limits

Precision and accuracy are the greatest and the detection limits the lowest for inorganic arsenic. The precision and accuracy of the inorganic arsenic determination is illustrated at two concentrations in Table 2-3. The standard seawater, NASS-1 (National Research Council of Canada) was run in 5.0-ml aliquots and the "standard river water" (National Bureau of Standards) was run in 100-µl aliquots. In either case, both the precision (RSD) and accuracy were about 5%. Precision begins to decrease, as the boiling point of the compound increases, as is illustrated in Table 2-4, for spiked river water. No standard reference material has been found for the organic species.

Table 2-3

REPLICATE DETERMINATIONS OF TOTAL INORGANIC ARSENIC IN SOME STANDARD WATERS

Replicate	Total (inorganic) arsenic, $\mu g \cdot l^{-1}$ NASS-1 Seawater	 NBS River water
1	1.579	81.5
2	1.556	74.5
3	1.591	71.8
4	1.493	79.0
5	1.529	79.3
N	5	5
$\bar{X}$	1.550	77.2
S	0.040	4.0
RSD	2.6%	5.2%
Certified	1.65	76.0
±	0.19	7.0

M - number of replicates.
$\bar{X}$ - mean
S - ± one standard deviation
RSD - relative standard deviation

Table 2-4

PRECISION DATA FOR THREE ARSENIC SPECIES, ILLUSTRATING THE DECREASE IN PRECISION WITH INCREASING BOILING POINT OF SPECIES. THESE SAMPLES WERE SPIKED RIVER WATER USED IN WATER STORAGE TESTS

	Arsenic concentrations, ng·l^{-1}		
Replicate	Inorganic arsenic	MMA	DMA
N (8-24-83)	3	3	3
X	937	2483	2173
S	44	79	181
RSD	4.7%	3.2%	8.3%
$\underline{N}$ (9-11-83)	3	4	4
$\bar{X}$	800	2342	2393
S	24	165	260
RSD	3.0%	7.0%	10.9%

The detection limit of this technique has not been explored to the extreme as the usual environmental sample benefits from less, not more sensitivity. For a chart recorder expansion of 600 mau full scale, and the parameters given in the text, and for a 30-ml sample aliquot, the following approximate detection limits are found: As(V), 0.006 µg·l^{-1} (twice the standard deviation of the blank); As(III) 0.003 µg·l^{-1} (0.5 chart units); MMA, 0.010 µg·$^{-1}$ as As (0.5 chart units); DMA, 0.012 µg·l^{-1} as As (0.5 chart units). For As(III), MMA and DMA, no contribution to the blank has been found due to reagents, except for the As(III) present in the river water used as a dilutant. As for As(V) a small contribution is found, mostly from the $NaBH_4$, and to a smaller extent from H_3PO_4. These may be minimized by selecting reagent lots of reagents found to be low in arsenic.

Water Storage Experiments

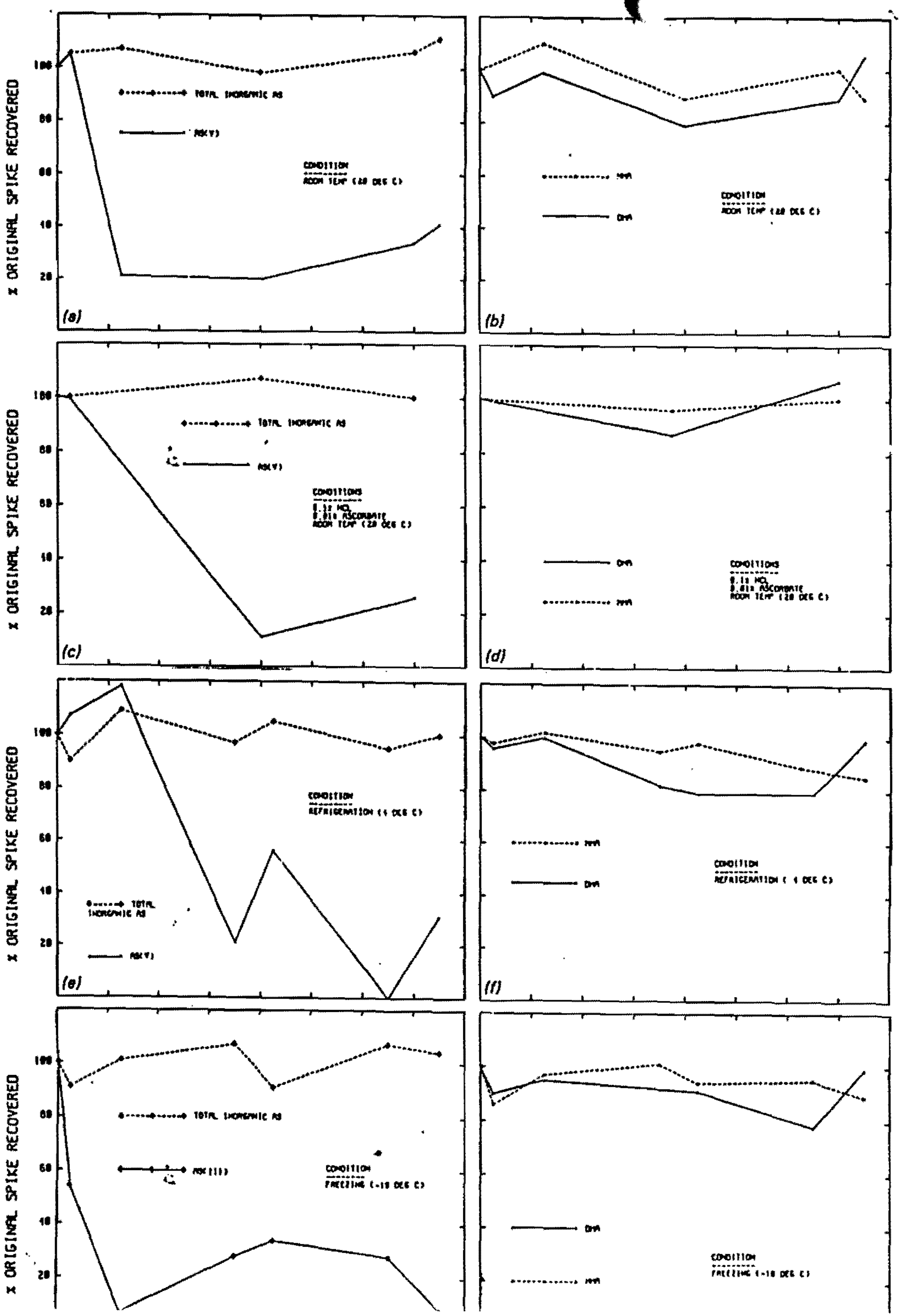
From the many experiments undertaken to determine a storage regime for arsenic species, the following general conclusion can be made: Almost any storage scheme will preserve the total arsenic, MMA, and DMA concentrations of river water in the µg·l^{-1} range. This is illustrated in the Figures 2-4a-p, where the final concentration of these parameters was within ±20% of the initial in all cases. The noise in the data is due mostly to the day-to-day analytical variability, which has been observed to be about twice that of same-day replicate analysis. On the other hand, these data also show that it is very difficult to preserve the original As(III)/As(V) ratio in samples, even for a short time. Two major observations are made: first, river water (Dungeness River water) tends to spontaneously reduce As(V) to As(III), even though the water has been filtered to 0.4 µ, thus removing most living creatures. This is also curious, as the natural equilibrium As(III)/As(V) ratio is about 0.2 in Dungeness River water. It is surmised that dissolved organic materials in the water are responsible for its reducing properties, a conclusion that is supported by work involving the reduction of Hg(II) to Hg(0) by humic acids (Bloom, unpublished work). The second observation is that the freezing of water inexplicably, but reproducibly causes the oxidation of As(III) to As(V) (Figure 2-4-g, i), except in the case of very rapid freezing by immersion in LN_2 (Figure 2-4-m, o).

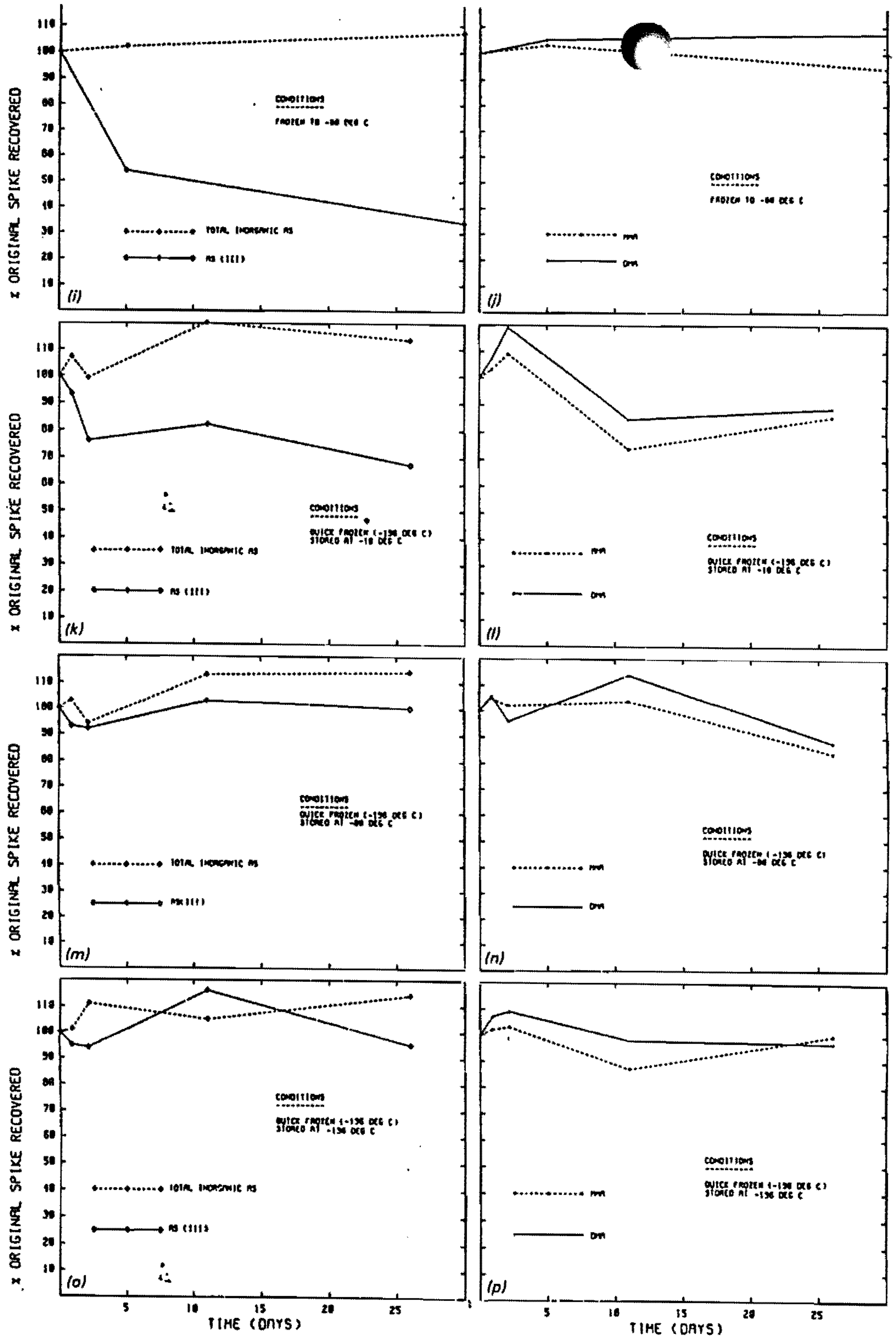
In light of these observations, the following storage regimes are recommended for arsenic in aqueous solution:

1. If only total inorganic arsenic plus MMA and DMA are to be determined, the sample should be stored at 0 to 4°C in polyethylene bottles until analysis. No chemical preservative is needed or desired and the analysis should be carried out as soon as possible.

