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THE LEADER IN ENVIRONMENTAL TESTING

Inorganic Arsenic Species Characterization and Monitoring

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Arsenic Affects Health Negatively

Cancer Research

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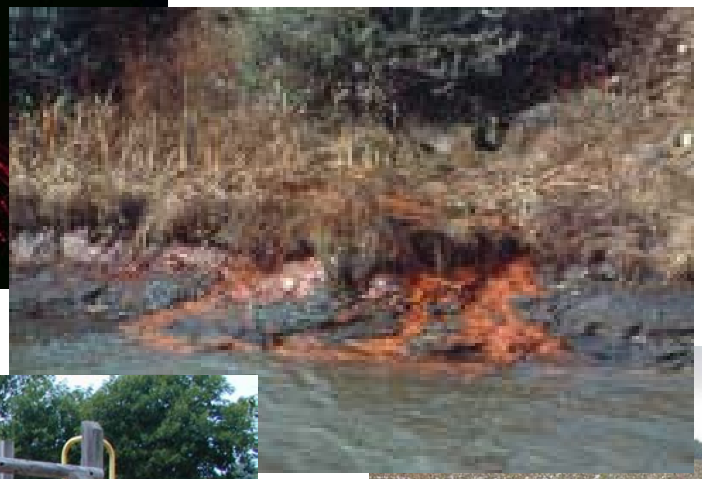
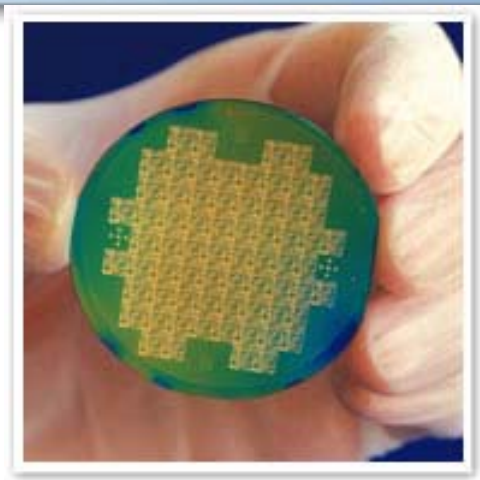
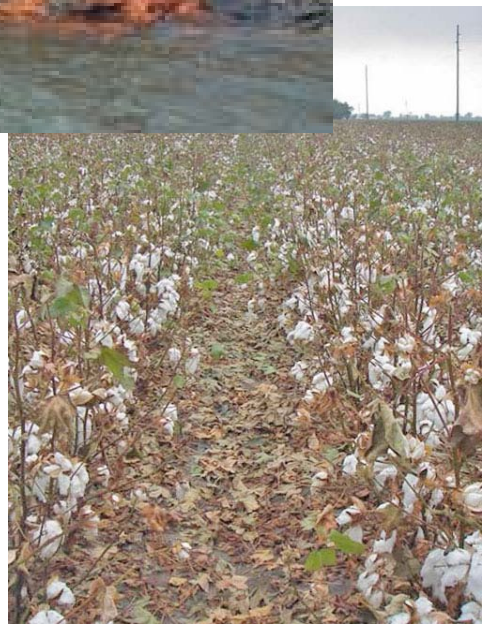
Many Ways to Release Arsenic







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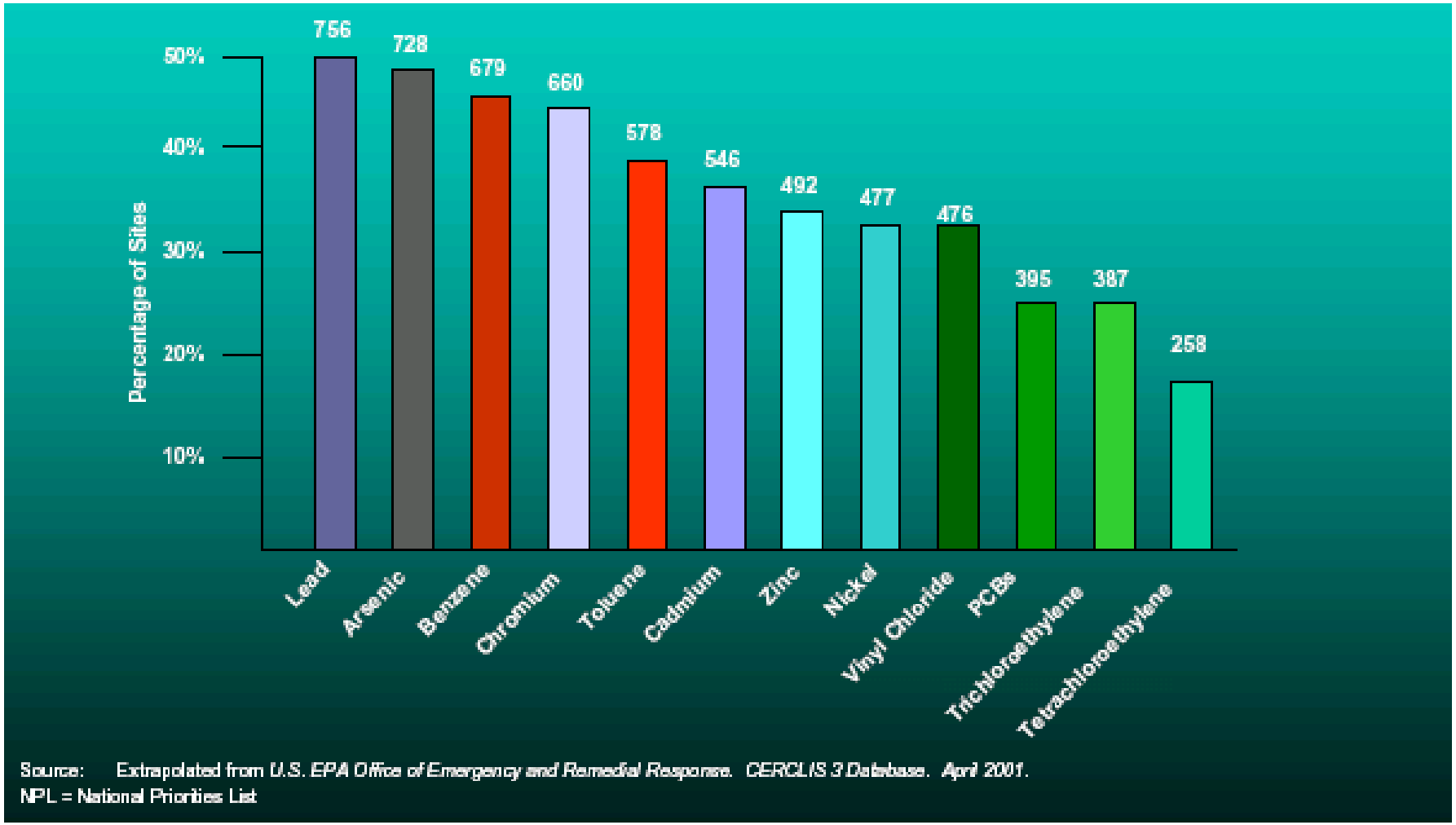
Arsenic is Common at Superfund NPL Sites



