WEBINAR

AGGRAVATIONS IN THE LAB: Solving Troubles with Tin and Mercury

THURSDAY, MAY 6
11:00AM–NOON EST

SPEAKERS:

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Chairman, Board of Directors

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Presentation Author

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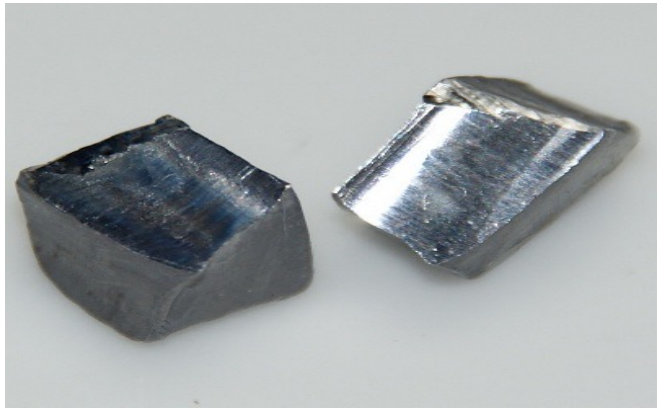
Issues with analyzing Mercury (Hg)

- Keeping Hg in solution
- Sample preparation
- ICP issues

Issues with analyzing Tin (Sn)

- Keeping Sn in solution
- Sample preparation
- ICP issues



Analyzing Hg

- Hg is one of the “problem-elements” and causes numerous problems/concerns for trace metals analysts
- Trace Hg analysis has many applications, including environmental, pharmaceutical, food/beverage, dental, emissions/air quality, consumer products, clinical, and more.
- Common methods:
  - EPA Methods: 200.8, 6020A, 3052, 1631E, 7473, 7470A, 7471B
  - USP 232/233 and ICH/Q3D
- Most questions related to ICP analysis of Hg
- **Hg MUST be in the Hg^{+2} form for accurate ICP measurements!**

Question #1

Which industry is your organization in?

A. Pharmaceutical
B. Environmental
C. Food/Beverage
D. Consumer Products
E. Petroleum
F. Mining
G. Medical
H. Dental
I. Other

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)

The Crux of the Matter

$Hg^0 + HNO_3 \rightarrow Hg^{2+} + NO_2$(brown fumes) + xs HNO_3 + heat to expel NO_2 $\rightarrow Hg^{2+}$ + xs HNO_3

$\rightarrow$Dilute with H_2O to make stock products/concentrates

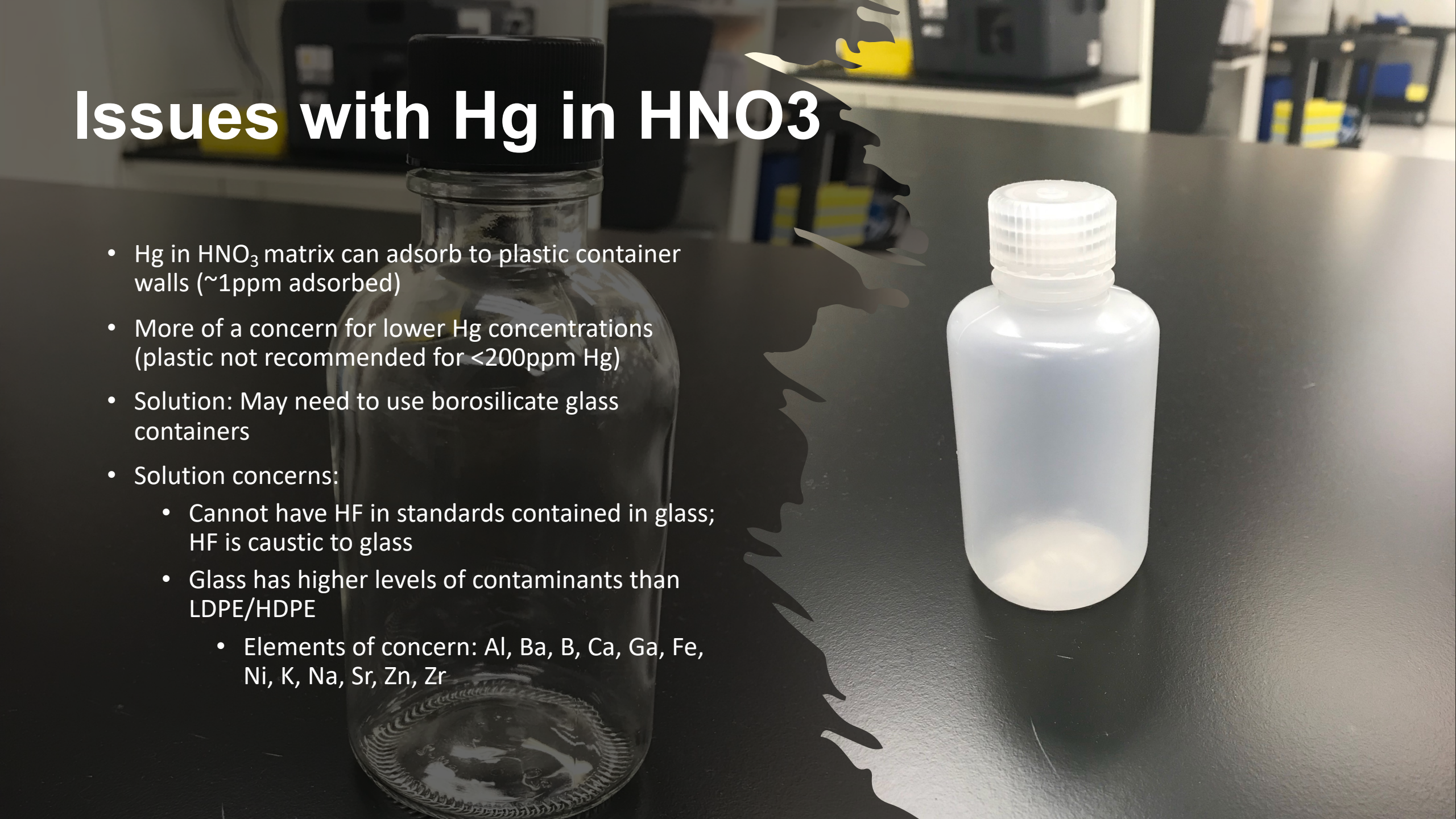
$Hg^0 + HNO_3 \rightarrow Hg^{2+} + NO_2$ + xs HNO_3

