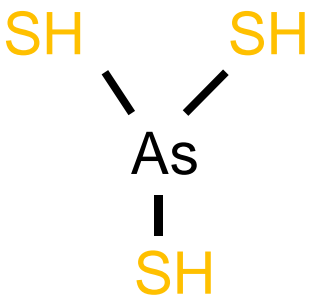
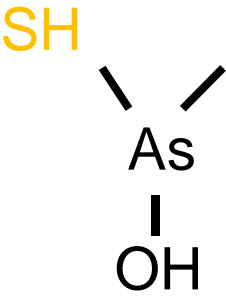
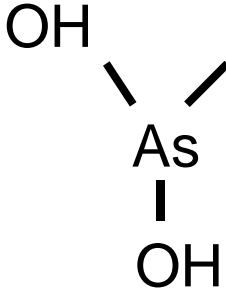
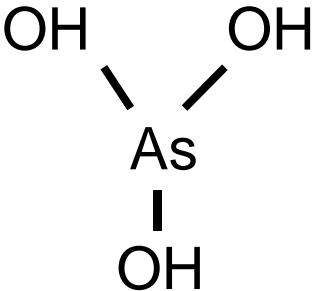


Arsenic speciation in sulfidic waters:
Reconciling contradictory spectroscopic and
chromatographic evidence

or: why does XAS see **thioarsenites**
and IC-ICP-MS **thioarsenates**?

Prof. Dr. Britta Planer-Friedrich
Group Seminar, 12.11.2010

Thioarsenites

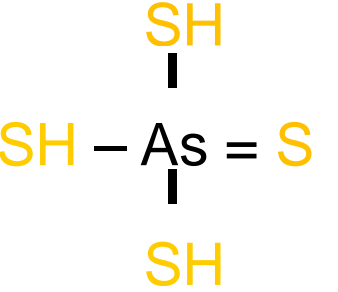
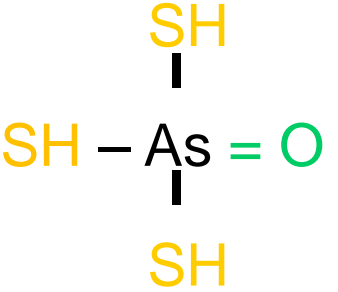
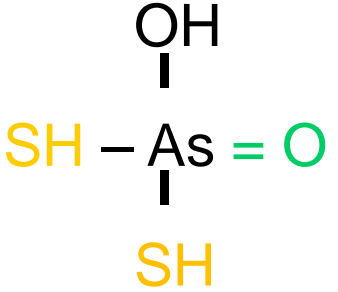
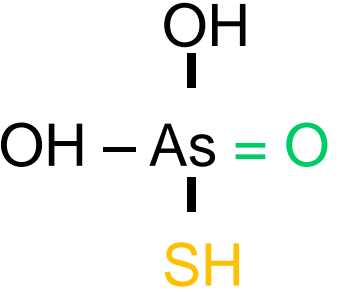
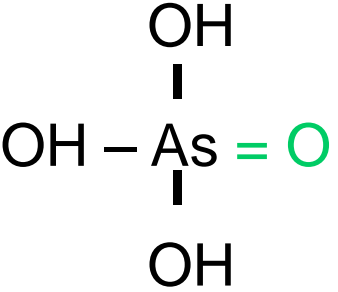


Mono~

Di~

Tri~

Tetra~



Thioarsenates

The early papers: Thioarsenates

Brauner, B. & Tomícek, F., Ueber die Einwirkung von Schwefelwasserstoff auf Arsensäure. Fresen. J. Anal. Chem. 27 (1), 508-513 (1888).

→ Precipitation of As_2S_5 (low pH, high H_2S , low temp.) vs. As_2S_3

McCay, L.W., Die Einwirkung von Schwefelwasserstoff auf Arsensäure Fresen. J. Anal. Chem. 27 (1), 632-634 (1888).

McCay, L.W., Die Einwirkung von Schwefelwasserstoff auf Arsensäure. Zeitschrift für anorganische Chemie 29, 36-50 (1901).

→ Isolation of monothioarsenate and dithioarsenate

McCay, L.W. Z. Anorg. Chem. 29, 36-50 (1902).

McCay, L.W. & Foster, W., Über die Trisulfoxyarsensäure. Zeitschrift für Anorganische Chemie 41, 452-473 (1904).

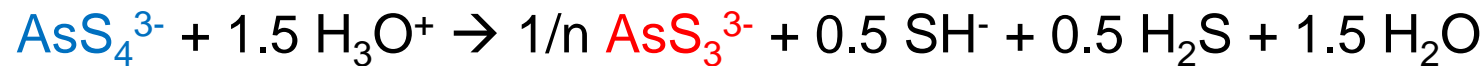
→ Alkalinizing As_2S_5 yields trithioarsenate at low OH concentrations; formation of mono-, di- and tetrathioarsenate at higher OH concentrations

Über Vorgänge bei der Bildung des Arsen(V)-sulfids beim Ansäuern von Tetrathioarsenatlösungen