Source: Extrapolated from *U.S. EPA Office of Emergency and Remedial Response. CERCLIS 3 Database. April 2001.*
NPL = National Priorities List

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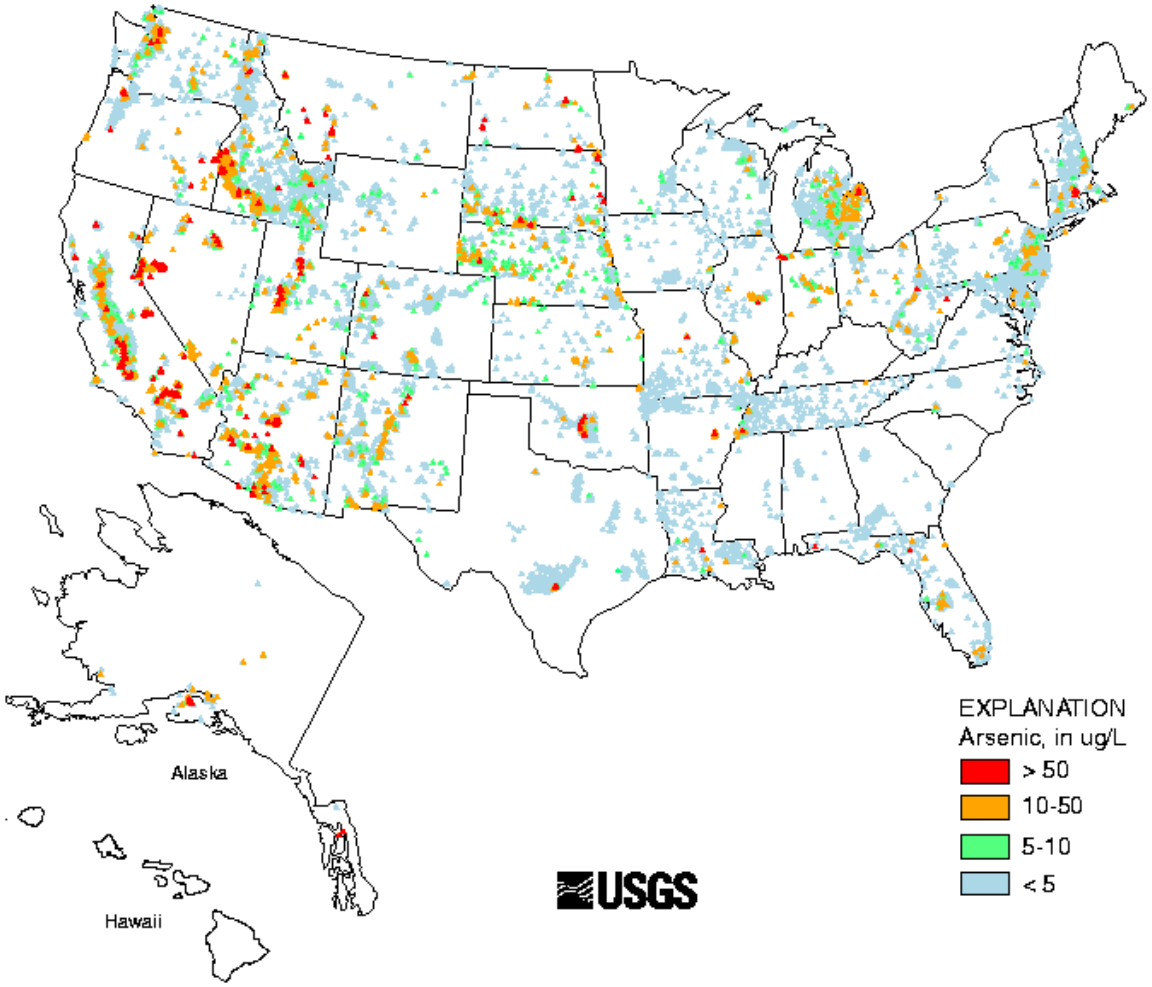
Arsenic is Common in U.S. Water Supplies



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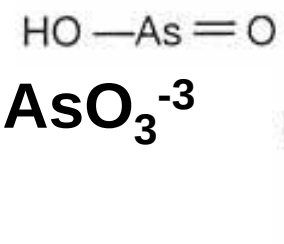
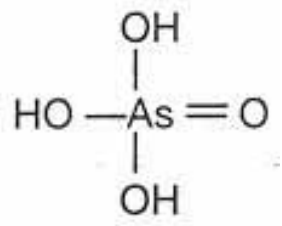
Inorganic Arsenic Species Found in the Environment

- **Arsenite (As^{3+})**
  - ~ **H_3AsO_3, $H_2AsO_3^-$, $HAsO_3^{-2}$, and AsO_3^{-3}**



- **Arsenate (As^{5+})**
  - ~ **H_3AsO_4, $H_2AsO_4^-$, $HAsO_4^{-2}$, and AsO_4^{-3}**



- **More protonation at low pH**
- **As^{3+} under reducing conditions**
  - ~ **flooded soils**
- **As^{5+} under oxidizing conditions**
  - ~ **oxygen-rich environments & well-drained soils**
- **As^{3+} more toxic than As^{5+}**

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Arsenic Regulatory Limits and Goals Drive Cleanups

- **Total arsenic**
  - ~ **Water**
    - ° **potable : 10 ug/L US EPA MCL**
    - ° **potable : 4 ng/L Final Public Health Goal - California**
    - ° **tap : 45 ng/L EPA Region 9 PRG target**
  - ~ **Soil**
    - ° **residential : 390 ug/kg EPA Region 9 PRG**
- **Arsenic (III)**
  - ~ **Marine water (chronic) - 36 ug/L AWQC**
- **Modified 7063 Reporting Limits**
  - ~ **water - 2 ug/L As^{3+} or As^{5+}**
  - ~ **soil - 100-400 ug/kg As^{3+} or As^{5+}**

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Arsenic Speciation Facilitates Site Assessments

- Ground water well
- Landfills
- Co-generation facility
- Steel mills
- Foundry
- Refinery
- Lead smelter
- Processing plant

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Ground Water Well

- **Site description**
  - ~ **Residential drinking water well**
  - ~ **New England**
- **Arsenic speciation drivers**
  - ~ **Characterize arsenic content**
  - ~ **Toxicity**
  - ~ **Selection of As removal system**

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Captive Landfill

- **Site description**
  - ~ **Active paper & fly ash landfill**
  - ~ **Monitoring wells > 10 ug/L total As**
  - ~ **Nearby commercial & residential development**
- **Arsenic speciation drivers**
  - ~ **Mobility**
  - ~ **Toxicity**

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Sanitary Landfill

- **Site description**
  - ~ **Closed landfill near flood plain of river**
  - ~ **Industrial area**
  - ~ **Monitoring wells in wetlands surrounding landfill**
  - ~ **Reducing environment**
- **Arsenic speciation drivers**
  - ~ **Source determination**
  - ~ **Mobility**

