

Sampling, Analysis and Interpretation for Arsenic

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General Info about Arsenic

- Arsenic is not a metal
- Arsenic in water likes oxygen

 Arsenic exists in water as an anion with negative charge (because of oxygen)

General Info about ArsenicArsenic (III and V) is very mobile in groundwater...

• So what mobilizes the arsenic from the mineral state?

 Chemical reactions between nitrate, iron, and oxygen can affect the mobility of trace amounts of arsenic (USGS 2006)

•presence of As(V) reducing microorganisms

Major As minerals occurring in nature

Mineral	Composition	Occurrence
Native arsenic	As	Hydrothermal veins
Native arsenic	As	Hydrothermal veins
Niccolite	NiAs	Vein deposits and norites
Realgar	AsS	Vein deposits, often associated with orpiment, clays and limestones, also deposits from hot springs
Orpiment	As ₂ S ₃	Hydrothermal veins, hot springs, volcanic sublimation products
Cobaltite	CoAsS	High-temperature deposits, metamorphic rocks
Arsenopyrite	FeAsS	The most abundant As mineral, dominantly in mineral veins
Tennantite	(Cu,Fe) ₁₂ As ₄ S ₁₃	Hydrothermal veins
Enargite	Cu ₃ AsS ₄	Hydrothermal veins
Arsenolite	As.O.	Secondary mineral formed by oxidation of arsenopyrite, native arsenic and other As minerals
Claudetite	As ₂ O ₃	Secondary mineral formed by oxidation of realgar, arsenopyrite and other As minerals
Scorodite	FeAsO ₄ .2H ₂ O	Secondary mineral



Ratio of Arsenite to Arsenate in Well Water



Sampling considerations

- Does my well have arsenic? Or am I being exposed to arsenic?
- Well testing will tell you what your average arsenic concentration is the day you collected the sample.
- Test the water out of the tap will tell you the concentration of arsenic you are exposed to the day you collected the sample.

Sampling

• The only way you can be exposed is by drinking the arsenic-contaminated water.

 The best point in the system to test the well water to determine if you are being exposed is at the tap because that is what you drink.

• Testing before and after treatment systems is a good way to determine the efficiency of arsenic removal.

How to take a sample from the tap

- Turn on the tap water and let it run for a minute
- Reduce the flow to a steady slow stream
- For a Total Arsenic determination, collect the water in a bottle preserved with nitric acid (#7 bottle from SHL) and fill up to the shoulder of the bottle – DO NOT OVERFILL
- Put the lid on the bottle and label the bottle with collector's name, date and time of collection

#7 Bottle with Nitric Acid



4mL 1:1 Nitric Acid

Collecting for Total Arsenic

- Fill out paperwork and sign chain of custody
- The sample is stable at room temperature as long as preserved with acid up to 6 months.

Collecting for Arsenic Speciation

- Collect sample the same way as Total As
- The preservative is not acid it is EDTA
- EDTA helps keep the Arsenic species from converting to different forms
- The stability of arsenic species tested in the arsenic speciation test have been evaluated to be 28 days.
- Keep bottle refrigerated.





Preserved with 5% EDTA

Sample Information Form (TRF)

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Chain of Custody

Chain of Custody/Tracking Signatures

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Analysis : What are our options?

• Use properties of arsenic to selectively measure its concentration.

Chemical properties – titration
Use known chemical reaction with visible endpoint.
Good precision and accuracy.
Typical quantitation limits: 1000 mg/L
Physical properties – optical spectroscopy
Each element has characteristic wavelengths of light that interact with atoms (or ions) in the gas phase.
Quantitation limits range from 1 to 0.01 mg/L.

Analysis : What are our options?

Physical properties – mass spectrometry
 Each element is composed of one or more isotopes of discrete mass.

Quantitation limits can be < 0.001 mg/L.

ICP-MS

Inductively-Coupled Plasma Mass Spectrometry



Interferences

- Other substances in the sample that produce a signal for arsenic.
- No other element has a stable, naturally occurring isotope at mass 75.
- But polyatomic ions can interfere:
 4ºAr³⁵Cl⁺

Quantitation Limits

• The lowest level that can be measured with confidence.

Factors that affect Quantitation Limits:

- Background noise Inherent in all electronic equipment
 Background signal Contamination from samples
- Characteristics of the element

Significant Figures

 Scientific instruments will generate a value consisting of many digits. It is up to the analyst to determine which of these digits are significant (real) and which are non-significant (noise)

SHL limits reportable values to two significant figures.Example:

0.0378 mg/L is reported as 0.038 mg/L

 But if the quantitation limit is 0.01 mg/L: 0.0378 mg/L is reported as 0.04 mg/L

Arsenic Speciation

- Requires separation of the different forms of arsenic before detection by the ICPMS.
- Chromatography takes advantage of the unequal interaction of substances dissolved in solution with a solid material.
- As the solution passes over the solid, some substances are retained on the solid more than others.
- Over time, the various substances are separated in the mobile solution...

Chromatography



Example Chromatogram



Liquid Chromatography - ICPMS



Be advised:

Total arsenic is commonly reported in mg/L.
Arsenic species are reported in units of ug/L.

In theory, the sum of arsenic species should equal total arsenic. For example, total arsenic = 0.012 mg/L, As(III) = 7 ug/L, and As(V) = 5 ug/L.

But if total arsenic = 0.015 mg/L it is not necessarily a cause for concern due to compounding of experimental error.

Irregularities - Sample #156992

- Total Arsenic = 0.19 mg/L
- Arsenic speciation = < 1.0 ug/L As(III), 17 ug/L As(V)

Total arsenic sample was preserved with nitric acid and contained visible solid material.

Speciation of filtered, acid-preserved sample = 68 ug/L As(III), 93 ug/L As(V)

Speciation of acid-digested sample = < 1.0 ug/L As(III), 190 ug/L As(V)

QUESTIONS?

Brian Wels

Don Simmons

• 515-725-1600