

# BE BOLD

2022 INORGANIC VENTURES WEBINAR SERIES

## A SYNOPSIS OF ICP Washout Techniques

**THURSDAY, JANUARY 20**  
**9:00–9:30AM EST**



PRESENTED BY:  
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Manager, Quality Control

# Key Topics

- Causes for washout issues
- Introduction system components
- Elements of concern
- Common rinse solutions / strategies
- Maintenance recommendations



# Causes for washout issues

- Solution matrix ( $\text{HNO}_3/\text{HCl}/\text{HF}/\text{NH}_4\text{OH}$ )
  - Could be from commercially available standards
  - Could be from specific sample preparation protocols
- Specific elemental affinity toward different types of plastics (Pump tubing, HF-resistant intro system)
- Spray chamber design (Single-pass, double-pass)
- Rinse protocols using the wrong acids/bases
- Rinse times are not long enough

# Solution Matrix

- Most elements are stable using only  $\text{HNO}_3$
- Some elements require HF for stability
  - HF stability often revolves around plastic surfaces
  - Some elements will precipitate in the presence of HF
- Some elements require HCl for stability
  - Only a few elements have issues in the presence of HCl
- Bromide/Iodide require basic matrices for stability
  - Some other elements are stable in basic pH



# Solution Matrix - HF

H	Not Checked by ICP																HF Elements					He						
Li	Be	HF "thieves"																Avoid HF					B	C	N	O	F	Ne
Na	Mg																	Al	Si	P	S	Cl	Ar					
K	Ca		Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr										
Rb	Sr		Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe										
Cs	Ba	*	Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn										
Fr	Ra	**	Lr	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	Nh	Fl	Mc	Lv	Ts	Og										

*	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb
**	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No

# Solution Matrix - HCl

H	Not Checked by ICP																HCl Elements					He						
Li	Be	Can work w/o HF																Avoid HCl					B	C	N	O	F	Ne
Na	Mg																	Al	Si	P	S	Cl	Ar					
K	Ca		Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr										
Rb	Sr		Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe										
Cs	Ba	*	Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn										
Fr	Ra	**	Lr	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	Nh	Fl	Mc	Lv	Ts	Og										

*	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb
**	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No

# Solution Matrix – TEA/NH<sub>4</sub>OH/H<sub>2</sub>O

H	Not Checked by ICP																Basic Elements					He	
Li	Be	Can work w/o HNO <sub>3</sub> /HF, but must be basic																B	C	N	O	F	Ne
Na	Mg																	Al	Si	P	S	Cl	Ar
K	Ca		Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr					
Rb	Sr		Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe					
Cs	Ba	*	Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn					
Fr	Ra	**	Lr	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	Nh	Fl	Mc	Lv	Ts	Og					

*	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb
**	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No

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# Spray Chambers

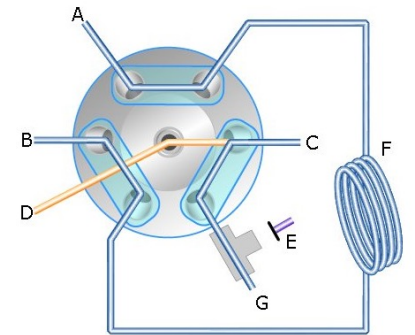
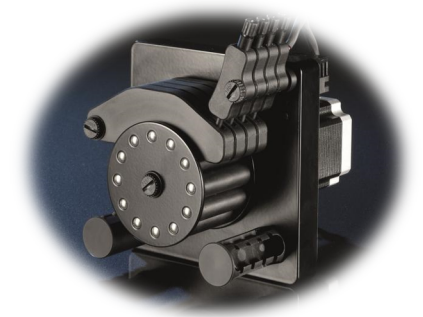
- Classical borosilicate glass
  - If HF is used, problems testing B and Si
  - B and Si will leach out of the spray chamber
- HF Resistant Systems (PTFE/PFA)
  - If high levels are run, B, Si, and Hg can stick around
  - No leaching of B and Si from the material
  - Coating is essential to help with performance
- Double pass spray chambers increase washout time significantly



