Sampling, Processing, and Instrumental Techniques for the Analysis of Silver in Natural Waters

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A complete re-evaluation of trace element levels in freshwaters has occurred over the past 5 years as a succession of studies have demonstrated previously published data to be erroneous. Severe contamination during sampling and processing, and inadequate analytical sensitivity plague historic data. Recently, several published studies have applied "standard" oceanographic analytical techniques, developed over the past 10-15 years, with the latest in "clean" techniques to accurately determine natural metal levels. In general, these methods rely on a preconcentration step, either liquid phase chelation/extraction or a solid phase extraction to provide the necessary enrichment for standard instrumental methods. Our group has been developing and applying to natural waters, techniques that allow quantification of many metals at natural levels without a non-instrumental preconcentration step. This paper outlines our field and analytical methods for the quantification of Ag and a select group of other trace elements at low ng L⁻¹ levels.

I. CONTAMINATION CONTROL - FIELD and LAB

The application of "clean" techniques to control contamination is an essential prerequisite for accurate quantification in all modern methods. Table 1 outlines some of the required steps and procedures followed in obtaining un-biased samples.

SAMPLERS
- Non-metallic, simple, isokinetic.
- Scrupulously acid-cleaned, blanked.

SAMPLE CONTAINERS
- Teflon bottles (FEP, PFA).
- Rigorously acid-cleaned (50% HCl, 50% HNO₃, 1% High Purity HNO₃).
- Double-bagged in clean-room.

FILTRATION - PHASE SEPARATION
- All Teflon holders, scrupulously acid-cleaned.
- Holders pre-loaded in clean-lab, double-bagged.
- Acid-leached polycarbonate track-etched filters.
- In-line or in field glove-box.
- Minimal surface contact - only filter holder/column - directly into Teflon filtrate bottle.
PRESERVATION
- Teflon vials, double-bagged in clean-room.
- Pre-dosed in clean-lab with 50% Ultrex HNO₃.

SAMPLE HANDLING
- Tyvek coveralls, poly gloves.
- "Clean-Hands" - "Dirty-Hands" Technique.
- Ultra-high purity reagents.

ENVIRONMENT
- Clean-lab processing, Class 100 benches for critical handling.

Scrupulously cleaned double-bagged Teflon sampling apparatus, gloved and garmented personnel, and "clean-hands" - "dirty-hands" techniques are standard elements of clean field protocols. Particulate contamination in equipment preparation and sample processing is controlled by working under clean-room environments.

The ability to accurately determine trace metal fluxes and yields depends not only on the collection of un-contaminated samples but also on obtaining representative samples as well. We approach this complex issue through the use of various clean compositing techniques (large rivers), or with direct compositing iso-kinetic samplers (wadable systems).

A meaningful field quality assurance program is essential for the demonstration, maintenance and documentation of data quality. In addition to the measures described above, the following categories of samples are obtained to track performance.

<table>
<thead>
<tr>
<th>TYPE</th>
<th>FREQUENCY OF COLLECTION</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bottle Blanks</td>
<td>20%</td>
</tr>
<tr>
<td>Filtration Blanks</td>
<td>20%</td>
</tr>
<tr>
<td>Analyte Spikes</td>
<td>15%</td>
</tr>
<tr>
<td>Complete Replicate</td>
<td>25%</td>
</tr>
</tbody>
</table>

II. ANALYTICAL METHODS

For analytical detection we have pursued two distinct approaches: Graphite Furnace Atomic Absorption (GFAA) methods for Ag levels >10 ng L⁻¹, and Inductively-Coupled Plasma Mass Spectrometry (ICP-MS) for Ag levels down to 0.5 ng L⁻¹. Automated multiple-pipetting is applied to increase sensitivity in GFAA, and a simplified matrix modification protocol controls interferences. GFAA operating conditions are summarized below.
GFAA OPERATING CONDITIONS

PE 5100Z Spectrophotometer
AS400 Furnace
AS40 Autosampler

Source Lamp: Hollow Cathode, 12 mA
Wavelength: 328.1 nm
Matrix Modifier: NH₄H₂PO₄ (400 µg in 20 µL)
Char Temperature: 750 °C
Atom. Temperature: 1800 °C
Sample Volume: 320 µL (8 x 40 µL pipettings)
Furnace Tube: L'vov platform in pyrolized tube
Purge Gas: Argon, grade 5

Table 2 summarizes figures of merit for GFAA when operated under specified conditions.

