# APPENDIX H

## A RECOMMENDED METHOD FOR INORGANIC ARSENIC ANALYSIS

Extracted from:

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# APPENDIX H

# A RECOMMENDED METHOD FOR INORGANIC ARSENIC ANALYSIS

**Note:** EPA is currently revising Method 1632: Determination inorganic arsenic in water by hydride generation flame atomic absorption to include fish tissue.

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 ithe 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% 0V-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 (nonpacked 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 flowir,g through it for 24 hours. This process, which further neutralizes active adsorption sites and purges the system of foreign volatiles, may be repeated whenever anaiate 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 wnpacked 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 H2 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.

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.

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 $l^{-1}$ 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 • $l^{-1}$ 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 µg $l^{-1}$ and less). Dilute As(III) standards are prepared daily.

Arsenate (As(V)) Standards. To prepare a 1000 mg • $l^{-1}$ stock solution, 4.16 g of reagent grade $Na_2HASO_4 • 7H_2O$ 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 • $l^{-l}$, 3.90 g of $CH_3AsO(ONa)_2 • 6H_2O$ 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 1000mg 1-l, 2.86 g of reagent grade (CW3)2AsO2Na 3H2O (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).

### 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 µ1) 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 naturalize 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 ot 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 cor,ditions described in this paper, the elusion 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 elusion. 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 nonlinear 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.

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.

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 • $1^{-1}$ (twice the standard deviation of the blank); As(III) 0.003 µg • $1^{-1}$ (0.5 chart units); MMA, 0.010 µg • $1^{-1}$ as As (0.5 chart units); DMA, 0.012 µg • $1^{-1}$ 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 DMh concentrations of river water in the $\mu \cdot 1^{-1}$ 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 (0ungeness River water) tends to spontaneously reduce As(V) to As(III), even though the water has been filtered to 0.4 ~, 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.

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 tfiis method (Table 2-6). In either case, all observed arsenic was in the inorganic form.

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 redigested 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.

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.

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 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.

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.

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 verify 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 $L^{-1}$.

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 that 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.

