WEBINAR

Washout Considerations for ICP Analyses

THURSDAY, MARCH 11
9:00–10:00AM EST

SPEAKERS:

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Production

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Key Topics

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

Audience Participation

- Today we are going to poll the audience throughout the presentation to better understand our collective challenges in the lab.
- Most of these questions will be multiple choice, and we will get to see the results after each question.
- Don’t fall asleep!

Question 1

- What type of instrument do you use in your laboratory?

A. ICP-OES
B. ICP-MS
C. Both ICP-OES & ICP-MS

Causes for washout issues

- Solution matrix (HNO_3/HCl/HF/NH_4OH)
  - 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
- Allowing for the appropriate amount of time to rinse

Solution Matrix

- Most elements are stable using only 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 base without HNO_3/HF

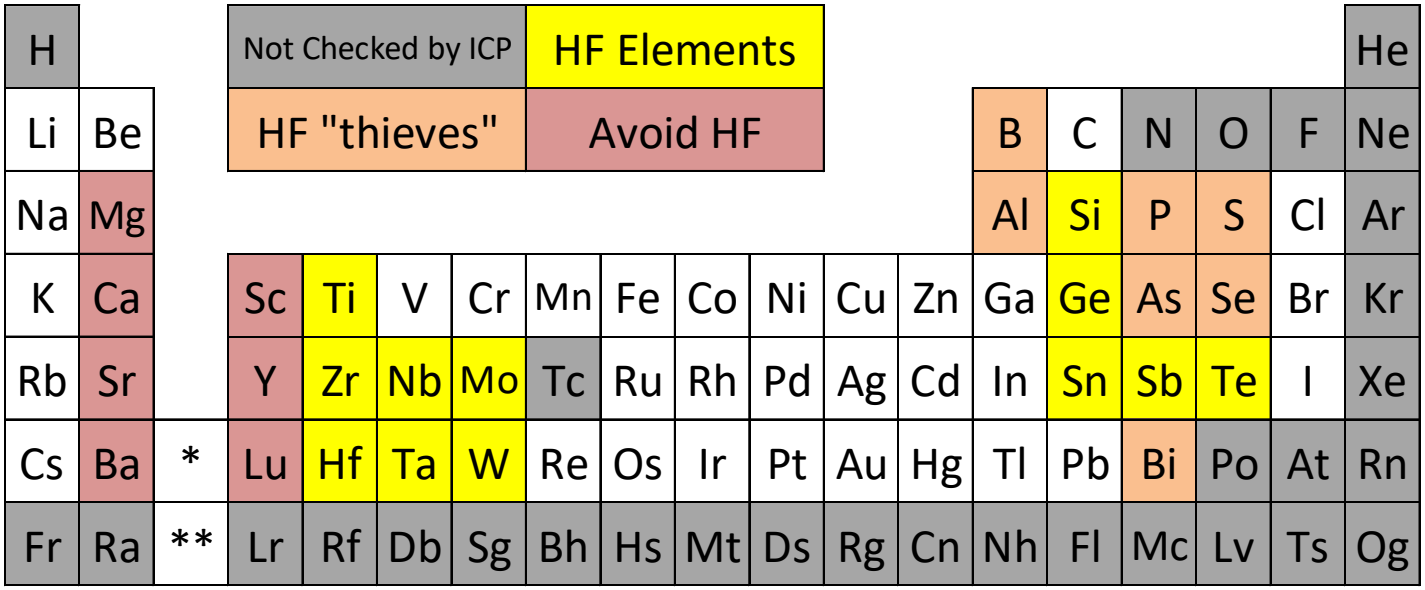
Question 2

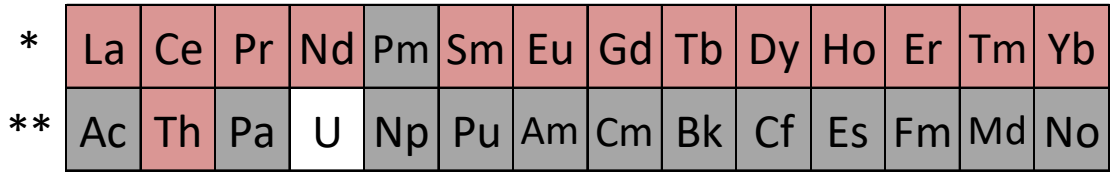
- Does your company forbid the use of HF in the laboratory?