TABLE 2. Silver: Multiple-Pipetting GFAA. Analytical Figures of Merit

<table>
<thead>
<tr>
<th>Criterion</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Typical Sensitivity (A*s/ppb)</td>
<td>0.7</td>
</tr>
<tr>
<td>Typical &quot;Noise&quot; (A*s)</td>
<td>0.003</td>
</tr>
<tr>
<td>S/N</td>
<td>250</td>
</tr>
<tr>
<td>Typical Blank Standard Deviation</td>
<td>2.5</td>
</tr>
<tr>
<td>IDL ng L⁻¹</td>
<td>7.5 (5 - 10)</td>
</tr>
</tbody>
</table>

IDL = 3 σ of 7 blank replicates

Ultrasonic nebulization coupled with a high efficiency interface and modern mass spectrometer provide the necessary sensitivity in our ICP-MS methods. When Mo and Zr spectral interferences, and background noise, are monitored and controlled, the ICP-MS can accurately quantify Ag abundances and isotope ratios of natural water systems. ICP-MS operating conditions are summarized below:
ICP-MS OPERATING CONDITIONS

VG Plasmaquad II STE
Cetac Ultrasonic Nebulizer 5100AT

Analyte Masses: 107, 109
Other Masses: 90, 95, 98, 99, 101, 104, 105, 106, 108
Solid State RF: 27.12 MHz
Forward Power: 1350 W
Reflected Power: <2 W
Argon Cool Gas: 13 L/min.
Argon Auxiliary Gas: 1.2 L/min.
Argon Nebulizer Gas: 0.8 L/min.
Sample Uptake: 1.5 - 2.5 mL/min.
Operating Vacuum: 1.2 x 10^{-6} mbar
Quad Mode: Peak Jump
Peak Dwell Time: 200 msec.
Points per Peak: 3
Acquisition Time: 90 sec., 5 cycles
Rinse Time: 360 sec.
Cones: 1 mm Nickel
USN: 140 °C heat, 2 °C cool

Table 3 summarizes figures of merit for ICP-MS when operated under specified conditions.


<table>
<thead>
<tr>
<th>Criterium</th>
<th>Ultrasonic Nebulization</th>
<th>Pneumatic Nebulization</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sensitivity (cps/ppb)</td>
<td>250,000 - 300,000</td>
<td>25,000 - 35,000</td>
</tr>
<tr>
<td>&quot;Noise&quot; (cps)</td>
<td>150 - 250</td>
<td>40 - 60</td>
</tr>
<tr>
<td>S/N</td>
<td>1400</td>
<td>600</td>
</tr>
<tr>
<td>Blank STD ng L⁻¹</td>
<td>0.15</td>
<td>0.4</td>
</tr>
<tr>
<td>IDL ng L⁻¹</td>
<td>0.45 (0.2 - 0.8)</td>
<td>1.2 (1 - 2)</td>
</tr>
</tbody>
</table>

IDL = 3 σ of 7 blank replicates
In both analytical techniques, filtrate samples are introduced to the instrument with no pre-treatment or pre-concentration. Total samples are taken through an in-bottle (original Teflon sample bottle) digestion at 60 °C for 12 hours with added Ultrex HNO₃ (1.6%), before instrumental analysis. This approach eliminates the contamination and recovery problems inherent in most pre-concentration schemes. The only surfaces the sample contacts prior to uptake into the instrument are the original Teflon sample bottle and polypropylene autosampler vial/tube.

Table 4 outlines the performance of the ICP-MS technique and associated field methods on a set of 49 river samples collected in Spring of 1993.