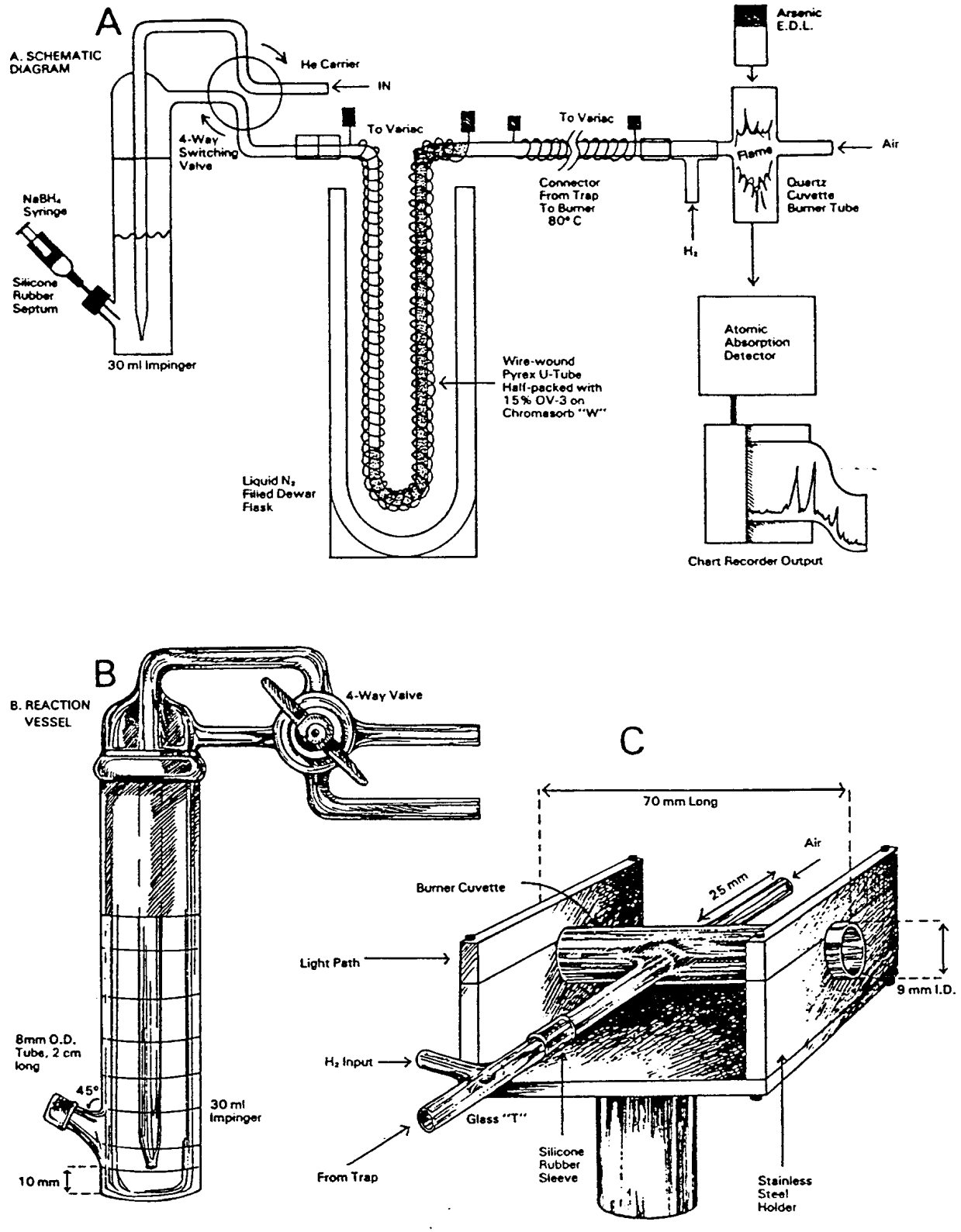


Figure 2-1. Arsenic Speciation Apparatus: (a) Schematic Diagram, (b) Reaction Vessel, (c) Quartz Cuvette Burner Tube.