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Closed Landfill

- **Site description**
  - ~ **Closed landfill**
  - ~ **Perimeter ground water monitoring wells**
- **Arsenic speciation drivers**
  - ~ **Source determination**
  - ~ **Mobility**
- **Also monitor redox parameters**

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Co-generation Facility

- Site description
  - ~ Waste fired boiler
    - ° Wood, tires, landfill gas
    - ° CCA treated wood waste
    - ° Stack gas waste
- NPDES exceedance for total As
- Arsenic speciation drivers
  - ~ Fate & transport
  - ~ Bioremediation management
  - ~ Source determination

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Steel Mill

- **Site description**
  - ~ **Scrap yard at steel mill**
- **Arsenic speciation drivers**
  - ~ **Distinguish between risk levels for arsenite and arsenate**
    - ° **Cancer endpoint**
  - ~ **Mobility**
  - ~ **Availability**

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Steel Mill

- **Site description**
  - ~ **Slag waste disposal area**
- **Arsenic speciation drivers**
  - ~ **Risk assessment**
    - ° **Cancer vs non-cancer endpoint**
    - ° **Reg 9 PRG change (late 2004)**
      - – **Non-cancer: 22 mg/kg to 0.39 mg/kg**
      - – **Cancer: 0.39 mg/kg**

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Foundry

- **Site description**
  - ~ **Closed waste pile**
  - ~ **Capped above ground landfill**
  - ~ **Sand from ceramics production**
  - ~ **Perimeter monitoring wells**
- **Arsenic speciation drivers**
  - ~ **Risk assessment**
  - ~ **Supplement to total and dissolved arsenic data**

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Refinery

- **Site description**
  - ~ **Operating refinery**
  - ~ **Ground water monitoring wells**
- **Arsenic speciation drivers**
  - ~ **Risk assessment**
  - ~ **Natural attenuation**
  - ~ **Mobility**

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Lead Smelter

- **Site description**
  - ~ **Century old lead smelter**
  - ~ **Industrial site, nearby residential area**
- **Arsenic speciation drivers**
  - ~ **Source determination**
  - ~ **Bioavailability**
  - ~ **Risk analysis**
- **Also monitor particle size**

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Processing Plant

- **Site description**
  - ~ **Mineral processing plant**
  - ~ **Arsenic contaminated sludge pit**
  - ~ **Ground water leaching, large plume**
- **Arsenic speciation drivers**
  - ~ **Monitor oxidative remediation process**
  - ~ **Mobility**
- **Also monitor DO and ORP**

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Target Analytes for modified 7063

- **Inorganic As^{3+}**
- **Inorganic As^{5+}**
- **Water soluble**
  - ~ **does not include insoluble species such as As_2S_3 and As_2S_5**
- **Does not include organo-arsenic species**

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Methodologies

- **EPRI EA-4641 (Battelle)**
  - ~ **Speciation of Selenium and Arsenic in Natural Waters and Sediments**
- **EPA 1632 (OW)**
  - ~ **Chemical Speciation of Arsenic in Water and Tissue by Hydride Generation Quartz Furnace Atomic Absorption Spectrometry**
- **EPA SW-846 7063 (OSW)**
  - ~ **Arsenic In Aqueous Samples And Extracts By Anodic Stripping Voltammetry (ASV)**

Sample Preservation

- **Water**
  - **1632A**
    - **pH <2 with HCl* in the field**
    - **refrigerated 4°C**
    - **28 days**
- **Soil/sediment**
  - **EPRI EA-4641**
    - **refrigerated 4°C**
    - **28 days**

**no free chlorine*

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Sample Preparation

- **Water**
  - ~ **As^{3+} (7063)**
    - ° **add HCl electrolyte**
  - ~ **As^{5+} by difference (Trace Detect & 7063)**
    - ° **add HCl electrolyte**
    - ° **reduce to As^{3+} with sodium thiosulfate**
- **Cleanup (optional)**
  - ~ **Copper remover cartridge**
  - ~ **non-polar SPE to remove electrode fouling organics**

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Sample Preparation

- **Soil / sediment**
  - ~ **leach with 0.1 M H_3PO_4**
  - ~ **centrifuge, decant**
  - ~ **leach with 0.1 M Na_3PO_4**
  - ~ **combine leachates**

  - ~ **As^{3+} (EPRI EA 4641 & 7063)**
    - ° **add HCl electrolyte**
  - ~ **As^{5+} by difference (EPRI & TD & 7063)**
    - ° **add HCl electrolyte**
    - ° **reduce to As^{3+} with sodium thiosulfate**

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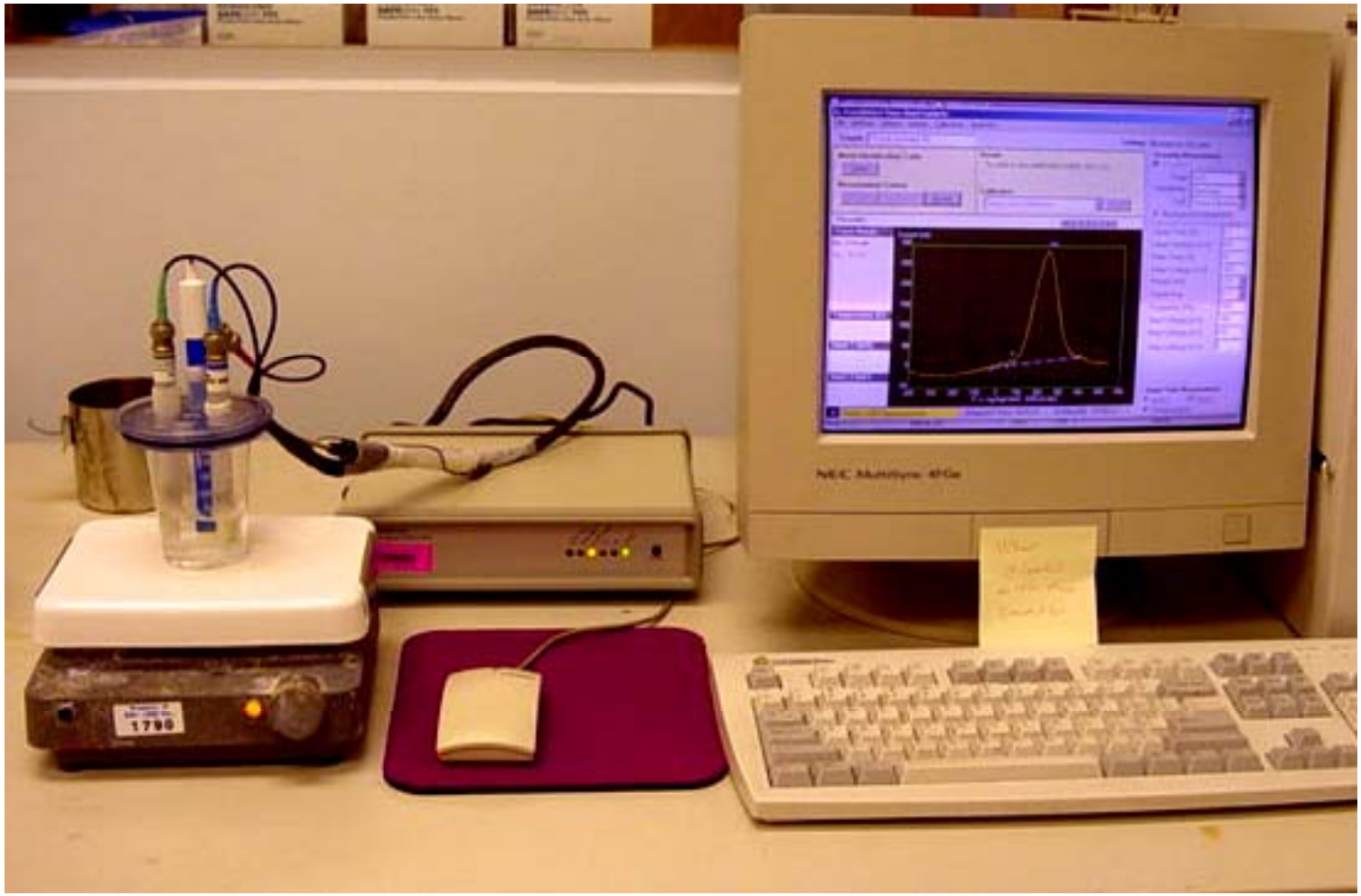
TraceDetect Nano-Band Explorer