A. Yes – HF is forbidden

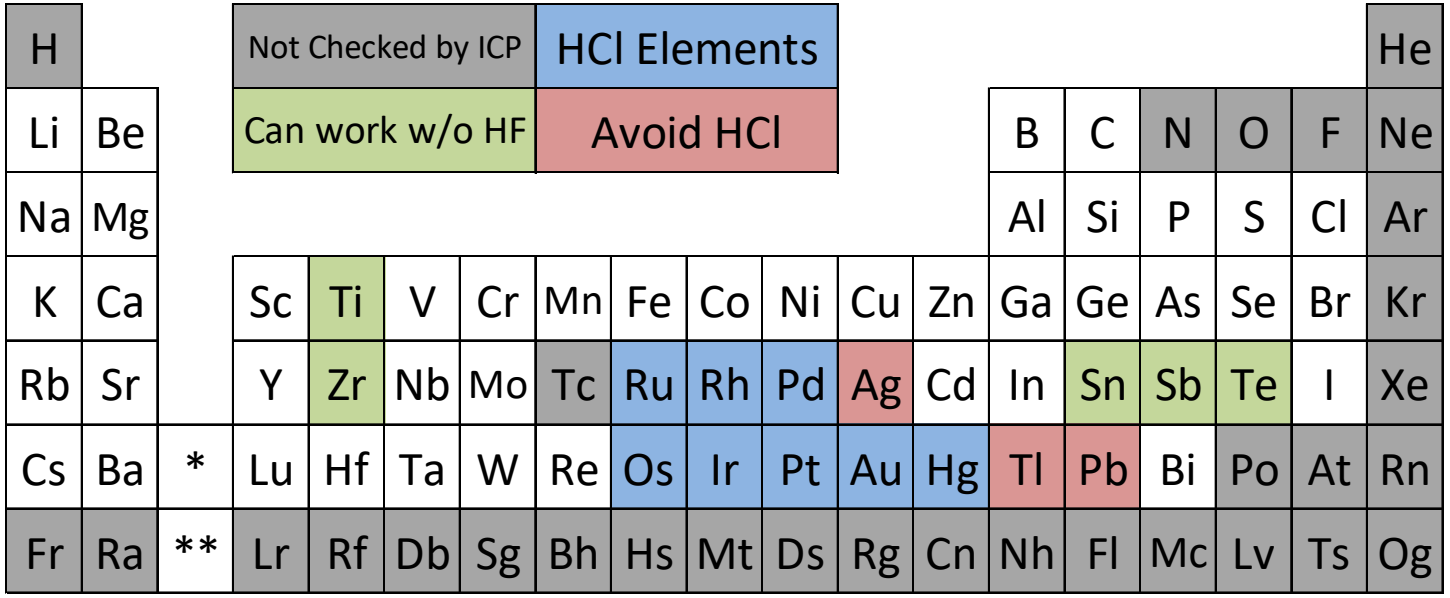
B. No – I can use HF

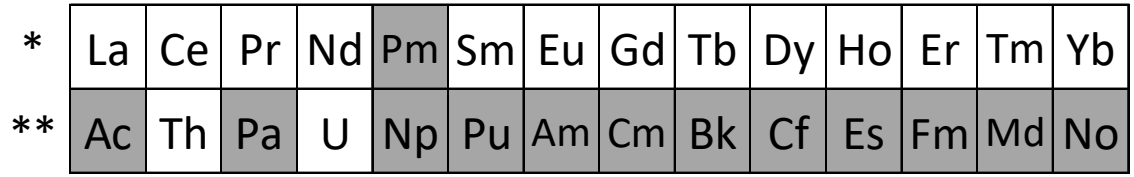
Solution Matrix - HF



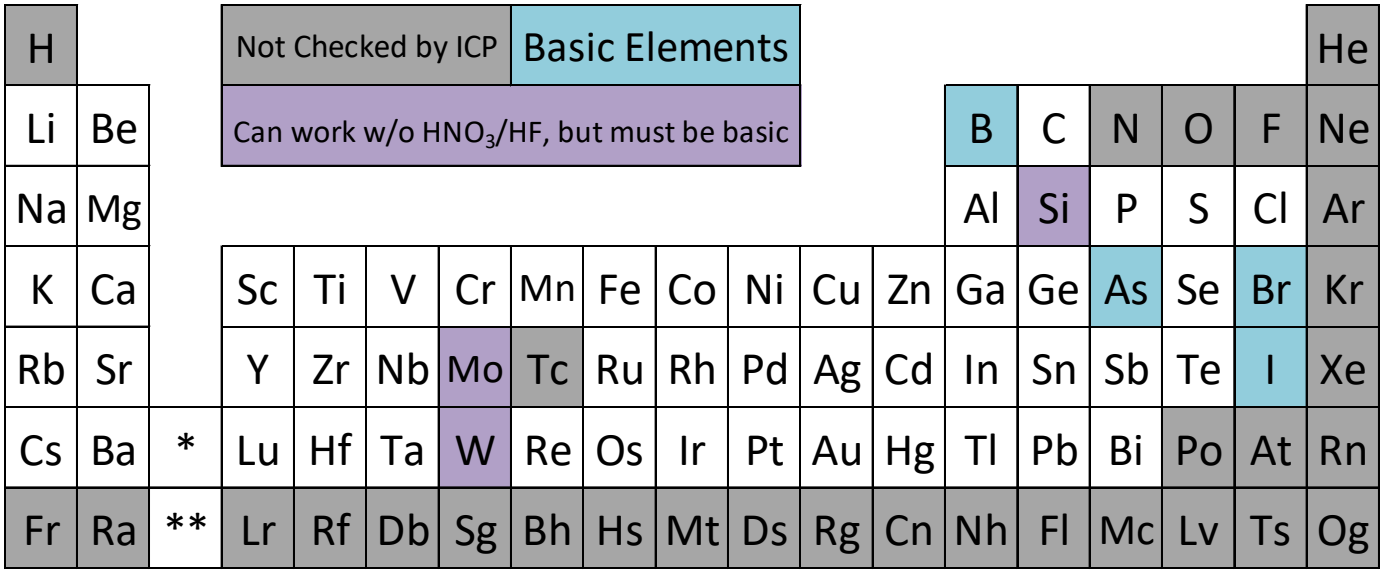


Solution Matrix - HCl





