CONSTITUENT SPECIES 5.6.4

ARSENIC SPECIATION 5.6.4.A

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Two sample-processing methods (field speciation and laboratory speciation) used at the USGS National Water Quality Laboratory (NWQL) are specific to sample analysis by inductively coupled plasma-mass spectrometry (ICP-MS) for determining the concentration of inorganic and organic arsenic species in a water sample. The field-speciation method requires NWQL Schedule 1729. The laboratory-speciation method requires use either of NWQL Schedule 1730, 1731, or 1732, as appropriate for study objectives. For either the field- or laboratory-speciation method, prior knowledge is needed of sample matrix-composition characteristics (that is, major-ion concentrations in filtered samples). Major-ion data are necessary to determine (1) the volume of ethylenediaminetetraacetic acid (EDTA) that will be required for sample preservation, and (2) if sample dilution is required.[1]

TECHNICAL NOTE:

- The field-speciation method (Schedule 1729) uses an SPE cartridge to separate inorganic arsenic species (arsenite and arsenate) in a filtered water sample. The eluate (containing arsenite) and the cartridge (containing arsenate) are sent to NWQL and analyzed by ICP–MS.
- The laboratory-speciation methods (Schedule 1730 or 1731) use a strong anion exchange column and high-performance liquid chromatography to separate inorganic (arsenite and arsenate) and organic arsenic species (monomethylarsonate, dimethylarsinate, and others) in a filtered water sample. As the species elute from the column, the corresponding arsenic concentration is determined using ICP–MS.

[1]The necessity for major-ion data is related to the sample preservative (EDTA) that is needed when ICP-MS analytical methods are used. For a discussion of other methods for As(III)/AS(V) species analysis, see McCleskey and others (2004).

Regardless of the speciation method used, all samples must be collected and filtered using standard USGS procedures, as described in NFM 4. For most applications, a laboratory speciation method (for example, Schedule 1730) should be selected unless the field method offers distinct advantages for a particular water-quality study. The field-speciation method involves relatively complex sample-processing steps, is applicable only for determination of inorganic arsenic species (arsenite and arsenate), is subject to interferences from other unknown charged arsenic species, and may require sample dilution due to the limited ion-exchange capacity of the SPE cartridge (see footnote below).

- **Field-speciation (separation) method** (NWQL Schedule 1729)
  - This method is used to determine concentrations of arsenite (As (III)) and arsenate (As (V)) by separation of the species using a solid-phase-extraction (SPE) cartridge in the field. The eluate and cartridge are submitted to NWQL for analysis.
  - Sample matrix composition can exceed the ion capacity of the SPE cartridge used to separate the arsenic species; therefore, the major-anion concentration must be known or closely estimated in advance to determine if sample dilution is required. Sample matrix information also is needed to determine the volume of EDTA to be added to preserve the sample.
  - As(V) results will be biased positively when monomethylarsonate (MMA), dimethylarsinate (DMA), or other arsenic species is present in a sample. If the presence of MMA and DMA is unknown, use the Schedule 1730 laboratory-speciation method.

- **Laboratory-speciation methods** (NWQL Schedules 1730, 1731, and 1732)
  - Select Schedule 1730 to determine concentrations of arsenite (As (III)), arsenate (As (V)), monomethylarsonate (MMA), and dimethylarsinate (DMA).
  - Select Schedule 1731 for a custom analysis; i.e., for determination of *other* organoarsenic species in addition to As(III), As (V), MMA, and DMA .
  - Schedules 1730 and(or) 1731 should be requested whenever there are questions about which inorganic and organic arsenic species are present in a sample and whenever the sample matrix composition (major-ion concentration) is unknown.
  - Sample matrix information (major-cation concentrations) is needed to determine the volume of EDTA to be added to preserve the sample. Samples must be collected in an opaque sample bottle.
  - Schedule 1732 is the laboratory-preparation analog of the field-speciation method and provides speciation only of As(III) and As(V). If the presence of MMA and DMA is unknown, Schedule 1730 should be requested.

Both field and laboratory arsenic speciation methods can be affected by the precipitation of metal oxides. Many suboxic or anoxic ground-water samples having arsenic concentrations greater than the drinking-water standard of 10 µg/L also can contain substantial concentrations of reduced aluminum, iron, or manganese. Oxidation of these metal species during sample collection and processing produces metal-oxide precipitates that can sorb arsenic, resulting in negatively biased data. Furthermore, arsenite can be oxidized to arsenate by photolytically produced free radicals; therefore, the exposure of the sample to light also should be minimized.