2. If the As(III)/As(V) ratio is to be maintained, the sample must be quick-frozen to -196°C in liquid nitrogen, and then stored at at least -80°C until analysis. Note that Figure 4-k shows that even in the case of rapid freezing to -196°C, followed by storage at -18°C, a definite oxidation of As(III) to As(V) was observed.

A convenient and safe way to quick-freeze samples is to place 55 ml of sample into a 60-ml narrow-mouth polyethylene bottle, screw on the cap (which has a 2 mm diameter hole) tightly, and drop into a Dewar flask full of liquid nitrogen. These bottles have been shown not to crack if less than 58 ml of water is placed in them, and not to float in the LN_2 if more than 50 ml is placed in them. After returning to the laboratory, the bottles may be placed into a low temperature freezer until analysis. Note of caution, if a small hole is not placed in the lid of the bottles, which are frozen in liquid nitrogen, the bottles may explode when removed from the liquid nitrogen.


% ORIGINAL SPIKE RECOVERED
100
80
60
40
20
TOTAL INORGANIC AS
AS(V)
CONDITION
ROOM TEMP (20 DEG C)
(a)
MMA
DMA
CONDITION
ROOM TEMP (20 DEG C)
(b)
TOTAL INORGANIC AS
AS(V)
CONDITIONS
0.1% HCL
0.01% ASCORBATE
ROOM TEMP (20 DEG C)
(c)
DMA
MMA
CONDITIONS
0.1% HCL
0.01% ASCORBATE
ROOM TEMP (20 DEG C)
(d)
CONDITION
REFRIGERATION (4 DEG C)
TOTAL INORGANIC AS
AS(V)
(e)
MMA
DMA
CONDITION
REFRIGERATION (4 DEG C)
(f)
TOTAL INORGANIC AS
AS(III)
CONDITION
FREEZING (-10 DEG C)
DMA
MMA
CONDITION
FREEZING (-10 DEG C)

% ORIGINAL SPIKE RECOVERED
110
100
90
80
70
60
50
40
30
20
10
CONDITIONS
FROZEN TO -80 DEG C
TOTAL INORGANIC AS
AS (III)
MMA
DMA
(i)
(j)
QUICK FROZEN (-196 DEG C)
STORED AT -10 DEG C
(k)
(l)
QUICK FROZEN (-196 DEG C)
STORED AT -80 DEG C
(m)
(n)
QUICK FROZEN (-196 DEG C)
STORED AT -196 DEG C
(o)
(p)
5
10
15
20
25
TIME (DAYS)

Determination of Arsenic Species in Sediments

Two procedures were investigated in the determination of arsenic in sediments. One, a wet-acid digestion was used to determine total arsenic. The second was a mild, pH-selective leach to remove various arsenic species intact.

Total Arsenic. In applying the hot HNO_3/H_2SO_4 digestion to standard sediments and air particulate matter, good agreement was attained between the established values and the measured values (Table 2-5). Also, in the case of estuarine and riverine sediments collected in the Puget Sound area, there was good agreement between X-ray fluorescence spectroscopy and this method (Table 2-6). In either case, all observed arsenic was in the inorganic form.

Table 2-5

TOTAL INORGANIC ARSENIC IN STANDARD SEDIMENTS BY HNO_3/H_2SO_4

	Total (inorganic) arsenic $\mu g \cdot g^{-1}$ dry weight basis			
Replicate	MESS-1 Estuarine sediment	BCSS-1 Estuarine sediment	NBS-1646 Estuarine sediment	NBS-1648 Air particulate matter
1	8.9	10.9	9.8	123.0
2	8.8	8.5	10.0	136.0
3	8.8	9.4	9.8	115.0
4	9.6	9.8	8.5	-
5	10.1	10.7	11.0	-
N	5	5	5	3
$\bar{X}$	9.2	9.9	9.8	125.0
S	0.6	1.0	0.9	11.0
RSD	6.5%	10.1%	9.2%	8.8%
Certified	10.6	11.1	11.6	115.0
±	1.2	1.4	1.3	10.0

Table 2-6

COMPARISON OF X-RAY FLUORESCENCE SPECTROSCOPY AND HYDRIDE GENERATION AA IN THE DETERMINATION OF TOTAL ARSENIC ENVIRONMENTAL SEDIMENTS. ALL REPRESENT TOTAL INORGANIC ARSENIC BY HOT ACID DIGESTION EXCEPT (*) SLWM, WHICH IS THE SUM OF SPECIES BY LEACHING

	Total Arsenic, $\mu g \cdot g^{-1}$ dry weight basis			
Type of Sediment	XRF		Hydride AA	
Lake Washington (silt)	14.6 ± 0.1	n=3	14.5 ± 1.1	n=6
Spiked Lake Washington (silt)	124.1 ± 3.4	n=3	120.0 ± 7.5	n=5*
BCSS-1, clean estuarine (mud)	11.7 ± 0.7	n=3	9.9 ± 1.0	n=5
Contaminated Puget Sound (sandy)	108.0 ± 24.0	n=3	93.0 ± 21.0	n=3
Duwamish River (sand)	8.0	n=1	2.6	n=1

However, when Lake Washington sediment spiked with inorganic as well as organic forms was analyzed by this method, the following was observed:

1. All of the MMA was recovered as MMA.
2. All of the inorganic arsenic was recovered as inorganic arsenic.
3. None of the DMA was recovered, but an unidentified higher boiling peak was generated.

This peak is clearly illustrated in Figure 2-5. Even after the above samples were re-digested to near-dryness (white fumes) in HNO_3 plus $HClO_4$, the same results were obtained. Therefore, at this point we recommend no hydride generation method to determine total arsenic in sediments, though this may be achieved using either neutron activation analysis or X-ray fluorescence spectroscopy. On the other hand, since no organic forms have been detected in any natural sediment and since both MMA and DMA give observable peaks if they are present, it is safe to assume as a general guideline that if only an inorganic arsenic peak is generated by a given sample, then it probably represents close to the total arsenic content of the sample.

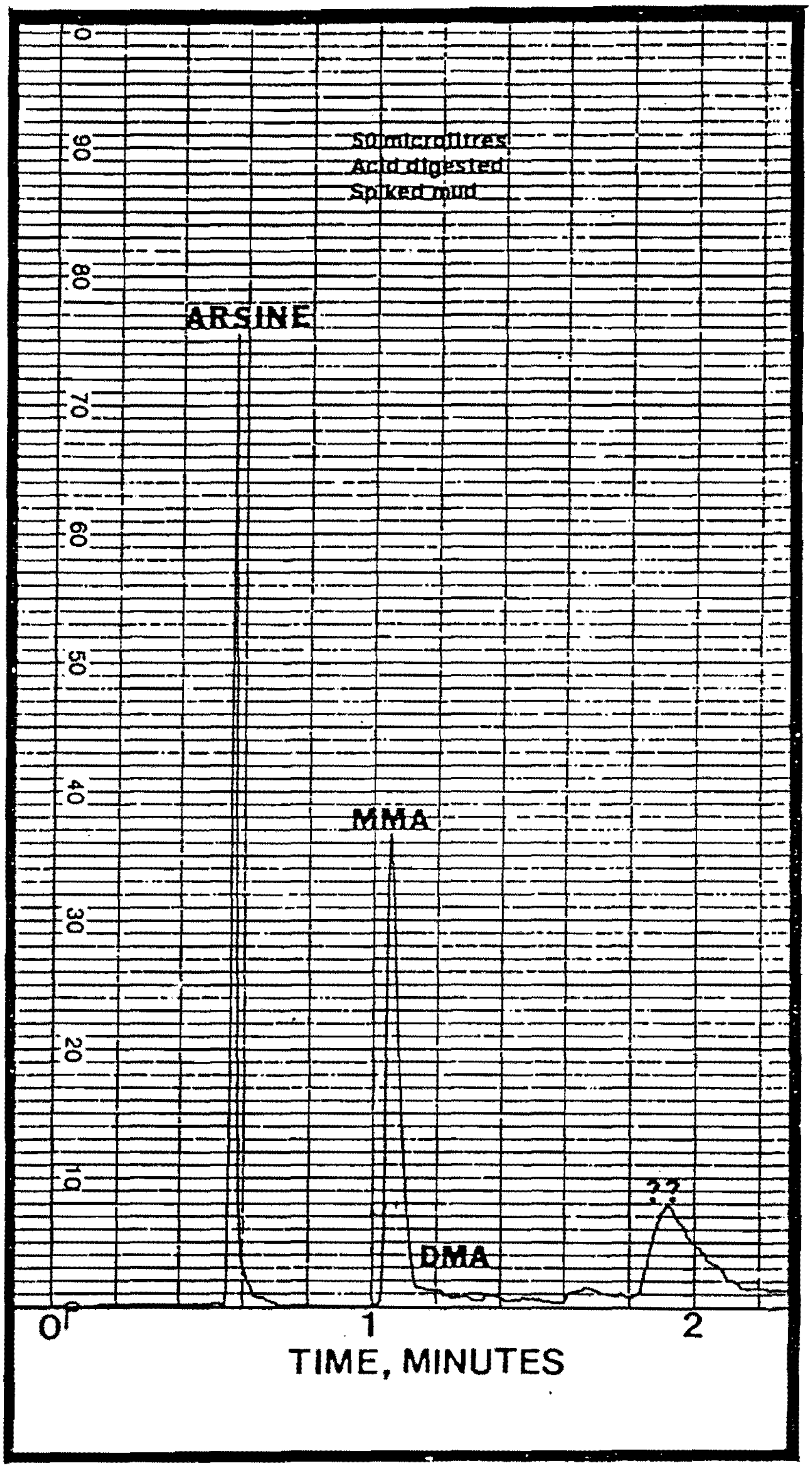


Figure 2-5. Chromatogram of digested (HNO_3/H_2SO_4) spiked Lake Washington mud. Vertical axis absorbance, horizontal axis time. Note absence of DMA peak and presence cf unidentified higher boiling compound.

Arsenic Speciation of Sediments. Maher (4) has shown that various arsenic species that may be removed from solids at different pH values. This approach was tested on a sample of spiked Lake Washington mud, over a wide range of pH using phosphate buffers. The results of these experiments, shown as arsenic recovered versus pH for all four species, are illustrated in Figure 2-6. Notice that the maximum recovery of As(III) occurs at about pH = 2.8 and that the maximum for As(V), MMA and DMA occur at pH >12. From these data, the two convenient buffers of 0.1 M H_3PO_4 (pH = 1.5) and Na_3PO_4 (pH = 12) were chosen to selectively extract the arsenic species from sediments. Samples extracted with H_3PO_4 (final pH = 2.3) are analyzed only for As(III) whereas those extracted with Na_3PO_4 (final pH = 11.9) are analyzed only for total As, which gives As(V), MMA and DMA, as As(III) is not extracted at this pH. On untested sediment types it would be wise to test this relationship to be sure it holds true before instituting an analytical regime.

Recovery of arsenic species from spiked Lake Washington mud is illustrated in Table 2-7. The calculated spike was added to the mud, which was then aged 14 days at 4°C before analysis. All analysis were carried out in quintuplicate. The yields are good and within the day-to-day variability for the respective species.