**TABLE 4. ICP-MS Performance Evaluation: Silver**

<table>
<thead>
<tr>
<th>Sample Type</th>
<th>Value</th>
</tr>
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<tbody>
<tr>
<td>Field Method Blanks (ng L⁻¹)</td>
<td>mean = 0.74, STD = 0.26, n = 31</td>
</tr>
<tr>
<td>Replicate Precision (Relative % Difference)</td>
<td>mean = 10.1, STD = 9.8, n = 52</td>
</tr>
<tr>
<td>Analyte Matrix Spike Recovery (%)</td>
<td>mean = 88.7, STD = 8.3, n = 16</td>
</tr>
<tr>
<td>Silver 107/109 Isotope Ratio</td>
<td>mean = 1.059, STD = 0.081, n = 166 accepted = 1.056</td>
</tr>
</tbody>
</table>

No aqueous, environmental matrix, Standard Reference Material is certified for Ag at low ng L⁻¹ levels. Accuracy of the Ag analyses is evaluated with dilutions of higher level certified SRM's, and with other internal checks. The Canadian NRC/IERT SRM SLRS-3 is run three times during a typical batch sequence of 20 samples, and serves well for most trace elements, however, Ag is not certified.
Questions & Answers: Sampling, Processing and Instrumental Techniques for the Analysis of Silver in Natural Waters

Q. DENISE SCHILDKRAUT (Eastman Kodak): I just wanted to make a comment. There is an NIST trace element freshwater sample that has certified silver concentration at 2.2 ppb. Would that be suitable for your purposes?

A. No, that's totally out of the realm of natural concentrations. We've obviously measured every CRM there is available for aqueous silver. You know, there's no problem measuring it. But you're a thousand times higher than natural concentrations. You have to dilute it down to get there, so the question becomes moot.

Q. GABOURY BENIOIT (Yale Univ.): Martin, I think a lot of us clean-technique chemists have done what you've done here, which is assume contamination at every single step along the process, and then try to eliminate it in all those steps. Have you done any work to try to identify where the major sources of contamination are? Because if we always have to do all of these steps, as you know, it's very costly and difficult work. It would be nice if we could narrow it down to some key spots in the procedure, perhaps.

A. We've done some intercomparison exercises with USGS and other groups, comparing different methods. And the filtration step is usually the biggest source of error here, as well as the acidification step, which is another real big potential problem. Once you get beyond those two steps, and assuming everyone's using a relatively decent sampler, then it becomes more difficult to trace the nature of the contamination. It seems to me like some kind of stochastic, random contamination, which you [might] have to go to extremes to eliminate. So it's hard to say don't do some of this stuff, because you could then get a couple of samples where you don't know whether they're real or contaminated. I don't think what we do is really that out of line. Most of it seems necessary.

Q. JIM KRAMER (McMaster Univ.): You certainly showed us the very eloquent needs that you have to have if you're going to get those kinds of detection levels, from an analytical point of view. I'd like to concentrate, though, a little bit upon what you showed us in context with the field side, and the variability there. Given that one does what you do, what would be the percent variability in an analysis — and maybe you've done this — such as, if you go to a particular site and get a particular sample, then go back and repeat the whole thing say, in another ten minutes, or within a time interval of whatever you want to use the data for. What is the variability, compared to the kinds of variability in the analytical part?

A. We've done a fair amount of that. The overall analytical precision depends on the metal, but most of it's analytical. It's a little more difficult to do for silver. For low level [elements] like cadmium and silver, overall, if we go out and sample half an hour, half an hour again, half an hour again, getting triplicates, it's on the order of 10 percent. Most of it analytical, almost all of it analytical. If we do things like zinc and copper, in a fairly large river, you're probably talking variability of a couple percent. And that's just sampling one point in the river. Now there's considerably more variability across a river. You get into issues of compositing. Different systems are going to behave differently as a function of time. But if you were able to collect a true replicate, instantaneous collection of three samples, the analytical error is going to be in the neighborhood of 10 percent, for the very low levels that we're talking about, and a couple percent for zinc and copper.