- Exposure of the sample to air and sunlight should be minimized to prevent metal-oxide precipitation.
- EDTA must be added immediately after sample filtration.

Quality Control

Collection and analysis of quality-control samples are required as an integral part of all water-quality investigations, and is the same whether using the field-separation or laboratory-speciation method. The final types, number, and distribution of quality-control samples generally are determined according to the design and data-quality requirements of the study (NFM 4.3).

The rule of thumb for studies collecting arsenic speciation data is to collect a set of blank, replicate, and spike QC samples with every 20 environmental samples, at a minimum, as follows:

1. Process an initial field blank to evaluate the potential for contamination associated with the field methods, materials used, and sampling environment. Distribute subsequent field blanks to address field-site concerns, the sampling timeframe, and data-quality requirements.
   - Use either inorganic- (IBW), pesticide- (PBW), or volatile/pesticide- (VPBW) grade blank water as the source solution for field blanks (table 5-9 or 5-10).
   - Process field blanks in the same manner and under the same environmental conditions as environmental samples (NFM 4.3.1.B). Take precautions to limit exposure of samples to air (NFM 4.0.3).
2. Collect and process replicate environmental samples to evaluate variability of the analytical results.
   - Duplicate or triplicate samples are collected and processed one after the other and in the same manner as the other environmental samples.
   - An additional replicate sample is collected and processed for use as a field spike.

3. Process an initial field-spike sample for an evaluation of matrix effects. Distribute subsequent field-spike samples to address field-site concerns, the sampling timeframe, and data-quality requirements. Use one of the replicate samples that has been processed as the spike sample. Always submit the spike sample for analysis along with an unspiked (duplicate) sample.
   a. Using a 100-µL micropipet and a clean micropipet glass bore or disposable plastic tip, dispense the spike solution into the replicate sample (table 5-9 or 5-10).
   b. Record spiking information on the worksheet (fig. 5-5 or 5-6 for the field- or laboratory-speciation methods, respectively) so that the percentage recovery can be calculated.

Calculation of diluent and EDTA volumes

Anions in the sample represent a potential source of method interference because they compete with arsenic for exchange sites on the strong anion exchange packing in the SPE cartridge. When using the field-speciation method, field personnel may need to dilute the samples with blank water (diluent) to alleviate this interference; diluent volume depends on the estimated anion concentration of the sample. The volume of EDTA preservative added to the sample (for either the field or laboratory method) depends on the estimated cation concentration of the sample filtrate.

Before beginning to process the sample using the field speciation method, calculate the volume of diluent as follows:

1. Estimate the concentration of anions in the sample using historical data for the sampling site or a representative site, if available. If prior knowledge of the sample matrix composition is unavailable, a laboratory method such as Schedule 1730 should be requested.

2. To calculate the anion concentration of the sample:

$$C_a = [HCO_3^- \times 1.6(10^{-4})] + [Cl^- \times 2.8(10^{-4})] + [NO_3^- \times 7.1(10^{-4})] + [HPO_4^{-2} \times 2.1(10^{-4})] + [SO_4^{-2} \times 2.1(10^{-4})]$$

where:

C_a = anion concentration in milliequivalents (meq) in 10-mL sample

HCO_3^- = bicarbonate concentration in mg/L as HCO_3^-

Cl^- = chloride concentration in mg/L as Cl^-

NO_3^- = nitrate concentration in mg/L as N

HPO_4^{-2} = phosphate concentration in mg/L as HPO_4^{-2}

SO_4^{-2} = sulfate concentration in mg/L as SO_4^{-2}

a. If the milliequivalents (meq) of total anions calculated for the sample exceeds the LC-SAX™ SPE cartridge capacity of 0.1 meq, the sample must be diluted with blank water to obtain a sample with 0.1 meq or less total anions.

b. **Do not excessively dilute samples because this results in diluting the arsenic species concentrations.**

c. Record the diluent volume on the worksheet (fig. 5-5) so that a dilution factor can be applied to the sample results. If the diluent volume is not provided, it will be assumed that the sample was not diluted.

For the field-speciation method: Estimate the total anion concentration of the sample to determine the diluent volume needed to prevent exceeding the ion-exchange capacity of the SPE cartridge.