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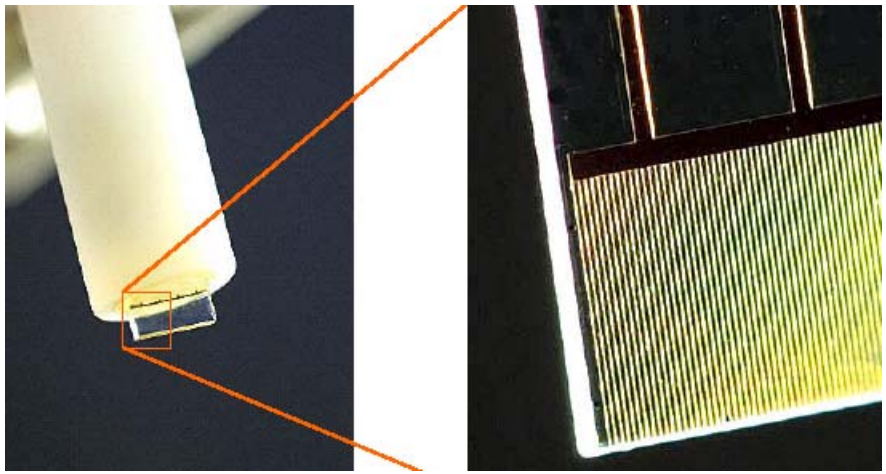
Modified 7063 Summary

- **Plate gold film electrode**
  - ~ **polish**
  - ~ **rinse**
  - ~ **plate 60 sec in gold solution while stirring**



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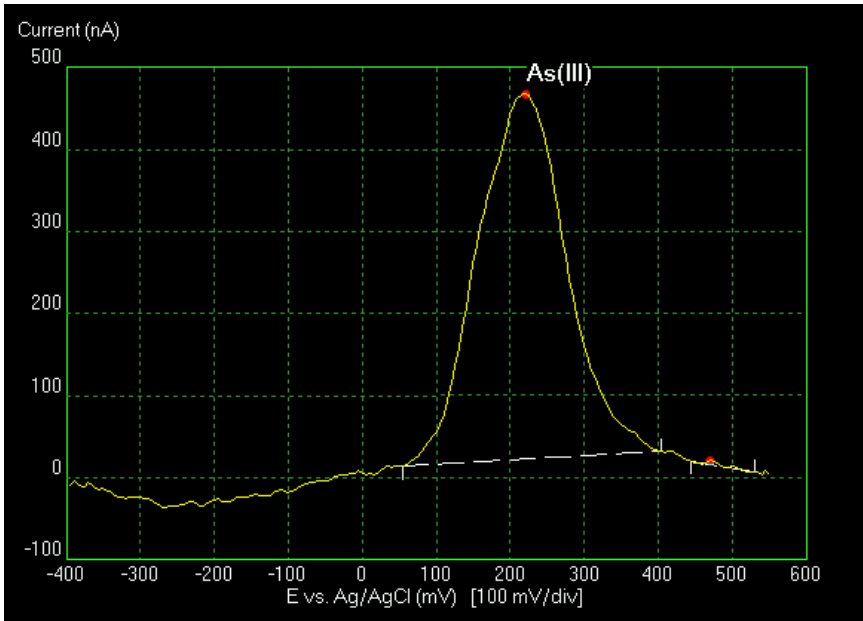
Modified 7063 Summary

- **Analyze standard or sample**
  - ~ **constant stirring**
  - ~ **plate As^{3+} at - 400 mV**
  - ~ **strip electrode by sweeping potential (-400 to +550 mV)**
  - ~ **record current (nA)**
  - ~ **Arsenic peak at ~250 mV**
  - ~ **peak height proportional to concentration**



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Modified 7063 QC

- **Method of Standard Additions (MSA)**
  - ~ **rather than Initial Cal and CCVs**
  - ~ **3 point MSA for samples with analyte present**
  - ~ **1 point MSA for non-detect samples at RL**
  - ~ **individual sample data sets stand on their own**
  - ~ **some samples can not support both As^{3+} & As^{5+}**
- **Reporting Limit Check Standard**
  - ~ **after samples with low MSA recovery**