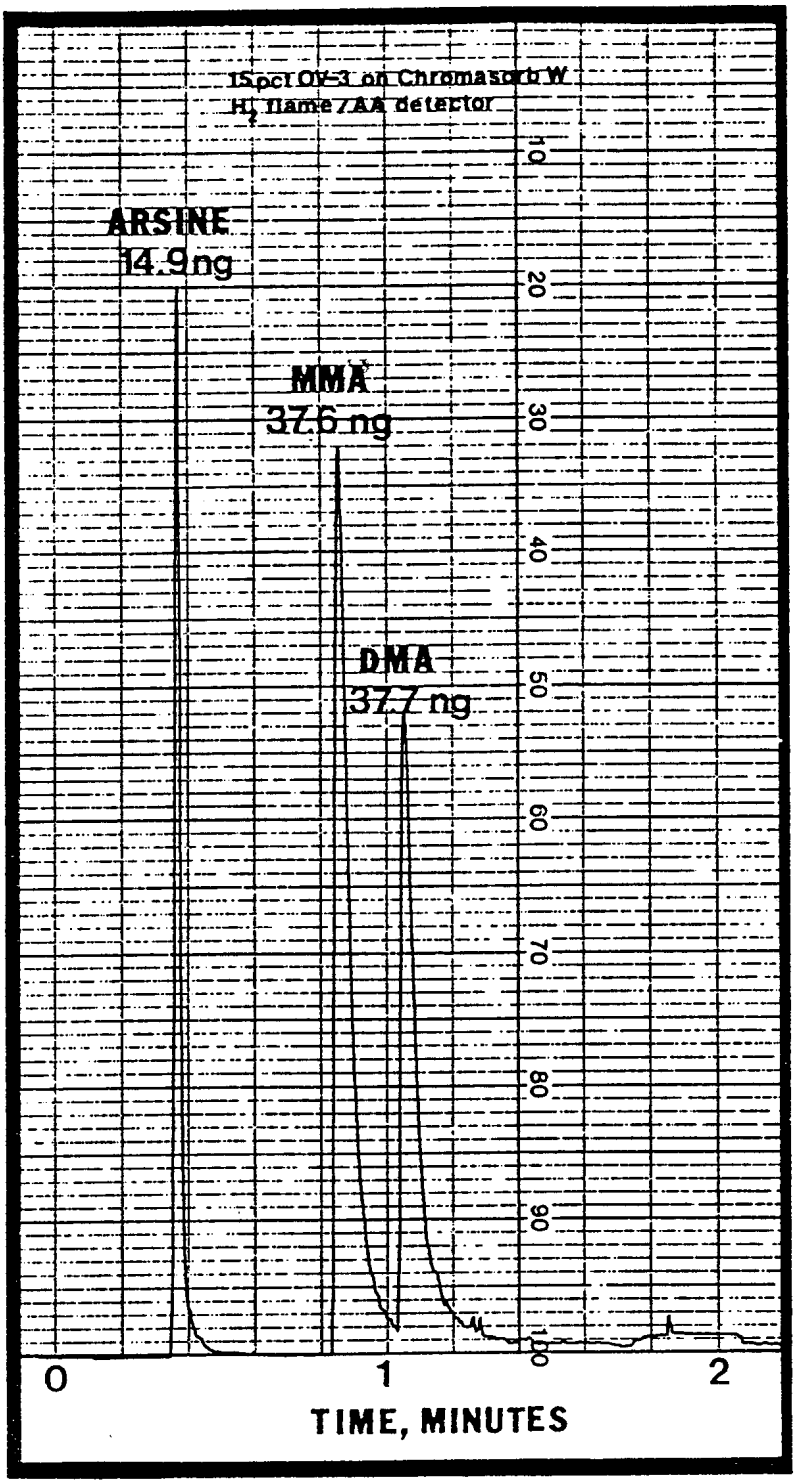


Figure 2-2. Typical chromatogram of arsenic hydride species. Vertical axis absorbance, horizontal axis time.

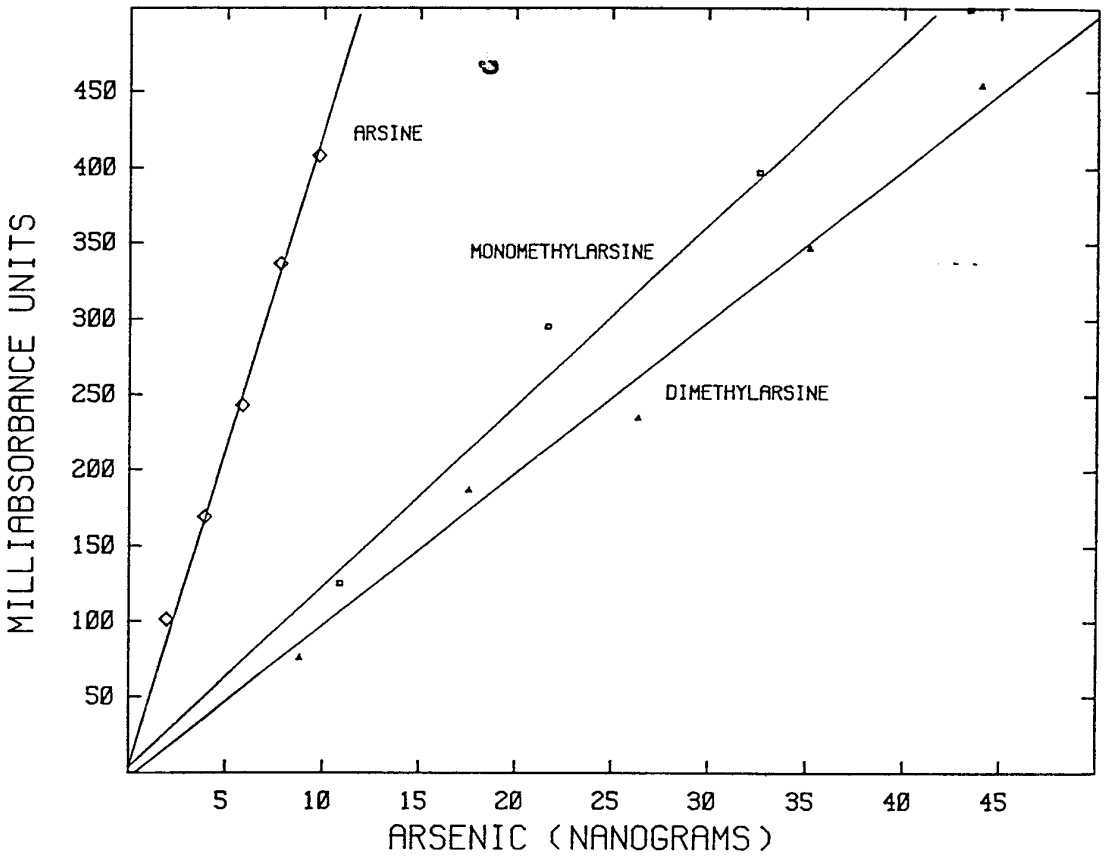


Figure 2-3. Standard curves, absorbance versus concentration for arsenic hydride species, atomic absorption detector.