To determine the volume of EDTA needed to preserve samples (NWQL Schedules 1729, 1730, 1731, and 1732), estimate the cumulative concentration of major cations in the sample, as follows:

1. Estimate the concentration of cations in the sample using historical data for the same site or a representative site, if available.
2. To calculate the volume of 250 mM (millimolar) EDTA required for a 10-mL sample:

$$V_{EDTA} = 4.0(10^{6}) \times ([Al \times 3.7(10^{-10})] + [Fe \times 1.8(10^{-10})] + [Mn \times 1.8\ (10^{-10})] + [Ca \times 2.5(10^{-7})] + [Mg \times 4.1(10^{-7})] + [Sr \times 1.1(10^{-10})])$$

where:

V_{EDTA}	= microliters of 250-mM EDTA required for a 10-mL sample
Al	= dissolved aluminum concentration, in µg/L as Al
Fe	= dissolved iron concentration, in µg/L as Fe
Mn	= dissolved manganese concentration, in µg/L as Mn
Ca	= dissolved calcium concentration, in mg/L as Ca
Mg	= dissolved magnesium concentration, in mg/L as Mg
Sr	= dissolved strontium concentration, in µg/L as Sr

3. If V_{EDTA} is less than 100 µL, add 100 µL of EDTA to the sample.
4. **If a sample is diluted for the field-speciation method, use the estimated cation concentration in the diluted sample in the equation above.**
5. Record the volume of EDTA added to the sample on the worksheet (fig. 5-5 or 5-6). If the EDTA volume is not provided, it will be assumed that 100 µL was added.

Sample processing

Sample-collection and -processing equipment should be cleaned according to USGS protocols for inorganic-constituent sampling (NFM 3.2.1). If an acid rinse is used, be sure to follow it with a thorough deionized-water rinse rinse. Do not acid rinse a filter membrane through which samples for arsenic analysis will be passed.

The field-speciation method of sample processing (NWQL Schedule 1729) is as follows:

1. Before leaving for the field:

   a. Fill out the header information on the worksheet for NWQL Schedule 1729 (fig. 5-5). Record the estimated anion and cation concentrations, diluent volume, and EDTA volume (see instructions in the section above). Referring to table 5-9, assemble the equipment needed.

   b. The strong anion exchange cartridge must be pre-conditioned before collecting samples. Prepare the cartridge-conditioning solutions as follows:

      ii. **pH $\geq$ 4** (Chloride-form LC-SAX cartridge): use methanol (CH_3OH, CAS 67-56-1) as received from the supplier. This is the most commonly used form for surface-water and ground-water matrices with pH $\geq$ 4.

      ii. **pH < 4** (Acetate-form LC-SAX cartridge): prepare a 1.7 M acetic acid solution by diluting trace-metals-grade acetic acid (CH_3COOH, CAS 64-19-7) by 1:10. This form works best to buffer samples with pH < 4. The 1.7 M acetic acid solution is stable for up to 30 days.

Always add acid to water, not water to acid.

2. At the field site, continue to fill out the sample worksheet for NWQL Schedule 1729 (fig. 5-5).

3. Assemble and organize on a clean work surface the necessary processing equipment and supplies (table 5-9).

4. Wear appropriate disposable, powder-free gloves. Before proceeding, prepare the 0.45-µm capsule filter (NFM 5.2.1.A, making sure that the capsule filter has been pre-

cleaned with DIW and is ready to be used. Study objectives may dictate use of a filter membrane with a smaller pore size (McCleskey and others, 2004); these also should be precleaned (NFM 5, table 5-3). **Do not rinse the filter with acid.**

5. Collect environmental (surface-water and ground-water) samples and quality-control samples using the "clean-sampling procedures prescribed for trace-element samples at low part-per-billion concentrations (NFM 4.0.1). Prevent exposure of samples to the atmosphere and light to prevent oxidation.

   - **Surface-water samples should be collected from a single vertical or a point and should not be composited.** If stream mixing conditions are a concern, multiple samples from different points in the cross section should be individually collected and processed, or a sample should be collected from a different cross section where mixing is not a concern. Collection of a multiple vertical, EWI, or EDI composite surface-water sample can result in substantial aeration of the sample, causing the distribution of arsenic species to change.
   - Ground-water samples are particularly susceptible to changes in arsenic species distribution when sampling waters with low dissolved-oxygen concentration and redox potential (Eh). Appropriate precautions should be taken to avoid the aeration or light exposure of ground-water samples (NFM table 4.4).

