



Sampling, Analysis and Interpretation for Arsenic

Don Simmons and Brian Wels
State Hygienic Laboratory
Ankeny, IA

General Info about Arsenic

- Arsenic is not a metal

<http://www.lenntech.com/periodic/periodic-chart.htm>

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

General Info about Arsenic

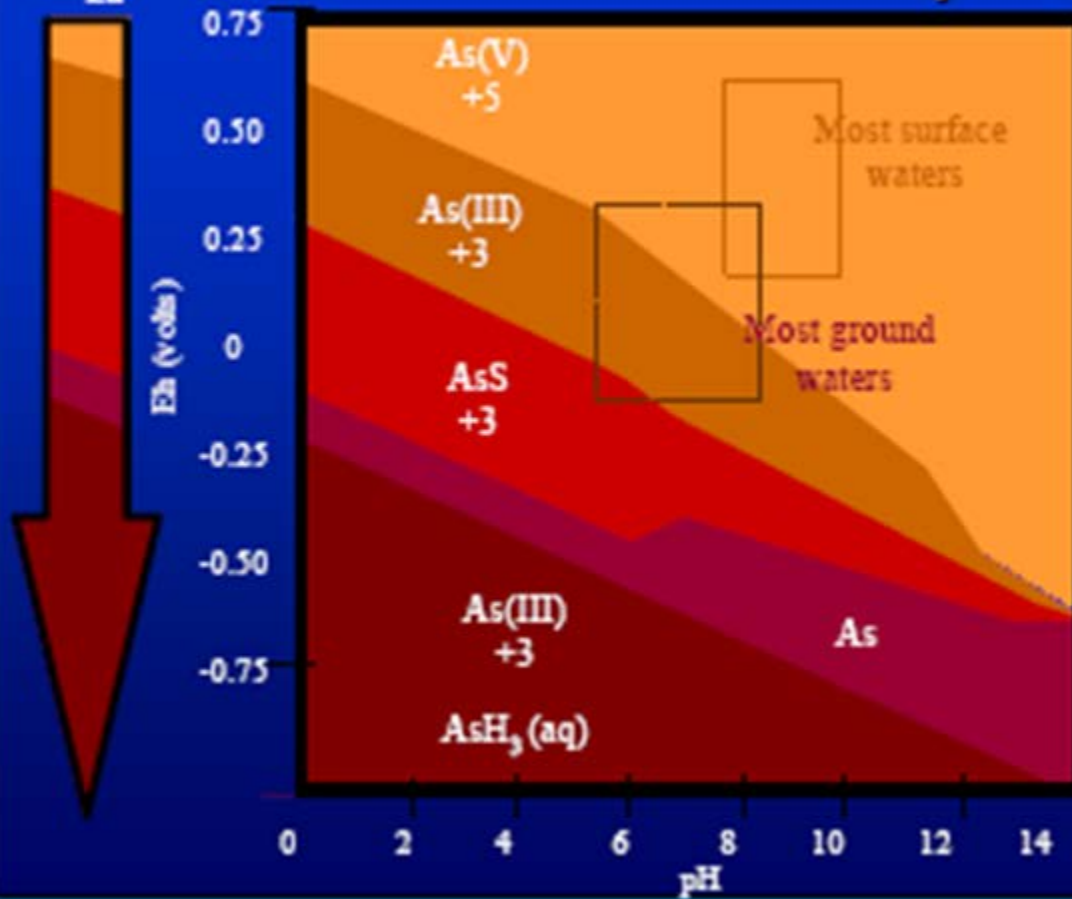
- Arsenic (III and V) is very mobile in groundwater...
- So what mobilizes the arsenic from the mineral state?
- Chemical reactions between nitrate, iron, and oxygen can affect the mobility of trace amounts of arsenic (USGS 2006)
- <http://www.sciencedirect.com/science/article/pii/S0169772206001100>
-presence of As(V) reducing microorganisms

Major As minerals occurring in nature

Mineral	Composition	Occurrence
Native arsenic	As	Hydrothermal veins
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Nicolite	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 ₄ O ₆	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