1970: Thioarsenites

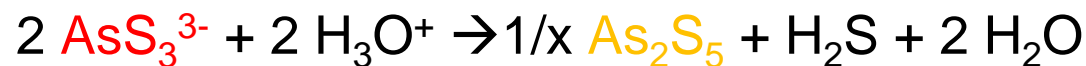
Von E. THILO, K. HERTZOG und A. WINKLER

at pH ca. 6



Tetrathioarsenate \rightarrow Trithioarsenite

at pH ca. 3



Trithioarsenite \rightarrow precipitation as As-S-mineral

Upon acidification, thioarsenates are stable as long as AsOH-groups can form; once the addition of further protons forces the formation of AsSH-groups, the ions become instable

\rightarrow hydrolysis to trithioarsenate can only be a minor reaction as tetrathioarsenate becomes immediately instable

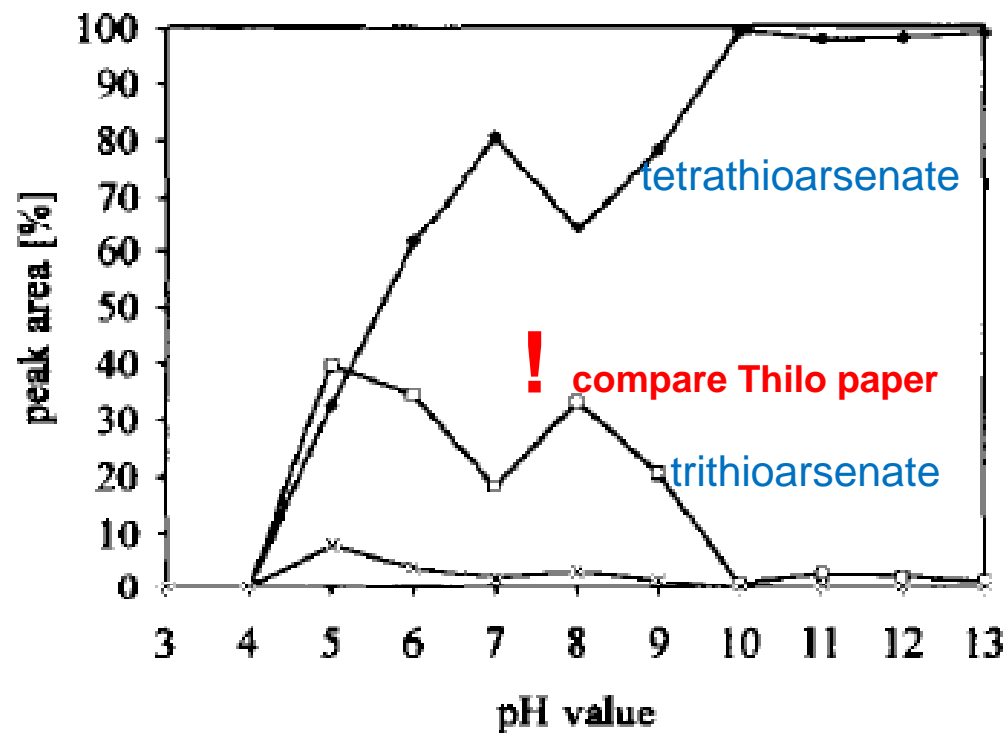
Separation of thio- and oxothioarsenates by capillary zone electrophoresis and ion chromatography

Georg Schwedt*, Melanie Rieckhoff

- First determination of thioarsenates by IC-ECD and CE
- Synthesis of mono-, di- and tetrathioarsenate

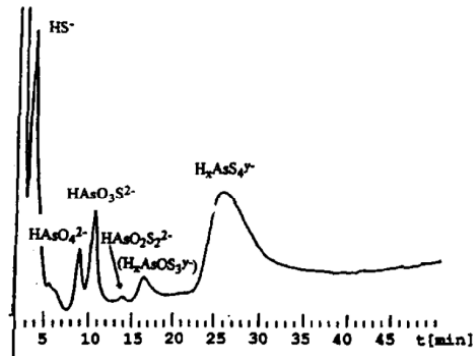
thioarsenate stability over pH:

- monothioarsenate entire pH range
- dithioarsenate max. pH 3, 5-6, 10
- tetrathioarsenate only pH 10-13



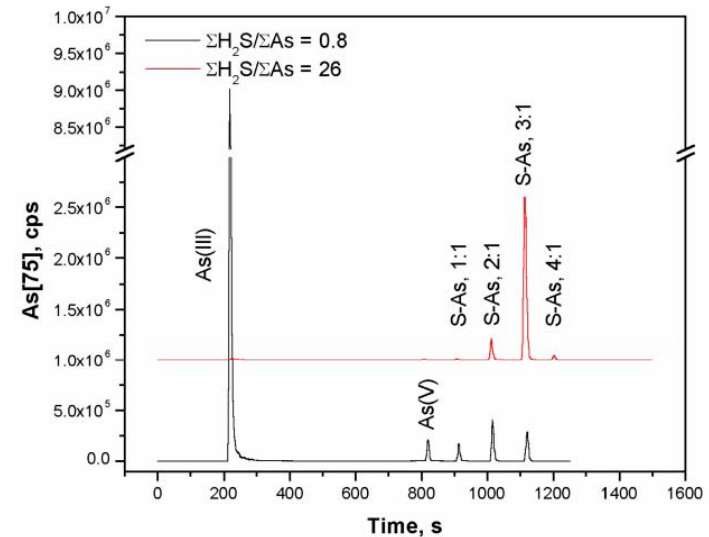
Speciation of arsenic in sulfidic waters

Richard T. Wilkin,^a Dirk Wallschläger^b and Robert G. Ford^a



--> compare to Schwedt

IC-ICP-MS: Thioarsenites



- o thioarsenic species can be determined by IC (20-100 mM NaOH) - ICP-MS (std. mode) at low concentrations!
- o based on their occurrence under reducing conditions (arsenite + sulfide) they are assigned as thioarsenites
- a problem occurs with the assignment of peak No. 4 → proposed $\text{AsS}_4\text{H}_x^{x-3}$, with no non-bonding electron pair
- o thermodynamic constants were derived → CAUTION! Those are WRONG!