Table 2-7

RECOVERY OF ARSENIC SPECIES FROM SPIKED LAKE WASHINGTON MUD BY SELECTIVE LEACHING

	$\mu g \cdot g^{-1}$ Arsenic, dry weight basis			
Arsenic species	Lake Washington mud	Spike added	Total recovered	Percent recovery
As(III)	2.2 ± 0.3	5.8	8.2 ± 14	103%
As(V)	4.4 ± 0.3	9.5	13.5 ± 17	96%
MMA	<0.8	58.0	51.3 ± 6.0	88%
DMA	<0.8	54.0	47.0 ± 4.2	87%

The values of the above analysis were then taken as the time zero values, and the mud divided and stored in one of two ways. Three aliquots each of Lake Washington

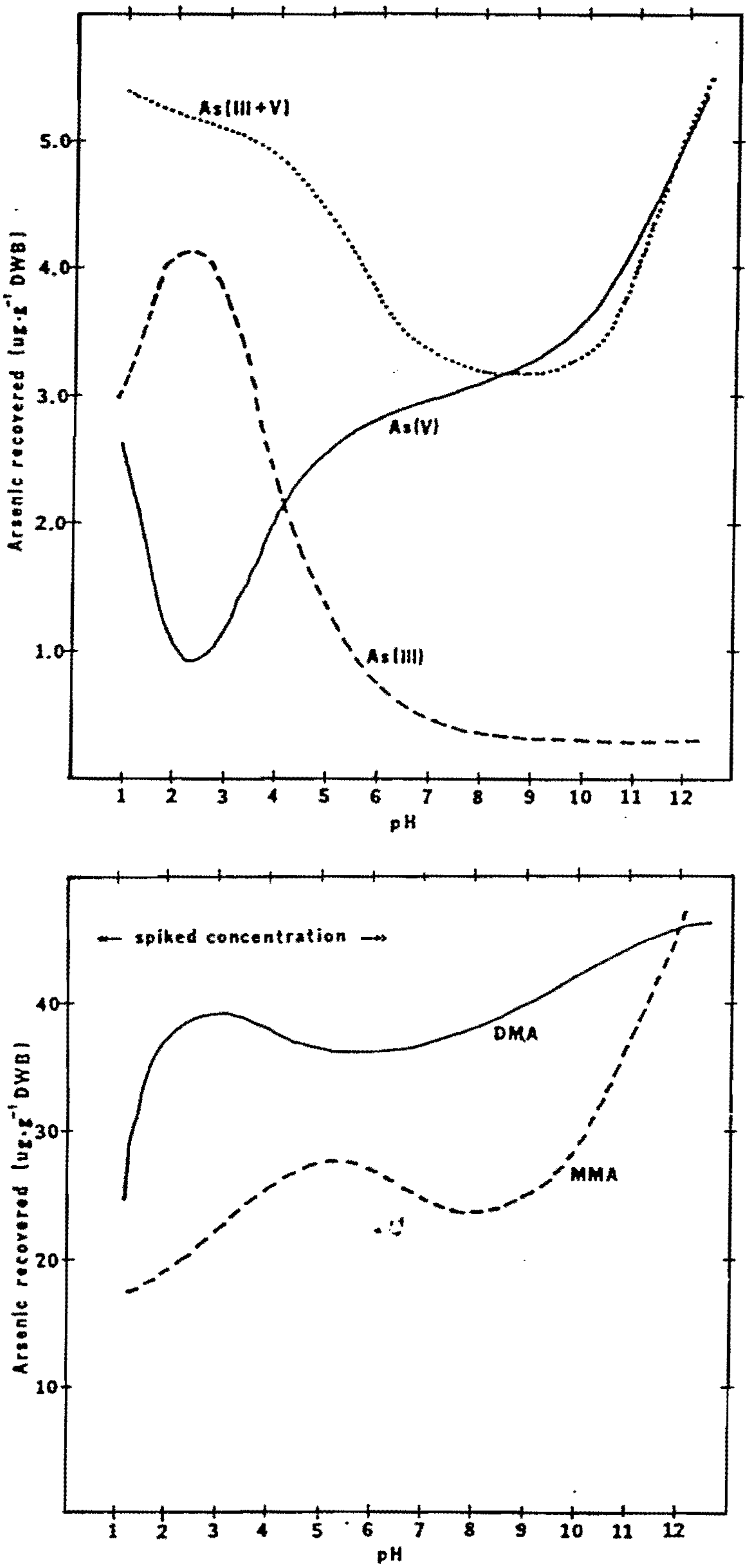


Figure 2-6. Arsenic species released from sediments as a function of solution pH. Plot of arsenic in sediment leached, μg g^{-1} dry weight basis (DWB), versus pH of leachate.

mud (LWM) and spiked LWM were placed into polyethylene bottles and frozen at -18°C, while three aliquots were kept refrigerated at 0 to 4°C. After 30 days these samples were analyzed for arsenic species, the results of which are shown in Table 2-8. These data indicate that small changes in the concentrations of the various species may be occurring, with significant decreases (20-30%) in the organic species being seen. These changes are small enough, however, that if the samples were analyzed as soon as possible after collection, they should not be of great importance.

Table 2-8

THIRTY-DAY STORAGE RESULTS FOR ARSENIC SPECIATION IN SEDIMENTS

Lake Washington mud

	$\mu g \cdot g^{-1}$ Arsenic, dry weight basis		
		Concentrations after 30-day aging	
Arsenic species	Initial concentration	Refrigerated, 0-4°C	Frozen, -18°C
As(III)	2.2 ± 0.3	2.2 ± 0.4	2.3 ± 0.3
As(V)	4.4 ± 0.3	5.2 ± 0.4	5.4 ± 0.4
MMA	<0.8	<0.8	<0.8
DMA	<0.8	<0.8	<0.8

Spiked Lake Washington mud

	$\mu g \cdot g^{-1}$ Arsenic, dry weight basis		
		Concentrations after 30-day aging	
Arsenic species	Initial concentration	Refrigerated, 0-4°C	Frozen, -18°C
As(III)	8.2 ± 1.4	7.1 ± 2.7	9.9 ± 1.3
As(V)	13.5 ± 1.7	13.8 ± 1.0	16.0 ± 0.5
MMA	51.3 ± 6.0	39.9 ± 1.6	46.2 ± 3.5
DMA	47.0 ± 4.2	46.5 ± 3.2	40.0 ± 2.4

Interstitial Water. Interstitial water is collected from mud by pressure filtration under nitrogen. An aliquot (~100 g) of mud is placed into a plastic pressure filtration vessel with 1.0 μ acid-cleaned filter, and tapped down to remove air bubbles. The system is pressurized to 75 psi, and after discarding the first 1 to 2 ml of filtrate, the interstitial water is collected into a 30-ml polyethylene bottle under nitrogen. The As(III) stability curve in Figure 2-7 was generated on a sample in contact with air. Within 5 minutes, the sample had changed from colorless to brown, indicating that Fe(II) had oxidized to Fe(III), and precipitated as colloidal $Fe(OH)_3$. If an aliquot of sediment is filtered under nitrogen and then frozen at -196°C, as for water samples, within 5 to 10 minutes, minimal changes in the As(III)/As(V) ratio should have taken place.

Using the above technique, a sample of spiked, Lake Washington sediment was analyzed for interstitial water arsenic speciation 30 days after spiking with arsenic. This data is presented in Table 2-9 and shows that the distribution coefficients (K_d) of the various species between the solid and aqueous phases increase in the following order: DMA<<MMA<As(III)<<As(V). In fact, a sizable fraction (4.3%) of the DMA is in the interstitial water in a given sample, a fact which is important considering the intimate interaction of the interstitial water and living creatures.

Table 2-9

ARSENIC SPECIATION OF SPIKED LAKE WASHINGTON MUD INTERSTITIAL WATER. K_d VALUES REPRESENT [As (DRY WEIGHT SEDIMENT]/[As (INSTERSTITIAL WATER)]

Species	Arsenic concentration $\mu g \cdot g^{-1}$ Dry sediment	Arsenic concentration $\mu g \cdot g^{-1}$ Interstitial water	K_d
AsV	20	<0.002	>10,000
AsIII	5.2	0.014	371
MMA	40	0.11	364
DMA	38	1.72	23

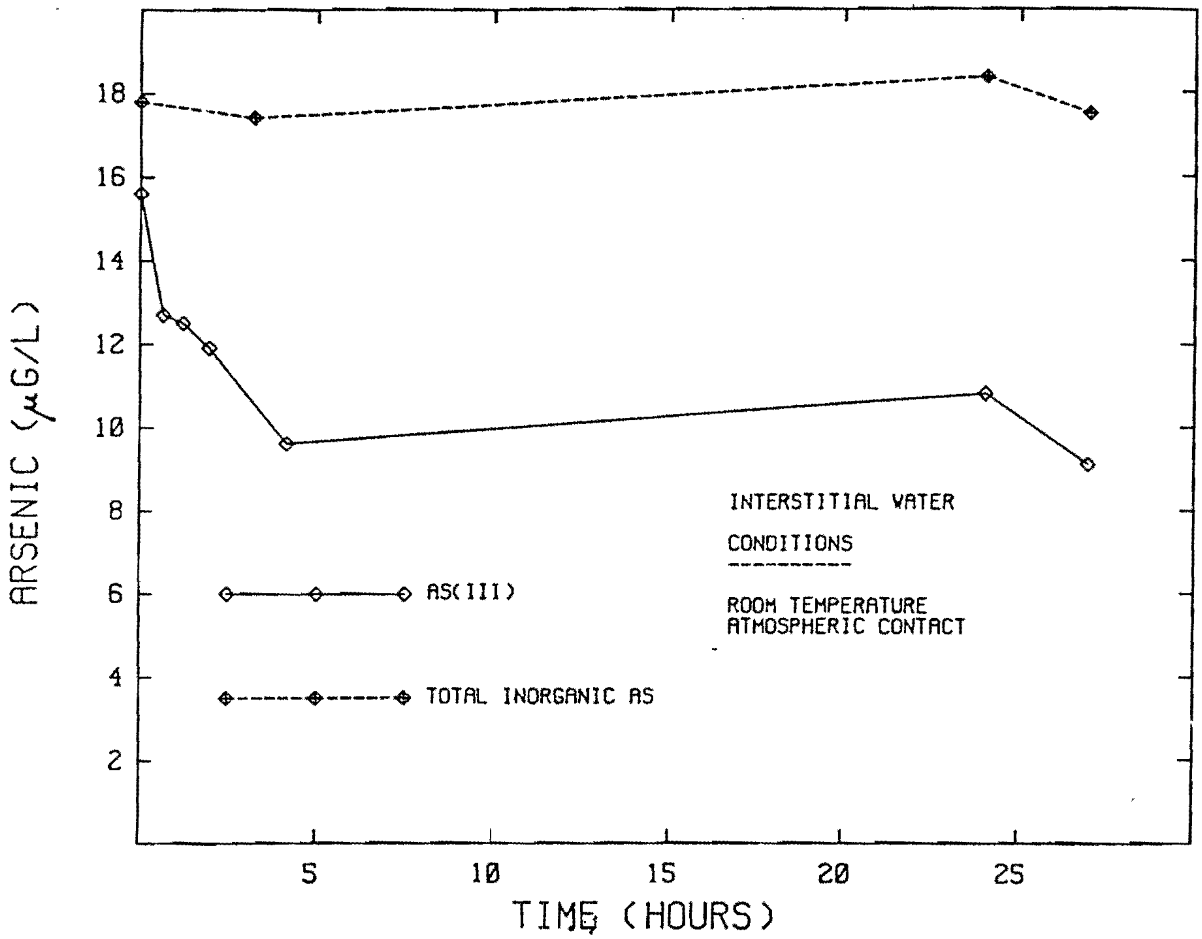


Figure 2-7. Plot of the concentration of AsIII and total inorganic arsenic versus storage time in interstitial water.

Interlaboratory Comparison

An interlaboratory comparison exercise was conducted between Battelle-Northwest (BNW) and Dr. M. O. Andreae of Florida State University (FSU) to demonstrate the effectiveness of the sample storage and shipping procedure and varify the accuracy of the anlaytical technique for determination of arsenic species in fresh water. Three samples were prepared as follows: (1) Dungeness River water (DRW) was filtered, (2) filtered DRW was spiked with nominally 0.45 μg L^{-1} of As (V) and 2 μg L^{-1} each of DMA and MMA, and (3) coal fly ash, standard reference material NBS-1633, was leached with DRW then filtered. All solutions were frozen immediately after preparation in liquid nitrogen then transferred and stored at -80°C. Samples were shipped on dry ice. Samples were analyzed at BNW and FSU the same week approximately two months after preparation. The results in Table 2-10 show good agreement between these two laboratories even for concentrations below 0.1 μg L^{-1}. We believe this interlaboratory exercise has demonstrated that these storage and shipping procedures are appropriate for freshwater samples and the analytical method used for arsenic speciation is sensitive and accurate for concentrations of inorganic arsenic greater than approximately 0.05 and for organic arsenic concentrations greater than 0.2 μg L^{-1}.