$\rightarrow$Dilute $H_2O \rightarrow 2Hg^{2+} + NO_2 \rightarrow Hg_2^{2+} + H_2O$

$Hg_2^{2+} + H_2O + HCl \rightarrow Hg^0 + Hg^{2+}$

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: https://www.inorganicventures.com/pub/media/wysiwyg/files/mercury_preservation_techniques.pdf)
- 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 Fresquez MR, Pappas RS, Watson CH. Establishment of Toxic Metal Reference Range in Tobacco from U.S. Cigarettes. J. Anal. Toxicol. 2013;37:298-304.)

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

Sample Preparation

Use a closed vessel or condenser for acid digestions

Avoid ashing! (Volatility and Toxicity of Hg^0)

For metal or oxide: dissolve in HNO3

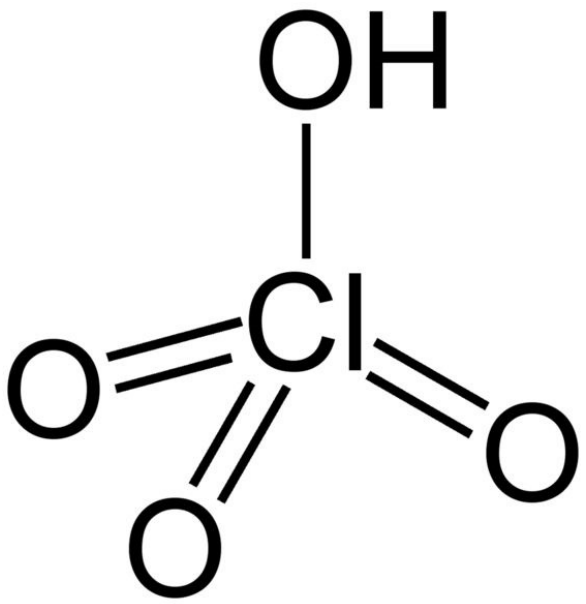
Organics: more complicated!