Minimize the amount of time the sample is exposed to air and light.

The remaining steps in the field-speciation method are time dependent; therefore, it is important to complete the previous steps before continuing.

6. Rinse centrifuge tubes **A** and **B** and syringe twice with blank water. Cap the tubes and set aside.

7. Remove the LC-SAX™ SPE cartridge from the shipping container. Noting the sample pH, condition the cartridge as follows:

   - **Sample pH ≥ 4:** Using the syringe, push about 2 mL of methanol followed by about 10 mL blank water through the chloride-form cartridge at a rate of 1 to 2 drops per second. Collect the methanol for proper disposal. Use the syringe to blow out excess water. **Use cartridge immediately after conditioning.**

   - **Sample pH < 4:** Using the syringe, push about 5 mL of 1.7 M acetic acid followed by about 10 mL of blank water through the acetate-form cartridge at a rate of 1 to 2 drops per second. Collect the acetic acid for proper disposal. Use the syringe to blow out excess water. **Use cartridge immediately after conditioning.**

8. If a sample dilution is required (see *"Calculation of diluent and EDTA volumes*"), add the appropriate volume of blank water (diluent) to centrifuge **tube A** (the centrifuge tube is graduated).

9. Using the micropipet and disposable glass bores or an adjustable micropipet and a clean tip, add the appropriate volume of EDTA solution to centrifuge **tube A** (see *"Calculation of diluent and EDTA volumes*"). If processing a spike sample, next add the field spike solution using a 100-µL micropipet and clean, disposable glass bore or plastic tip.

   a. If more than 100 µL of EDTA is needed, use either an adjustable volume micropipet that is capable of delivering the calculated volume of EDTA, or use a 100-µL micropipet and round the calculated volume of EDTA up to the nearest 100-µL increment.

   b. Be careful not to add excessive EDTA to the field speciation sample. An excess of EDTA will compete with arsenic species for ion-exchange sites in the SPE cartridge, thus causing positive bias in the As(III) results.

10. Filter 10.0±0.2 mL (or 10.0 mL minus the diluent volume) of sample directly into the centrifuge tube. Cap **tube A** tightly, and mix well. **The EDTA and the filtered sample must be combined in tube A immediately after filtration.**

    - Filter the environmental samples using in-line procedures as described in NFM 5.2.
    - Take precautions to prevent oxidation of chemical species when filtering ground water; the risk of oxidation is of lesser concern for aerated surface water.

11. Remove the plunger from the syringe barrel. Connect the barrel to the SPE cartridge using the red cartridge adapter.

12. Pour the contents of **tube A** into the syringe barrel attached to the cartridge. Carefully insert the plunger into the syringe barrel.

    a. Slowly push the plunger to elute the sample through the cartridge at a rate of 1 to 2 drops per second, collecting the eluate in the centrifuge tube labeled **B**.

    b. Pass the entire sample volume through the cartridge. Use the syringe to blow out any remaining sample from the cartridge.

    c. Tightly cap **tube B**. Label **tube B** with station ID, date, and time. Discard **tube A** and the syringe.

13. Label the cartridge and the container into which the cartridge will be placed with station ID, date, and time. Place the cartridge into its original container, and cap tightly.

14. Complete the NWQL Schedule 1729 worksheet (fig. 5-5). Retain the original copy of the worksheet in station folder.

15. Place **tube B**, the SPE cartridge, and a copy of the completed worksheet (fig. 5-5) into the original kit bag. Label the bag with the station ID, date, and time. **Chill and maintain at 4°C. The cartridge and eluate are stable for up to 7 weeks; however, both should be shipped to NWQL to arrive within 14 days of sample collection.**

Laboratory-speciation methods of sample processing (NWQL Schedules 1730, 1731, and 1732):

1. Before processing samples, begin to fill out the sample worksheet (fig. 5-6), indicating the NWQL Schedule being requested (Schedule 1730, 1731, or 1732).
2. Assemble and organize on a clean work surface the necessary processing equipment and supplies (table 5-10).
3. Wear appropriate disposable, powder-free gloves. Before proceeding, prepare the 0.45-µm capsule filter (NFM 5.2.1.A), making sure that the capsule filter has been pre-cleaned with DIW and is ready to be used. Study objectives may dictate use of a filter membrane with a smaller pore size (McCleskey and others, 2004); these also should be precleaned (NFM 5, table 5-3). **Do not rinse the filter with acid.**
4. Collect environmental (surface-water and (or) ground-water) samples and quality-control samples, using the prescribed procedures for samples with trace-element concentrations at the part-per-billion level. (NFM 4). Prevent exposure of samples to the atmosphere and light to prevent oxidation.
   - **Surface-water samples should be collected from a single vertical or a point and should not be composited.** If stream mixing conditions are a concern, multiple samples from different points in the cross section should be individually collected and processed or a sample should be collected from a different cross section where mixing is not a concern. Collection of a multiple vertical, EWI, or EDI composite surface-water sample can result in substantial aeration of the sample, causing the distribution of arsenic species to change.

