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The Determination of Ambient Metals in Aqueous Ecosystems by ICP-MS and Cold Vapor Atomic Fluorescence Spectroscopy

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Abstract

USEPA water quality criteria for metals have created extraordinary interest in the determination of ultra-trace metals in aqueous ecosystems. To help determine compliance with these water quality criteria, the Washington State Department of Ecology has developed a set of integrated protocols for the sampling and analysis of freshwater ecosystems for metals.

The sampling protocols include the use of specially precleaned Teflon sampling bottles, the use of high purity acid for sample preservation, and the use of precleaned filters and filter apparatus for the determination of dissolved metals. The analytical protocols used include inductively coupled plasma/mass spectrometry for most metals, and cold vapor atomic fluorescence for the determination of mercury. Currently available analytical protocols were modified to include the use of reference materials developed from aqueous ecosystems and the use of very low level standards to validate calibration. Rigorous quality assurance protocols were used to validate all aspects of these new protocols.

Real-world ambient data were presented for numerous rivers and streams in Washington State. The data focused on several toxic metals -- mercury, cadmium, lead, nickel, copper, zinc, and uranium -- and the occurrence of these dissolved metals throughout Washington State.

The determination of ambient metals in aqueous ecosystems by ICP/MS and cold vapor atomic fluorescence

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real-world determination of ultra-trace metals - integrated approach

- **Study performed in 1994 by Washington State Department of Ecology**
- **Study integrated advanced analytical techniques with protocols for cleaning and validation of sample containers and reagents**
- **Study focused on fresh water rivers and streams in Washington with problematic metals data (303d list)**

sampling considerations

- **how and where the samples are taken is critical for the success of ultra-trace metals projects**
- **our work uses teflon sampling bottles (PFA) and Teflon preservative acid vials**
- **for dissolved metals a disposable polystyrene filter apparatus with a 0.45 micron pore size filter element is used**

labware cleaning requirements

- **for cleaning operations Manchester operates a “clean” room (most room surfaces are plastic, $500K investment)**
- **the clean room contains a class 100 clean hood for critical cleaning and drying operations**
- **clean hood is laminar flow, polypropylene, effective particle control**

teflon labware cleaning protocol

- **72 hour soak in 1:1 nitric acid (reagent)**
- **72 hour soak in DI**
- **72 hour soak in 1:1 nitric acid**
- **final DI rinse**
- **stored filled with DI until use**
- **cleaned bottles and vials validated by ICP/MS before shipment to clients**

polystyrene filter cleaning

- **filters purchased commercially**
- **clean-up in lab consisting of:**
  - 500 ml 1:1 reagent nitric acid
  - 500 ml DI
- **both volumes passed through filter**
- **filter cleaning takes place in clean hood**
- **air dry in clean hood - reassembly**
- **storage till use in plastic bags (resealable)**

Reagent Considerations

- **Acids used are all high purity (Ultrex) grade or redistilled in a Teflon still**
- **Reagent water goes through 3 stages of deionization and polishing**
- **All other reagent used in sample preparation are purchased as highest purity available and then purified further as appropriate**

Ultra-trace Mercury Determination

- **based on EPA method 245.7**
- **cold vapor atomic fluorescence technique**
- **disposable PETG tissue culture bottles used for sample prep (low permeability)**
- **samples collected in PFA teflon 500 ml bottles**
- **lab reporting limit -- 1 ng/L (ppt)**
- **free bromine digestion technique**

Ultra-trace Mercury Determination

- **Questron/PSA instrument used**
- **CVAF technique proven to be robust**
- **Method has been in production status for 2 years at Manchester**
- **Lab developing real data on fresh water mercury contamination for the first time**
- **Time of analysis (5 min per) issue**

bromine digestion technique

- **KBr -- $KBrO_3$ -- HCl reagent**
- **forms free bromine**
- **mixed reagent provides quantitative oxidation of mercury species in less than 10 minutes**
- **effective for salt water and freshwater**
- **PETG bottles precleaned/stored containing digestion reagent**

mercury method summary

- **over 95% of results on ambient waters below EPA chronic fresh water quality criteria of 12 ng/L**
- **quality assurance data indicates reliability and robustness of method**
- **blanks uniformly under 1 ng/L**