Table 2-10

ARSENIC SPECIATION INTERCOMPARISON EXERCISE

	μg ℓ$^{-1}$							
	As (III)		As (V)		MMA		DMW	
Sample	BNW	Andreae	BNW	Andreae	BNW	Andreae	BNW	Andreae
DRW	0.061 ±0.004	0.067	0.042 ±0.008	0.023	<0.01	0.002	<0.01	0.067
SDRW	0.061 ±0.005	0.066	0.468 ±0.028	0.421	1.96 ±0.11	1.67	1.92 ±0.13	1.82
FA	0.052 ±0.006	0.031	12.9 ±0.2	12.0	<0.01	ND	<0.01	ND

Intercomparison exercise results with Meinrat O. Andreae for arsenic speciation in limnological samples. DRW is filtered Dungeness River water; SDRW is Dungeness River water spiked with nominally 0.45 μg·ℓ$^{-1}$ As (V), and 2 μg·ℓ$^{-1}$ each DMA and MMA. FA is the filtrate of 1000 mg·ℓ$^{-1}$ NBS coal fly ash leached with DRW. BNW results are the mean of (3) determinations. ND means not detected. ± = one standard deviation.

Precision for Sediments and Water

The precision or reproducibility for replicate analyses of arsenic species in field samples is shown in Table 2-11. Collection of these field samples is described in Section 3 of this report. The sediment was analyzed for leachable As (III) and As (V). Interstitial water and water from Hyco Reservoir were also analyzed for As (III) and (V). The results indicate that the relative standard deviations (RSD) for arsenic (III) and (V) in sediment are approximately 20% while the RSD for these species in interstitial water and in the water column are approximately 15% and 7%.

CONCLUSIONS AND RECOMMENDATIONS FOR FURTHER WORK

Arsenic speciation of a variety of materials in the limnological environment is simply and reproducibly achieved using selective hydride generation/low-temperature trapping techniques in conjunction with atomic absorption detection. The most difficult problem is the unambiguous determination of total arsenic in solids by this technique. Other related techniques which might be investigated include dry ashing, lithium metaborate fusion, and graphite furnace atomic absorption. An alternate method is to analyze select samples by X-ray fluorescence spectrometry.

Table 2-11

PRECISION OF ARSENIC SPECIATION HYCO RESERVOIR
(February 1984)

	Sediment As, Sta. 5 $\mu g\ g^{-1}$ dry wt			Interstitial As, Sta. 5 $\mu g\ L^{-1}$			Water column, Sta. 4 $\mu g\ L^{-1}$		
Replicate	Total	As(V)	As(III)	Total	As(V)	As(III)	Total	As(V)	As(III)
1	38.33	25.15	13.18	75.8	41.1	34.7	1.222	1.128	0.094
2	36.61	21.74	14.87	67.1	29.9	37.2	1.082	0.983	0.099
3	25.27	15.24	10.03	77.2	32.0	45.2	1.186	1.079	0.107
4	21.28	12.75	8.53	--	--	--	--	--	--
5	29.49	17.26	12.23	--	--	--	--	--	--
6	28.71	16.97	11.74	--	--	--	--	--	--
N	6	6	6	3	3	3	3	3	3
$\bar{X}$	29.95	18.19	11.76	73.4	34.4	39.0	1.163	1.063	0.100
S	6.53	4.51	2.26	5.5	6.0	5.5	0.073	0.074	0.007
RSD	21.8%	24.8%	19.2%	7.5%	17.4%	14.1%	6.3%	6.9%	6.6%

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Section 3

ARSENIC SPECIATION IN HYCO RESERVOIR

INTRODUCTION

Hyco Reservoir was selected as the water body to sample for field testing the sampling, storage, transport and analytical techniques that were developed under this contract (2020-2) and described in Section 2 of this report. Hyco Reservoir is a power plant cooling impoundment located near Roxboro, North Carolina. The reservoir, constructed by Carolina Power and Light Company (CP&L), receives cooling water and coal fly ash pond effluent. Previous studies conducted by CP&L indicated the reservoir contained elevated concentrations of arsenic and other trace elements, probably due to ash pond effluent.

The main purpose of the field sampling was to apply the methods that were developed and tested in the laboratory to a coal combustion waste receiving water body. Also of interest were the determination of seasonal distributions of arsenic species in Hyco Reservoir and the comparison of these results with the arsenic speciation predicted by the geochemical equilibrium speciation model described in Section 1 of this report.

HYCO RESERVOIR SAMPLING

Water and sediments were collected on February 27, 1984 and July 10-11, 1984. Three stations in the reservoir and effluent from the fly ash pond were sampled. The sampling stations, shown in Figure 3-1, are Carolina Power and Light routine monitoring stations. Surface bottom sediment and one or two depths were sampled in the water column at the three reservoir stations. Station 3, the background station, is located upstream of the power plant discharge area and therefore is not likely to be affected by coal combustion waste. Station 4 is near the cooling water and fly ash pond discharge. Station 5 is located downstream of Station 4, near the cooling water intake for the power plant.

Water column samples were taken with a General Oceanics Go-Flow teflon-coated PVC 10 liter water bottle. The water samples were taken to the shore where they were

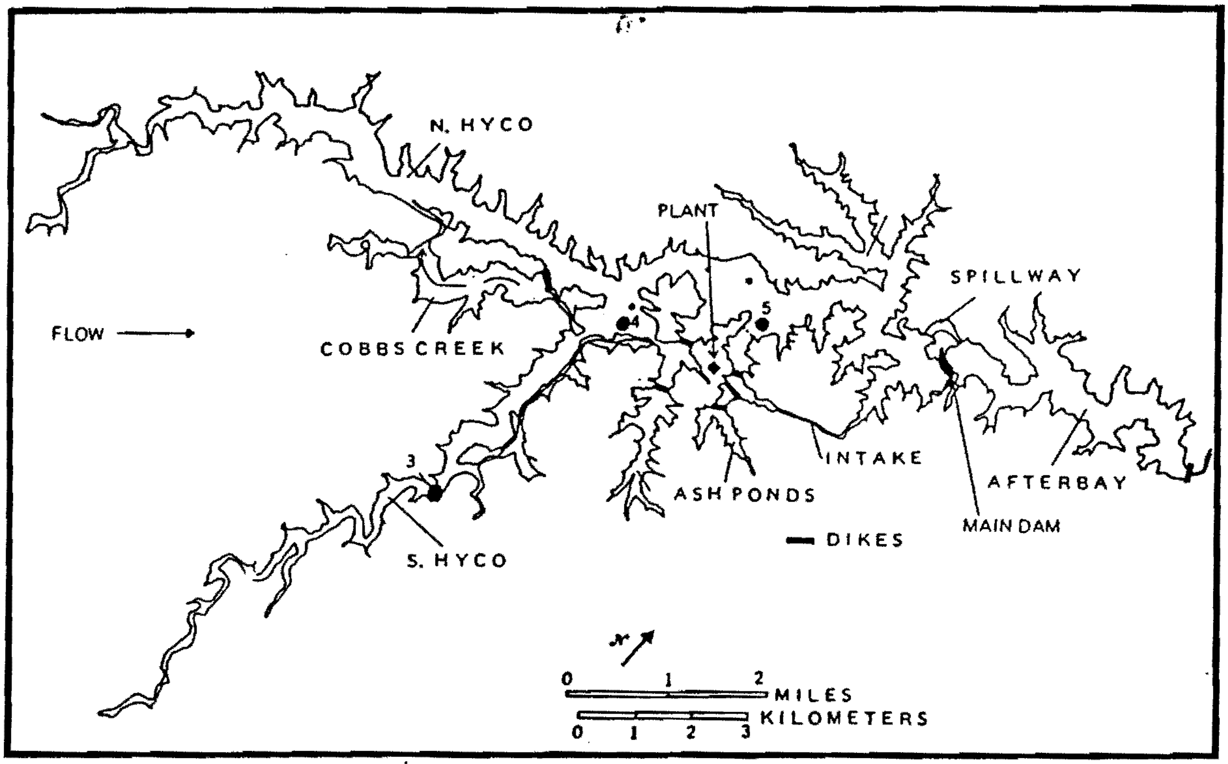

Figure 3-1. Hyco Rservoir Water and Sediment Sampling Stations

pressure filtered through 0.4 μm pore Unipore® membrane filters using nitrogen gas. Filtered water and filters were frozen in liquid nitrogen for transport to the laboratory.

Sediments were collected with a Ponar grab sampler. In the shore laboratory, sediment was placed in an Amicon® pressure filter chamber and squeezed, using nitrogen gas, through an 0.4 μm pore Unipore© filter to collect interstitial water. The containers collecting the interstitial water were continually flushed with nitrogen gas to prevent oxidation of chemicals in the interstitial water samples. Both sediment and interstitial samples were stored and shipped in liquid nitrogen. The effluent from the fly ash pond was collected and processed the same as the reservoir water column samples.

ANALYTICAL METHODS

The analytical methods used to determine the concentrations of arsenic species in water, suspended particulate matter, and sediments are described in Section 2. During the July 1984 field sampling trip several parameters were measured to characterize the physical and chemical conditions in the reservoir. The pH was determined with a pH electrode. The electrical potential (E^H) was measured with a platinum electrode (Orion 96-78-00). This redox electrode was calibrated in redox buffers. Field measurements are corrected for reference potential and results reported as E^H, with reference to a hydrogen electrode potential of 0.0 volts. The alkalinity was determined by potentiometric titration and results reported as mg L^{-1} as $CaCO_3$ (1). The concentrations of soluble ferric ion (Fe^{+3}) and soluble ferrous ion (Fe^{+2}) were determined by spectrophotometry (2).

RESULTS AND DISCUSSION

Water Column

The concentrations of dissolved and particulate arsenic in the water column and ash pond of Hyco Reservoir are shown in Tables 3-1 and 3-2. Arsenic concentrations at Station 3, the background station, are lower than at Stations 4 and 5, which are influenced by effluent from the ash pond. Approximately half of the arsenic is dissolved in the water column. In July 1984, the temperature of the water sampled indicated the lake was stratified (Table 3-3). Although the physical and chemical parameters shown in Table 3-3 were not measured in February 1984, the suspended load in February was fairly constant with depths indicating the water column was not stratified in the winter.

Table 3-1

TOTAL ARSENIC IN HYCO RESERVOIR WATER COLUMN
(February 1984)

Station	Depth	Susp. load mg·L^{-1}	Arsenic, µg L^{-1} Total	Diss.	Part.	Percent % Diss.
3	1	28.4	0.18	0.08	0.10	44
4	1	45.5	2.79	1.37	1.42	49
4	8	49.1	2.26	1.16	1.10	51
5	1	51.8	2.26	1.05	1.21	46
5	11	31.5	2.06	1.27	0.80	62
Ash pond	0.1	72.9	36.4	24.6	11.8	68

Table 3-2

TOTAL ARSENIC IN HYCO RESERVOIR WATER COLUMN
(July 1984)

Station	Depth	Susp. load mg·L^{-1}	Arsenic, µg L^{-1} Total	Diss.	Part.	Percent Diss.
3	1	7.0	<0.97	0.78	<0.19	>80
4	1	11.7	2.59	1.82	0.77	70
4	9	46.3	3.94	1.95	1.99	49
5	1	11.8	2.54	1.88	0.66	74
5	11	38.7	3.72	0.97	2.16	31
Ash pond	0.1	17.3	--	na	1.33	--

Table 3-3

PHYSICAL AND CHEMICAL MEASUREMENTS OF WATER COLUMN AND SEDIMENT INTERSTITIAL WATER FROM HYCO RESERVOIR

(July 1984)

Station	Depth (m)	Temperature (C°)	pH	Alkalinity mg L^{-1}	Fe^{+3}/Fe^{+2}
3 water	1	26.5	7.74	24	*
3 sediment	n.d.	n.d.	7.01	n.d.	0.39
4 water	1	30.0	7.33	14	*
4 water	9	18.5	6.99	22	*
4 sediment	10.5	13.4	6.87	n.d.	<0.05
5 water	1	28.5	7.28	13	*
5 water	12	16.0	7.37	21	*
5 sediment	13	12.5	7.19	n.d.	<0.02

---

n.d. - No data

* - Total soluble Fe below detection limit of 3.9 μg L^{-1}.