- Ground-water samples are particularly susceptible to changes in arsenic species distribution when sampling waters with low dissolved-oxygen concentration and redox potential (Eh). Appropriate precautions should be taken to avoid the aeration or light exposure of ground-water samples (NFM table 4-4).

5. Rinse an opaque polyethylene sample bottle twice with blank water.
6. Using the micropipet and disposable glass bores or plastic tips or an adjustable micropipet and a clean tip, add at least 100 µL of EDTA solution to the sample bottle (see "*Calculation of diluent and EDTA volumes*"). If more than 100 µL of EDTA is needed, use either an adjustable volume micropipet that is capable of delivering the calculated volume of EDTA, or use a 100-µL micropipet and round the calculated volume of EDTA up to the nearest 100-µL increment.
7. If processing a spike sample, add the field spike solution (N1613) using a 100-µL micropipet and clean, disposable glass bore or plastic tip.
8. Record the volumes of EDTA solution and spike solution used on the laboratory-speciation methods worksheet (fig. 5-6). If the EDTA volume is not provided, it will be assumed that 100 µL was added.
9. Filter the sample, filling the opaque sample bottle to the top. Do not fill to overflowing. The opaque sample bottle holds about 11.5± 0.1 mL when completely full. The bottle must be filled completely to the brim so that the dilution factor and spike recovery can be accurately calculated. Cap bottle tightly.
   - Filter the environmental samples using in-line procedures as described in NFM 5.2.
   - Take precautions to prevent oxidation of chemical species when filtering ground water; the risk of oxidation is of lesser concern for aerated surface water.
10. Label bottle with station ID, date, and time.

11. Complete the worksheet (fig. 5-6). Retain the original copy of the worksheet in the station folder and place a copy in a sealed bag with the sample bottle.

12. Chill and maintain the sample at 4°C. The sample is stable for up to 3 months; however, the sample should be shipped to the NWQL to arrive within 14 days of sample collection.

Selected References

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McCleskey, R.B., Nordstrom, D.K., and Maest, A.S., 2004, Preservation of water samples for arsenic(III/V) determinations: an evaluation of the literature and new analytical results: Applied Geochemistry, v. 19, p. 995-1009.
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Table 5-9. Checklist of supplies and equipment required for arsenic speciation using the field-separation method (NWQL Schedule 1729)

[mL, milliliter; mg, milligram; µg-As/L, micrograms-arsenic per liter; <, less than; SPE, solid-phase extraction cartridge; mM, millimoles per liter; M, moles per liter; EDTA, ethylenediamine-tetraacetic acid; L, microliter; As(III), arsenite; As(V), arsenate]

√	Supplies	Description	Number required	Supplier and One Stop Shopping item number for USGS studies
	Blank water	• Inorganic-grade (IBW), or • Pesticide-grade (PBW), or • Volatile-organic/pesticide-grade (VPBW)	As needed	Q386FLD, N1600, N1570
	Field speciation kit (arsenic)	• Tube A, graduated, 15 mL for sample filtrate • Tube B, graduated, 15 mL for cartridge eluate • LC-SAX™ SPE cartridge • Syringe, 10 mL	1 per sample	N1610
	EDTA solution (store at room temperature)	25 mL of 250 mM EDTA for sample preservation. EDTA shelf life is one year from date of preparation and is printed on each bottle. See footnote below for proper disposal.	As needed	N1611
	Schedule 1729 spike solution (store at room temperature)	10 mL of 2,500 µg-As/L of As(III) and As(V). Spike solution shelf life is 90 days from date of preparation and is printed on each bottle. See footnote below for proper disposal.	As needed for Schedule 1729	N1612
	Methanol *or* acetic acid	Methanol (high purity grade, CAS 67-56-1), certified with <1 µg-As/L contamination; Acetic acid (CAS 64-19-7), certified with <1 µg-As/L contamination (trace-element grade). See footnote below for proper disposal.	As needed	Open market
	Micropipet	100-µL fixed volume or adjustable-volume, for EDTA and spikes	1	N1370 (fixed volume) or Open market
	Glass bores or plastic micropipet tips	Disposable glass bores, for 100-µL fixed-volume micropipet or disposable 100-µL fixed-volume or larger volume plastic tips for adjustable-volume micropipets	Ample supply	N1300 (glass bores) or Open market (plastic tips)
	Pipet	1- to 10-mL variable volume with tips, for sample dilution	1	Open market
	SPE tube adapter	For 3-mL SPE cartridge (field speciation only)	1, reusable	N1614
	Wash bottles: • Teflon® • Polyethylene	• 500 mL, for methanol or 1.7 M acetic acid for SPE cartridge conditioning • 250 mL or 500 mL, for blank water	1	Open market

