Glass or Plastic?
The Challenges and Solutions of Analyzing Mercury by ICP

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Outline

- Motivation
- Hg in Solution
- Standard/Sample preparation
- In the Instrument
- Analysis/Troubleshooting

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Why Mercury?

Prevalent in a wide array of applications

-chemical manufacturing, electroplating, dentistry

Various forms extremely toxic to humans/animals

-neurological effects, Minamata disease, etc.

Physical/chemical nature of Hg makes it difficult to measure reliably by ICP-OES/ICP-MS

-vapor pressure of the metal, oxidation states in solution

Methods for Hg determination

Cold Vapor Atomic Absorption – EPA Methods
1631E, 3052, 7473, 7470A, 7471B

ICP-MS – EPA Method 200.8, 6020A, 3052

ICP-MS/ICP-OES – USP 232/233 & ICH/Q3D

***Class 1 impurity, cannot be excluded by Risk Assessment**

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Hg Certified Reference Materials

Commercially available from ppb range to 10,000 ppm+ in various matrices.

Typically produced using Hg metal and HNO_3/H_2O with heat, or various salts (application-specific).

Can be combined with all ICP-visible elements, although certain complex combinations have compatibility problems.

Hg metal reacting with HNO_3 in H_2O

Species of Hg in solution

Mercury can exist in aqueous solutions as Hg^{2+}, Hg_2^{2+} or a number of different organometallic species.

Reducing environments can convert Hg^{2+} to the Hg_2^{2+} dimer or the metallic form with relative ease.

$$2Hg^{2+} + 2e^- \leftrightarrow Hg_2^{2+},\ E^0 = 0.920V$$

$$Hg_2^{2+} + 2e^- \leftrightarrow 2Hg^0,\ E^0 = 0.797V$$

Hg in Solution

Keeping Hg in the Hg^{2+} state is necessary for reliable measurements by ICP.

Mercury in the Hg_2^{2+} state presents issues with both matrix compatibility and ICP instrumentation.

Metallic Hg is volatile, poses not only health hazards but instrumentation effects.

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Standard/Sample Preparation

The success of Hg analyses are heavily dependent on preparation:

- Choice of matrix/matrices
- Container materials

Hg has shown long term stability in a number of matrices and container materials…however several factors must be accounted for.

Low-density polyethylene (LDPE)

Borosilicate

Standard Preparation – HNO_3

Hg in HNO_3 solutions has a tendency to stick to plastic (up to ~1ppm adsorbed); the loss of Hg to plastic and the reduction of Hg^{2+} are thought to be related.

Gold chloride can mitigate this by acting as an oxidizing agent or possibly blocking sites on the plastic surface.

$$AuCl_4^- + 3e^- \leftrightarrow Au + 4Cl^-, E^0 = 1.00V$$

Alternatively, borosilicate glass containers can be used, although contamination can be an issue for certain analytes (Al, B, Ca, Na, Ni, Zn) and use of HF is not advised.

Standard Preparation – HNO_3

Hg^{2+} can also reduce to the Hg_2^{2+} dimer over time if any NO_x gases remain from the stock standard production process.

Adding HNO_3 and boiling can convert it back to the Hg^{2+}, although recertification will be required.

Standard Preparation – HCl

Hg^{2+} tends to be stable in HCl (exists as $HgCl_4^{2-}$ in solution); the Hg_2^{2+} dimer, however, will precipitate in the presence of Cl^-.

$HgCl_4^{2-}$ (E^0 = 0.41V) is more difficult to reduce to the dimer than Hg^{2+} in HNO_3 (E^0 = 0.92V), could be a potential reason we don't observe Hg sticking to plastic in HCl solutions.

We don't normally see issues with Hg sticking to plastic in mixed HNO_3/HCl matrices.

Standard Preparation - General

Hg appears to be stable in dilute HF; we don't have stability data to indicate any adverse interactions between Hg and HF thus far.

Carbon-containing species can reduce Hg^{2+} to the metallic form; standards containing Sb and Hg present an array of challenges involving matrices and container materials.

Standard Preparation - Summary

Most preferable to least:

Hg in HCl (boro or plastic)

Hg in HNO_3 + HCl (boro or plastic)

Hg>200ppm in HNO_3 (plastic)

Hg in HNO_3 (boro)

Hg in HNO_3 with Au (plastic)

Hg<200ppm in HNO_3 (plastic)

Consider what is important to your analysis; a proper risk assessment can be pivotal in setting up successful methods/analyses.

Sample Preparation - General

Consider all components present in standards/samples.

If any components of the sample or reagents can act as a reducing agent, any Hg^{2+} in solution could get reduced.

Be mindful of any container materials involved with handling/preparation/storage.

Contact Inorganic Ventures for detailed sample preparation info.