E^H - Electrical potential referenced to the hydrogen electrode.

Alkalinity - mg L^{-1} $CaCO_3$.

The majority of dissolved arsenic is in the As (V) oxidation state in the water column except at Station 3, which is only one-third As (V) and two-thirds As (III) (Tables 3-4 and 3-5). The source of the As (V) appears to be the fly ash pond which contained 24 μg L^{-1} As (V) in February. Both of the organo-arsenic compounds were below detection in the water column.

Table 3-4

DISSOLVED ARSENIC SPECIES IN HYCO RESERVOIR WATER COLUMN
(February 1984)

		$\mu g\ L^{-1}$					Percent
Station	Depth (m)	As (Total)	As (III)	As (V)	MMA	DMA	As(V)
3	1	0.080 ± 0.013	0.053 ± 0.007	0.027 ± 0.017	<0.03	<0.03	33.8
4	1	1.37	0.080	1.29	<0.03	<0.03	94.2
4	8	1.16 ± 0.07	0.100 ± 0.007	1.06 ± 0.07	<0.03	<0.03	91.4
5	1	1.05	0.080	0.97	<0.03	<0.03	92.4
5	11	1.27	0.057	1.21	<0.03	<0.03	95.3
Ash Pond	0.1	24.6	0.21	24.4	0.5	<0.3	99.2

Table 3-5

DISSOLVED ARSENIC SPECIES IN HYCO RESERVOIR WATER COLUMN
(July 1984)

		µg L⁻¹					Percent
Station	Depth (m)	As (Total)	As (III)	As (V)	MMA	DMA	As(V)
3	1	0.78 ± 0.09	0.55 ± 0.04	0.23 ± 0.13	<0.04	<0.06	29.5
4	1	1.82 ± 0.27	0.24 ± 0.03	1.58 ± 0.24	<0.04	<0.06	86.8
4	9	1.95 ± 0.08	0.19 ± 0.01	1.75 ± 0.08	<0.04	<0.06	89.7
5	1	1.88 ± 0.06	0.18 ± 0.05	1.70 ± 0.10	<0.04	<0.06	90.4
5	12	0.97 ± 0.11	0.06 ± 0.01	0.91 ± 0.11	<0.04	<0.06	93.8

Suspended Particulate Matter

The concentration of arsenic in particulate matter collected from Hyco Reservoir ranges from <27 to 66 $\mu g\ g^{-1}$ dry wt (Tables 3-6 and 3-7). The higher concentrations are from the stations near the fly ash pond discharge. The concentrations of arsenic in particulate matter collected from the ash pond where higher than in the reservoir. The percentage of total arsenic that was leachable ranged from 46 to 91% with most of the leachable arsenic present as As (V).

Table 3-6

TOTAL AND LEACHABLE ARSENIC IN HYCO RESERVOIR
PARTICULATE MATTER
(February 1984)

		$\mu g\ g^{-1}$ dry wt					
Station No.	Depth (m)	Total As	Total leached	Percent leached	As (V)	As (III)	Percent As (V)
3[a]	1	3.9[a]	30.0[a]	>100%	29.6[a]	0.4[a]	99
4	1	31	28.2	91	27.7	0.5	98
4	8	22	19.0	86	18.5	0.5	97
5	1	23	19.7	86	19.3	0.4	98
5	11	25	21.3	85	20.6	0.7	97
Ash Pond	0.1	162	99.2	61	98.5	1.7	99

[a] Small hole in filter.

Table 3-7

TOTAL AND LEACHABLE ARSENIC IN HYCO RESERVOIR PARTICULATE MATTER
(July 1984)

		µg g^{-1} dry wt					
Station No.	Depth (m)	Total As	Total leached	Percent leached	As (V)	As (III)	Percent As (V)
3	1	<27	14.17	>53	9.56	4.61	67
4	1	66	37.24	56	36.50	0.74	98
4	9	43	27.70	64	25.11	2.59	91
5	1	56	27:28	49	26.12	1.16	96
5	12	56	26.01	46	24.15	1.86	93
Ash Pond	0.1	78	na	--	na	na	--

na = not analyzed.

Sediments and Interstitial Water

The concentrations of arsenic in surface sediments are similar to the concentrations in suspended particulate matter from the same stations (Tables 3-8 and 3-9). The concentrations of arsenic in sediments from Stations 4 and 5 are three times greater than at Station 3 reflecting input from the ash pond. The amount and species of leachable arsenic in sediments are similar to that of suspended matter. Between 33 and 84% of the total arsenic in the sediment was leachable, with the majority being present in the As (V) valence state. Organo-arsenic species were not detected.

Table 3-8

TOTAL AND LEACHABLE ARSENIC SPECIES IN HYCO RESERVOIR SEDIMENT (February 1984)

	$\mu g\ g^{-1}$ dry wt							
				Leached As Species, ppm				Percent
Station	Total As	Total As leached	Percent leached	As(V)	As(III)	MMA	DMA	As(V)
3	12.6	5.90	46.8	3.95	1.95	<0.01	<0.02	66.9
4	40.7	31.95	78.5	18.19	11.76	<0.01	<0.02	56.9
5	35.8	29.95	83.7	22.72	9.18	<0.01	<0.02	75.9

Table 3-9

TOTAL AND LEACHABLE ARSENIC IN HYCO RESERVOIR SEDIMENT (July 1984)

	$\mu g\ g^{-1}$ dry wt					
				Leached As Species		
Station No.	Total As	Total As leached	Percent leached	As (V)	As (III)	Percent As (V)
3	13.9	5.3	38.1	4.7	0.5	88.7
4	37.3	24.2	64.9	21.7	2.5	89.7
5	39.3	18.6	47.3	15.6	3.0	83.9

The concentrations of arsenic in interstitial water are much greater than in the water column and vary with the total arsenic concentration in sediment (Tables 3-10 and 3-11). The dissolved arsenic is almost equally divided between the As (III) and (V) valence states indicating the sediments are chemically more reducing than the overlying water column which contains primarily As (V).

Table 3-10

DISSOLVED ARSENIC SPECIES IN HYCO RESERVOIR INTERSTITIAL WATER (February 1984)

	Arsenic Species µg L^{-1}					Percent
Station	Total AS	As(V)	As(III)	MMA	DMA	As(V)
3	5.37	2.79	2.58	<0.1	<0.1	52
4	96.1	48.4	47.7	<0.2	<0.2	50
5	73.4	34.4	39.0	<1.4	<1.4	46

Table 3-11

DISSOLVED ARSENIC SPECIES IN HYCO RESERVOIR INTERSTITIAL WATER (July 1984)

	Arsenic Species µg·L^{-1}					Percent
Station	Total As	As (V)	As (III)	MMA	DMA	As (V)
3	7.4	4.1	3.3	<0.04	<0.06	55
4	69.7	51.1	18.6	<0.04	<0.06	73
5	68.4	25.9	42.5	<0.04	<0.06	38

Comparison of Field Data with Geochemical Modeling Data

A comparison of the arsenic valence state results for Hyco Reservoir with those arsenic species predicted by the geochemical model indicates general agreement exists. The model predicted that As (V) would be the dominant arsenic valence state for high E^H environments and As (III) would be dominant in low E^H environments. Also, the model predicted arsenic would be relatively soluble in surface waters and sorption of As (V) on metal oxides could control arsenic concentrations in natural waters. Arsenic is primarily in the As (V) form in the water column of the reservoir except at Station 3 where As (III) predominates. The presence of As (III) at Station 3 does not agree with the E^H-pH diagram (Figure 3-1) which predicts only in the sediment interstitial water would As (III) predominate. The pH and E^H values for the interstitial water (Table 3-3) fall in the region of the E^H-pH diagram (Figure 3-1) where As (III) predominates over As (V). The Fe^{+3}/Fe^{+2} ratio for the interstitial waters indicates these waters are reducing with respect to this couple. However, Lindberg and Runnells (3) have pointed out that there is usually poor agreement between platinum electrode measurements and multiple redox couples for field samples because of internal disequilibrium. Based on the few measurements we have made of redox couples and E^H, we are not yet able to address the agreement between the model and the field data. As part of a proposed follow-on contract we plan to examine this aspect of arsenic geochemistry.

As predicted by the model, arsenic is relatively mobile (that is soluble) in the water column with approximately 50% dissolved. Also in agreement with the model is the adsorption of arsenic As (V) on suspended particulate matter and sediment. Usually greater than 70% of the leachable arsenic is As (V).

CONCLUSIONS AND RECOMMENDATIONS

Methods for sampling, storage and quantification of arsenic species in freshwater and sediment have been developed and demonstrated to be appropriate for field studies of coal combustion waste receiving waters. Analyses of standard reference materials and interlaboratory comparison samples indicate these methods produce accurate results.

The speciation of arsenic in Hyco Reservoir is in agreement with the predominant inorganic forms of arsenic that were predicted for freshwater using the geochemical model MINTEQ. Organo-arsenic compounds were not detected in Hyco Reservoir. The major source of arsenic to Hyco Reservoir appears to be the effluent from the fly ash pond. A significant quantity of arsenic is removed from the reservoir by sedimentation. Most of the arsenic on the sediments is in the As (V) valence state.

Recommendations for future research includes determination of seasonal changes in arsenic speciation and improvement of the predictability of arsenic speciation for a wide range of natural waters using a combined approach of field data and the geochemical speciation model MINTEQ.

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Appendix A

ACTIVITIES OF AQUEOUS SPECIES AND SATURATION INDEXES OF SOLID PHASE FOR ARSENIC

LOG ACTIVITY OF AQUEOUS SPECIES FOR LOW DISSOLVED SOLIDS WATER

(Concentration units in μg L^{-1} for S(II) and As)

pH = 5

Aqueous Species	Valence	Eh(mV)=100 S(-II)=.1 As=.0001	Eh(mV)=100 S(-II)=10 As=.0001	Eh(mV)=400 S(-II)=.1 As=.0001	Eh(mV)=400 S(-II)=10 As=.0001	Eh(mV)=100 S(-II)=.1 As=.01	Eh(mV)=100 S(-II)=10 As=.01	Eh(mV)=400 S(-II)=.1 As=.01	Eh(mV)=400 S(-II)=10 As=.01
$H_4AsO_3^+$	III	-14.180	-14.180	-20.617	-20.617	-12.180	-12.180	-18.616	-18.616
$H_3AsO_3^o$	III	-8.875[a]	-8.875[a]	-15.312	-15.312	-6.875[a]	-6.875[a]	-13.311	-13.311
$H_2AsO_3^-$	III	-13.367	-13.367	-19.803	-19.803	-11.367	-11.367	-17.803	-17.803
$HAsO_3^{-2}$	III	-20.776	-20.776	-27.212	-27.212	-18.776	-18.776	-25.212	-25.212
AsO_3^{-3}	III	-29.433	-29.433	-35.870	-35.870	-27.433	-27.433	-33.869	-33.869
$H_3AsO_4^o$	V	-15.973	-15.973	-11.730	-11.730	-13.973	-13.973	-9.729	-9.729
$H_2AsO_4^-$	V	-13.148	-13.148	-8.904[a]	-8.904[a]	-11.148	-11.148	-6.904[a]	-6.904[a]
$HAsO_4^{-2}$	V	-14.937	-14.937	-10.694	-10.694	-12.937	-12.937	-8.693	-8.693
AsO_4^{-3}	V	-21.708	-21.708	-17.464	-17.464	-19.708	-19.708	-15.464	-15.464
$HAsO_3F^-$	V	-18.464	-18.464	-14.220	-14.220	-16.464	-16.464	-12.220	-12.220
AsO_3F^{-2}	V	-19.333	-19.333	-15.090	-15.090	-17.333	-17.333	-13.089	-13.089