Sample Preparation: Organics

- **Extremely toxic**! Please use extreme caution when working with organomercury compounds.
- Must be kept in solution with oxidizing agent to prevent loss as the metallic form!
- Hg in biological material: heat with H_2SO_4 or HNO_3 or both and potassium permanganate (in excess)
  - Oxidizing agent: permanganate
  - H_2SO_4 alone may not fully free all Hg
  - Use a closed vessel!
  - Low heat (~50-60^{0}C)
- *Can also use perchloric acid instead of permanganate
- Microwave digestion method based on EPA Method 3051a (for sediments, sludges, soils, and oils)

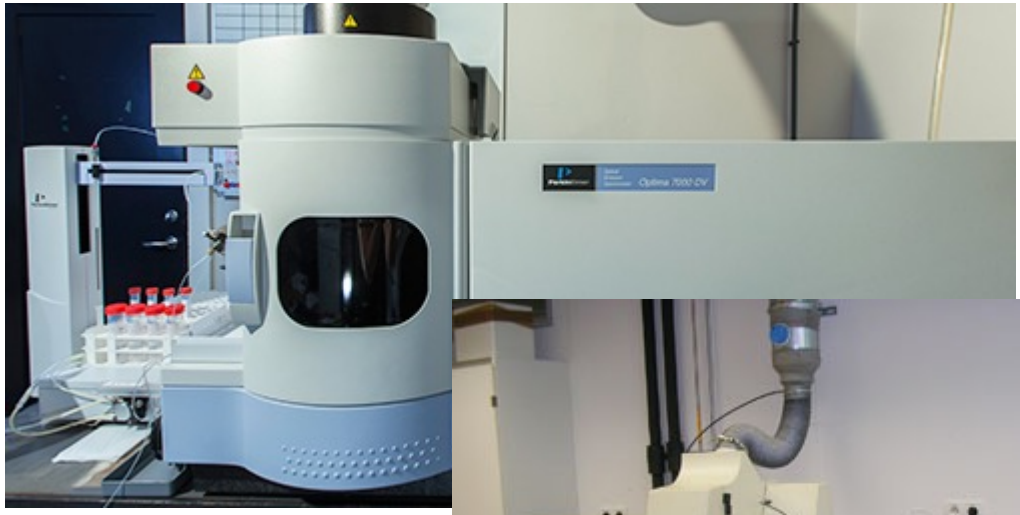
Paul's thoughts/suggestions for using Perchloric Acid

For tips and safe use of perchloric acid and other acid digestions, please see Section 12 of our Trace Analysis Guide: https://www.inorganicventures.com/trace-analysis-guide/acid-digestions-of-organic-samples



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

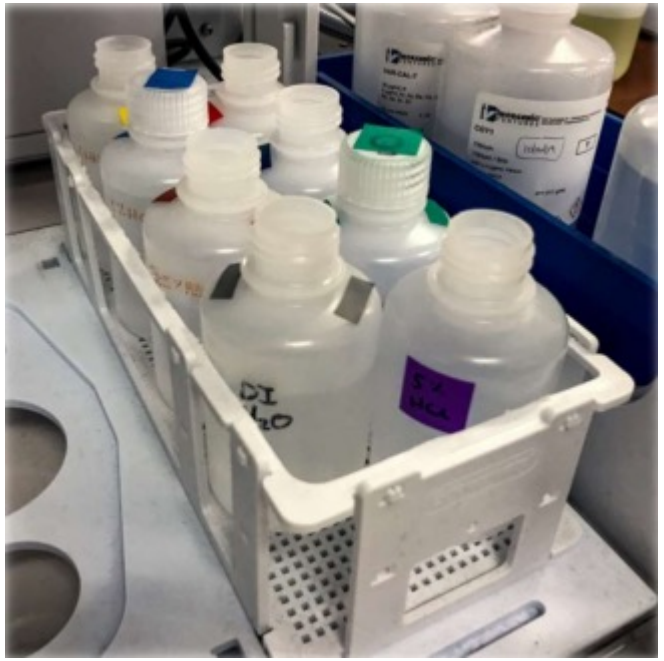
Question #2

Do you use ICP-OES or ICP-MS for your analyses?

A. OES only
B. MS only
C. We use both!

Rinse solutions

- For OES, we recommend reconditioning the spray chamber surface with RBS™-25 (2.5%) → will make the surface less “sticky”
  - Not recommended for MS (high Na)
- Sample lines are the main issue for Hg sticking (especially PVC tubing)
- 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



Interferences

Atomic Spectroscopic Information: (red text indicates severe at ~ concs.)