Thioarsenates in Sulfidic Waters

S. STAUDER,* B. RAUE, AND F. SACHER

IC-ICP-MS: Thioarsenates

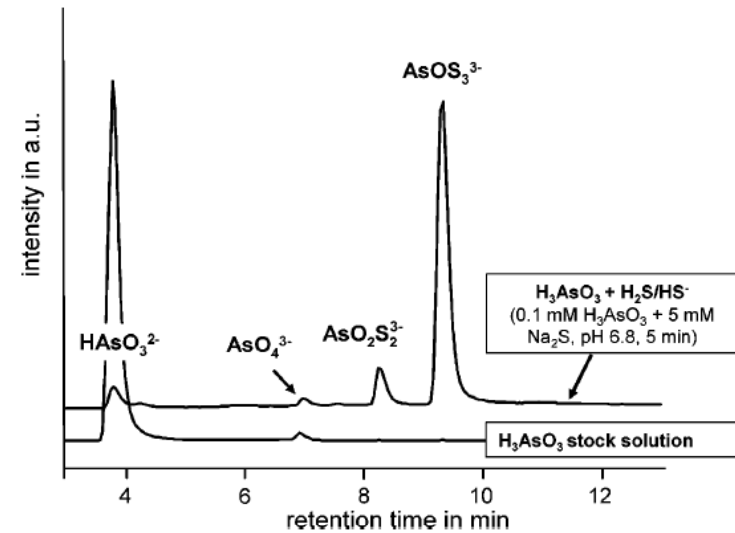


FIGURE 3. Results of arsenic speciation by IC–ICP/MS in oxygen-free arsenite and arsenite/hydrogen sulfide samples.

- used same method as Wilkin et al. 2003 (IC-ICP-MS) on arsenite-sulfide solutions and natural samples
- based on comparison with synthesized stds. and old literature reviews identification as thioarsenates (not thioarsenites as Wilkin et al. 2003)
- occurrence of thioarsenic species (mainly tri-) in groundwater of a former paper mill (sulfur acid production pyrite-burning) → environmental relevance!
- proposed mechanism: disproportionation $\text{As(III)} + \text{S(-II)} \rightarrow \text{As(V)-S} + \text{As(0)}$
- problem: we see no „missing“ As(0) ; disproportionation questionable

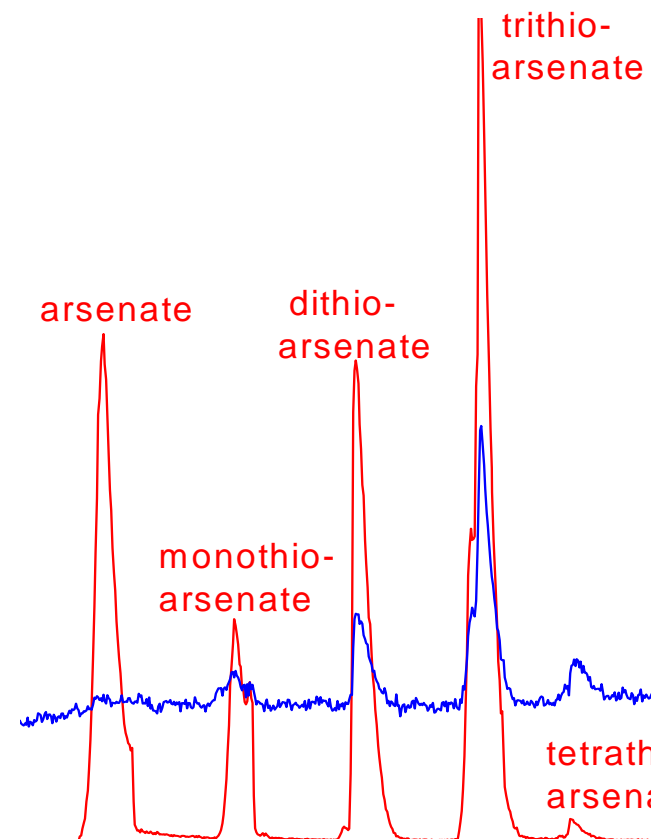
Determination of (Oxy)thioarsenates in Sulfidic Waters

Dirk Wallschläger*[†] and Christopher J. Stacey[‡]

IC-ICP-MS: Thioarsenates

- S/As ratios determined in synthetic samples as 1:1 to 4:1
 - ES/MS characterisation of IC-fractions as thioarsenates
- What we measure with IC are definitely thioarsenates!

problem: are the original mixtures of arsenite + sulfide really thioarsenates or only oxidized by IC-ICP-MS and ES-MS?