LOG SI FOR MINERALS FOR LOW DISSOLVED SOLIDS WATER

(Concentration units in $\mu g\ L^{-1}$ for S(II) and As)

pH = 5

Solid Phases Composition	Name	Eh(mV)=100 S(-II)=.1 As=.0001	Eh(mV)=100 S(-II)=10 As=.0001	Eh(mV)=400 S(-II)=.1 As=.0001	Eh(mV)=400 S(-II)=10 As=.0001	Eh(mV)=100 S(-II)=.1 As=.01	Eh(mV)=100 S(-II)=10 As=.01	Eh(mV)=400 S(-II)=.1 As=.01	Eh(mV)=400 S(-II)=10 As=.01
AsI_3		-51.537		-57.974		-49.537		-55.973	
As_2O_5		-38.841	-38.841	-30.353	-30.353	-34.841	-34.841	-26.352	-26.352
As_4O_6	Arsenolite	-32.080	-32.08	-57.825	-57.825	-24.08	-24.080	-49.824	-49.824
As_4O_6	Claudetite	-31.858	-31.858	-57.602	-57.602	-23.853	-23.853	-49.602	-49.602
As_2S_3	Orpiment	-0.697[a]	5.503[b]	-13.570	-7.369	3.303[b]	9.503[b]	-9.569	-3.369
AsS	Realgar	-10.423	-8.356	-22.199	-20.132	-8.423	-6.356	-20.199	-18.132
$Ba_3(AsO_4)_2$		-13.616	-5.128		-9.616		-1.128		
$Cu_3(AsO_4)_2 \cdot 6H_2O$		-32.639	-33.207	-24.151	-24.151	-28.639	-29.207	-20.151	-20.718
$FeAsO_4 \cdot 2H_2O$		-13.631	-13.631	-9.388	-9.388	-11.631	-11.631	-7.387	-7.387
$Mn_3(AsO_4)_2 \cdot 8H_2O$		-36.043	-36.043	-27.555	-27.555	-32.043	-32.043	-23.555	-23.555
$Ni_3(AsO_4)_2 \cdot 8H_2O$	Annabelite	-40.506	-40.506	-32.018	-32.018	-36.506	-36.506	-28.017	-28.077
$Pb_3(AsO_4)_2$		-37.578		-29.090		-33.578		-25.090	
$Zn_3AsO_4 \cdot 22.5H_2O$		-40.244	-40.244	-31.757	-31.757	-36.244	-36.248	-27.756	-27.760
$Ca_3(AsO_4)_2 \cdot 6H_2O$		-35.037	-35.073	-26.585	-26.585	-31.073	-31.073	-22.585	-22.585
$AlAsO_4 \cdot 2H_2O$		-14.469	-14.469	-10.225	-10.225	-12.469	-12.469	-8.225	-8.225

LOG ACTIVITY OF AQUEOUS SPECIES AND LOG SI FOR MINERALS FOR LOW DISSOLVED SOLIDS WATER

(Concentration units in μg L^{-1} for S(II) and As)

pH = 5

Solid Phases Composition	Name	Eh(mV)=100 S(-II)=.1 As=.0001	Eh(mV)=100 S(-II)=10 As=.0001	Eh(mV)=400 S(-II)=.1 As=.0001	Eh(mV)=400 S(-II)=10 As=.0001	Eh(mV)=100 S(-II)=.1 As=.01	Eh(mV)=100 S(-II)=10 As=.01	Eh(mV)=400 S(-II)=.1 As=.01	Eh(mV)=400 S(-II)=10 As=.01
$BaSO_4$	Barite	-0.874		-0.874		-0.874		-0.874	
$BaCO_3$	Witherite	-8.182		-8.182		-8.182		-8.182	
FeOOH	Ferrihydrite	-2.157	-2.157	-2.157	-2.157	-2.157	-2.157	-2.157	-2.157
Fe_2O_3	Maghemite	-0.895	-0.895	-0.895	-0.895	-0.895	-0.895	-0.895	-0.895
$Fe_3(OH)_8$		-11.421	-11.421	-11.421	-11.421	-11.421	-11.421	-11.421	-11.421

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[a] Dominant aqueous species.

[b] Solid phases that are supersaturated or in equilibrium.

LOG ACTIVITY OF AQUEOUS SPECIES FOR LOW DISSOLVED SOLIDS WATER

(Concentration units in μg L^{-1} for S(II) and As)

pH = 7.5

Aqueous Species	Valence	Eh(mV)=100 S(-II)=.1 As=.0001	Eh(mV)=100 S(-II)=10 As=.0001	Eh(mV)=400 S(-II)=.1 As=.0001	Eh(mV)=400 S(-II)=10 As=.0001	Eh(mV)=100 S(-II)=.1 As=.01	Eh(mV)=100 S(-II)=10 As=.01	Eh(mV)=400 S(-II)=.1 As=.01	Eh(mV)=400 S(-II)=10 As=.01
$H_4AsO_3^+$	III	-20.776	-20.776	-31.456	-31.456	-18.776	-18.776	-29.456	-29.456
$H_3AsO_3^o$	III	-12.971	-12.971	-23.651	-23.651	-10.971	-10.971	-21.651	-21.651
$H_2AsO_3^-$	III	-14.963	-14.963	-25.643	-25.643	-12.963	-12.963	-23.552	-23.643
$HAsO_3^{-2}$	III	-19.872	-19.872	-30.552	-30.552	-17.872	-17.872	-28.552	-28.552
AsO_3^{-3}	III	-26.029	-26.029	-36.709	-36.709	-24.029	-24.029	-37.709	-34.709
$H_3AsO_4^o$	V	-15.069	-15.069	-15.069	-15.069	-13.069	-13.069	-13.069	-13.069
$H_2AsO_4^-$	V	-9.744	-9.744	-9.744	-9.744	-7.744	-7.744	-7.744	-7.744
$HAsO_4^{-2}$	V	-9.033[a]	-9.033[a]	-9.033[a]	-9.033[a]	-7.033[a]	-7.033[a]	-7.033[a]	-7.033[a]
AsO_4^{-3}	V	-13.304	-13.304	-13.304	-13.304	-11.304	-11.304	-11.304	-11.304
$HAsO_3F^-$	V	-17.537	-17.537	-17.537	-17.537	-15.537	-15.537	-15.537	-15.537
AsO_3F^{-2}	V	-15.906	-15.906	-15.906	-15.906	-13.906	-13.906	-13.906	-13.906

LOG SI FOR MINERALS FOR LOW DISSOLVED SOLIDS WATER

(Concentration units in μg L^{-1} for S(II) and As)

pH = 7.5

Solid Phases Composition	Name	Eh(mV)=100 S(-II)=.1 As=.0001	Eh(mV)=100 S(-II)=10 As=.0001	Eh(mV)=400 S(-II)=.1 As=.0001	Eh(mV)=400 S(-II)=10 As=.0001	Eh(mV)=100 S(-II)=.1 As=.01	Eh(mV)=100 S(-II)=10 As=.01	Eh(mV)=400 S(-II)=.1 As=.01	Eh(mV)=400 S(-II)=10 As=.01
AsI_3		-63.141		-73.821		-61.141		-71.821	
As_2O_5		-37.033	-37.033	-37.033	-37.033	-33.033	-33.033	-33.033	-33.033
As_4O_6	Arsenolite	-48.464	-48.464	-91.184	-91.184	-40.464	-40.464	-83.184	-83.184
As_4O_6	Claudetite	-48.242	-48.242	-90.962	-90.962	-40.242	-40.242	-82.962	-82.962
As_2S_3	Orpiment	-10.890	-4.352	-32.250	-25.712	-6.890	-0.352[b]	-28.250	-21.712
AsS	Realgar	-17.686	-15.507	-33.706	-31.527	-15.686	-13.507	-31.706	-29.527
$Ba_3(AsO_4)_2$		3.162[b]		3.162[b]		7.161[b]		7.162[b]	
$Cu_3(AsO_4)_2 \cdot 6H_2O$		-19.910	-32.561	-19.910	-32.561	-15.910	-28.561	-15.910	-28.561
$FeAsO_4 \cdot 2H_2O$		-10.388	-10.388	-10.388	-10.388	-8.388	-8.388	-8.388	-8.388
$Mn_3(AsO_4)_2 \cdot 8H_2O$		-19.279	-19.279	-19.279	-19.279	-15.279	-15.279	-15.279	-15.279
$Ni_3(AsO_4)_2 \cdot 8H_2O$	Annabelite	-26.358	-26.358	-26.358	-26.358	-22.358	-22.358	-22.358	-22.358
$Pb_3(AsO_4)_2$		-24.447		-24.447		-20.447		-20.447	
$Zn_3AsO_4 \cdot 22.5H_2O$		-23.775	-27.562	-23.775	-27.562	-19.775	-23.562	-19.775	-23.562
$Ca_3(AsO_4)_2 \cdot 6H_2O$		-18.303	-18.303	-18.303	-18.303	-14.303	-14.303	-14.303	-14.303
$AlAsO_4 \cdot 2H_2O$		-10.628	-10.628	-10.628	-10.628	-8.628	-8.628	-8.628	-8.628

LOG ACTIVITY OF AQUEOUS SPECIES AND LOG SI FOR MINERALS FOR LOW DISSOLVED SOLIDS WATER

(Concentration units in μg L^{-1} for S(II) and As)

pH = 7.5

Solid Phases Composition	Name	Eh(mV)=100 S(-II)=.1 As=.0001	Eh(mV)=100 S(-II)=10 As=.0001	Eh(mV)=400 S(-II)=.1 As=.0001	Eh(mV)=400 S(-II)=10 As=.0001	Eh(mV)=100 S(-II)=.1 As=.01	Eh(mV)=100 S(-II)=10 As=.01	Eh(mV)=400 S(-II)=.1 As=.01	Eh(mV)=400 S(-II)=10 As=.01
$BaSO_4$	Barite	-0.893		-0.893		-0.893		-0.893	
$BaCO_3$	Witherite	-4.271		-4.271		-4.271		-4.271	
FeOOH	Ferrihydrite	0.183	0.183	0.183	0.183	0.183	0.183	0.183	0.183
Fe_2O_3	Maghemite	3.784	3.784	3.784	3.784	3.784	3.784	3.784	3.784
$Fe_3(OH)_8$		-1.753	-1.753	-1.753	-1.753	-1.753	-1.753	-1.753	-1.753

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[a] Dominant aqueous species.

[b] Solid phases that are supersaturated.