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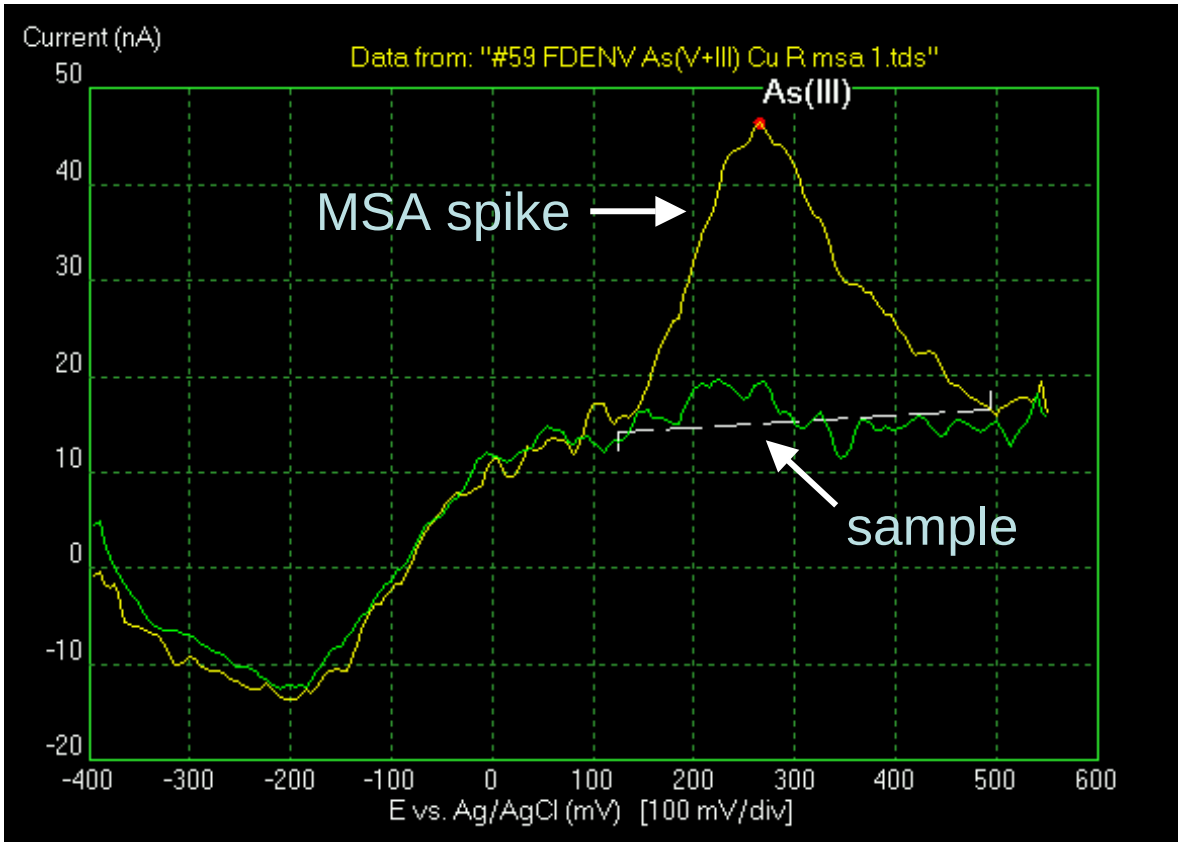
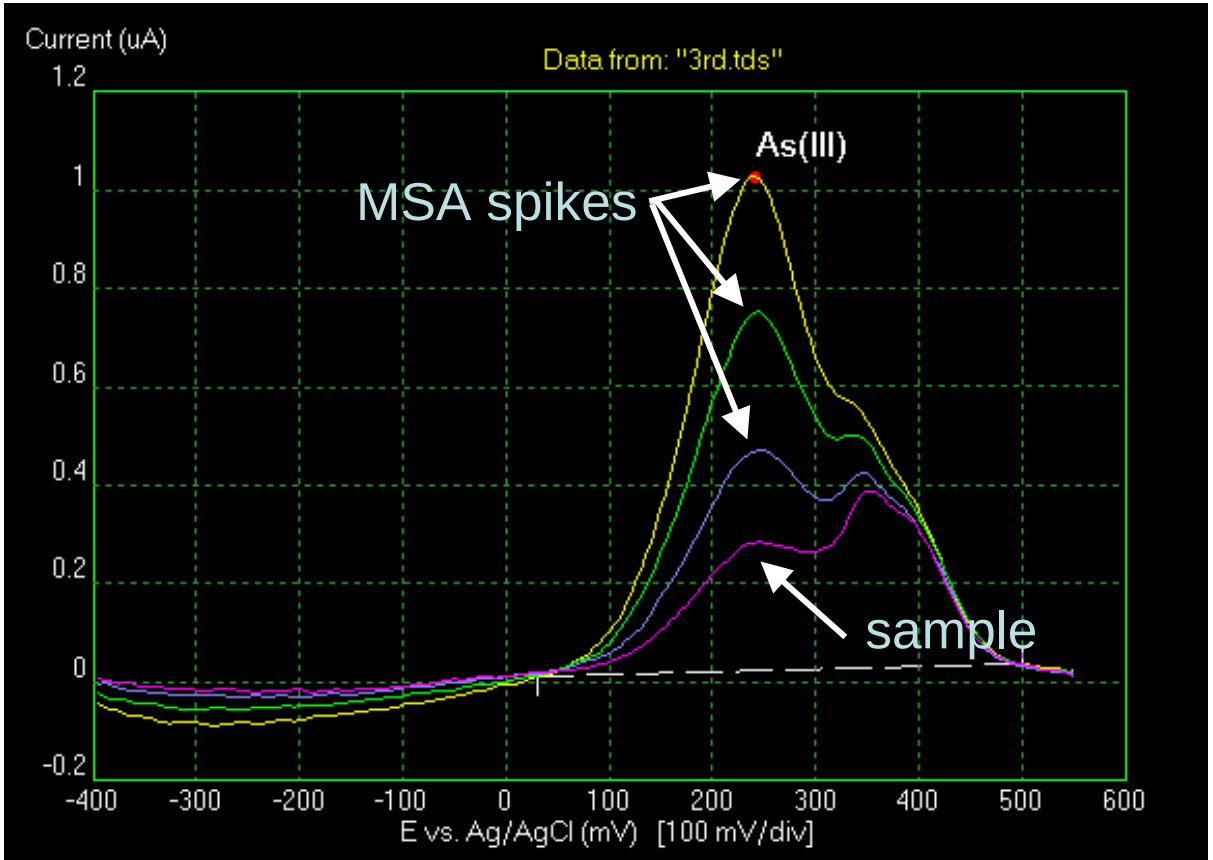
Non-Detect Sample

