BE BOLD

2022 INORGANIC VENTURES WEBINAR SERIES

Quick Tips for Working with Tin and Mercury

THURSDAY, AUGUST 18
9:00–9:30AM EST

PRESENTED BY:
Autumn Phillips
R&D Chemist

Analyzing Hg

- Hg is one of the “problem-elements” and causes numerous problems/concerns for trace metals analysts
- Common methods:
  - EPA Methods: 200.8, 6020A, 3052, 1631E, 7473, 7470A, 7471B
  - USP 232/233 and ICH/Q3D
- **Hg MUST be in the Hg^{+2} form for accurate ICP measurements!**

Keeping Hg in the Hg^{+2} form

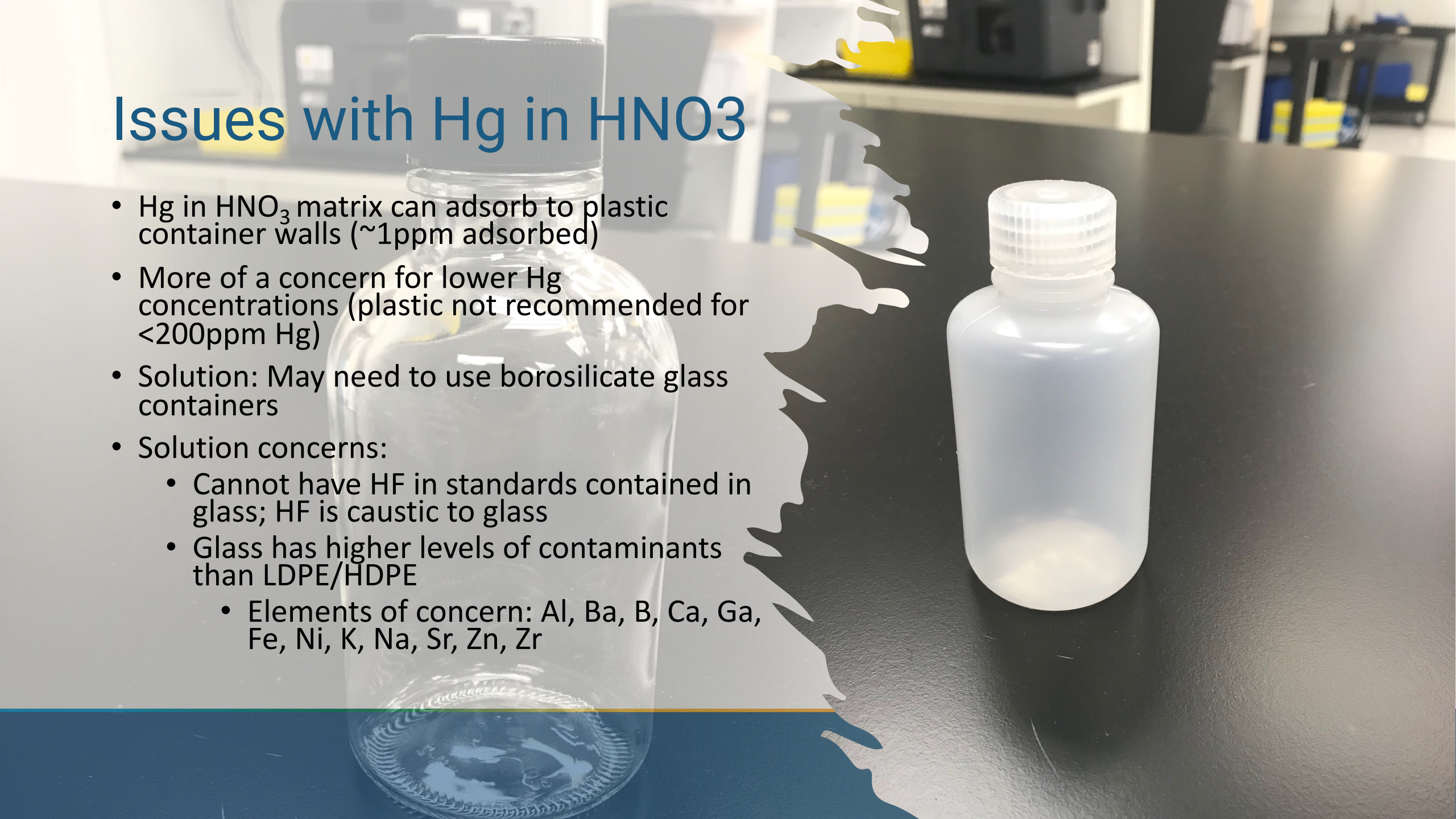
- Avoid neutral/basic media → insoluble carbonate
- Avoid mixing with tartrate → will be reduced to the metallic form
- Reducing environments can convert Hg^{2+} to the Hg_2^{2+} dimer or the metallic form.
- Hg_2^{2+} disproportionation into metallic mercury and Hg^{2+}:

$$Hg_2^{2+} \xleftrightarrow{Cl^-} Hg^0 + Hg^{2+}$$

- Hg^{2+} can reduce to Hg_2^{2+} if NO_2 gases remain in the container from reaction/production process
- Adding HNO_3 and boiling can convert Hg_2^{2+} back to the Hg^{2+} (recertification may be required)

Issues with Hg in HNO3

- Hg in HNO_3 matrix can adsorb to plastic container walls (~1ppm adsorbed)
- More of a concern for lower Hg concentrations (plastic not recommended for <200ppm Hg)
- Solution: May need to use borosilicate glass containers
- Solution concerns:
  - Cannot have HF in standards contained in glass; HF is caustic to glass
  - Glass has higher levels of contaminants than LDPE/HDPE
    - Elements of concern: Al, Ba, B, Ca, Ga, Fe, Ni, K, Na, Sr, Zn, Zr



Issues with Hg in HNO3 cont.

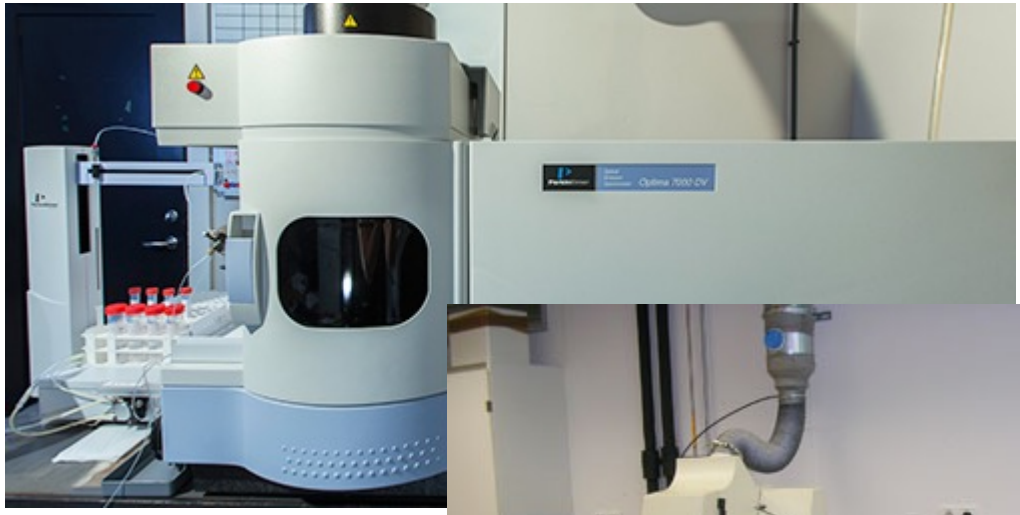
- Alternative solution: add 1ppm $AuCl_3$ to stabilize Hg to avoid adsorption to plastic (EPA bulletin)
- Solution concerns: Cl from $AuCl_3$ can cause interferences in ICP-MS (polyatomic interference for As and Se)
- Include $AuCl_3$ in matrix of blank, standards, and samples.
- *There are also methods for stabilizing Hg with L-cysteine in dilute HNO3, but we have not used this methods in-house yet. (See here)

Hg in HCl matrix

- Hg is stable in HCl at any concentration (exists as $HgCl_4^{2-}$ in solution)
- We recommend using HCl matrix for Hg standards if possible
- Concerns:
  - Cl interference issues for As and Se on ICP-MS → use collision cell (He mode)
  - Hg_2^{2+} form may precipitate in the presence of Cl^-. Can boil with excess HNO3 prior to adding HCl to make sure dimer is not present
  - If Ag is present, excess chloride will need to be added to keep Ag in solution and the solution will be photosensitive.
  - If Tl is present, it should be in the Tl^{+3} state as Tl^{+1} may precipitate as the chloride

Running Hg solutions on ICP

- Hg sticks to plastic in HNO_3 matrices → many intro system components are composed of plastic!
- Glass intro system preferred
- Initial analyses should not be affected, however memory effects due to Hg washing out over time can affect subsequent analyses.
- Solution: Run Thiourea or higher HCl rinses to help with washout issues



Running Hg solutions on ICP cont.