Arsenic Mobility

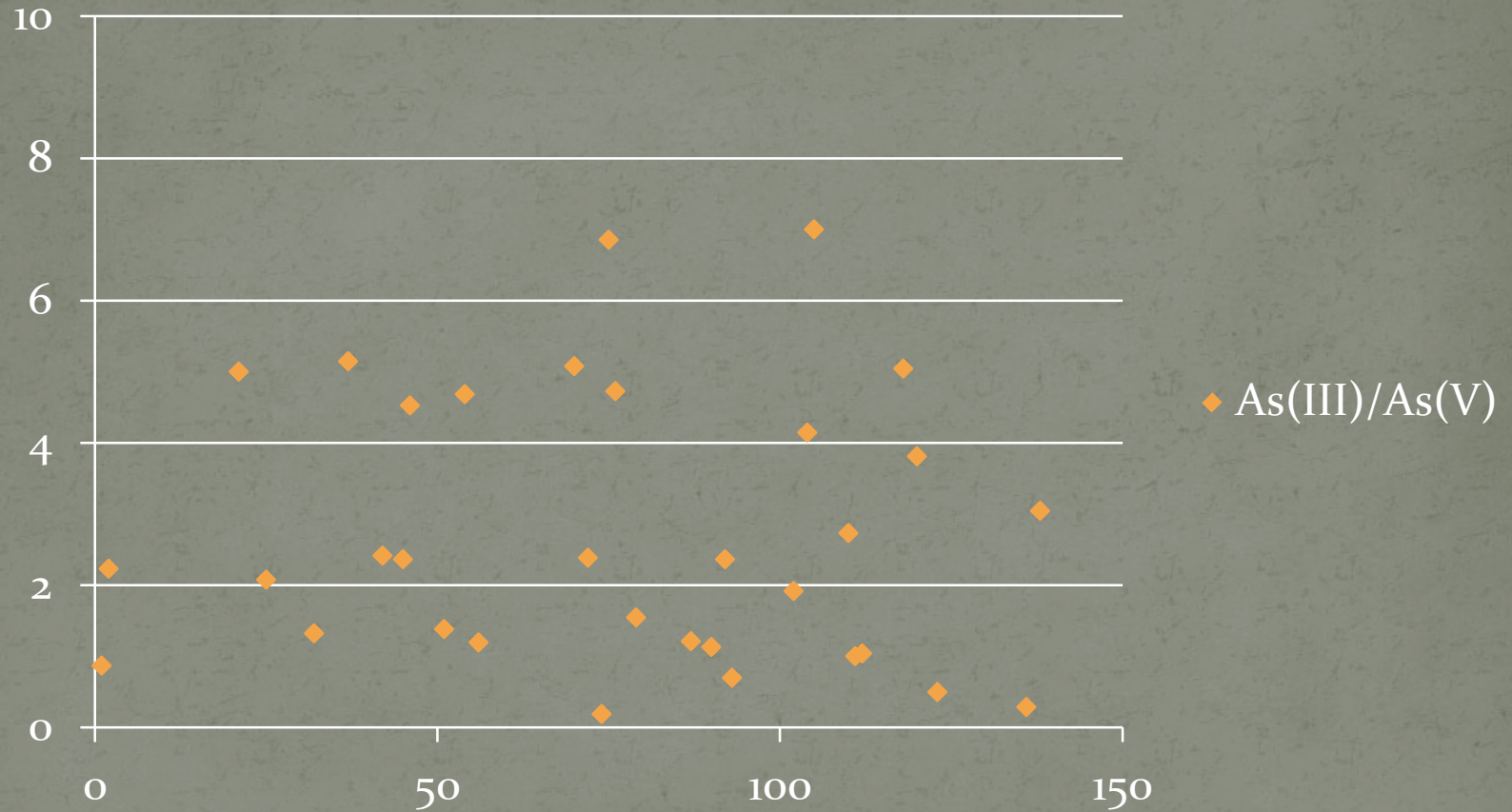
Reducing O₂ & E_h



Eh-pH diagram

measure of system state (aerobic/ anaerobic)

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.

70
Bottle



Preserved
with 5%
EDTA

Complete Form

Order #: 84380



Pages in Order: 1 of 1

Containers in Order: 1

REPORT TO:

3201



DONALD SIMMONS

SHL ANKENY

IOWA LABORATORIES COMPLEX

2220 S ANKENY BLVD

ANKENY, IA 50023

BILL TO:

3201



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Requested Analyses/Tests

Metals (multi) EPA 200.8- Arsenic

Complete or correct the following information

Environmental
Sample Collection Form

Collected Date: _____

yyyy-mm-dd

Client Reference: _____

Location: _____

kitchen sink, plant tap, etc.

Collector Phone: _____

000/111-2222

Collected Time: _____

24 hour format hh:mm

Collector: _____

Print last, first name

Location City: _____

Description: _____

Chain of Custody

Chain of Custody/Tracking Signatures

Relinquished By: _____

Date/Time: _____
 year / mm / dd Military Time

SHL Sample Receiving Custodian: _____

Date/Time: _____
 year / mm / dd Military Time

Relinquished By: _____

Date/Time: _____
 year / mm / dd Military Time

SHL Sample Receiving Custodian: _____

Date/Time: _____
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Analysis : What are our options?