Mineralogical Magazine, October 2005, Vol. 69(5), pp. 781–795

XAS: Thioarsenites

In situ analysis of thioarsenite complexes
in neutral to alkaline arsenic sulphide solutions

B. C. BOSTICK^{1,2,*} S. FENDORF² AND G. E. BROWN JR.^{2,3}

All XAS paper report **thioarsenites** (ONLY!), no thioarsenates

Environ. Sci. Technol. 2008, 42, 1643–1650

**Examination of Arsenic Speciation in
Sulfidic Solutions Using X-ray
Absorption Spectroscopy**

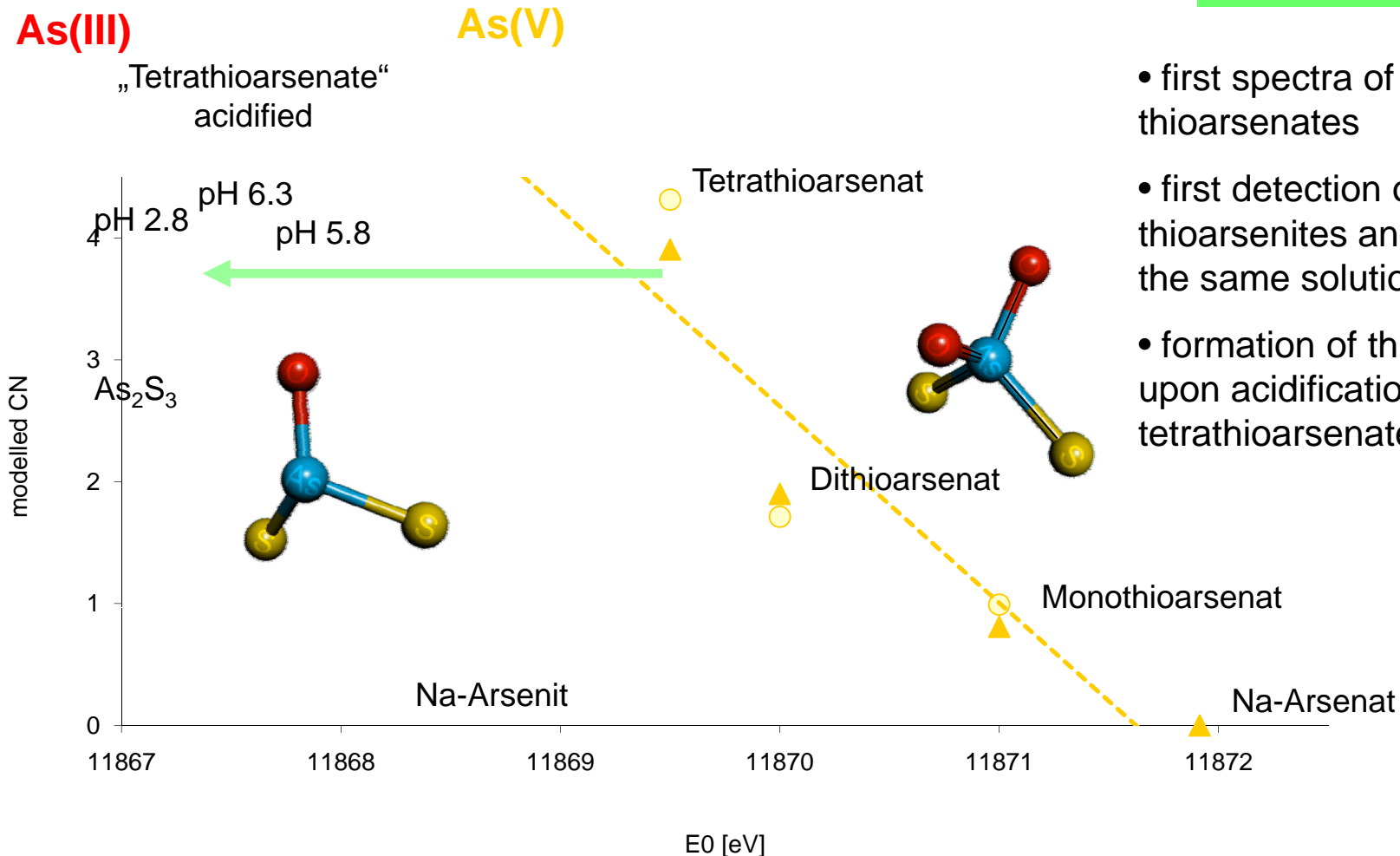
DOUGLAS G. BEAK,^{*,†}
RICHARD T. WILKIN,[†]
ROBERT G. FORD,[†] AND SHELLY D. KELLY[‡]

Discrimination of Thioarsenites and Thioarsenates

by X-ray Absorption Spectroscopy

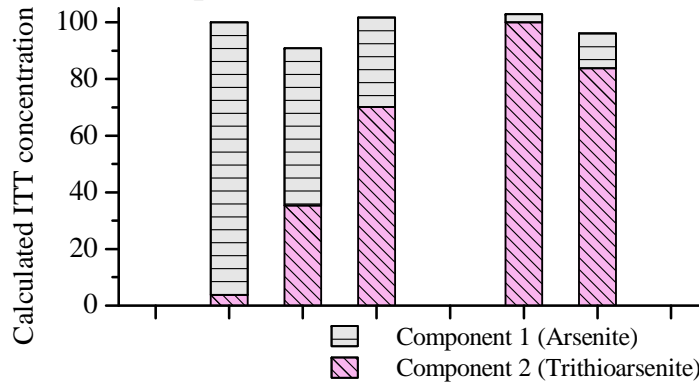
Elke Suess,^{*,†,‡} Andreas C. Scheinost,^{§,||} Benjamin C. Bostick,[⊥] Broder J. Merkel,[‡] Dirk Wallschlaeger,[#] and Britta Planer-Friedrich[†]

