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 (in press).

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 anionic 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), dimethylarsinate (DMA), and other organoarsenic species.
  - Select Schedule 1731 for a custom analysis; for example, for determination of 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-ion 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.

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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.