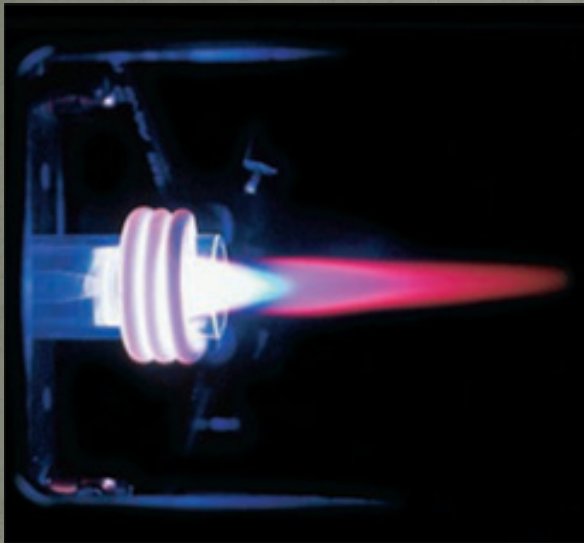
- Use properties of arsenic to selectively measure its concentration.
- Chemical properties – titration
 - Use known chemical reaction with visible endpoint.
 - Good precision and accuracy.
 - Typical quantitation limits: 1000 mg/L
- Physical properties – optical spectroscopy
 - Each element has characteristic 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:
 - $^{40}\text{Ar}^{35}\text{Cl}^+$

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

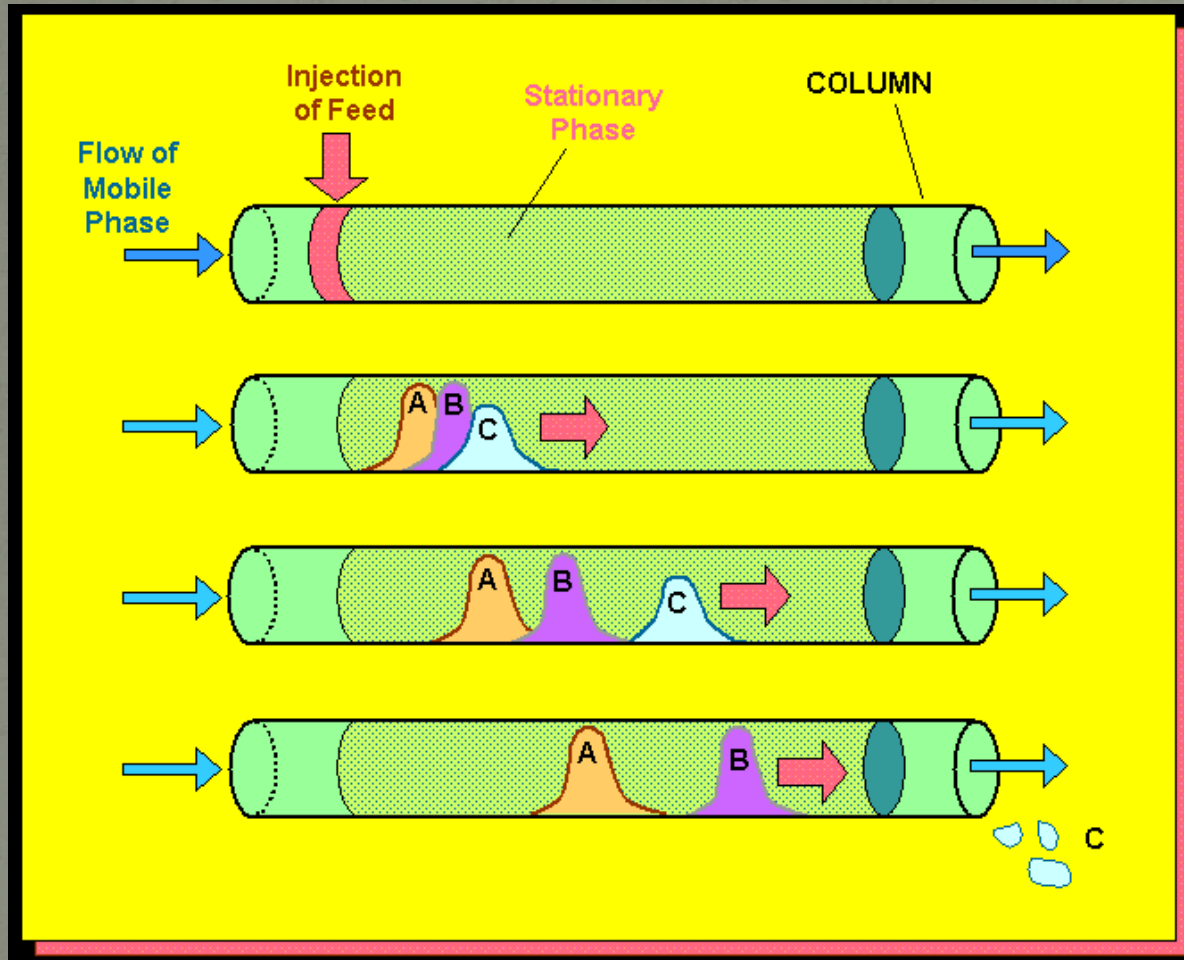
Significant Figures

- 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:
 - o.0378 mg/L is reported as 0.038 mg/L
- But if the quantitation limit is 0.01 mg/L:
 - o.0378 mg/L is reported as 0.04 mg/L