- **sample 1 - ND**
- **sample 1 + RL MSA spike (1 ppb)**



Sample with As(III) Present

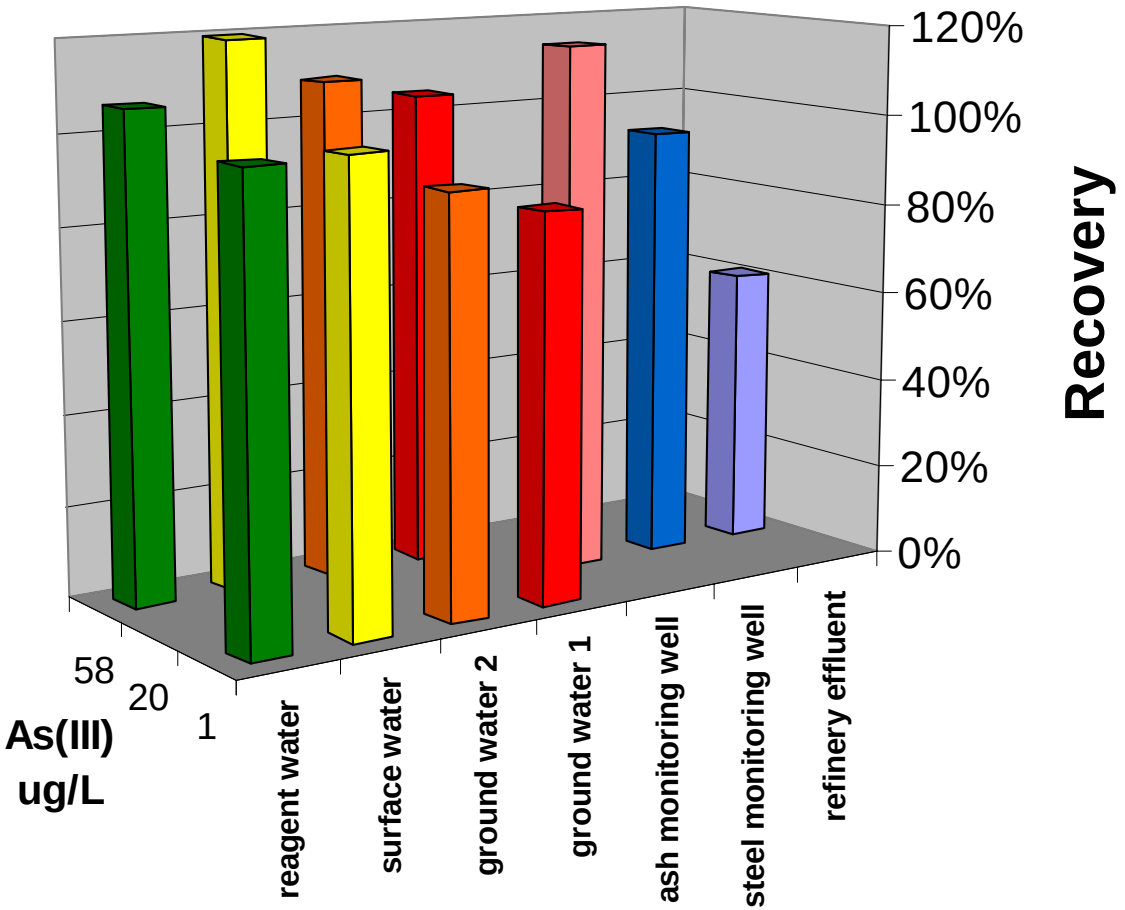
- **sample 2 - low level hit**
- **MSA spikes**