Study results

- **set of studies performed in 1994**
- **Typical results:**
  - Columbia River - The Dalles 1.2 ng/L
  - Sanpoil River 9.8 ng/L
  - Nisqually River 1.1 ng/L
  - Fife Ditch 6.4 ng/L
  - Deschutes River 1.1 ng/L
  - Spokane River 0.81 ng/L

Ultra-trace mercury QA data

- **Digestion blank data**
  - For study n=28
  - mean blank 0.12 ng/L
- **Reference material data**
  - NIST 1641c was used
  - diluted to true value of 29.4 ng/L
  - mean recovery 93.8%
  - n=24

Ultra-trace mercury QA data

- **Spike recovery data**
  - spiking level ranged from 2 to 20 ng/L
  - spike recovery ranged from 80 - 126%
  - mean spike recovery 100.05% -- n=19
- **Method Detection Limits**
  - freshwater 0.34 ng/L
  - nearshore salt water 1.2 ng/L

Final details on method

- **Stability study shows samples stable over 30 days**
- **bromide - bromate reagents muffled at 400 C for purification**
- **solid analytical capability at 1 ng/L**
- **with attention, blanks attainable at 0.5 ng/L**
- **QA data solid**

ICP/MS for ultra-trace metals

- **Method modified EPA 200.8**
- **Manchester currently coordinating SM 3125 - metals by ICP/MS**
- **focus on ranges under 1 ppb**
- **matrix - freshwater**
- **~20 elements determined**
- **study on dissolved constituents**
- **internal standard method**

ICP/MS analyte list and masses

Be 9	**Al 27**	**Ti 47**	**V 51**	**Cr 53**	**Mn 55**
Co 59	**Ni 60**	**Cu 63**	**Zn 66**	**As 75**	**Se 77**
Sr 88	**Mo 95**	**Ag 107**	**Cd 111**	**Sb 123**	**Ba 135**
Tl 205	**Pb 208**	**U 238**			

ICP/MS calibration

- **Sciex/PE 5000 used for study**
- **internal standards are used**
  - Li Sc Rh Ho Th
- **tuning solution as recommended in 200.8**
  - 10 ppb Mg Pb Rh Ce Ba
- **calibration regime**
  - 0 5 10 20 50 100 ug/L stds

ICP/MS reporting limits (ppb)

- **0.01 U**
- **0.02 Mn Co Ag Cd Pb**
- **0.05 Be Ni Cu Tl**
- **0.1 V**
- **0.2 As Se**
- **0.4 Zn Cr**
- **1 Al**

ICP/MS Quality Assurance

- **1643c and SLRS-2 Reference Materials**
- **Calibration verification standards at 50 ppb, 1 ppb and 0.3 ppb**
- **Sample bottle blanks, field filtration blanks**
- **Continuing calibration blanks at 10%**
- **Spikes at 50 ppb**
- **Field Replicates**

EPA water quality criteria

- **Hardness based for most metals**
- **Spring run-off brings high solids, low hardness and potential for violations**
- **Chronic criteria most likely to be violated are: (assuming hardness at 25 mg/L)**
  - Cadmium @ 0.330 ug/L
  - Lead @ 0.374 ug/L
  - Copper @ 3.12 ug/L

ICP/MS 0.30 ppb QA results

analyte	mean	% rec	StdDev
Be 9	0.296	98.5	0.066
Ni 60	0.281	93.7	0.060
Cu 63	0.342	113.9	0.069
Ag 107	0.289	96.2	0.011
Cd 111	0.297	98.9	0.019
Pb 208	0.311	103.8	0.037