Solution Matrix – TEA/NH_4OH/H_2O



*	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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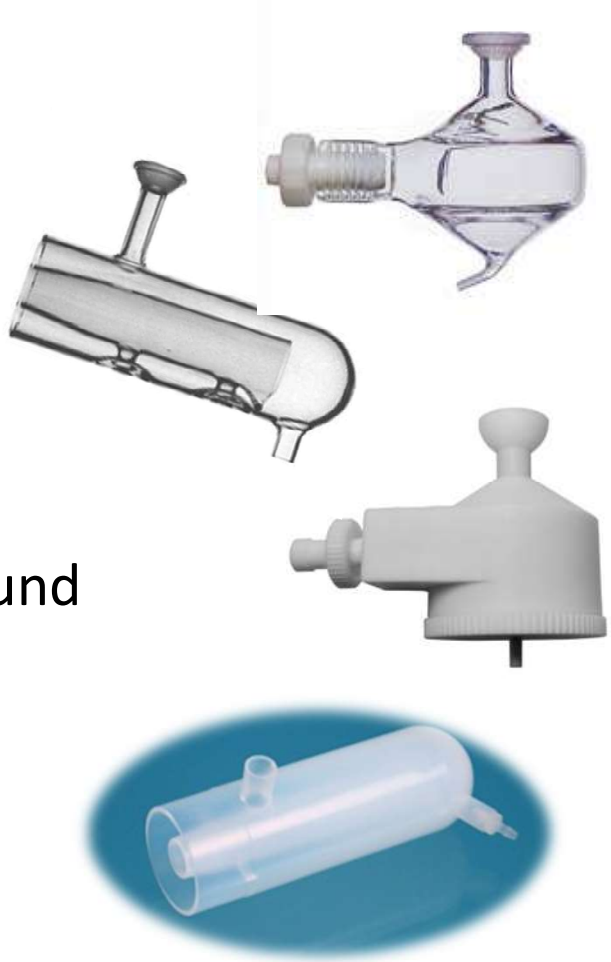
Spray Chambers