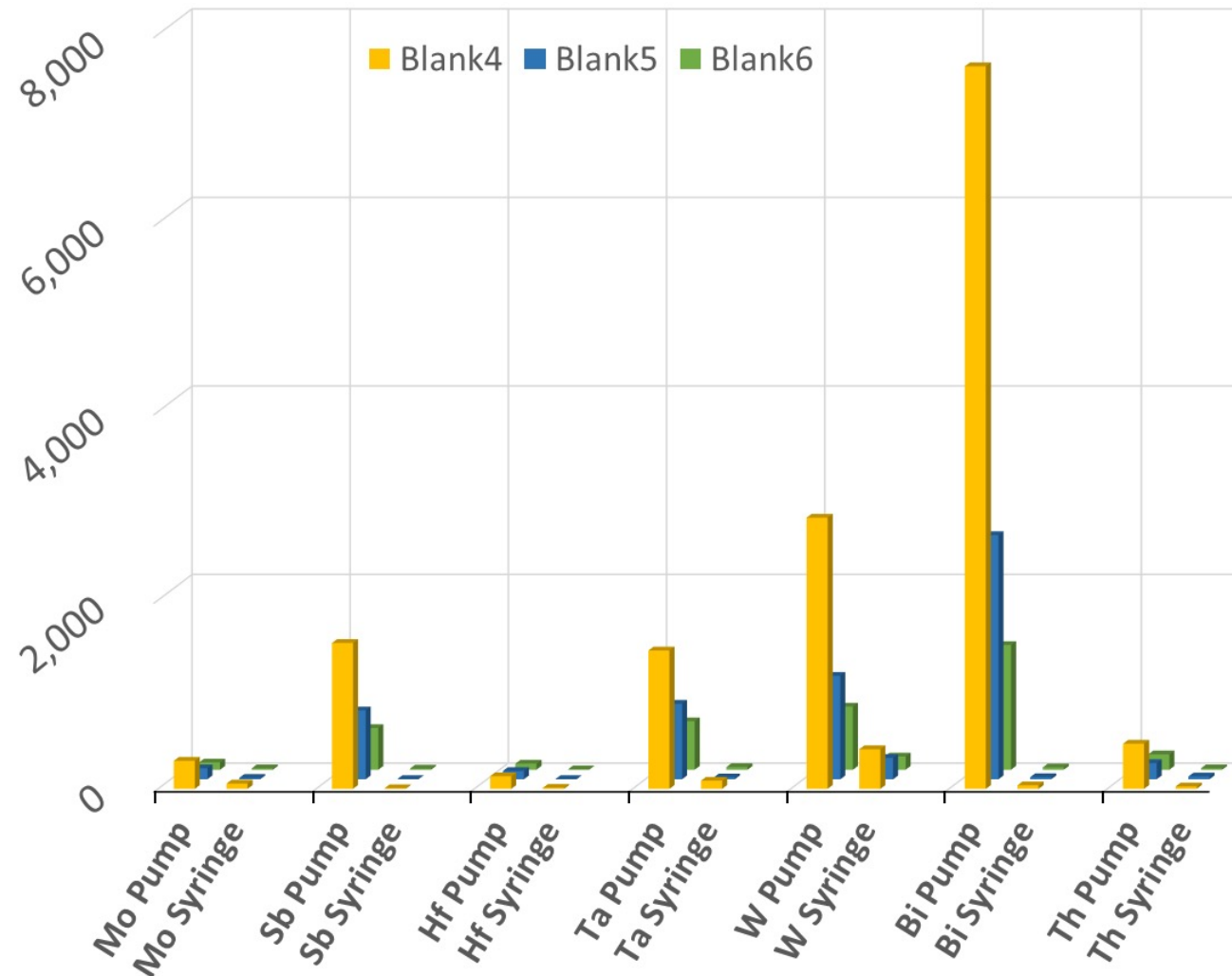


# Sample Delivery

- **Peristaltic Pump**
  - Sample is introduced from autosampler probe through peristaltic pump tubing before it reaches the nebulizer
  - Many elements stick to the PVC peristaltic pump tubing
- **Syringe Drive / Switching Valve Systems**
  - Sample is loaded into a sample loop without passing through peristaltic pump tubing
  - PVC tubing is eliminated, but a switching valve is added to the equation



- Washout of select “sticky” elements after a 4ppb spike containing over 60 elements.
- Bi is by far the worst.
- PVC tubing is used for peri-pump introduction systems.
- Faster washout of elements using syringe drive systems allows us to run more samples free of “memory” interferences.
- This results in less maintenance when running high TDS samples.