- Hg_2^{2+} can be converted to a mix of Hg^{2+} and Hg^0 in the presence of chloride or other ligands.
- If Hg is present, even in small part, as the metallic (Hg^0) species, the nebulization/transport efficiency will be significantly higher for Hg and signal could increase several hundred percent.
- Extremely high recoveries → reduced Hg species
- Low results → Hg loss due to adsorption or precipitation of Hg_2^{2+} with chloride
- Recommended rinse solutions:
  - HCl / Thiourea
    - 1-10% v/v HCl
    - 0.5% w/v Thiourea
    - Also good for Au
  - NH4OH
    - 1-5% v/v for OES or MS

Analyzing Tin

- Primary issues with analyzing Sn are volatility and tendency to hydrolyze (forms semi-colloidal suspension)
- Poor recoveries for Sn can generally be attributed to either an incomplete sample digestion, or instability of Sn in the digested sample

Forms of Sn in solution

- Sn exists in solution as Sn^{4+} and Sn^{2+} which form complex ions.
- Sn^{4+} hydrolyzes much more readily than Sn^{2+}

$$Sn + HCl \rightarrow \overset{(Sn^{+2})}{SnCl_4^{2-}} + \text{air and time} \rightarrow \overset{(Sn^{+4})}{SnCl_6^{2-}}$$

- In HCl:
  - Sn(II) forms $SnCl_4^{2-}$ and Sn(IV) forms $SnCl_6^{2-}$
  - Requires large excess of chloride to stabilize!
  - Sn^{2+} is easily oxidized to Sn^{4+} by oxygen in the air
- Not stable in HNO_3 alone → will oxidize to insoluble SnO_2 (stannic oxide):

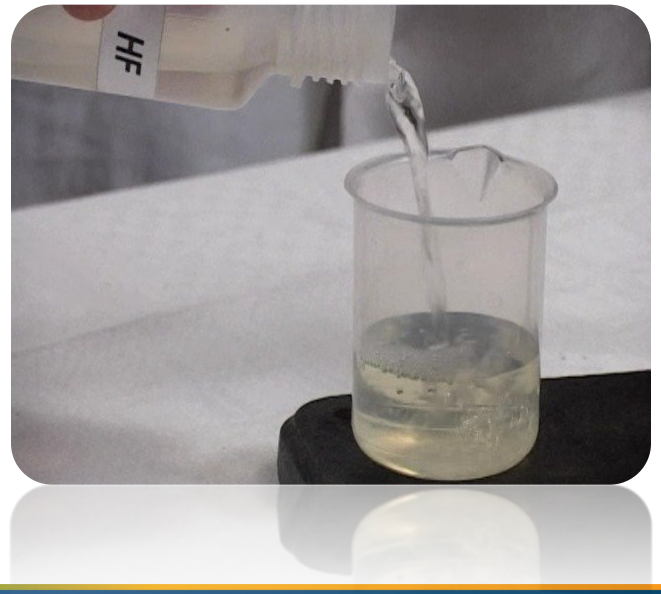
$$Sn^{4+} + 4HNO_3 \rightarrow SnO_2 + 4NO_2 + 2H_2O$$

Keeping Sn in solution

- Hydrolysis and oxidation are the primary concerns.
- Basic media: not stable! Sn will fall out as insoluble hydroxides and sulfide.
- Organotin compounds: adsorb to sediments.
- Can be stabilized in HCl, alone, but will need a large excess of HCl.
- The age of the solution also matters as the Sn species can oxidize over time, changing the ratios of different forms in solution and potentially precipitating out as the oxide.

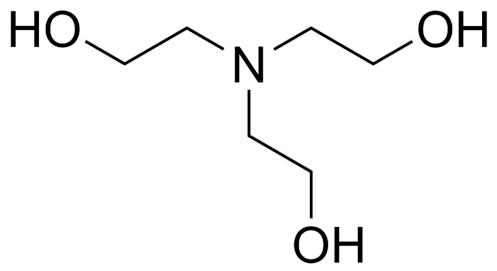
Keeping Sn in solution

- Best option is to stabilize Sn with HF.
- HF will “fix” Sn in solution forming SnF_2 , SnF_4 , and other fluorostannates.
- Fluoride ions will surround and stabilize the Sn ions, and will not be displaced by other components in the solution