LOG ACTIVITY OF AQUEOUS SPECIES FOR LOW DISSOLVED SOLIDS WATER

(Concentration units in μg L^{-1} for S(II) and As)

pH = 9

Aqueous Species	Valence	Eh(mV)=100 S(-II)=.1 As=.0001	Eh(mV)=100 S(-II)=10 As=.0001	Eh(mV)=400 S(-II)=.1 As=.0001	Eh(mV)=400 S(-II)=10 As=.0001	Eh(mV)=100 S(-II)=.1 As=.01	Eh(mV)=100 S(-II)=10 As=.01	Eh(mV)=400 S(-II)=.1 As=.01	Eh(mV)=400 S(-II)=10 As=.01
$H_4AsO_3^+$	III	-28.214	-28.214	0	0	-26.214	-26.214	-36.894	-36.894
$H_3AsO_3^0$	III	-18.909	-18.909	-29.589	-29.589	-16.909	-16.909	-27.589	-27.589
$H_2AsO_3^-$	III	-19.401	-19.401	-30.081	-30.081	-17.401	-17.401	-28.081	-28.081
$HAsO_3^{-2}$	III	-22.810	-22.810	-33.490	-33.490	-20.810	-20.810	-31.490	-31.490
AsO_3^{-3}	III	-27.467	-27.467	0	0	-25.467	-25.467	-36.147	-36.147
$H_3AsO_4^0$	V	-18.007	-18.007	-18.007	-18.007	-16.007	-16.007	-16.007	-16.007
$H_2AsO_4^-$	V	-11.182	-11.182	-11.182	-11.182	-9.182	-9.182	-9.182	-9.182
$HAsO_4^{-2}$	V	-8.971[a]	-8.971[a]	-8.971[a]	-8.971[a]	-6.971[a]	-6.971[a]	-6.971[a]	-6.971[a]
AsO_4^{-3}	V	-11.742	-11.742	-11.742	-11.742	-9.742	-9.742	-9.742	-9.742
$HAsO_3F^-$	V	-20.475	-20.475	-20.475	-20.475	-18.475	-18.475	-18.475	-18.475
AsO_3F^{-2}	V	-17.343	-17.343	-17.344	-17.344	-15.344	-15.344	-15.344	-15.344

LOG SI FOR MINERALS FOR LOW DISSOLVED SOLIDS WATER

(Concentration units in μg L^{-1} for S(II) and As)

pH = 9

Solid Phases Composition	Name	Eh(mV)=100 S(-II)=.1 As=.0001	Eh(mV)=100 S(-II)=10 As=.0001	Eh(mV)=400 S(-II)=.1 As=.0001	Eh(mV)=400 S(-II)=10 As=.0001	Eh(mV)=100 S(-II)=.1 As=.01	Eh(mV)=100 S(-II)=10 As=.01	Eh(mV)=400 S(-II)=.1 As=.01	Eh(mV)=400 S(-II)=10 As=.01
AsI_3		-73.580		-84.261		-71.580		-82.260	
As_2O_5		-42.908	-42.908	-42.909	-42.908	-38.908	-38.908	-38.908	-38.908
As_4O_6	Arsenolite	-72.215	-72.215	-114.936	-114.936	-64.216	-64.216	-106.936	-106.936
As_4O_6	Claudetite	-71.993	-71.993	-114.714	-114.713	-63.993	-63.993	-106.713	-106.713
As_2S_3	Orpiment	-26.965	-20.610	-48.325	-41.970	-22.965	-16.610	-44.325	-37.970
AsS	Realgar	-26.523	-24.405	-42.544	-40.425	-24.523	-22.405	-40.543	-38.425
$Ba_3(AsO_4)_2$		6.282^b		6.281^b		10.282^b		10.282^b	
$Cu_3(AsO_4)_2 \cdot 6H_2O$		-25.370	-29.834	-25.370	-29.834	-21.370	-25.834	-21.370	-25.834
$FeAsO_4 \cdot 2H_2O$		-13.760	-13.760	-13.760	-13.760	-11.760	-11.760	-11.760	-11.760
$Mn_3(AsO_4)_2 \cdot 8H_2O$		-16.166	-16.166	-16.167	-16.166	-12.166	-12.166	-12.166	-12.166
$Ni_3(AsO_4)_2 \cdot 8H_2O$	Annabelite	-27.674	-27.674	-27.674	-27.674	-23.674	-23.674	-23.674	-23.674
$Pb_3(AsO_4)_2$		-25.890		-25.891		-21.890		-21.890	
$Zn_3AsO_4 \cdot 22.5H_2O$		-24.381	-25.398	-24.381	-25.398	-20.381	-21.398	-20.381	-21.398
$Ca_3(AsO_4)_2 \cdot 6H_2O$		-15.223	-15.223	-15.223	-15.223	-11.223	-11.223	-11.223	-11.223
$AlAsO_4 \cdot 2H_2O$		-13.972	-13.972	-13.972	-13.972	-11.972	-11.972	-11.972	-11.972

LOG ACTIVITY OF AQUEOUS SPECIES AND LOG SI FOR MINERALS FOR LOW DISSOLVED SOLIDS WATER

(Concentration units in µg L^{-1} for S(II) and As)

pH = 9

Solid Phases Composition	Name	Eh(mV)=100 S(-II)=.1 As=.0001	Eh(mV)=100 S(-II)=10 As=.0001	Eh(mV)=400 S(-II)=.1 As=.0001	Eh(mV)=400 S(-II)=10 As=.0001	Eh(mV)=100 S(-II)=.1 As=.01	Eh(mV)=100 S(-II)=10 As=.01	Eh(mV)=400 S(-II)=.1 As=.01	Eh(mV)=400 S(-II)=10 As=.01
$BaSO_4$	Barite	-0.895		-0.895		-0.895		-0.895	
$BaCO_3$	Witherite	-2.758		-2.758		-2.758		-2.758	
FeOOH	Ferrihydrite	-0.252	-0.252	-0.252	-0.252	-0.252	-0.252	-0.252	-0.252
Fe_2O_3	Maghemite	2.915	2.915	2.915	2.915	2.915	2.915	2.915	2.915
$Fe_3(OH)_8$		0.345	0.345	0.345	0.345	0.345	0.345	0.345	0.345

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[a] Dominant aqueous species.

[b] Solid phases that are supersaturated.

LOG ACTIVITY OF AQUEOUS SPECIES FOR HIGH DISSOLVED SOLIDS WATER

(Concentration units in μg L^{-1} for S(II) and As)

pH = 5

Aqueous Species	Valence	Eh(mV)=100 S(-II)=.1 As=.0001	Eh(mV)=100 S(-II)=10 As=.0001	Eh(mV)=400 S(-II)=.1 As=.0001	Eh(mV)=400 S(-II)=10 As=.0001	Eh(mV)=100 S(-II)=.1 As=.01	Eh(mV)=100 S(-II)=10 As=.01	Eh(mV)=400 S(-II)=.1 As=.01	Eh(mV)=400 S(-II)=10 As=.01
$H_4AsO_3^+$	III	-14.179	-14.179	-20.689	-20.689	-12.179	-12.179	-18.689	-18.689
$H_3AsO_3^o$	III	-8.874[a]	-8.874[a]	-15.384	-15.384	-6.874[a]	-6.874[a]	-13.384	-13.384
$H_2AsO_3^-$	III	-13.356	-13.356	-19.867	-19.867	-11.356	-11.356	-17.867	-17.867
$HAsO_3^{-2}$	III	-20.755	-20.755	-27.266	-27.266	-18.755	-18.755	-25.266	-25.266
AsO_3^{-3}	III	-29.404	-29.404	-35.915	-35.915	-27.404	-27.404	-33.915	-33.915
$H_3AsO_4^o$	V	-15.931	-15.931	-11.762	-11.762	-13.931	-13.931	-9.762	-9.762
$H_2AsO_4^-$	V	-13.108	-13.108	-8.939[a]	-8.939[a]	-11.108	-11.018	-6.939[a]	-6.939[a]
$HAsO_4^{-2}$	V	-14.896	-14.896	-10.727	-10.727	-12.896	-12.896	-8.727	-8.727
AsO_4^{-3}	V	-21.661	-21.661	-17.492	-17.492	-19.661	-19.661	-15.492	-15.492
$HAsO_3F^-$	V	-18.174	-18.174	-14.005	-14.005	-16.174	-16.174	-12.005	-12.005
AsO_3F^{-2}	V	-19.043	-19.043	-14.874	-14.874	-17.043	-17.043	-12.874	-12.874

LOG SI FOR MINERALS FOR HIGH DISSOLVED SOLIDS WATER

(Concentration units in µg L^{-1} for S(II) and As)

pH = 5

Solid Phases Composition	Name	Eh(mV)=100 S(-II)=.1 As=.0001	Eh(mV)=100 S(-II)=10 As=.0001	Eh(mV)=400 S(-II)=.1 As=.0001	Eh(mV)=400 S(-II)=10 As=.0001	Eh(mV)=100 S(-II)=.1 As=.01	Eh(mV)=100 S(-II)=10 As=.01	Eh(mV)=400 S(-II)=.1 As=.01	Eh(mV)=400 S(-II)=10 As=.01
As_2O_5		-38.748	-38.748	-30.409	-30.409	-34.748	-34.748	-26.409	-26.409
As_4O_6	Arsenolite	-32.092	-32.092	-58.135	-58.135	-24.092	-24.092	-50.135	-50.135
As_4O_6	Claudetite	-31.869	-31.869	-57.911	-57.911	-23.869	-23.869	-49.911	-49.911
As_2S_3	Orpiment	-8.531	5.387[b]	-21.552	-7.923	-4.531	9.387[b]	-17.552	-3.923
AsS	Realgar	-13.037	-8.398	-24.888	-20.345	-11.037	-6.398	-22.888	-18.345
$Ba_3(AsO_4)_2$		-11.337	-11.337	-2.997	-2.997	-7.337	-7.337	1.003[b]	1.003[b]
$Cu_3(AsO_4)_2 \cdot 6H_2O$		-33.092	-33.120	-21.052	-21.281	-29.092	-29.120	-17.052	-17.281
$FeAsO_4 \cdot 2H_2O$		-19.985	-19.985	-10.478	-10.478	-17.985	-17.985	-8.478	-8.478
$Mn_3(AsO_4)_2 \cdot 8H_2O$		-34.458	-34.458	-26.119	-26.119	-30.458	-30.458	-22.119	-22.119
$Ni_3(AsO_4)_2 \cdot 8H_2O$	Annabelite	-37.337	-37.337	-28.998	-28.998	-33.337	-33.337	-24.998	-24.998
$Ca_3(AsO_4)_2 \cdot 6H_2O$		-32.878	-32.878	-24.539	-24.539	-28.878	-28.878	-20.539	-20.539
$AlAsO_4 \cdot 2H_2O$		-14.513	-14.513	-10.344	-10.344	-12.513	-12.513	-8.344	-8.344

LOG ACTIVITY OF AQUEOUS SPECIES AND LOG SI FOR MINERALS FOR HIGH DISSOLVED SOLIDS WATER

(Concentration units in μg L^{-1} for S(II) and As)

pH = 5

Solid Phases Composition	Name	Eh(mV)=100 S(-II)=.1 As=.0001	Eh(mV)=100 S(-II)=10 As=.0001	Eh(mV)=400 S(-II)=.1 As=.0001	Eh(mV)=400 S(-II)=10 As=.0001	Eh(mV)=100 S(-II)=.1 As=.01	Eh(mV)=100 S(-II)=10 As=.01	Eh(mV)=400 S(-II)=.1 As=.01	Eh(mV)=400 S(-II)=10 As=.01
$BaSO_4$	Barite	1.235[b]	1.235[b]	1.235[b]	1.235[b]	1.235[b]	1.235[b]	1.235[b]	1.235[b]
$BaCO_3$	Witherite	-7.052	-7.052	-7.052	-7.052	-7.052	-7.052	-7.052	-7.052
FeOOH	Ferrihydrite	-8.552	-8.552	-3.215	-3.215	-8.552	-8.552	-3.215	-3.215
Fe_2O_3	Maghemite	-13.686	-13.686	-3.011	-3.011	-13.686	-13.686	-3.011	-3.011
$Fe_3(OH)_8$		-24.558	-24.558	-13.886	-13.866	-24.558	-24.558	-13.886	-13.886

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[a] Dominant aqueous species.

[b] Solid phases that are supersaturated.