# Key Topics

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# Problem Elements

H	Not Checked by ICP																Elements with washout issues																He						
Li	Be																																	B	C	N	O	F	Ne
Na	Mg																																	Al	Si	P	S	Cl	Ar
K	Ca			Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr																				
Rb	Sr			Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe																				
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# Why?

H	Not sure, PVC tubing?																HNO <sub>3</sub> makes it sticky																He						
Li	Be	Lack of HF makes it sticky																HCl makes it precipitate																B	C	N	O	F	Ne
Na	Mg																	Al	Si	P	S	Cl	Ar																
K	Ca		Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr																					
Rb	Sr		Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe																					
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# Common Rinse Solutions

- $\text{HNO}_3$

- 5-10% on an OES
- 1-2% on a MS

- $\text{HCl}$

- 5-10% on an OES
- 1-2% on a MS

- RBS-25

- 2.5% on an OES
- Not Recommended on MS due to high Sodium

- $\text{H}_2\text{O}$

- Can be effective enough for Na, K, Ca, etc.

# Rinse Solutions with HF

- $\text{HNO}_3$

- 5-10% on an OES
- 1-2% on a MS

- HF

- 0.1-2% on an OES
- 0.05-0.5% on a MS

- If using borosilicate glass nebulizer and spray chamber



- Limit HF to a max of 0.2%
- B and Si results will be unreliable

- If using an HF resistant nebulizer and spray chamber



- Can go up to 2-3%
- >3% HF degrades the coating

# Specialty Rinse Solutions

- $\text{NH}_4\text{OH}$

- 1-5% for OES or MS
- Use for B, Br, I, Hg

- $\text{HCl}$  / Thiourea

- 1-10%  $\text{HCl}$
- 0.5% Thiourea
- Use for Hg, Au, Os

- $\text{HCl}$  / Hydroxylamine· $\text{HCl}$

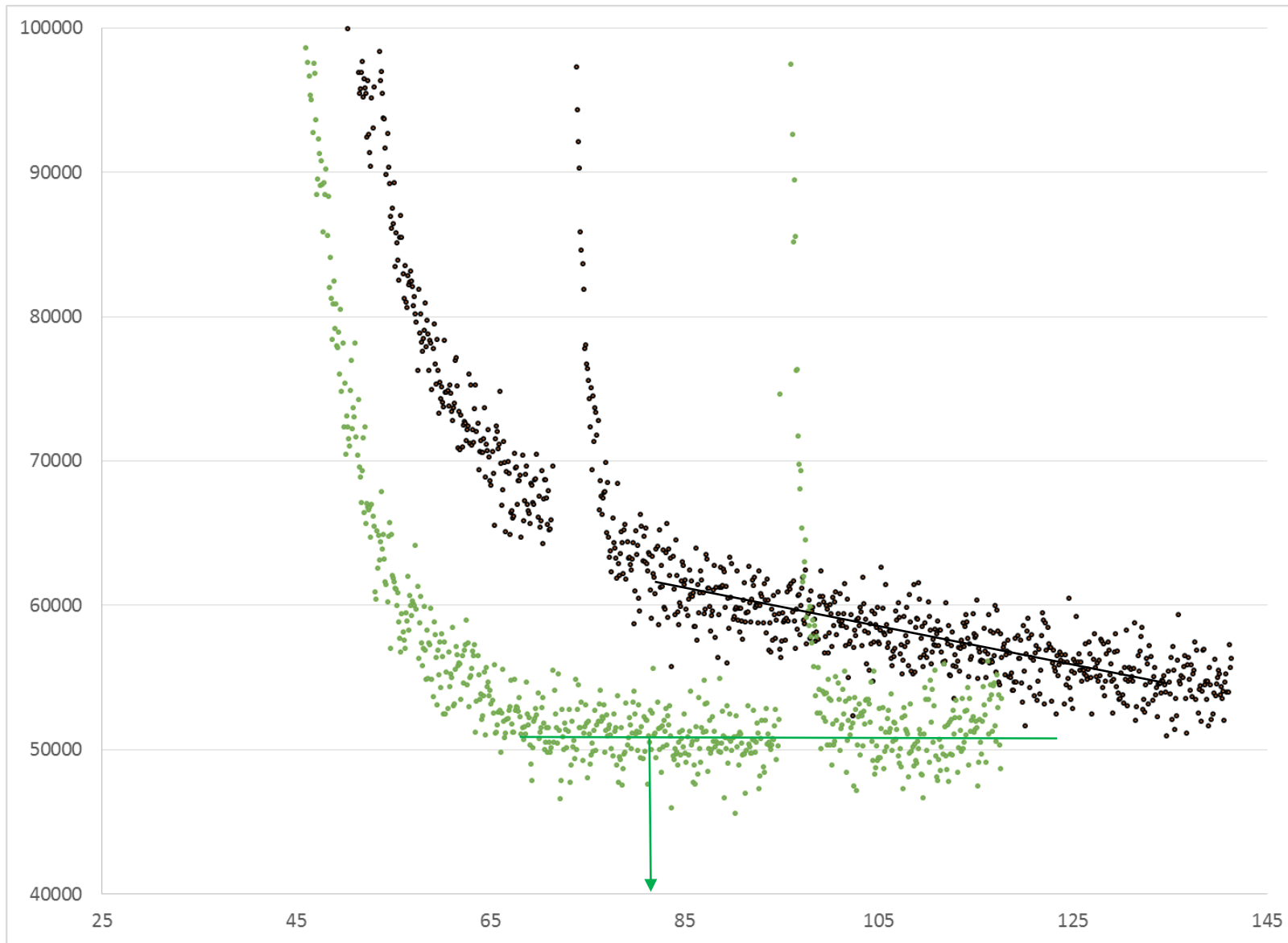
- 10%  $\text{HCl}$
- 0.5%  $\text{NH}_2\text{OH}\cdot\text{HCl}$
- Use for Os