XAS: Thioarsenites upon destruction of Thioarsenates

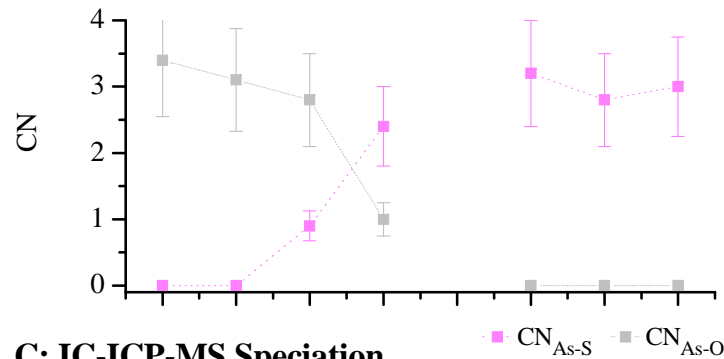


- first spectra of synthesized thioarsenates
- first detection of thioarsenites and -nates in the same solution
- formation of thioarsenites upon acidification of tetrathioarsenate

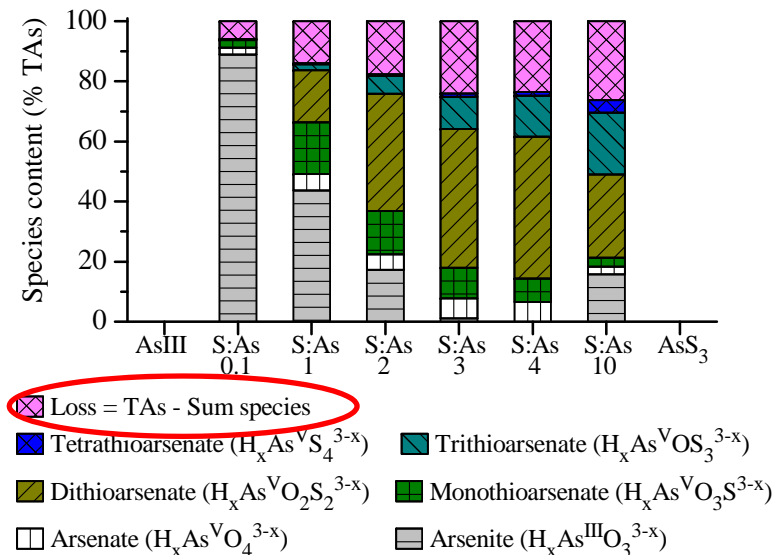
A: EXAFS Speciation



B: EXAFS Coordination Numbers



C: IC-ICP-MS Speciation

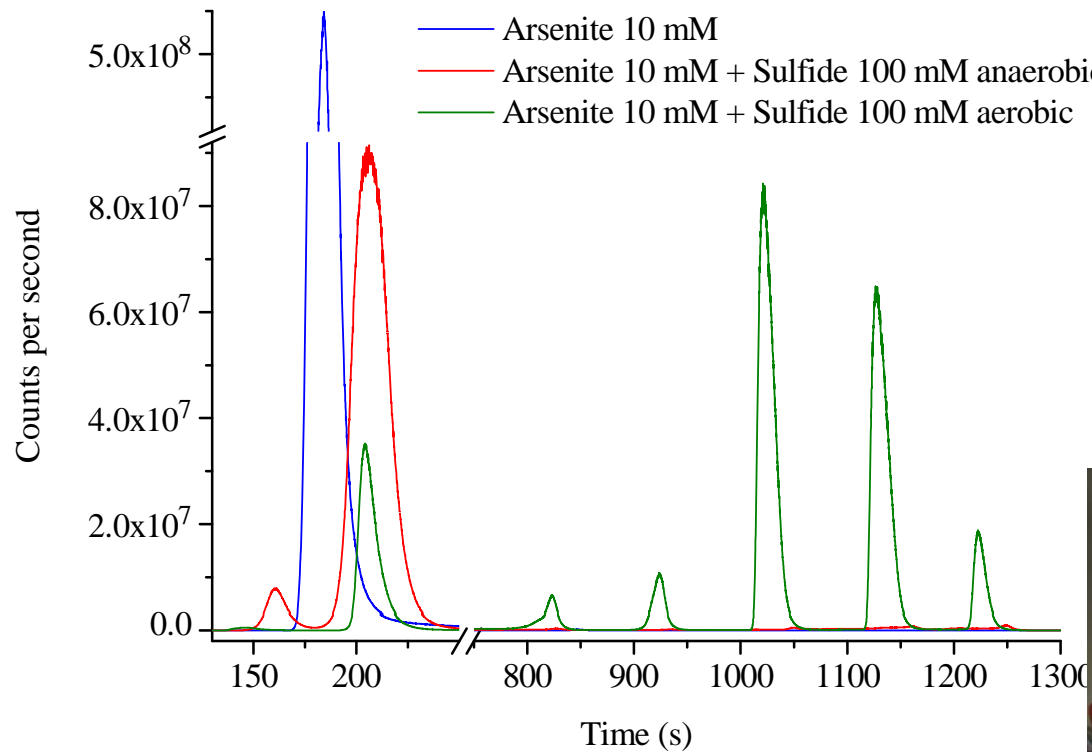


XAS: Trithioarsenite
forms from Arsenite + Sulfide

IC-ICP-MS: Dithioarsenate
forms from Arsenite + Sulfide

- ~~• co-elution of thioarsenites and thioarsenates?~~
- **oxidation** of thioarsenites?
- hydrolysis of thioarsenites?