TECHNICAL NOTE: Material Safety Data Sheets are supplied with the EDTA and arsenic field spike solutions. Persons using these materials should become familiar with the associated warnings and safety guidelines prior to using the materials in the field. Expired EDTA and spike solutions, methanol, and acetic acid must be disposed of according to Federal, State, and local regulations. The District safety officer and water-quality specialists can be consulted for proper disposal methods.

Table 5-10. Checklist of supplies and equipment required for arsenic speciation using the laboratory-speciation methods (NWQL Schedules 1730, 1731, or 1732)

[mL, milliliter; µg-As/L, micrograms-arsenic per liter; mM, millimoles per liter; EDTA, ethylenediaminetetraacetic acid; µL, microliter; As(III), arsenite; As(V), arsenate; DMA, dimethylarsinate; MMA, monomethylarsonate]

√	Supplies	Description	Number required	Supplier and One Stop Shopping item number for USGS studies
	Blank water	• Inorganic-grade (IBW), or • Pesticide-grade (PBW), or • Volatile-organic/pesticide-grade (VPBW)	As needed	Q386FLD, N1600, N1570
	Schedules 1730 and 1731 spike solution (store at room temperature)	10 mL of 2,500 µg-As/L of As(III), As(V), DMA, and MMA. Spike solution shelf life is 90 days from date of preparation and is printed on each bottle. See footnote below for proper disposal.	As needed for Schedules 1730 or 1731	N1613
	Schedule 1732 spike solution (store at room temperature)	10 mL of 2,500 µg-As/L of As(III) and As(V). Spike solution shelf life is 90 days from date of preparation and is printed on each bottle. See footnote below for proper disposal.	As needed for Schedule 1732	N1612
	EDTA solution (store at room temperature)	25 mL of 250 mM EDTA for sample preservation. EDTA shelf life is one year from date of preparation and is printed on each bottle. See footnote below for proper disposal.	As needed	N1611
	Micropipet	100-µL fixed volume or adjustable-volume, for EDTA and spikes.	1	N1370 (fixed volume) or Open market
	Glass bores or plastic micropipet tips	Disposable glass bores, for 100-µL fixed-volume micropipet or disposable 100-µL fixed-volume or larger volume plastic tips for adjustable-volume micropipets.	Ample supply	N1300 (glass bores) or Open market (plastic tips)
	Sample bottles	Opaque (brown) “8-mL”, polyethylene (holds 11.5 mL of sample when full).	1 per sample	N1615

TECHNICAL NOTE: Material Safety Data Sheets are supplied with the EDTA and arsenic field spike solutions. Persons using these materials should become familiar with the associated warnings and safety guidelines prior to using the materials in the field. Expired EDTA and spike solutions must be disposed of according to Federal, State, and local regulations. The District safety officer and water-quality specialists can be consulted for proper disposal methods.

Arsenic Field-Speciation Method Checklist and Worksheet
(Schedule 1729)

Site ID: _____*Date/Time:* _____
Site Name: _____ *Collector:* _____

_ Filter sample using 0.45-µm capsule filter; do not clean media with acid
_ SPE Cartridge Conditioning for samples with pH greater than or equal to 4:
2 mL methanol and 10 mL deionized water

or

_ SPE Cartridge Conditioning for samples with pH < 4: 5 mL 1.7 M acetic acid and 10 mL deionized water
_ Estimated anion milliequivalents in 10 ml sample:_____ meq