Running Sn solutions on ICP

- Sn is best stabilized in solution with HF
- HF is caustic to glass → many intro systems are glass!
- If you do not have an HF-resistance (plastic) intro system, we recommend neutralizing the HF with TEA prior to running on the instrument.
  - Add TEA to slight excess (pH 7-8)
  - The fluoride ion itself does not attack glass, HF does.
  - **Switch out wash solution after using TEA before Hg analysis



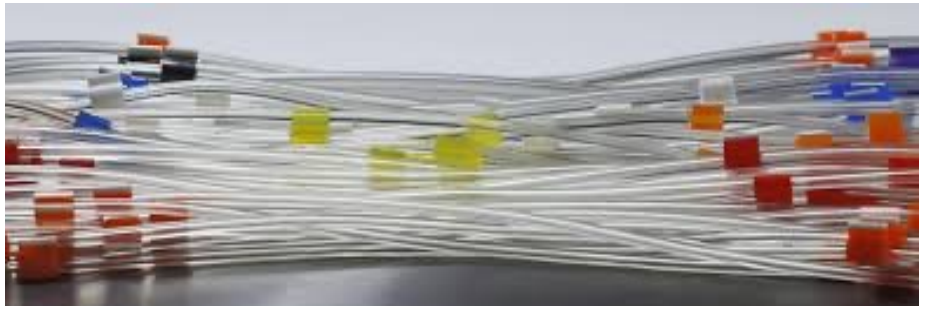
Running Sn solutions on ICP cont.

- If Sn is stabilized with HCl, chloride can cause interference issues for other elements in ICP-MS (especially for As and Se)
  - These issues can be mitigated by using a collision cell
- $SnCl_4$ will also cause a vaporization interference: more Sn gets into the plasma due to high vapor pressure. If there are different ratios of Sn(II) and Sn(IV) in standards and samples, this causes issues.
  - Best to “fix” with small amount of HF

Running Sn solutions on ICP cont.

- Issues if the Sn has undergone hydrolysis → forms a semi-colloidal suspension (tin(IV) hydroxide)
- Make sure the solution is “crystal clear” prior to analysis
  - If the particulate is <8microns, varying amounts of Sn will reach the plasma → low or sporadic results
  - You can test for a semi-colloidal suspension by running the solution through a micron filter (0.3micron Millipore) which will break up the semi-colloidal suspension, allowing it to make it into the system (signal will increase)
  - Again, the best option is to add HF to stabilize

Rinse solutions

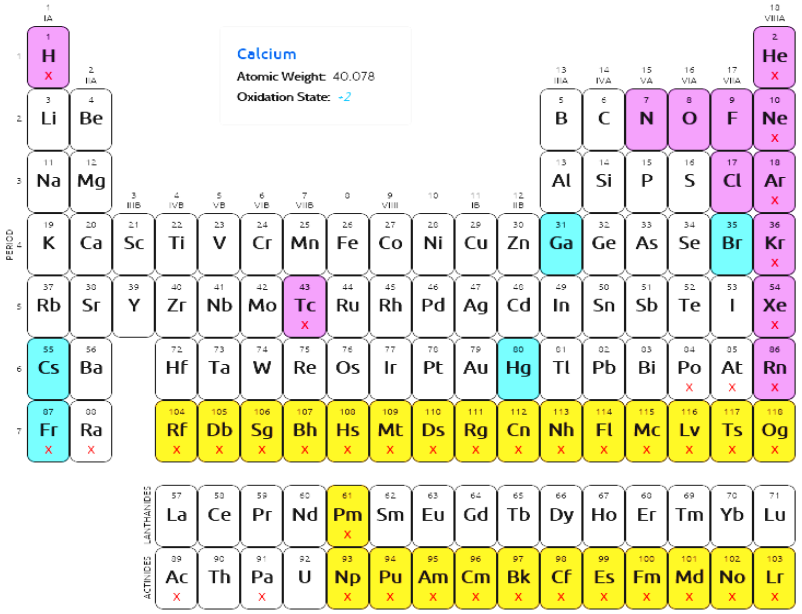


- Sticking is more of an issue for MS than OES
- Start out with 10-20% HCl
- Adding HF to the rinse solution will help purge Sn from the system
  - HF limits:
    - 0.1-2% v/v for OES
    - 0.05-0.5% v/v for MS
    - Max of 0.2% v/v HF for borosilicate glass nebulizer and spray chamber (B and Si results will be unreliable)
    - Up to 2-3% v/v HF for HF-resistant systems (>3% HF will degrade the coating)
- Replace tubing

*For more information go to Technical Videos | Ask a Chemist (inorganicventures.com) and check out our webinar “Aggravations in the lab: Solving Troubles with Tin and Mercury”

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.