# Utilize real-time output monitoring

- Some instrument software packages allow you to monitor a line in real time and record the signal vs time
- This can help with method development activities in determining appropriate rinse times between samples
- It can also be helpful in assessing the effectiveness of different rinse solutions







Monitoring Washout  
on B 208.959nm

Rinse w/ 5% HNO<sub>3</sub>

Rinse w/ 5% NH<sub>4</sub>OH

5% HNO<sub>3</sub> doesn't go to baseline  
even within 2 minutes.

5% NH<sub>4</sub>OH rinses it out within 80  
seconds.

# Experiment with different rinse strategies

- Switching valve and syringe drive systems pose an extra challenge to washout due to the use of a dedicated carrier solution.
- Most ICP-MS users prefer to use  $\text{HNO}_3$  to prevent  $^{40}\text{Ar}^{35}\text{Cl}^+$  &  $^{40}\text{Ar}^{37}\text{Cl}^+$  from interfering on  $^{75}\text{As}$  &  $^{77}\text{Se}$ .
- Running rinse solutions as samples in varying order can help determine which types of rinses are more effective for certain elements and intro-system setups.

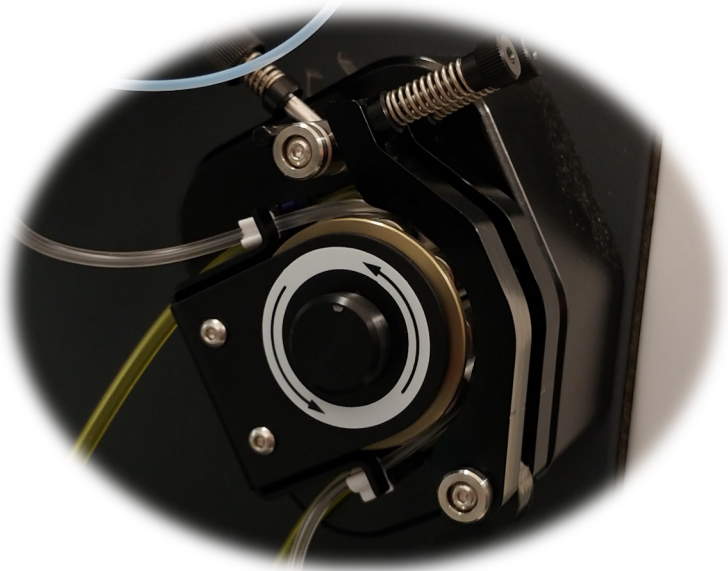
# Key Topics

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- **Maintenance recommendations**