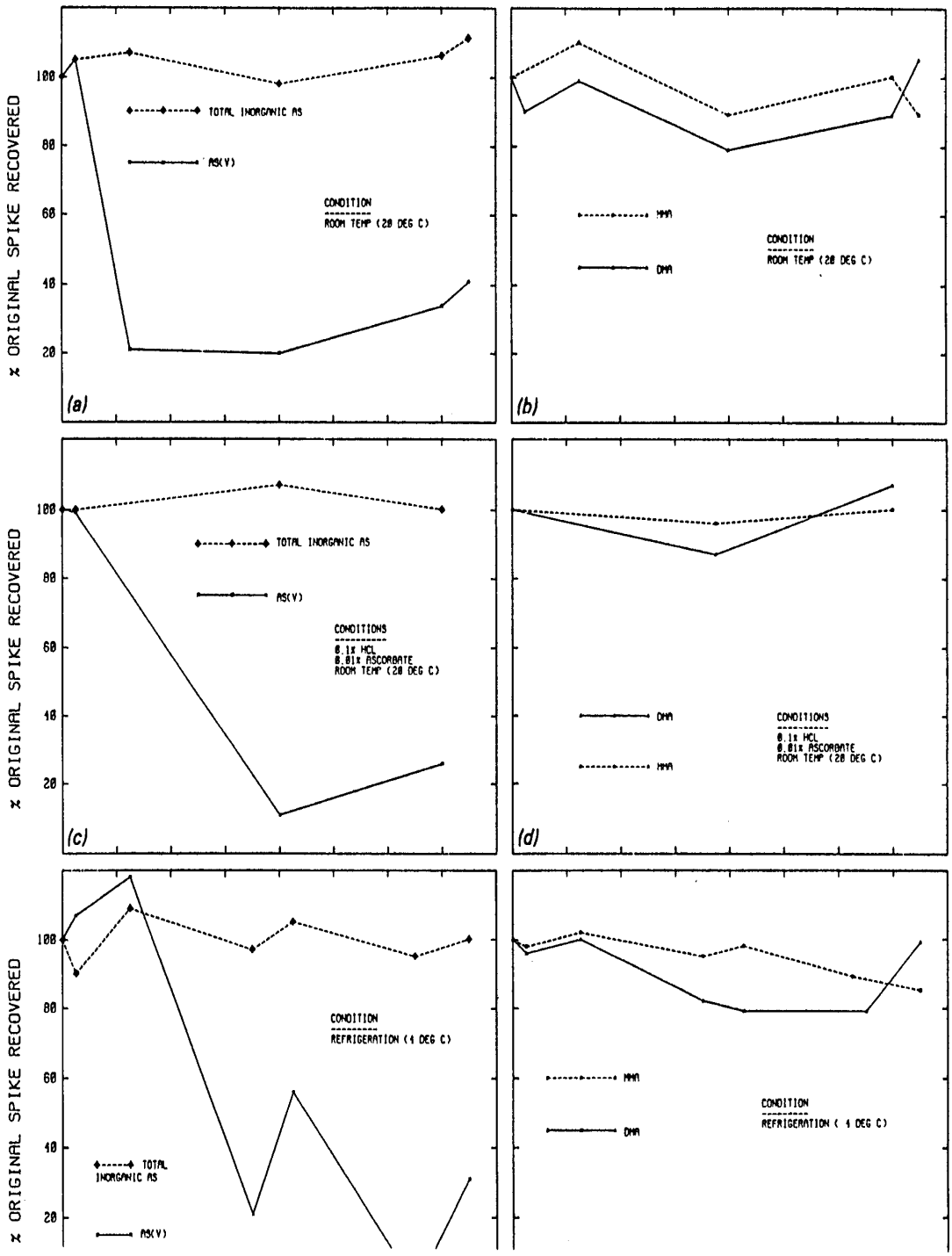


Figure 2-4a-p. Results of aqueous arsenic species storage tests. Plotted are the percentages of soluble arsenic species remaining versus storage time.