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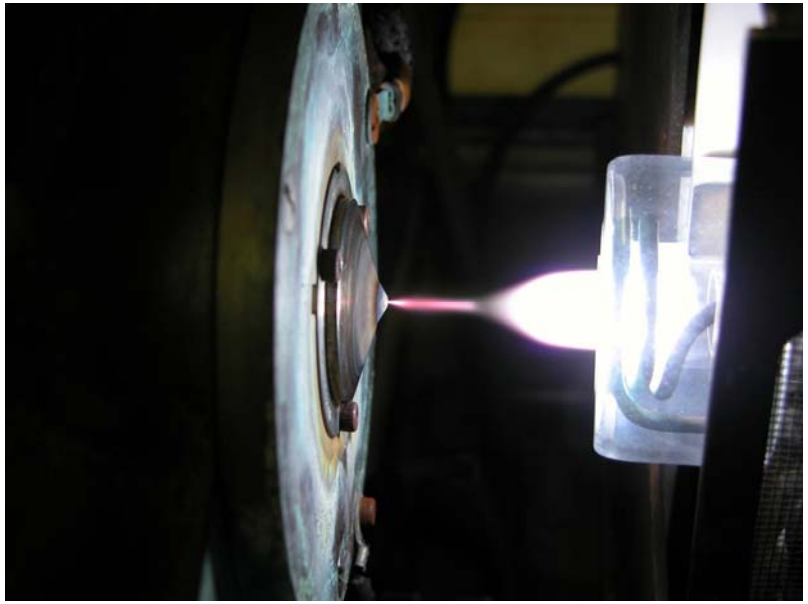


In the Instrument

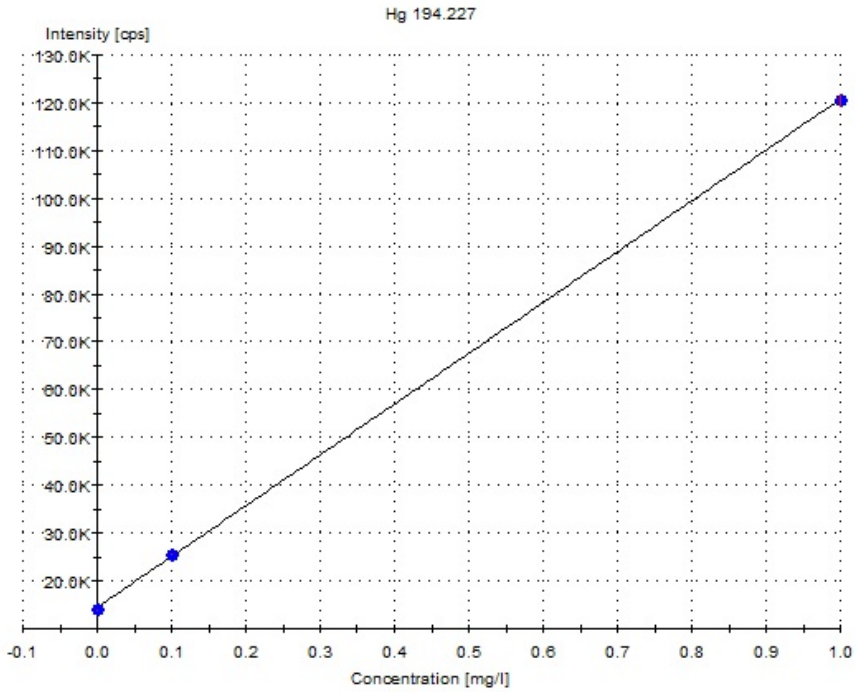
Hg has a number of serviceable options across the ICP methods.

Preferable lines/masses:

ICP-OES: 184.950nm, 194.227nm, 253.652nm

ICP-MS: 199, 201, 202

See www.inorganicventures.com/periodic-table for more detailed information.



In the Instrument – Introduction System

Hg sticks to plastic in HNO_3 matrices; many intro system components are composed of plastic!

Initial analyses should not be affected, however memory effects due to Hg washing out over time can affect subsequent analyses.

Thiourea, higher HCl rinse solutions can help with washout issues.

Running Au through the system prior to Hg standards/samples could potentially mitigate this; Inorganic Ventures plans to investigate.

HF-resistant introduction system

In the Instrument – Intro System/Plasma

If Hg is present as the Hg_2^{2+} species, the nebulization efficiency will be significantly higher for Hg and signal could increase several hundred percent.

Half of the Hg dimer converts to the Hg^{2+}, other half converts to the metal; vapor from metal produces false-high results when it reaches the plasma.

$$Hg_2^{2+} \rightarrow Hg^{2+} + Hg^0$$

Mercury dimer disproportionation

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Analysis/Troubleshooting

Determining the source of error with Hg recoveries can be difficult due to the variety of avenues it can come from.