- 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



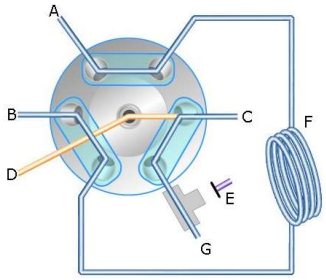
Question 3

- What type of spray chamber do you use on your primary ICP?

A. Borosilicate Glass Cyclonic
B. Borosilicate Glass Scott Style
C. HF-Resistant Teflon Cyclonic
D. HF-Resistant Teflon Scott Style

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

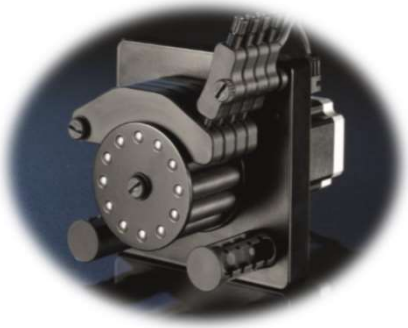
Question 4

- What type of sample delivery system do you use on your primary ICP?

A. Standard Peristaltic Pump
B. Peristaltic Pump with Switching Valve
C. Syringe Drive with Switching Valve

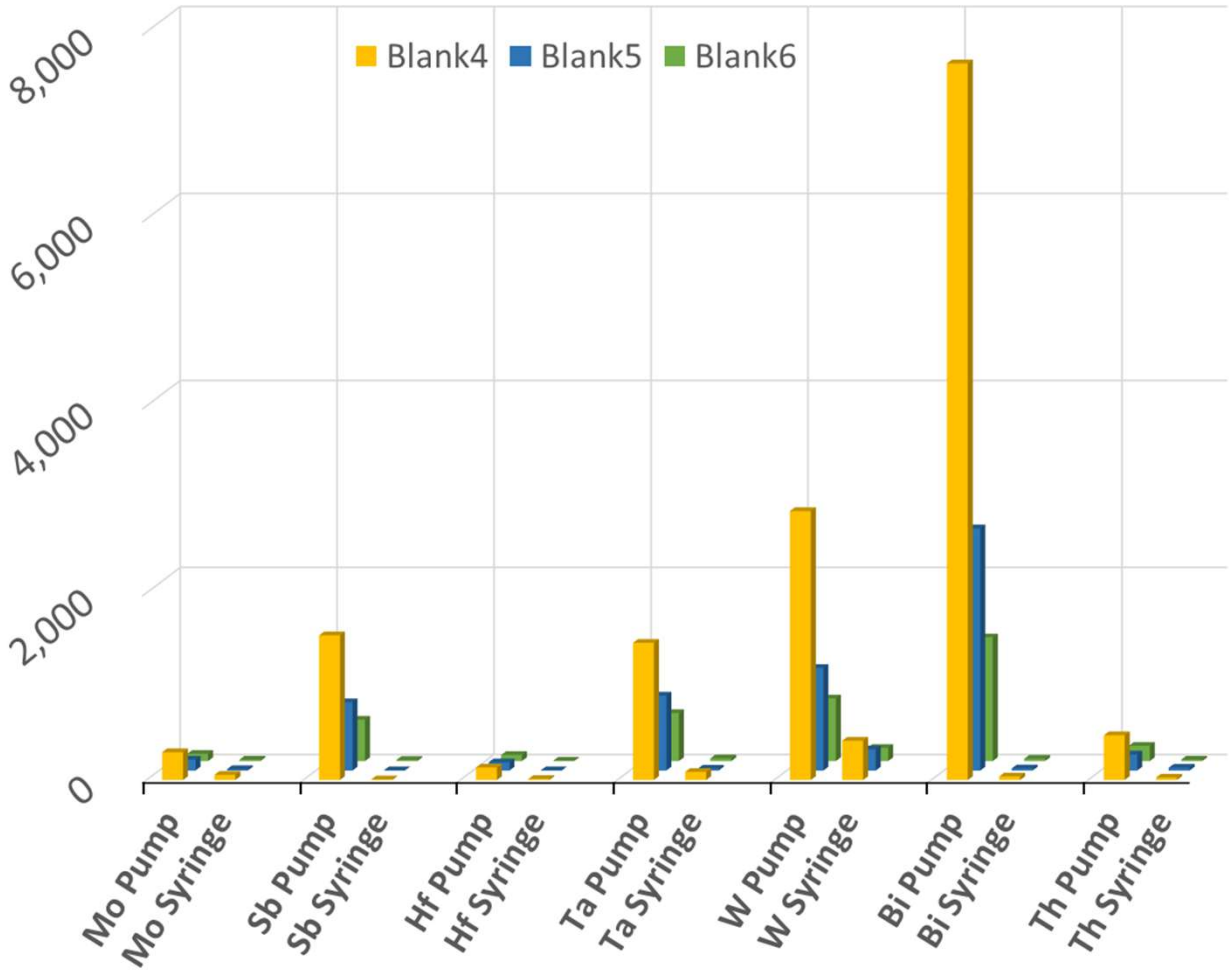
Peri-Pump vs. Syringe Drive on MS

	Blank1	Blank2	Blank3	Sample	+4ppb Spike	Blank4	Blank5	Blank6	
95Mo	6	6	12	1,229	28,443	**297**	**116**	**77**	Peri Pump
95Mo	17	11	13	756	28,443	**56**	**15**	**15**	Syringe Drive
121Sb	17	9	23	437	70,605	**1,547**	**731**	**443**	Peri Pump
121Sb	9	2	4	193	70,605	**7**	**2**	**11**	Syringe Drive
178Hf	36	18	26	5	134,673	**134**	**87**	**64**	Peri Pump
178Hf	0	0	0	4	134,673	**11**	**2**	**4**	Syringe Drive
181Ta	34	55	43	27	461,654	**1,467**	**801**	**514**	Peri Pump
181Ta	20	13	11	7	461,654	**87**	**20**	**29**	Syringe Drive
184W	85	58	58	394	127,417	**2,876**	**1,097**	**669**	Peri Pump
184W	35	26	44	150	127,417	**420**	**226**	**141**	Syringe Drive
209Bi	78	75	50	131	271,275	**7,664**	**2,590**	**1,323**	Peri Pump
209Bi	18	18	31	51	271,275	**38**	**22**	**24**	Syringe Drive
232Th	5	35	12	1,467	349,163	**478**	**173**	**163**	Peri Pump
232Th	15	7	6	15	349,163	**26**	**30**	**15**	Syringe Drive



The sample run in this example is 100µg/g Mn in 1% v/v HNO_3.

- 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.