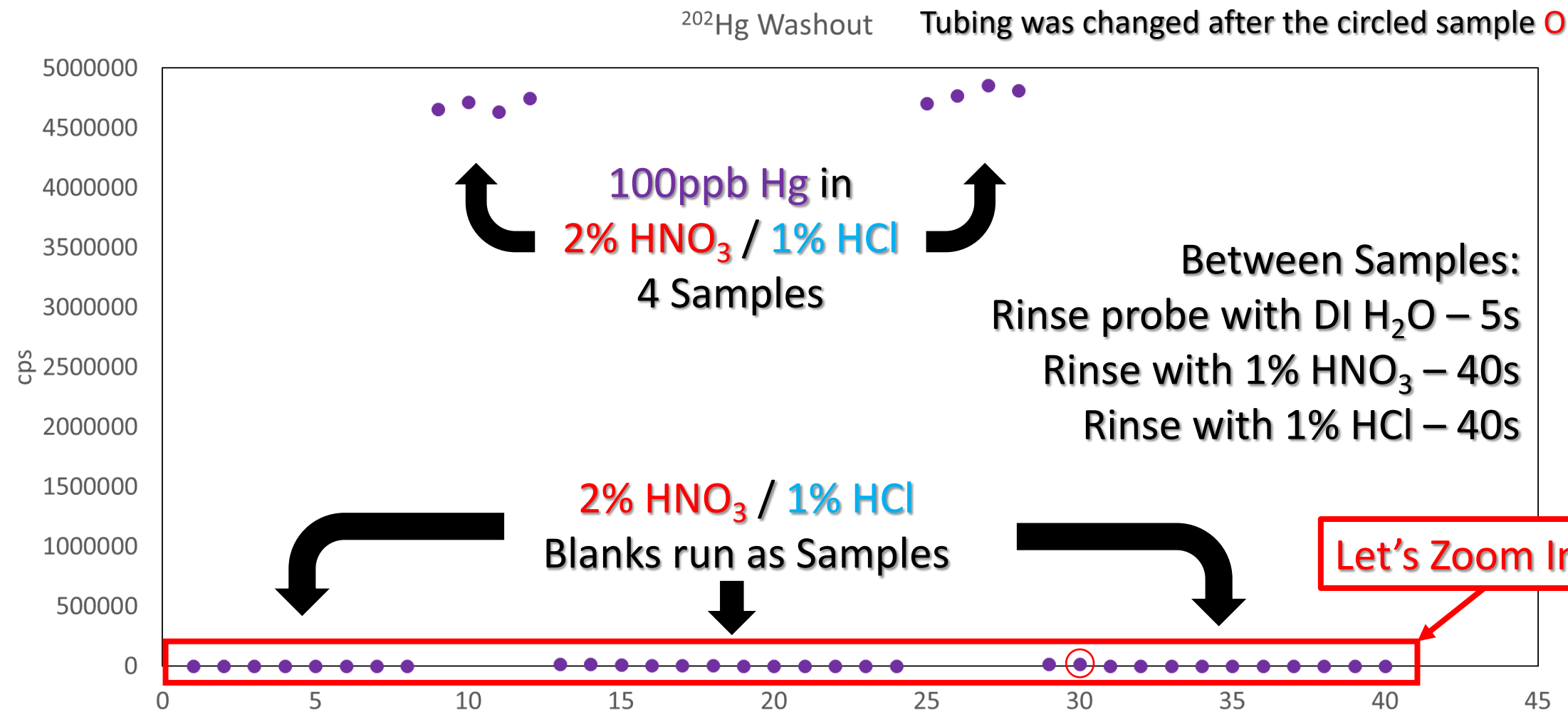


# Peristaltic Pump Tubing

- If using peristaltic pump tubing for sample delivery...
  - Consider changing the tubing daily
  - Or directly after a run with “sticky” elements