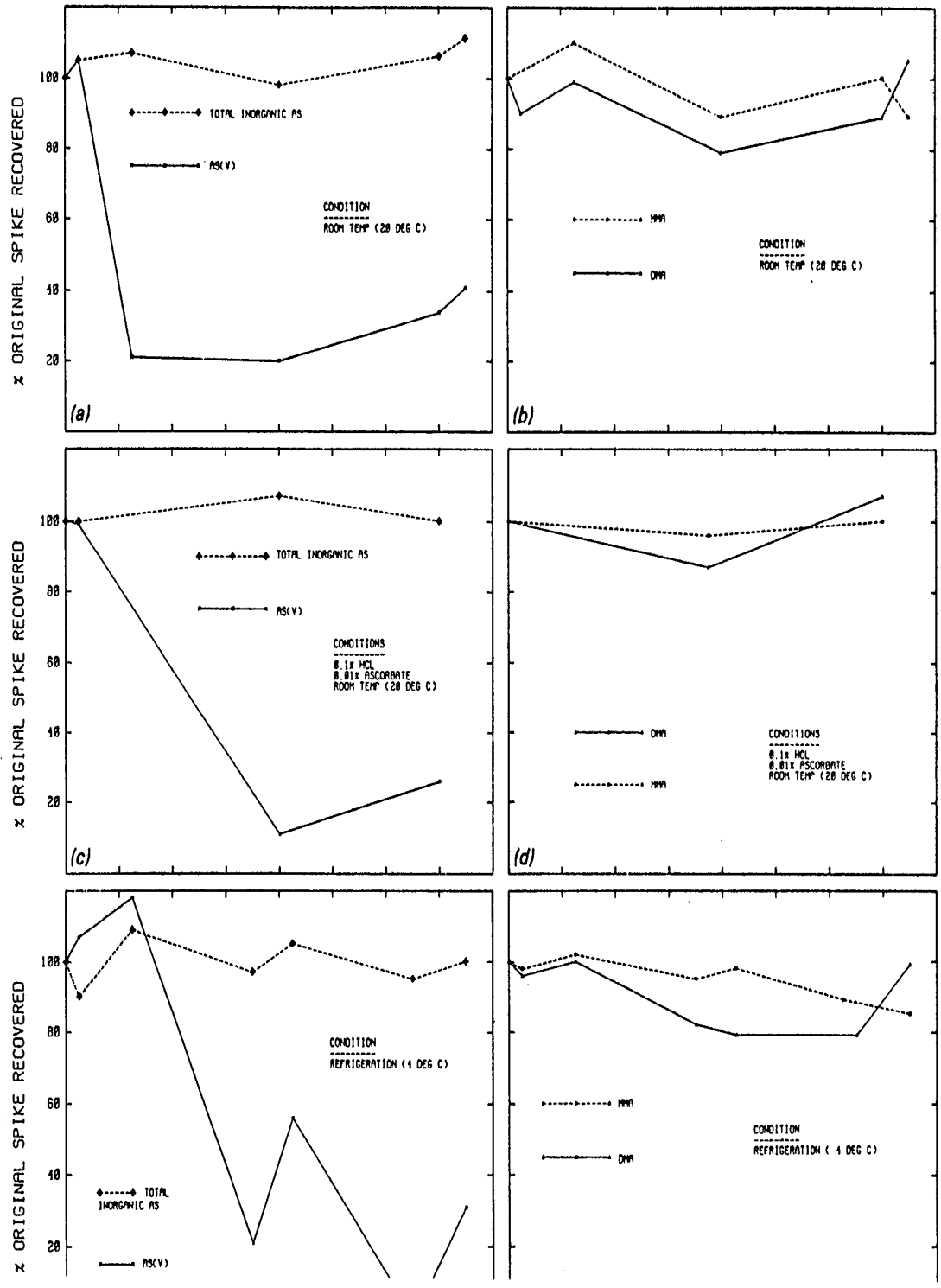


Figure 2-4a-p. (continued)