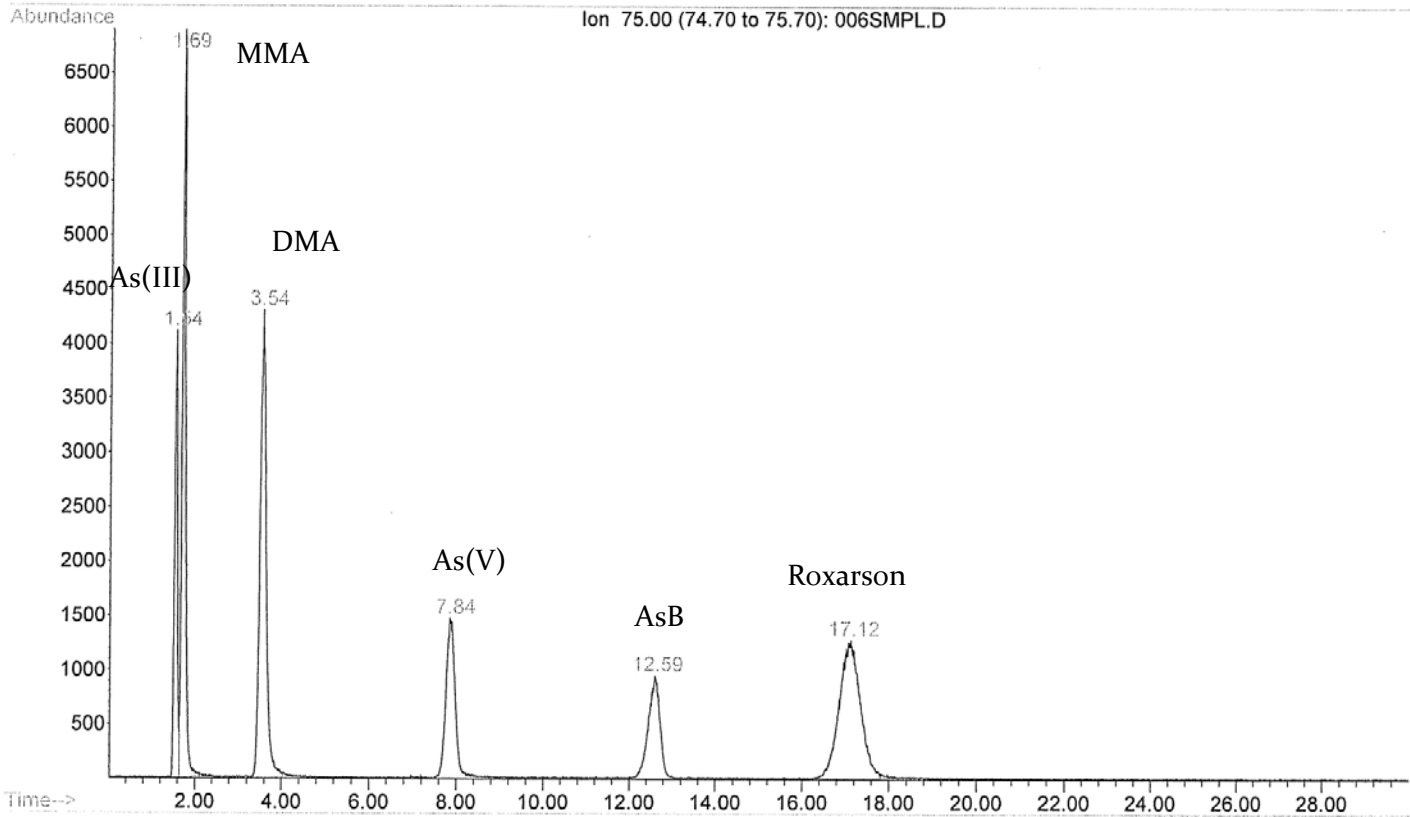
Arsenic Speciation

- 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 brian-wels@uiowa.edu
- Don Simmons donald-simmons@uiowa.edu
- 515-725-1600