LOG ACTIVITY OF AQUEOUS SPECIES FOR HIGH DISSOLVED SOLIDS WATER

(Concentration units in μg L^{-1} for S(II) and As)

pH = 7.5

Aqueous Species	Valence	Eh(mV)=100 S(-II)=.1 As=.0001	Eh(mV)=100 S(-II)=10 As=.0001	Eh(mV)=400 S(-II)=.1 As=.0001	Eh(mV)=400 S(-II)=10 As=.0001	Eh(mV)=100 S(-II)=.1 As=.01	Eh(mV)=100 S(-II)=10 As=.01	Eh(mV)=400 S(-II)=.1 As=.01	Eh(mV)=400 S(-II)=10 As=.01
$H_4AsO_3^+$	III	-20.931	-20.931	-31.612	-31.612	-18.931	-18.931	-29.611	-29.611
$H_3AsO_3^0$	III	-13.126	-13.126	-23.807	-23.806	-11.126	-11.126	-21.806	-21.806
$H_2AsO_3^-$	III	-15.109	-15.109	-25.789	-25.789	-13.109	-13.109	-23.789	-23.789
$HAsO_3^{-2}$	III	-20.008	-20.008	-30.688	-30.688	-18.008	-18.008	-28.688	-28.688
AsO_3^{-3}	III	-26.931	-26.931	-36.837	-36.837	-24.157	-24.157	-34.837	-34.837
$H_3AsO_4^0$	V	-15.183	-15.183	-15.184	-15.183	-13.183	-13.183	-13.183	-13.183
$H_2AsO_4^-$	V	-9.861	-9.861	-9.861	-9.861	-7.861	-7.861	-7.861	-7.861
$HAsO_4^{-2}$	V	-9.149[a]	-9.149[a]	-9.149[a]	-9.149[a]	-7.149[a]	-7.149[a]	-7.149[a]	-7.149[a]
AsO_4^{-3}	V	-13.414	-13.414	-13.414	-13.414	-11.414	-11.414	-11.414	-11.414
$HAsO_3F^-$	V	-17.393	-17.393	-17.394	-17.394	-15.393	-15.393	-15.393	-15.393
AsO_3F^{-2}	V	-15.762	-15.762	-15.763	-15.763	-13.762	-13.762	-13.762	-13.762

LOG SI FOR MINERALS FOR HIGH DISSOLVED SOLIDS WATER

(Concentration units in μg L^{-1} for S(II) and As)

pH = 7.5

Solid Phases Composition	Name	Eh(mV)=100 S(-II)=.1 As=.0001	Eh(mV)=100 S(-II)=10 As=.0001	Eh(mV)=400 S(-II)=.1 As=.0001	Eh(mV)=400 S(-II)=10 As=.0001	Eh(mV)=100 S(-II)=.1 As=.01	Eh(mV)=100 S(-II)=10 As=.01	Eh(mV)=400 S(-II)=.1 As=.01	Eh(mV)=400 S(-II)=10 As=.01
As_2O_5		-37.253	-37.253	-37.254	-37.258	-33.253	-33.253	-33.253	-33.253
As_4O_6	Arsenolite	-49.103	-49.103	-91.824	-91.824	-41.103	-41.103	-83.823	-83.823
As_4O_6	Claudetite	-48.879	-48.879	-91.600	-91.599	-40.879	-40.879	-83.599	-83.599
As_2S_3	Orpiment	-24.536	-8.045	-45.897	-29.921	-20.536	-4.045	-41.896	-25.921
AsS	Realgar	-22.290	-16.793	-38.311	-32.985	-20.290	-14.793	-36.310	-30.985
$Ba_3(AsO_4)_2$		5.138[b]	5.138[b]	5.138[b]	5.138[b]	9.138[b]	9.138[b]	9.137[b]	9.138[b]
$Cu_3(AsO_4)_2 \cdot 6H_2O$		-17.539	-23.950	-16.746	-18.271	-13.539	-19.950	-12.746	-14.271
$FeAsO_4 \cdot 2H_2O$		-11.745	-11.745	-9.371	-9.370	-9.745	-9.745	-7.370	-7.370
$Mn_3(AsO_4)_2 \cdot 8H_2O$		-18.002	-18.002	-18.003	-18.002	-14.002	-14.002	-14.002	-14.002
$Ni_3(AsO_4)_2 \cdot 8H_2O$	Annabelite	-23.944	-23.944	-23.945	-23.944	-19.944	-19.944	-19.944	-19.944
$Ca_3(AsO_4)_2 \cdot 6H_2O$		-16.411	-16.411	-16.412	-16.411	-12.411	-12.411	-12.411	-12.411
$AlAsO_4 \cdot 2H_2O$		-10.366	-10.366	-10.366	-10.366	-8.366	-8.366	-8.366	-8.366

LOG ACTIVITY OF AQUEOUS SPECIES AND LOG SI FOR MINERALS FOR HIGH DISSOLVED SOLIDS WATER

(Concentration units in μg L^{-1} for S(II) and As)

pH = 7.5

Solid Phases Composition	Name	Eh(mV)=100 S(-II)=.1 As=.0001	Eh(mV)=100 S(-II)=10 As=.0001	Eh(mV)=400 S(-II)=.1 As=.0001	Eh(mV)=400 S(-II)=10 As=.0001	Eh(mV)=100 S(-II)=.1 As=.01	Eh(mV)=100 S(-II)=10 As=.01	Eh(mV)=400 S(-II)=.1 As=.01	Eh(mV)=400 S(-II)=10 As=.01
$BaSO_4$	Barite	1.224[b]	1.224[b]	1.224[b]	1.224[b]	1.224[b]	1.224[b]	1.224[b]	1.224[b]
$BaCO_3$	Witherite	-3.176	-3.176	-3.176	-3.176	-3.176	-3.176	-3.176	-3.176
FeOOH	Ferrihydrite	-1.060	-1.060	1.315	1.315	-1.060	-1.060	1.315	1.315
Fe_2O_3	Maghemite	1.298	1.298	6.048	6.048	1.298	1.298	6.048	6.048
$Fe_3(OH)_8$		-4.582	-4.582	-2.797	-2.797	-4.582	-4.582	-2.797	-2.797

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[a] Dominant aqueous species.

[b] Solid phases that are supersaturated.

LOG ACTIVITY OF AQUEOUS SPECIES FOR HIGH DISSOLVED SOLIDS WATER

(Concentration units in µg L^{-1} for S(II) and As)

pH = 9

Aqueous Species	Valence	Eh(mV)=100 S(-II)=.1 As=.0001	Eh(mV)=100 S(-II)=10 As=.0001	Eh(mV)=400 S(-II)=.1 As=.0001	Eh(mV)=400 S(-II)=10 As=.0001	Eh(mV)=100 S(-II)=.1 As=.01	Eh(mV)=100 S(-II)=10 As.01	Eh(mV)=400 S(-II)=.1 As=.01	Eh(mV)=400 S(-II)=10 As=.01
$H_4AsO_3^+$	III	-28.381	-28.381	0	0	-26.381	-26.381	0	0
$H_3AsO_3^o$	III	-19.076	-19.076	-29.756	-29.756	-17.076	-17.076	-27.756	-27.756
$H_2AsO_3^-$	III	-19.558	-19.558	-30.238	-30.238	-17.558	-17.558	-28.238	-28.238
$HAsO_3^{-2}$	III	-22.957	-22.957	-33.637	-33.637	-20.957	-20.957	-31.637	-31.637
AsO_3^{-3}	III	-27.606	-27.606	0	0	-25.606	-25.606	-36.286	-36.286
$H_3AsO_4^o$	V	-18.133	-18.133	-18.133	-18.133	-16.133	-16.133	-16.132	-16.133
$H_2AsO_4^-$	V	-11.310	-11.310	-11.310	-11.310	-9.310	-9.310	-9.310	-9.310
$HAsO_4^{-2}$	V	-9.098[a]	-9.098[a]	-9.098[b]	-9.098[b]	-7.098[a]	-7.098[a]	-7.098[a]	-7.098[a]
AsO_4^{-3}	V	-11.863	-11.863	-11.863	-11.863	-9.863	-9.863	-9.863	-9.863
$HAsO_3F^-$	V	-20.342	-20.342	-20.342	-20.342	-18.342	-18.342	-18.342	-18.342
AsO_3F^{-2}	V	-17.211	-17.211	-17.211	-17.211	-15.211	-15.211	-15.211	-15.211

LOG SI FOR MINERALS FOR HIGH DISSOLVED SOLIDS WATER

(Concentration units in µg L^{-1} for S(II) and As)

pH = 9

Solid Phases Composition	Name	Eh(mV)=100 S(-II)=.1 As=.0001	Eh(mV)=100 S(-II)=10 As=.0001	Eh(mV)=400 S(-II)=.1 As=.0001	Eh(mV)=400 S(-II)=10 As=.0001	Eh(mV)=100 S(-II)=.1 As=.01	Eh(mV)=100 S(-II)=10 As=.01	Eh(mV)=400 S(-II)=.1 As=.01	Eh(mV)=400 S(-II)=10 As=.01
As_2O_5		-43.151	-43.151	-43.151	-43.151	-39.151	-39.151	-39.151	-39.151
As_4O_6	Arsenolite	-72.900	-72.899	-115.619	-115.619	-64.900	-64.899	-107.619	-107.620
As_4O_6	Claudetite	-72.676	-72.675	-115.396	-115.396	-64.676	-64.675	-107.619	-107.396
As_2S_3	Orpiment	-40.935	-24.346	-62.295	-43.943	-36.935	-20.346	-58.295	-39.943
AsS	Realgar	-31.239	-25.710	-47.259	-41.142	-29.239	-23.710	-45.259	-39.142
$Ba_3(AsO_4)_2$		8.238[b]	8.239[b]	8.239[b]	8.239[b]	12.238[b]	12.239[b]	12.239[b]	12.239[b]
$Cu_3(AsO_4)_2 \cdot 6H_2O$		-21.898	-29.999	-21.896	-22.782	-17.898	-25.999	-17.896	-18.782
$FeAsO_4 \cdot 2H_2O$		-12.759	-12.759	-12.758	-12.758	-10.759	-10.759	-10.758	-10.758
$Mn_3(AsO_4)_2 \cdot 8H_2O$		-14.907	-14.906	-14.906	-14.906	-10.907	-10.906	-10.906	-10.907
$Ni_3(AsO_4)_2 \cdot 8H_2O$	Annabelite	-25.434	-25.434	-25.434	-25.434	-21.434	-21.434	-21.434	-21.434
$Ca_3(AsO_4)_2 \cdot 6H_2O$		-13.366	-13.366	-13.366	-13.366	-9.366	-9.366	-9.366	-9.366
$AlAsO_4 \cdot 2H_2O$		-13.777	-13.777	-13.777	-13.777	-11.777	-11.777	-11.777	-11.777

LOG ACTIVITY OF AQUEOUS SPECIES AND LOG SI FOR MINERALS FOR HIGH DISSOLVED SOLIDS WATER

(Concentration units in μg L^{-1} for S(II) and As)

pH = 9

Solid Phases Composition	Name	Eh(mV)=100 S(-II)=.1 As=.0001	Eh(mV)=100 S(-II)=10 As=.0001	Eh(mV)=400 S(-II)=.1 As=.0001	Eh(mV)=400 S(-II)=10 As=.0001	Eh(mV)=100 S(-II)=.1 As=.01	Eh(mV)=100 S(-II)=10 As=.01	Eh(mV)=400 S(-II)=.1 As=.01	Eh(mV)=400 S(-II)=10 As=.01
$BaSO_4$	Barite	1.226[b]	1.227[b]	1.227[b]	1.227[b]	1.226[b]	1.226[b]	1.226[b]	1.226[b]
$BaCO_3$	Witherite	-1.683	-1.683	-1.683	-1.683	-1.683	-1.683	-1.683	-1.683
FeOOH	Ferrihydrite	0.875	0.875	0.876	0.876	0.875	0.875	0.876	0.876
Fe_2O_3	Maghemite	5.169	5.169	5.172	5.172	5.169	5.169	5.172	5.172
$Fe_3(OH)_8$		-0.276	-0.276	-5.612	-5.612	-0.276	-0.276	-5.612	-5.612

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[a] Dominant aqueous species.

[b] Solid phases that are supersaturated.