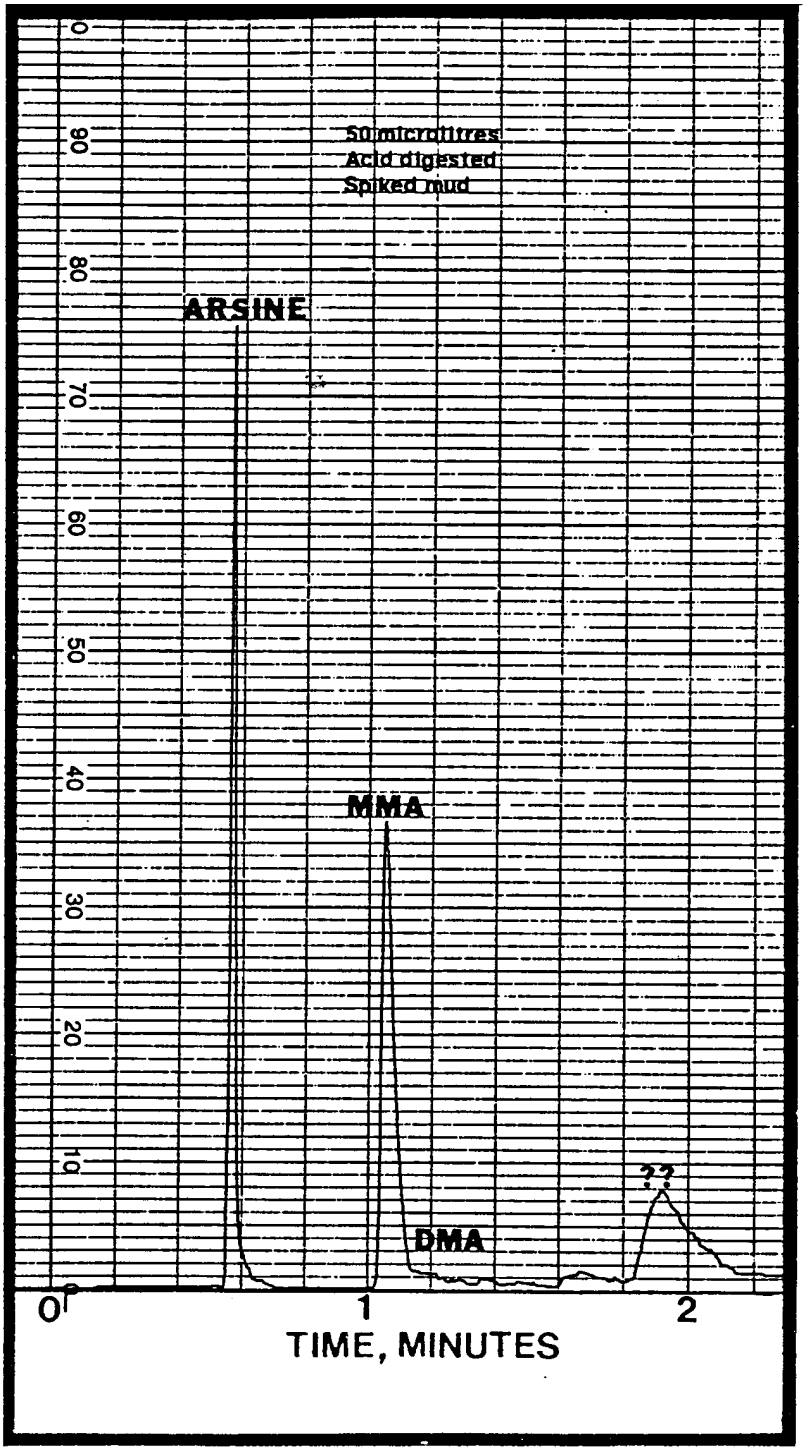


Figure 2-5. Chromatogram of digested ($HNO_3/H_2SO_4$) spiked Lake Washington mud. Vertical axis absorbance, horizontal axis time. Note absence of DMA peak and presence of unidentified higher boiling compound.