Arsenic (III) Method Performance

- **Water Sample Matrix Spikes**

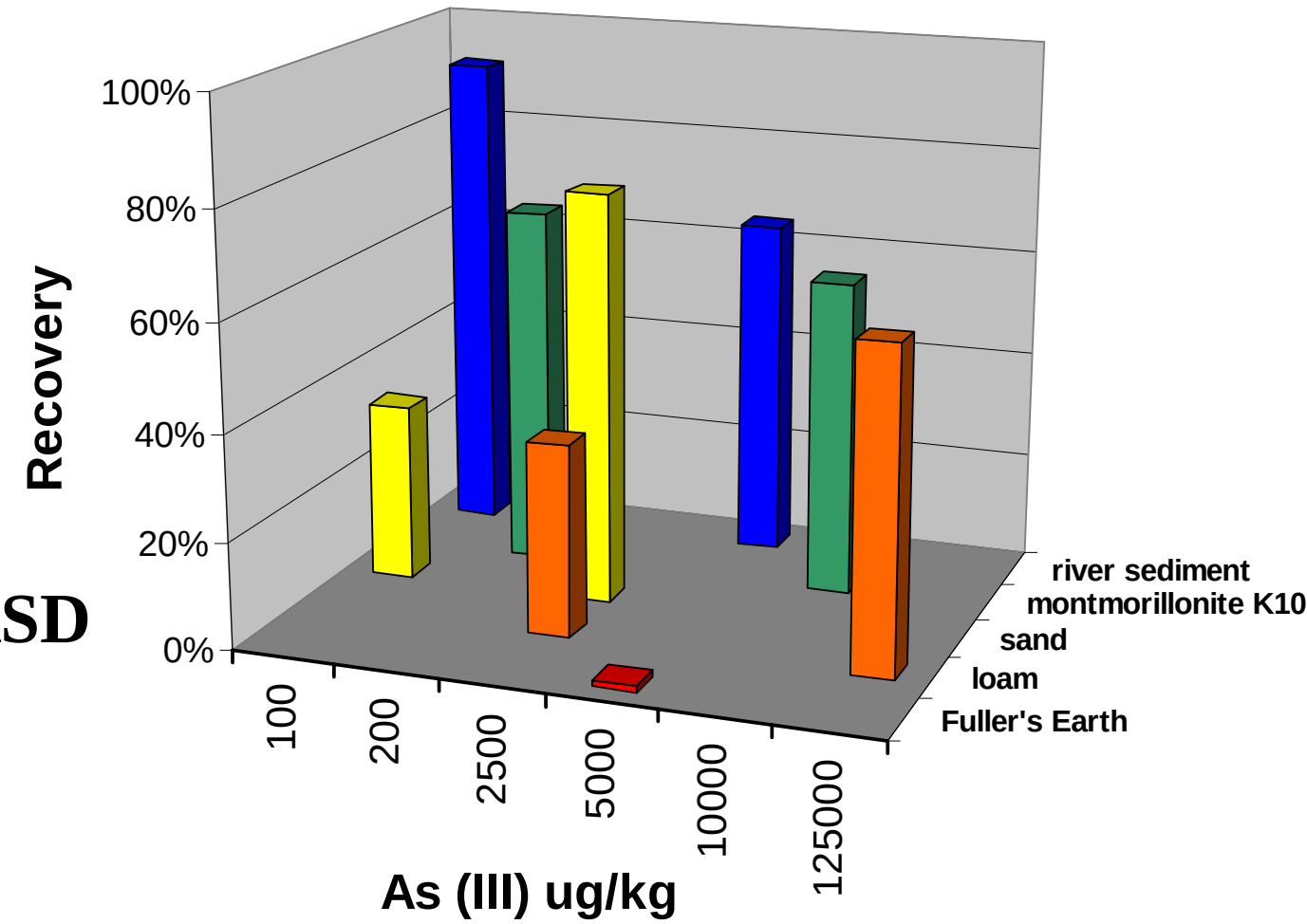
avg
102% R
6.1% RSD



Arsenic (III) Method Performance

- **Soil/Sediment Sample Matrix Spikes**

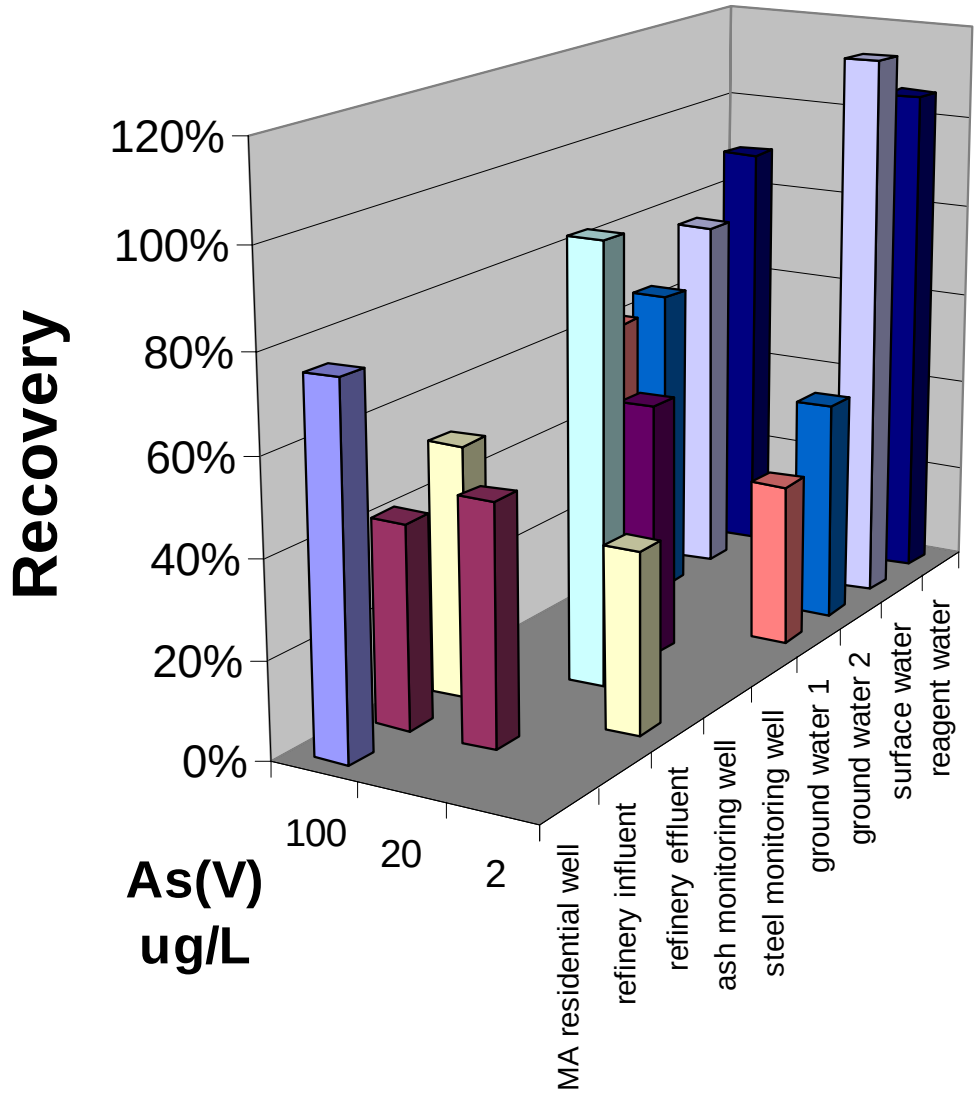
avg
61% R
10.3% RSD



Arsenic (V) Method Performance

- **Water Sample Matrix Spikes**

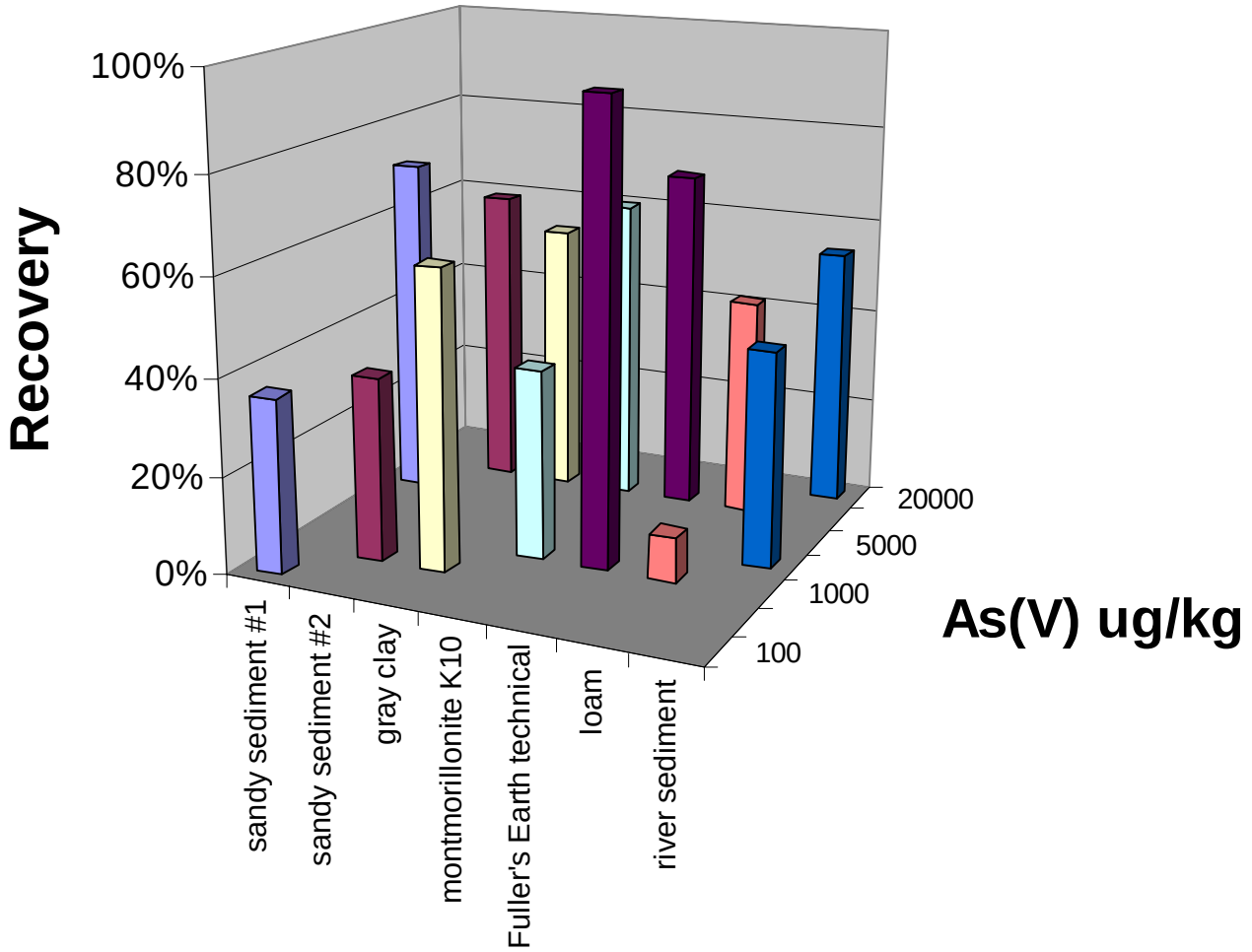
avg
67% R
8.9% RSD



Arsenic (V) Method Performance

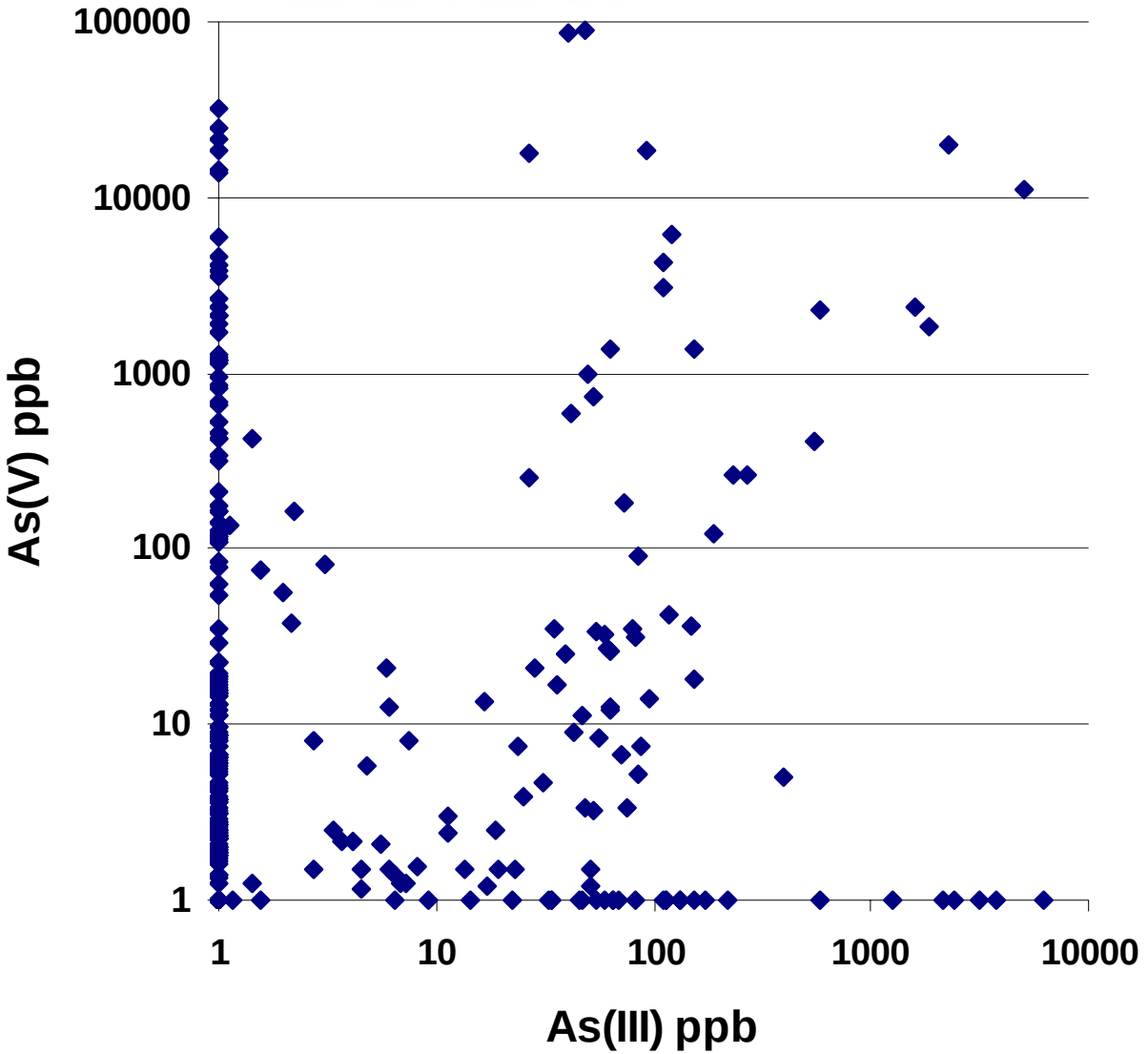
- **Soil/Sediment Sample Matrix Spikes**

avg
53% R
8.2% RSD



Wide range of Species Results

- ~500 samples
- No As(III) in most
- No As(V) in some



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Further Information

- **Arsenic Fact Sheet**
  - ~ http://www.in.gov/isdh/programs/environmental/factsheets/arsenic.htm
- **CLU-IN Contaminant Focus**
  - ~ http://clu-in.org/contaminantfocus/default.focus/sec/arsenic/cat/Overview/

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Conclusions

- Many uses of species data
  - ~ Monitoring, fate & transport, risk assessment
- Anodic stripping voltammetry of water
  - ~ direct determination of As^{3+}
    - reporting limit: 2 ug/L
  - ~ As^{5+} determined by chemical reduction and difference
    - reporting limit: 2 ug/L
- Soil/Sediment extracted
  - ~ H_3PO_4 and Na_3PO_4 overnight leaching
    - reporting limit: 100-400 ug/kg
- Method of Standard Additions
- EPA OSW Inorganic workgroup
  - ~ Submitted for inclusion in SW-846

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Species Measurements Needed

"The toxicity and fate of waterborne metal contaminants was shown to be highly dependent on chemical form, and it was realized that analytical measurement of these forms would be more meaningful than data for total element concentrations."

CSIRO

Graeme Batley

(1989)

Chiefl Research Scientist

Commonwealth Scientific and Industrial Research Organization

New South Wales, Australia

Acknowledgments

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Rev: 8/6/07

TestAmerica North Canton
Inorganic Arsenic Speciation Analysis
(Anodic Stripping Voltammetry)

TestAmerica North Canton provides analysis of arsenic (III) and arsenic (V) in water and aqueous extracts of soil and sediment by anodic stripping voltammetry, a new analytical technique for analysis of inorganic arsenic species at parts per billion (ppb) levels.