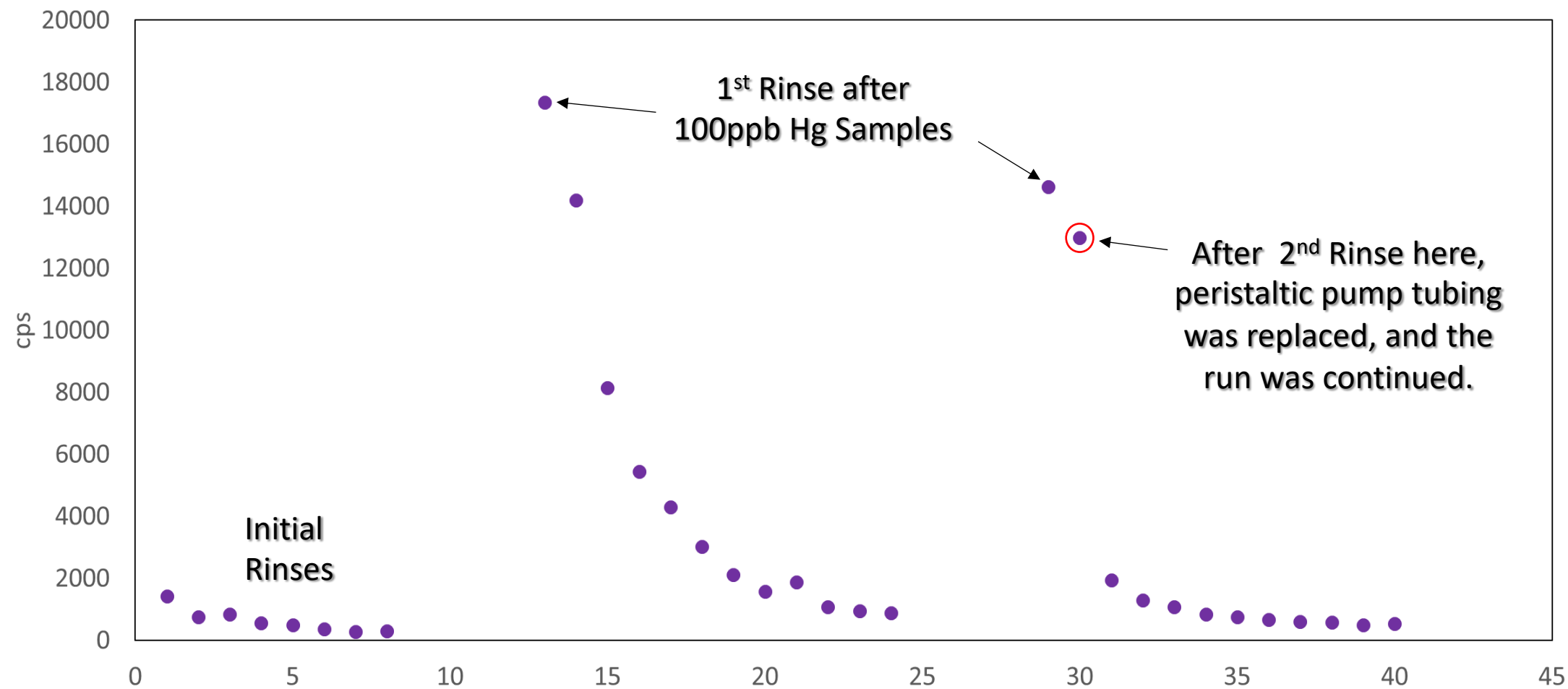
# Example of effect of changing tubing





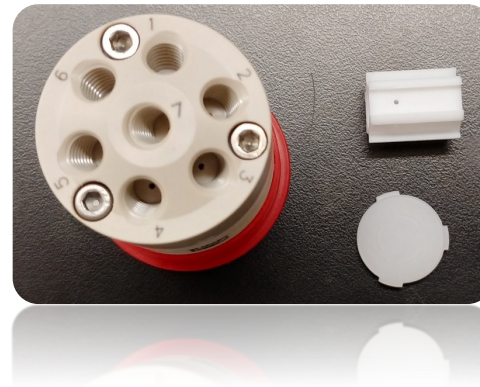
# Example of effect of changing tubing

$^{202}\text{Hg}$  Washout



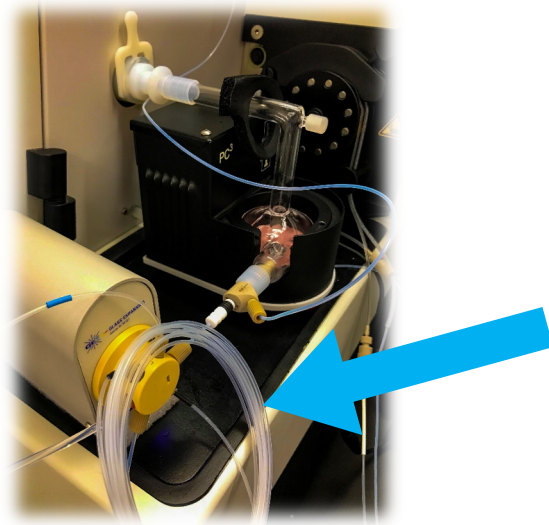
# Switching Valve Systems

- Sample loops do inevitably become dirty
- When not in use, make sure carrier solution flows through the sample loop to continuously clean it
- Replacing valve sleeves can help when routine cleaning no longer helps.