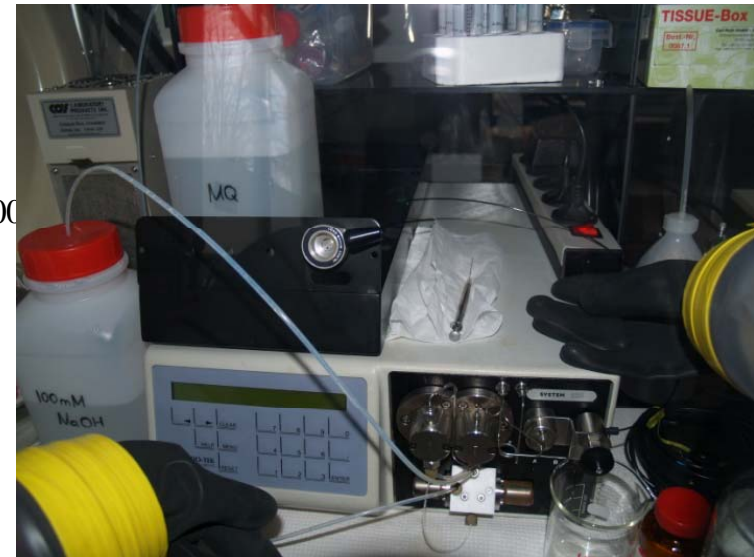
Thioarsenates in chromatography from arsenite-sulfide solutions are an oxidation artefact!

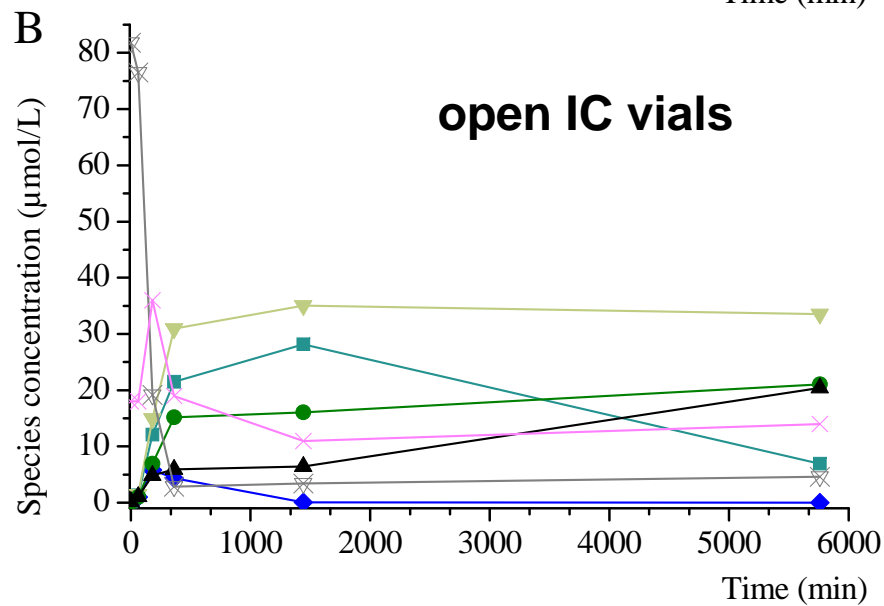
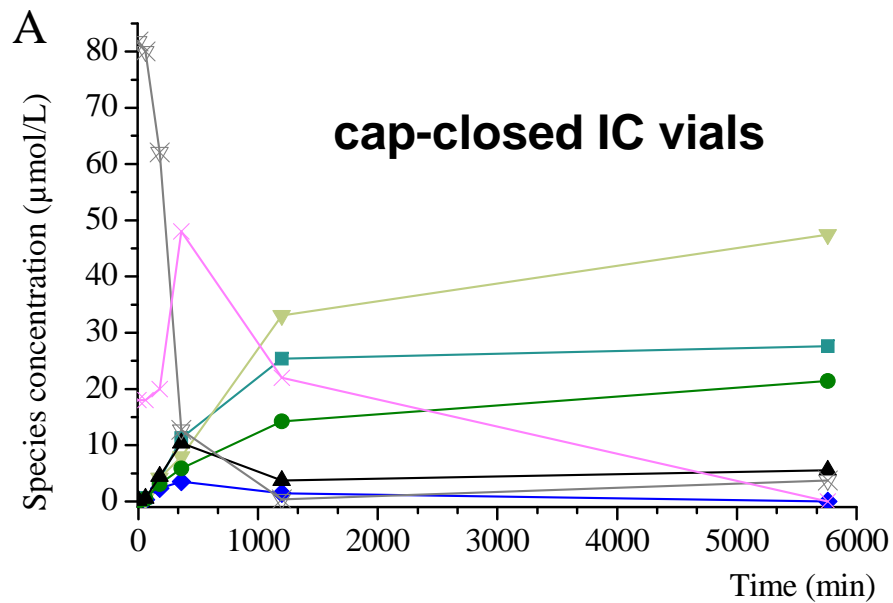