Incorporating check solutions and an internal standard should help point to issues with either the standards or the samples.

Internal Standards: Pt, Ir, Bi for ICP-MS; Cd, Be for ICP-OES.

Analysis/Troubleshooting

If HNO_3-only matrices are unavoidable, solutions must be prepared and stored in glass or Au-treated plastic.

Extremely high (>200% versus expected) signal/counts generally point to reduced Hg species (Stock or preparation) that experience higher nebulization efficiencies.

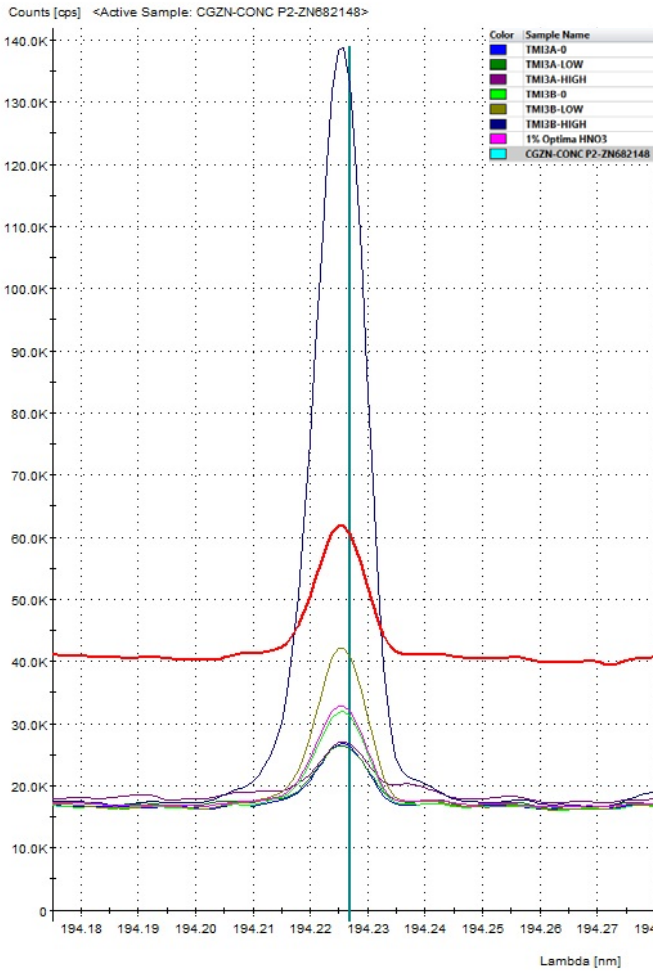
Precipitation caused by Hg_2^{2+}/Cl^- interaction should point back to the stock Hg standard.

Boiling the stock standard in HNO_3 can help oxidize the Hg dimer back to the Hg^{2+} species.

Analysis/Troubleshooting

Check the raw counts/spectra for calibration curves. Memory effects are prevalent in Hg analyses, consider using different solutions for rinses if issues arise.

A working stability program of your standards can be extremely useful in analyses/validations; comparing freshly prepared standards against stored standards can provide insight to the effectiveness of your storage/preparation methods.



Summary

Understanding the species of Hg in solution will prove useful for troubleshooting.

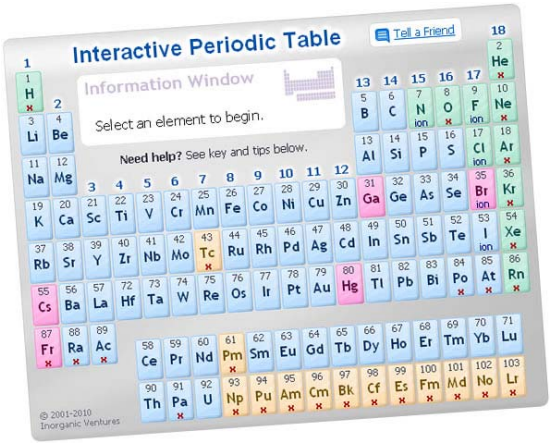
Consider matrices/container materials before setting up analyses.

Freshly-prepared standards can help identify stability issues.

Most issues with Hg can be traced back to container materials and the species of Hg present in solutions; eliminating opportunities for reduction of Hg^{2+} and adsorption gives the best chance for reliable Hg measurements.

Technical Support – Available to Everyone

Online Resources at inorganicventures.com



Customers can visit our website's *Tech Center*, which includes:

- **Interactive Periodic Table**
- **Sample Preparation Guide**
- **Trace Analysis Guide**
- **ICP Operations Guide**
- **Expert Advice**
- **And much, much more.**

Questions?

Thank you!