Technique / Line	Estimated D.L.*	Order	Type	Interferences
ICP-OES 184.950 nm	0.03/.005 µg/mL	1	atom	
ICP-OES 194.227 nm	0.03/.005 µg/mL	1	ion	V
ICP-OES 253.652 nm	0.1 /.03 µg/mL	1	atom	Ta, Co, Th ,Rh , Fe, U
ICP-MS 202 amu	9 ppt	n/a	M^+	$^{186}W^{16}O$

*ICP-OES D.L.'s are given as radial / axial view

Additional preferred lines:
ICP-OES: 435.835 nm
ICP-MS: 199amu, 200amu, *201amu (best line if W is in the sample, do not use if Re is in sample)

On the horizon for Hg testing applications

- More applications in Cannabis testing as the cannabis industry broadens and products become more strictly regulated
- Baby Food Safety Act of 2021: consistent limits across all manufacturers for heavy metals in baby foods (https://www.cnn.com/2021/03/25/health/baby-food-toxic-metals-legislation-wellness/index.html)
  - All products tested instead of just individual ingredients
  - Heavy metals have neurotoxic effects which are of particular concern for a babies developing brain.

Why Tin?

- Common applications for Sn:
  - Plating
  - Mining
  - Coating for food containers/cookware
  - Solder
  - Pharmaceutical (USP 232, Class 3)
  - Dental
  - Environmental
  - Manufacturing
  - Consumer products
  - Much more

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+}
- 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.

Question #3

Does your company allow the use of HF in the lab?

A. Yes!

B. No – HF is not allowed.

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

Sample Preparation: Metal

- Soluble in HNO3/HF and HCl
- For HCl: keep vessel closed or heat under reflux
  - Loss of tin(IV) chloride is a concern
  - BP of tin(IV) chloride is only 114^{O}C

The Crux of the Matter

(Sn^{+2}) (Sn^{+4})

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

Sample Preparation: Alloys

- First treat with concentrated H_2SO_4 (~100mL per 1 gram of sample)
- Boil until alloy disintegrates and nearly all H_2SO_4 is expelled
- Then add either water and concentrated HCl (2:1 ratio), or concentrated HF (~10mL per 1g sample) and heat gently
- If using HF, must first transfer to a plastic container!

Sample Preparation: Ores

- Fusion with Na_2CO_3, followed by dissolution with HCl and a small amount of HF
  - Na_2CO_3 is clean, easy to use, and allows for use of Pt crucible (much better than using Ni or Fe crucibles)
- Other fusion mixtures:
  - Na_2S + S (after oxidation with HNO3)
  - Na_2O_2 + NaOH
- Please use extreme caution when using Na_2O_2! Very dangerous!

Paul's thoughts on using Na_2CO_3 for fusion mixtures

Sample Preparation: Organotin compounds

- **Toxic!**
- Volatility of the tetrachloride and precipitation of the insoluble stannic oxide are problems
- Dry ashing is not recommended because of errors with volitization of $SnCl_4$ or reaction between SnO_2 and the crucible

Sample Preparation: Organotin compounds cont.

- Oxidation w/ H_2O_2 and H_2SO_4: Heat w/ conc H_2SO_4 to fumes, then add 30% H_2O_2 **dropwise** to finish oxidation
- Make sure there is always an EXCESS of H_2SO_4
- Be ***patient*** and proceed ***slowly***!
- Take extra precaution when using this method to avoid build-up of H_2O_2 in the mixture → can lead to an explosion!
- Works well for PVC

Sample Preparation: Oxide

- SnO - soluble in HCl
- SnO_2 - very resistant to all acids including HF!
  - Fusion with Na_2CO_3, followed by dissolution in HCl or HCl/HF is the best option
  - Fusion with equal parts of Na_2CO_3 and S is also soluble in water or dilute acids as the thiostannate

Question #4

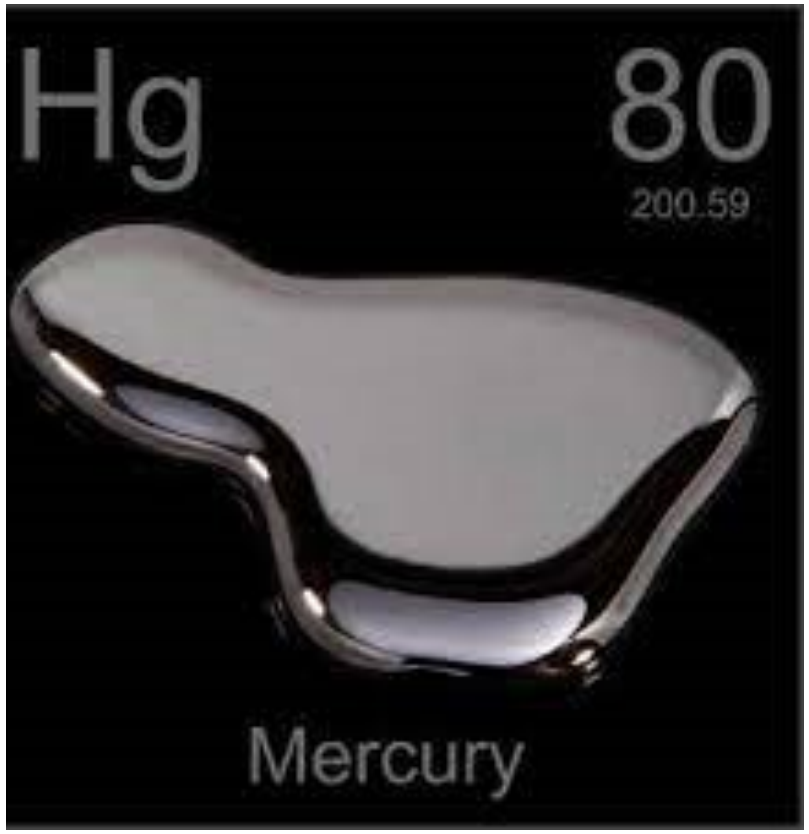
Do you have an HF-resistant introduction system on your instrument?