2 „arsenite“ peaks, when

- S:As \uparrow
- Total As \uparrow
- NaOH \downarrow

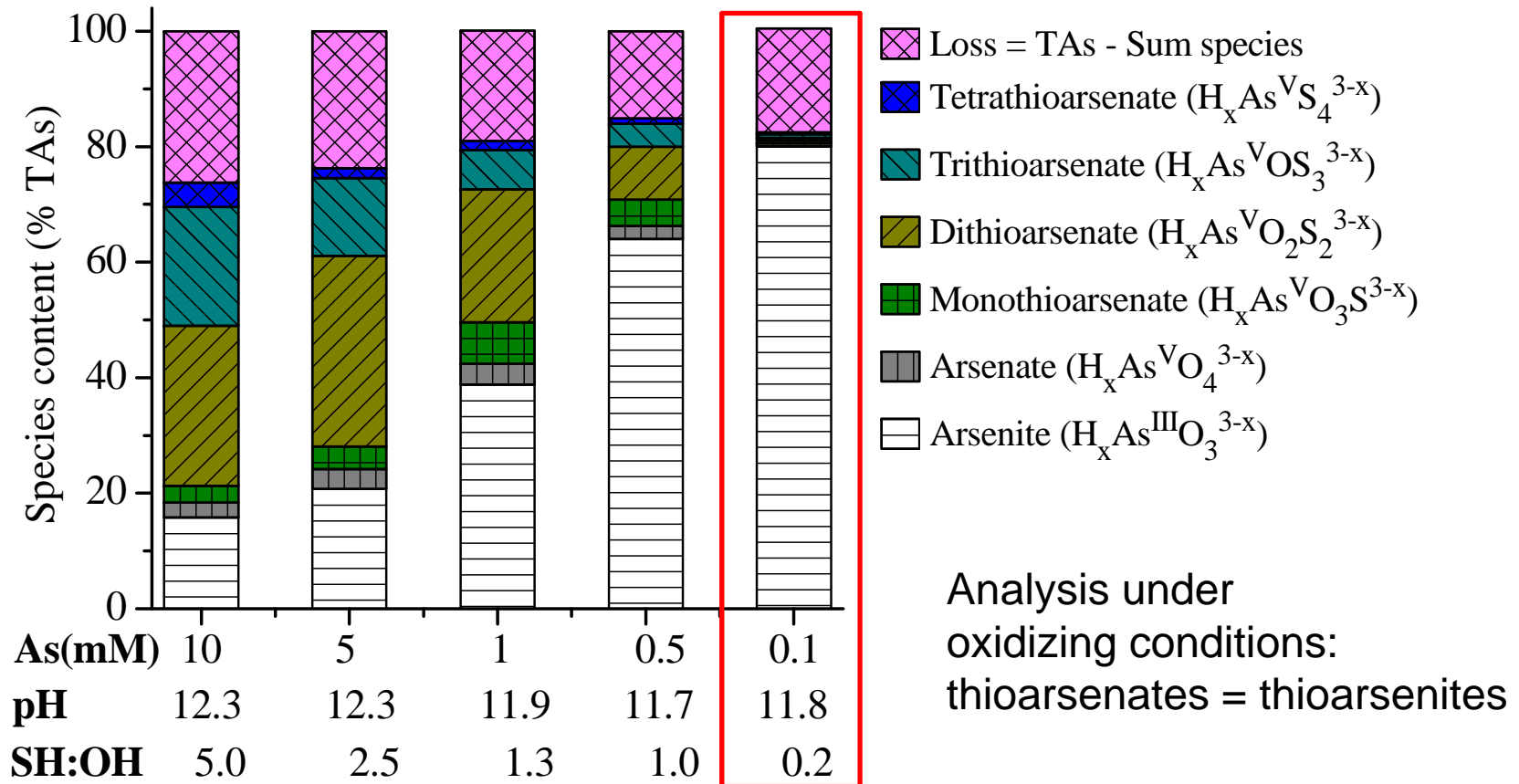
no sulfur in either of the 2 peaks





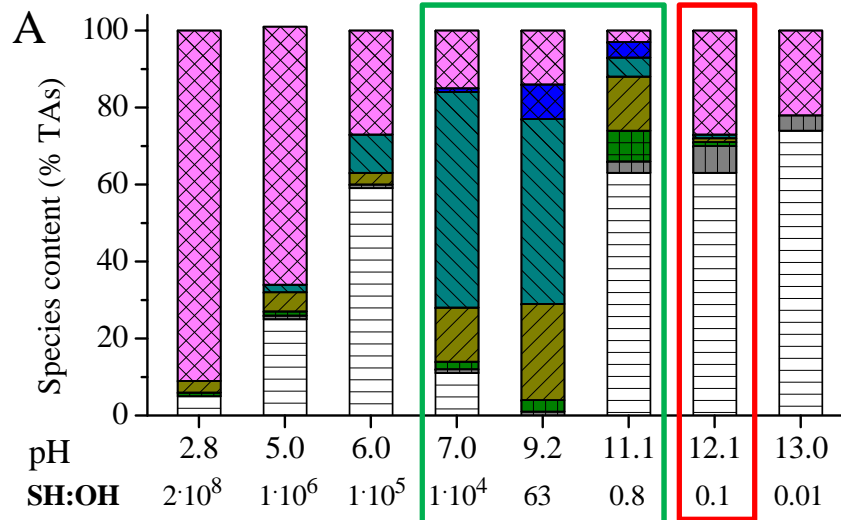
Oxidation kinetics of a solution containing 0.1 mM arsenite + 1 mM sulfide

Why arsenite instead of thioarsenites?