$C_a = [HCO_3^- \times 1.6(10^{-4})] + [Cl^- \times 2.8(10^{-4})] + [NO_3^- \times 7.1(10^{-4})] + [HPO_4^{-2} \times 2.1(10^{-4})] + [SO_4^{-2} \times 2.1(10^{-4})]$

where: C_a = anion concentration in milliequivalents in 10-mL sample
HCO_3^- = bicarbonate concentration in mg/L as HCO_3^-
Cl^- = chloride concentration in mg/L as Cl^-
NO_3^- = nitrate concentration in mg/L as N
HPO_4^{-2} = phosphate concentration in mg/L as HPO_4^{-2}
SO_4^{-2} = sulfate concentration in mg/L as SO_4^{-2}

_ Diluent (blank water) volume added to tube A to give <0.1 anion milliequivalents in 10-mL sample _____ mL
_ EDTA preservative added to tube A _____µL
(100 µL or the volume calculated below, whichever is greater)

(Note: if sample is diluted, account for dilution factor when using the following equation):

$V_{EDTA} = 4.0(10^6) \times ([Al \times 3.7(10^{-10})] + [Fe \times 1.8(10^{-10})] + [Mn \times 1.8\ (10^{-10})] + [Ca \times 2.5(10^{-7})] + [Mg \times 4.1(10^{-7})] + [Sr \times 1.1(10^{-10})])$

where: V_{EDTA} = microliters of 250-mM EDTA required per sample
Al = dissolved aluminum concentration, in µg/L as Al
Fe = dissolved iron concentration, in µg/L as Fe
Mn = dissolved manganese concentration, in µg/L as Mn
Ca = dissolved Ca concentration, in mg/L as Ca
Mg = dissolved magnesium concentration, in mg/L as Mg
Sr = dissolved strontium concentration, in µg/L as Sr

_ Sample volume added to tube A
(10.0±0.2 or 10.0 mL minus diluent volume)_____ mL
_ Spike Solution lot number_____**F**
Solution concentration_____ µg/L
Volume added_____ µL
_ Push all the sample through cartridge at 1 to 2 drops per second.
_ Collect eluate in tube B; cap tightly.
_ Write Station ID, date, and time on the cartridge, tube B, and shipping container.
_ Place tube B, cartridge (inside its shipping container), and copy of worksheet inside the kit bag. Label bag with station ID, date, and time.
_ Maintain at 4 °C. Ship chilled sample and a copy of the worksheet to the NWQL within 14 days of collection.

COMMENTS:

Figure 5-5. Worksheet for field-speciation method to determine arsenic species in water samples.

Arsenic Laboratory-Speciation Methods Checklist and Worksheet
(Schedule 1730, 1731, or 1732)

Site ID: _____ *Date/Time:* _____
Site Name: _____ *Collector:* _____
Lab schedule requested: _____

Laboratory-speciation methods Schedules 1730, 1731, or 1732

_ Filter sample using 0.45-µm disposable capsule filter;
do not clean media with acid
_ EDTA preservative added to opaque bottle_____µL
(100 µL or the volume calculated below, whichever is greater)

$$V_{EDTA} = 4.0(10^{-6}) \times ([Al \times 3.7(10^{-10})] + [Fe \times 1.8(10^{-10})] + [Mn \times 1.8\ (10^{-10})] + [Ca \times 2.5(10^{-7})] + [Mg \times 4.1(10^{-7})] + [Sr \times 1.1(10^{-10})])$$

where: V_{EDTA} = microliters of 250-mM EDTA required per sample
Al = dissolved aluminum concentration, in µg/L as Al
Fe = dissolved iron concentration, in µg/L as Fe
Mn = dissolved manganese concentration, in µg/L as Mn
Ca = dissolved Ca concentration, in mg/L as Ca
Mg = dissolved magnesium concentration, in mg/L as Mg
Sr = dissolved strontium concentration, in µg/L as Sr

_ Spike Solution lot number_____**L or F**
(circle one)
Solution concentration_____ µg/L
Volume added _____ µL

Spiked or unspiked sample volume completely fill bottle, but do not overflow.

Note “8-mL” opaque bottle contains 11.5 ± 0.1 mL when completely full: 11.5 mL

_ Write Station ID, date, and time on bottle.
_ Maintain at 4 °C. Ship chilled sample and a copy of the worksheet to the NWQL within 14 days of collection.

COMMENTS:

Figure 5-6. Worksheet for laboratory-speciation methods to determine arsenic species in water samples.