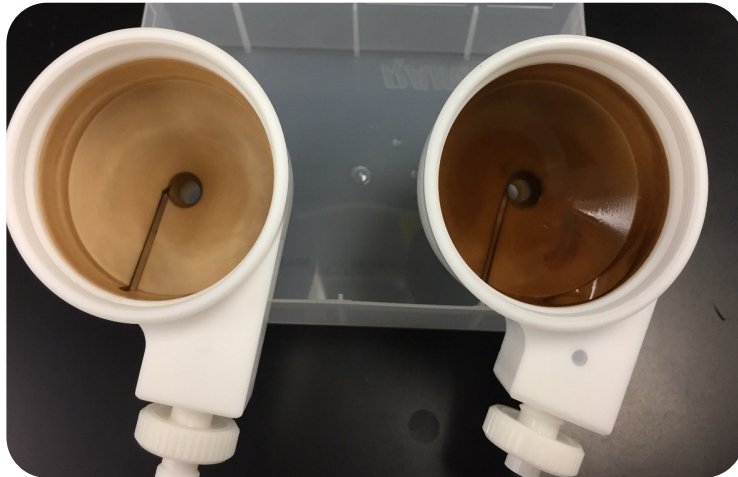
# Switching Valve Systems

- If using a sample loop, shaking the loop while it is rinsing can help clear out stuck elements.
- This phenomenon can be observed using real-time display



# Weekly Soaking of Various Parts

- Soak dirty spray chambers, nebulizers, and valve sleeves in 25% solution of RBS-25.
- Rinse with lots of DI H<sub>2</sub>O.

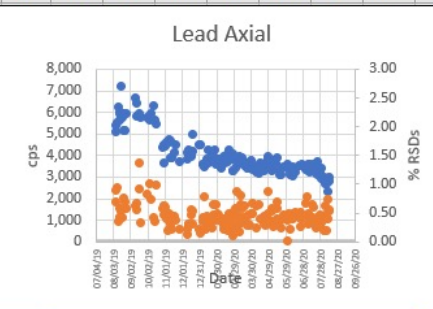
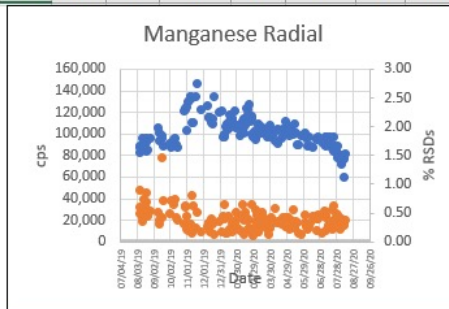
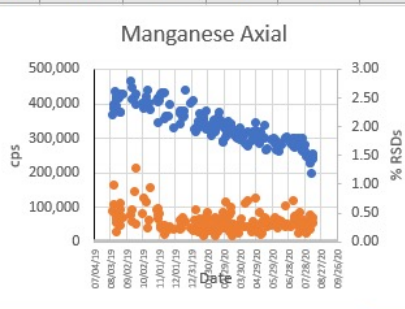
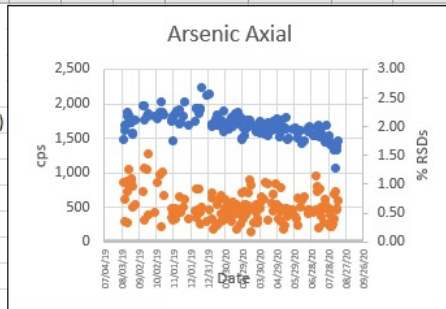


# More tips and tricks for washout issues

- Keep up with routine instrument maintenance to prevent other washout issues.
  - Torch parts, cones/interface, tubing, autosampler probe, rinse station reservoirs
  - Keep a detailed log of maintenance steps and record performance report data



# Example of a Daily Maintenance Log

[illegible]

# Final Thoughts

- Identify the elements that give you trouble
- Experiment with different rinse solutions
- Keep up with routine instrument maintenance
- Identify specific causes for washout issues
- Develop methods that include effective rinse strategies and only the elements you require



# Technical Support – Available to Everyone

## Online Resources at [inorganicventures.com](http://inorganicventures.com)

Periodic table showing elements. Calcium (Ca) is highlighted with a callout box showing its Atomic Weight: 40.078 and Oxidation State: -2.



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.