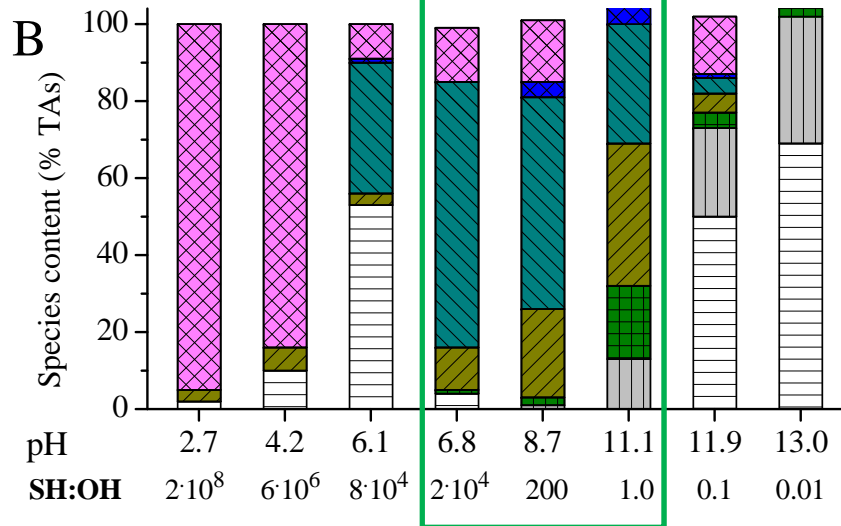


- Dilution (even when preserving pH) leads to a decrease in the SH:OH ratio
→ with an excess of OH thioarsenites are instable and transform to arsenite (hydrolysis, „competitive dissociation“)
- Without initial formation of thioarsenites, no thioarsenates form!

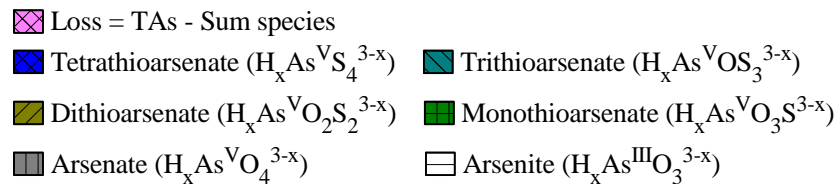
Effect of pH



immediately after preparation
in the glovebox



after one week in the glovebox



Rapid decomposition of thioarsenites to arsenite but relatively slow formation from arsenite → electrostatic repulsion of negatively charged arsenite and sulfide?

Summary of what happens during ion chromatography

SH ⁻ :OH ⁻ ratio	Species formed under anaerobic conditions	Species analyzed by chromatography under anaerobic conditions	Species analyzed by chromatography under aerobic conditions
SH ⁻ > OH ⁻	thioarsenites	arsenite (artifact: transformation of thioarsenites to arsenite due to excess of OH ⁻ by elution at pH 13)	thioarsenates (artifact: oxidation of thioarsenites before alkaline transformation to arsenite; thioarsenates are stable at excess OH ⁻)
SH ⁻ = OH ⁻	initially arsenite, after some days thioarsenites	arsenite (initially true speciation, later artifact)	initially arsenite (true speciation), then thioarsenates (artifact)
SH ⁻ < OH ⁻	arsenite (thioarsenites are unstable due to excess of OH ⁻)	arsenite	arsenite (true speciation, even though there is oxygen, there is no formation of thioarsenates without initial formation of thioarsenites)

Summary interpretation of previous observations

thioarsenites are determined in **XAS** because arsenite and thus sulfide concentrations (10-100 mM) are high compared to OH-concentrations (pH 11-12 – 1-10 mM)

- dilution necessary for **IC** (nM - μ M range) and analysis at highly alkaline pH leads to a decrease in the SH/OH ratio, thioarsenites decompose to **arsenite** (anaerobic cond.) or oxidize to **thioarsenates** (aerobic cond.)
- preparation of arsenite and sulfide at high pH prevents formation of thioarsenites, no thioarsenates form, only **arsenite** is detected under aerobic cond. → thioarsenites are necessary **intermediate key species** for thioarsenate formation

Implications

- we need to explicitly **determine thioarsenites**
 - analytical challenge → ion pair chromatography?
 - synthesis of trithioarsenite?
 - what is the “loss”?
 - prove pathway of formation (“oxidative thio-lation”)?
 - role of polysulfides?
- what are the **field studies** worth reporting thioarsenate occurrence with IC-ICP-MS?
 - improve sampling methods (O₂-exclusion!)
 - look for thioarsenites under anaerobic conditions
 - role of polysulfides?