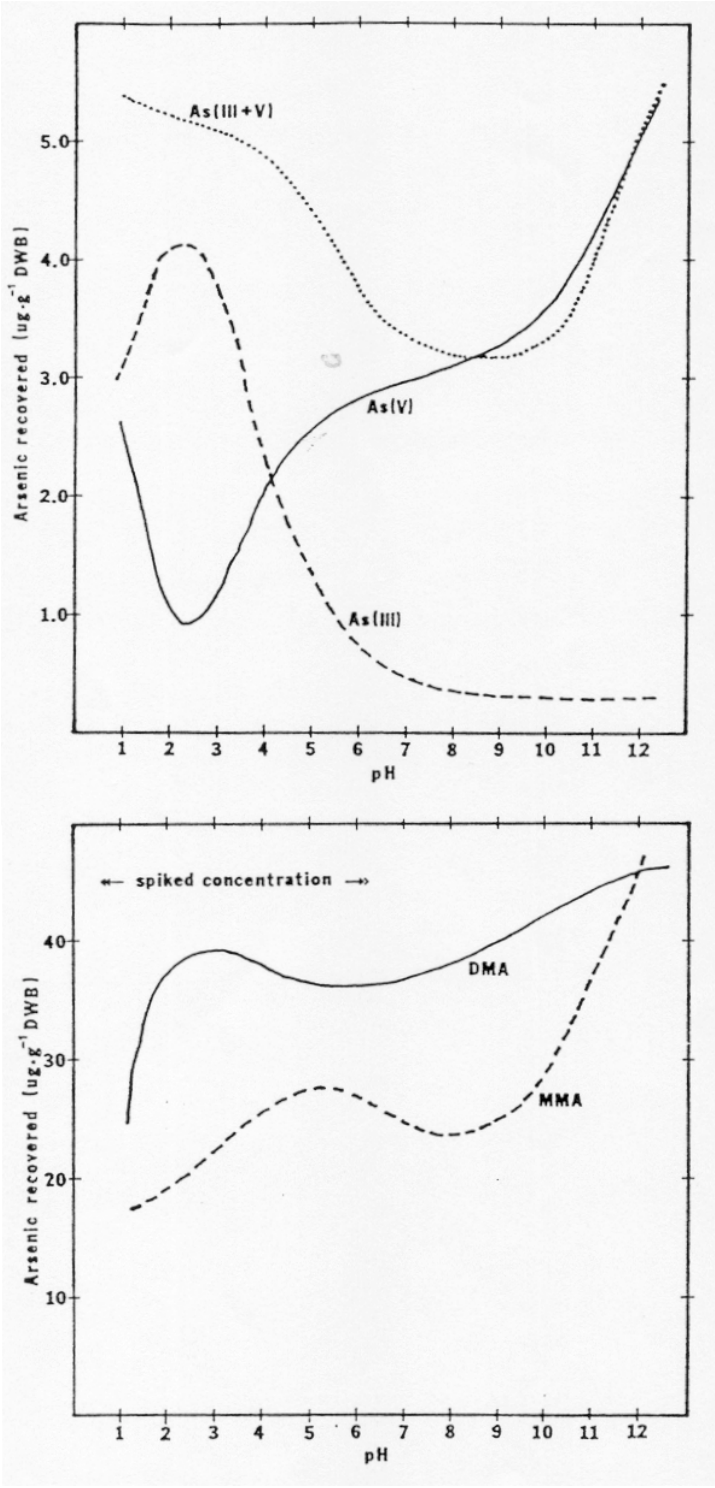


Figure 2-6. Arsenic species released from sediments as a function of solution pH. Plot of arsenic in sediment leached, µg $g^{-1}$ dry weight basis (DWB), versus pH of leachate.

