

CONSTITUENT SPECIES 5.6.4

ARSENIC SPECIATION 5.6.4.A

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The speciation method used at the USGS National Water Quality Laboratory (NWQL), Lab Code LC 3142¹, uses liquid chromatography to separate inorganic and organic arsenic species and inductively coupled plasma-mass spectrometry (ICP-MS) to measure the associated arsenic concentration. When using this speciation method, prior knowledge is needed of the major-cation concentrations present in the filtered sample. The major-cation 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. The necessity for major-ion data is related to the amount of sample preservative (EDTA) that is required.

TECHNICAL NOTE:

This speciation method (LC 3142) uses a strong anion exchange column and high-performance liquid chromatography to separate inorganic (arsenite and arsenate) and organic arsenic species (monomethylarsonate, dimethylarsinate) in a filtered water sample. As the species elute from the column, the corresponding arsenic concentration is determined using ICP-MS.

All samples must be collected and filtered using standard USGS procedures, as described in NFM 4 and NFM 5, respectively.

➤ **Laboratory-speciation method** (NWQL Lab Code 3142)

- Select Lab Code 3142 to determine concentrations of arsenite (As (III)), arsenate (As (V)), monomethylarsonate (MMA), dimethylarsinate (DMA).²
- Samples must be collected in an opaque sample bottle (One-Stop #N1615).
- Sample matrix information (major-cation concentrations) is needed to determine the volume of EDTA to be added to preserve the sample.

The laboratory arsenic speciation method can be affected by the precipitation of metal oxides. Many suboxic or anoxic ground-water samples having arsenic concentrations greater than the USEPA 10- $\mu\text{g/L}$ drinking-water standard 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.**

¹ The following NWQL laboratory schedules (LS) were replaced by LC 3142 as of April 1, 2010: LS1729, LS1730, LS1731, and LS1732.

² For a discussion of other methods for As(III)/As(V) species analysis, see McCleskey and others, 2004.

Quality Control

Collection and analysis of quality-control samples are required as an integral part of all USGS water-quality investigations. 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 general recommendation for studies collecting arsenic speciation data is to collect, at a minimum, a set of blank, replicate, and spike QC samples with every 20 environmental samples, as follows:

1. Process an initial field blank to evaluate the potential for contamination associated with the field methods and materials used, and the sampling environment. Distribute subsequent field blanks to address field-site concerns, the sampling timeframe, and data-quality requirements.
 - Use inorganic (IBW) blank water as the source solution for field blanks (table 5.6.4.A—1).
 - 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 sampling, sample processing, and analytical measurement.
 - 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 was processed as the spike sample.
 - Always submit the spike sample for analysis along with an unspiked (duplicate) sample.
 - a. Using a 100- μ L micropipet and a clean micropipet glass bore or disposable plastic tip, dispense the spike solution into the replicate sample (table 5.6.4.A—1).
 - b. Record spiking information on the laboratory-speciation method worksheet (fig. 5.6.4.A—1) so that the percentage recovery can be calculated.

Calculation of diluent and EDTA volumes

The volume of EDTA preservative added to the sample depends on the estimated cation concentration of the sample filtrate.

To determine the volume of EDTA needed to preserve samples (NWQL LC 3142), 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:

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

where:

V_{EDTA} = microliters of 250-mM EDTA required for a 10-mL sample

Al = dissolved aluminum concentration, in $\mu\text{g/L}$ as Al

Fe = dissolved iron concentration, in $\mu\text{g/L}$ as Fe

Mn = dissolved manganese concentration, in $\mu\text{g/L}$ 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 $\mu\text{g/L}$ as Sr

3. If V_{EDTA} is less than 100 μL , add 100 μL of EDTA to the sample.
4. Record the volume of EDTA added to the sample on the worksheet (fig. 5.6.4.A—1). If the EDTA volume is not provided, it will be assumed that 100 μL was added.