A. Yes

B. No, our intro system has glass components

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



Paul’s Suggestions for switching out wash solution after using TEA

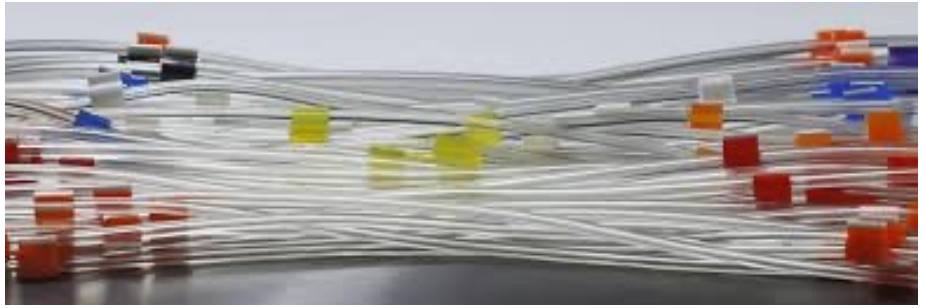
Running Sn solutions on ICP cont.

- 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

Interferences

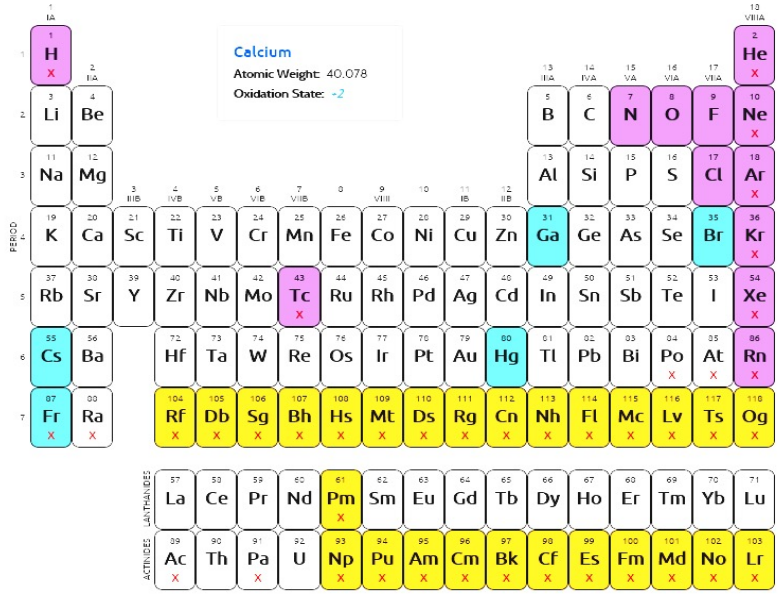
Atomic Spectroscopic Information: (red text indicates severe at ~ concs.)

Technique / Line	Estimated D.L.*	Order	Type	Interferences
ICP-OES 189.989 nm	0.03/.003 µg/mL	1	ion	Gd
ICP-OES 242.949 nm	0.1/.01 µg/mL	1	atom	W, Mo, Rh ,Ta, Co
ICP-MS 120 amu	5 ppt	n/a	M^+	^{120}Te, $^{104}Ru^{16}O$, $^{104}Pd^{16}O$

*ICP-OES D.L.'s are given as radial / axial view

- The 189.926 nm line is the best with respect to sensitivity and freedom from spectral interference
- Wavelength (189.926 nm or 189.989 nm) will depend on the type of grating
- For MS, also check 117, 118, and 119 amu

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.