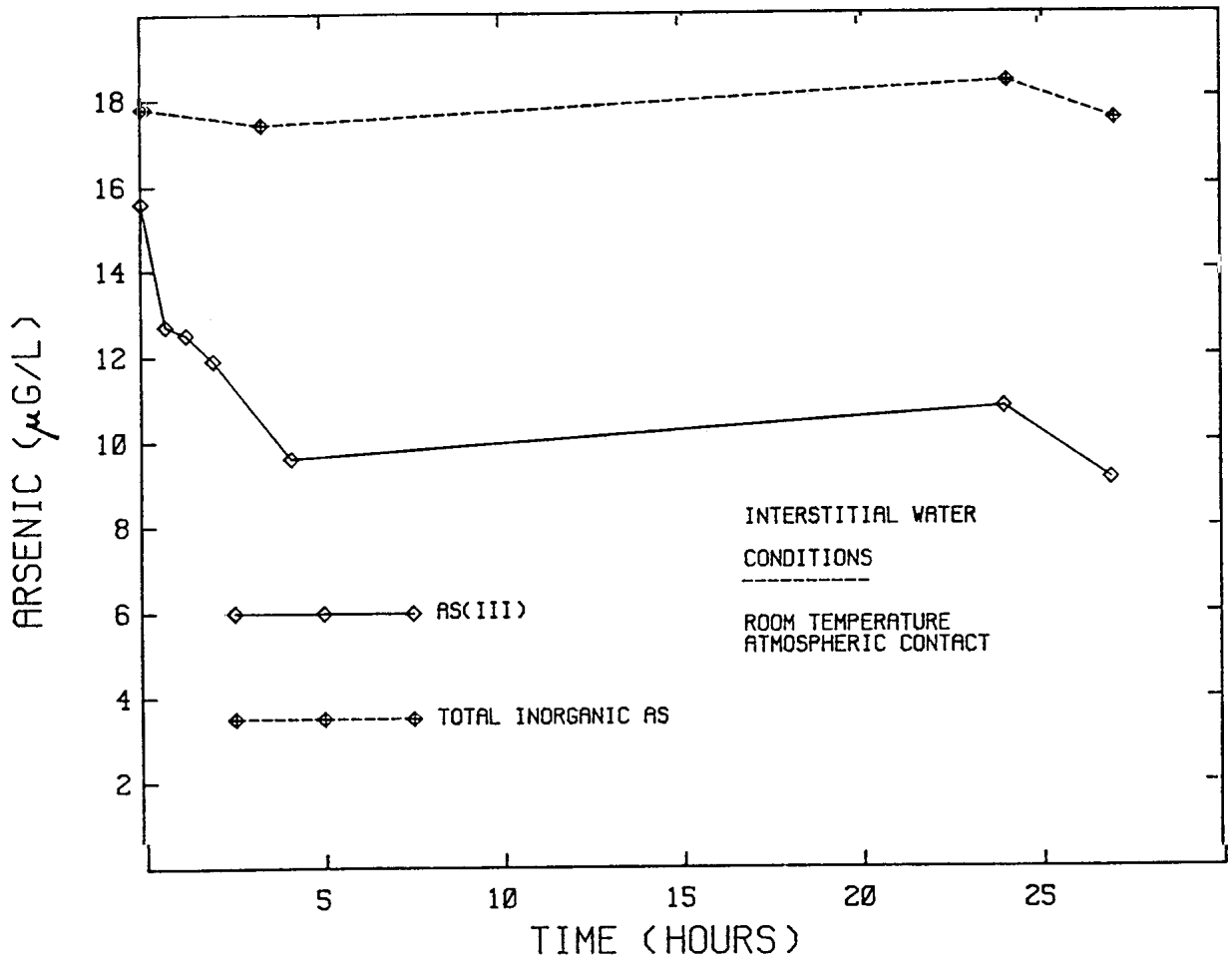


Figure 2-7. Plot of the concentration of As(III) and total inorganic arsenic versus storage time in interstitial water.

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 |

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 |

Table 2-3

Replicate Determinations of Total Inorganic Arsenic in Some Standard Waters

| | Total (inorganic) arsenic, $\mu g \cdot 1^{-1}$ | |
|---|---|---|
| Replicate | 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 |
| $\overline{X}$ | 1.550 | 77.2 |
| S | 0.040 | 4.0 |
| RSD | 2.6% | 5.Z% |
| Certified | 1.65 | 76.0 |
| ± | 0.19 | 7.0 |

M = number of replicates.
$\overline{X}$ = 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, $ng \cdot 1^{-1}$ | | |
|---|---|---|---|
| Replicate | Inorganic arsenic | MMA | DMA |
| N (8-24-83) | 3 | 3 | 3 |
| $\overline{X}$ | 937 | 2483 | 2173 |
| S | 44 | 79 | 181 |
| RSD | 4.7% | 3.2% | 8.3% |
| N (9-11-83) | 3 | 4 | 4 |
| $\overline{X}$ | 800 | 2342 | 2393 |
| S | 24 | 165 | 260 |
| RSD | 3.0% | 7.0% | 10.9% |

Table 2-5

Total Inorganic Arsenic in Standard Sediments by $HNO_3/H_2SO_4$

| | Total (inorganic) arsenic µg•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 |
| 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 |
| $\pm$ | 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 Enyironmental 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 | | | |
|---|---|---|---|---|
| Types 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 |

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% |

Table 2-8

Thirty-day Storage Results for Arsenic Speciation in Sediments

Lake Washington mud

| Arsenic species | µg • $g^{-1}$ Arsenic, dry weight basis | | |
|---|---|---|---|
| | Initial concentration | Concentrations after 30-day aging | |
| | | 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

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

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 µg • $g^{-1}$ | | |
|---|---|---|---|
| | Dry sediment | Interstitial water | $K_d$ |
| As(V) | 20 | <0.002 | >10,000 |
| As(III) | 5.2 | 0.014 | 371 |
| MMA | 40 | 0.11 | 364 |
| DMA | 38 | 1.72 | 23 |

Table 2-10

Arsenic Speciation Intercomparison Exercise

| | µg $\ell^{-1}$ | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | 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 0. Andreae for arsenic speciation in limnological samples. DRW is filtered Dungeness River water; SDRW is Dungeness River water spiked with nominally 0.45 µg • $\ell^{-1}$ As (V), and 2 µg • $\ell^{-1}$ each DMA and MMA. FA is the filtrate of 1000 mg Q-1 NBS coal fly ash leached with DRW.
BNW results are the mean of (3) determinations. ND means not detected. ± = one standard deviation.

Table 2-11

Precision of Arsenic Speciation HYCO Reservoir
(February 1984)

| | Sediment As, Sta. 5 µg $g^{-1}$ dry wt | | | Interstitial As, Sta. 5 µg $L^{-1}$ | | | Water column, Sta. 4 µg $L^{-1}$ | | |
|---|---|---|---|---|---|---|---|---|---|
| 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% |

REFERENCES

1. Braman, R. S., L. L. Johnson, C. C. Foreback, J. M. Ammons and J. L. Bricker. “Separation and determination of nanogram amounts of inorganic arsenic and methylarsenic compounds.” *Analytical Chemistry* 49 (4):621-625 (1977).

2 Andreae, M. O. “Determination of arsenic species in natural waters.” *Analytical Chemistry* 49:820, May 1977.

3. Andreae, M. O. “Methods of Seawater Analysis.” Arsenic (by hydride generation/AAS), pp. 168-173 Verlag Chemie, Florida, (1983).

4. Maher, W. A. “Determination of inorganic and methylated arsenic species in marine organisms and sediments.” *Analytica Chemica Acta* 126:157-165 (1981).