Sample Processing for Laboratory Arsenic-Speciation Method

Equipment for sample collection and processing 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. **Do not acid rinse a filter membrane** through which samples for arsenic analysis will be passed.

To process samples for arsenic speciation analysis by NWQL LC3142:

1. Before processing samples, begin to fill out the sample worksheet (fig. 5.6.4.A—1), specifying NWQL LC 3142.
2. Assemble and organize on a clean work surface the necessary processing equipment and supplies (table 5.6.4.A—1).
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 precleaned 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 or groundwater 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.
 - o **Surface-water samples should be collected from 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.
 - o Groundwater 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 groundwater samples (NFM table 4-4).
5. Rinse an opaque polyethylene sample bottle twice with IBW.
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 (One-Stop # 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. 5.6.4.A—1). 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 plus 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.
 - o Filter the environmental samples using in-line procedures as described in NFM 5.2.
 - o Take precautions to prevent oxidation of chemical species when filtering groundwater; 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. 5.6.4.A—1). 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. Although the sample is stable for up to 3 months, the **sample should be shipped to the NWQL to arrive within 14 days of sample collection.**

Selected References

- Bednar, A.J., Garbarino, J.R., Ranville, J.F., Wildeman, T.R., 2002, Preserving the distribution of inorganic arsenic species in groundwater and acid mine drainage samples: *Environmental Science and Technology*, v. 36, p. 2213-2218.
- Garbarino, J.R., Bednar, A.J., and Burkhardt, M.R., 2002, Methods of analysis by the U.S. Geological Survey National Water Quality Laboratory—Arsenic speciation in natural-water samples using laboratory and field methods: U.S. Geological Survey Water-Resources Investigations Report 02-4144, 40 p.
- 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.
- Nordstrom, D.K., 2002, Worldwide occurrence of arsenic in ground water: *Science*, v. 296, no. 5576, p. 2143-2145.
- Nordstrom, D.K., and Archer, D.G., 2002, Arsenic thermodynamic data and environmental geochemistry, *in* Welch, A.H., and Stollenwerk, K.G., eds., *Arsenic in Ground Water: Geochemistry and Occurrence*, Boston, Kluwer Academic Publishers, p. 1-26.

Table 5.6.4.A—1. Checklist of supplies and equipment required for arsenic speciation using the laboratory-speciation methods (NWQL Lab Code 3142)

[mL, milliliter; $\mu\text{g-As/L}$, 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)	As needed	Q378FLD
	Lab Code 3142 spike solution (store at room temperature)	10 mL of 2,500 $\mu\text{g-As/L}$ 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 Lab Code 3142	N1613
	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. USGS NWQL or local or regional safety officers can be consulted for proper disposal methods.

**Arsenic Laboratory-Speciation Methods Checklist and Worksheet
(Lab Code 3142)**

Site ID: _____

Date/Time: _____

Site Name: _____

Collector: _____

Lab schedule requested: LC 3142

- Filter sample using 0.45- μ m disposable capsule filter; do not clean media with acid
- EDTA preservative added to opaque bottle: _____ μ L
(100 μ L or the volume calculated below, whichever is greater)

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

where:

V_{EDTA} = microliters of 250-mM EDTA required per sample

Al = dissolved aluminum concentration, in _____ I = disso

Fe = dissolved iron concentration, in _____ Fe = diss

Mn = dissolved manganese concentration, in _____ = dissoMn

Ca = dissolved Ca concentration, in mg/L as Ca

Mg = dissolved magnesium concentration, in mg/L as Mg

Sr = dissolved strontium concentration, in _____ = dissoSr

- Spike Solution lot number: _____ **L or F** (circle one)
 Solution concentration: _____ μ g/L
 Volume added: _____ μ L

- Spiked or unspiked sample volume: 11.5 mL
Note: When completely full, the "8-mL" opaque bottle contains 11.5 ± 0.1 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 5.6.4.A—1. Worksheet for laboratory-speciation methods to determine arsenic species in water samples