Advantages of Analysis by Method 7063 - modified

Low Detection Limits –

As(III)	Water	RL: 2 ug/L	/ MDL: 1.1 ug/L
	Soil	RL: 400 ug/kg	/ MDL: 56 ug/kg
As(V)	Water	RL: 2 ug/L	/ MDL: 0.85 ug/L
	Soil	RL: 400 ug/kg	/ MDL: 42 ug/kg

Reporting limits are similar to total arsenic limits by ICP/MS. This method is sensitive enough to meet most total arsenic and arsenic (III) action levels.

Improves identification of environmental hazard

- Arsenic (III) is the most toxic arsenic species commonly found in the environment, and is considered a toxic pollutant across most regulatory programs (air, water, hazardous waste & pollution prevention). It is persistent and harmful to human health and the environment at low levels.
- Speciation analysis can help provide a more accurate risk assessment and facilitate fate and transport evaluations.
- Method 7063-mod differentiates between arsenic (III) and other forms of arsenic. Since many risk calculations assume total arsenic concentrations to be equivalent to arsenic (III), the costs of cleanup can be lowered by proving otherwise.

Limitations of the Arsenic Speciation by ASV Method

Sampling procedure – Sample exposure to air should be minimized to avoid oxidation of arsenic (III) to arsenic (V). Preservation with HCl reduces co-precipitation with iron oxides. (Do not use oxidizers such as HNO_3.)

Interferences – Antimony and bismuth are chemically similar to arsenic resulting in positive bias. High organic content may suppress sensitivity, requiring sample dilution. High copper concentrations may over ride lower arsenic concentrations requiring sample cleanup.

More information

Sample volume – Water: One 1-Liter plastic bottle per sample. Solid: 2 oz glass jar.

Sample preservation – Water: HCl (ensure no free Cl_2) preserved and bottle filled to the top to exclude air and cool to 4° C. Solid: cool to 4°C.

Holding time – Currently Method 7063-mod has a 28 day holding time for HCl preserved water samples. Soil and sediment samples when refrigerated at 4°C have a 28 day holding time.

For more information on Arsenic Speciation analyses, contact your local Account Executive or Customer Service Manager at the email addresses listed to the left.