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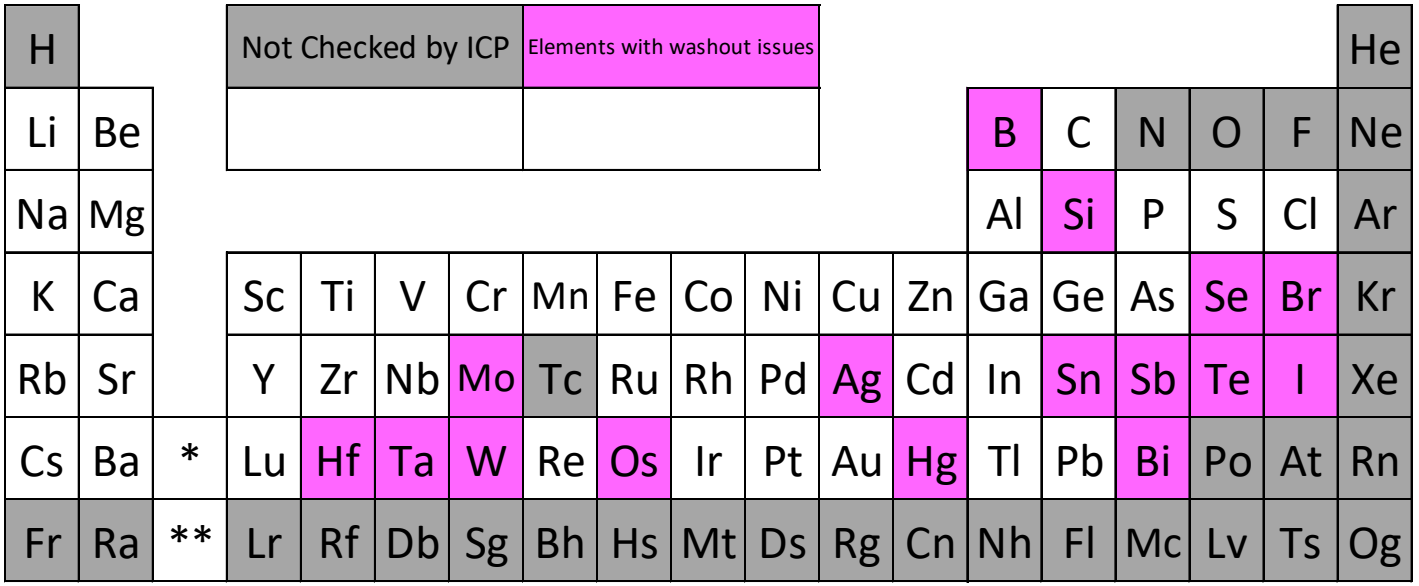
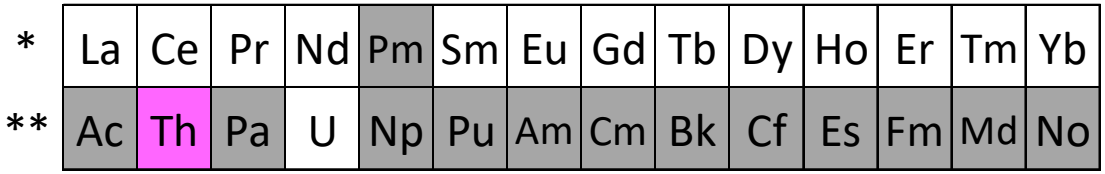
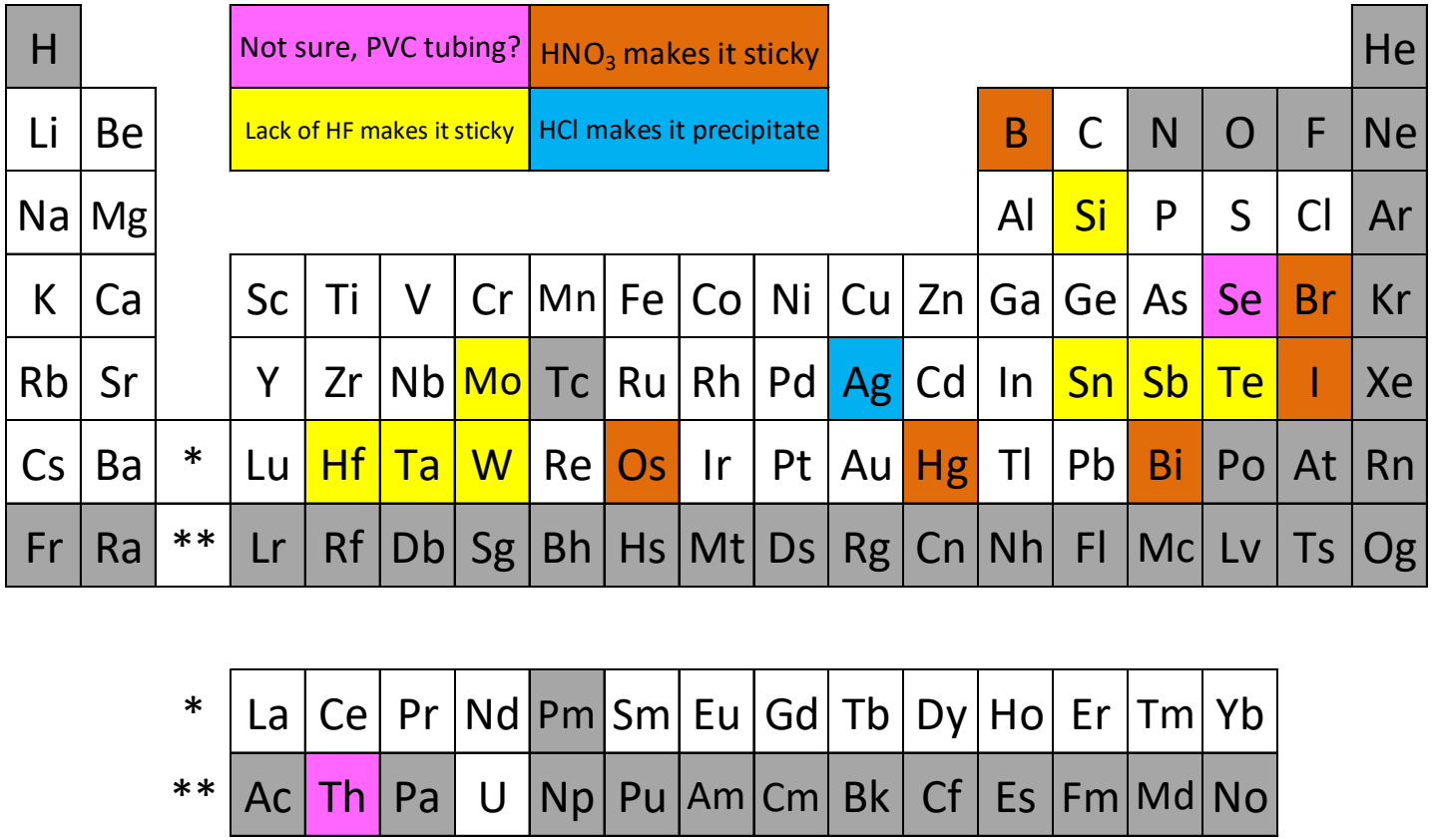
Problem Elements





Why?


Not sure, PVC tubing?
HNO_3 makes it sticky
Lack of HF makes it sticky
HCl makes it precipitate
H
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
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Lr
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Tb
Dy
Ho
Er
Tm
Yb
**
Ac
Th
Pa
U
Np
Pu
Am
Cm
Bk
Cf
Es
Fm
Md
No

Are you running elements you don’t need?

- Custom solutions can help you rid your analyses of unnecessary problematic elements
- Concentration ranges can be high (for user dilution)
- Or they can be ready made to save time at the bench
- IV can ensure that your solutions will be stable and suitable for your methods
- We can even make recommendations for elemental/matrix compatibility

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Common Rinse Solutions

- HNO_3
  - 5-10% on an OES
  - 1-2% on a MS
- 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
- H_2O
  - Can be effective enough for Na, K, Ca, etc.

Rinse Solutions with HF

- 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

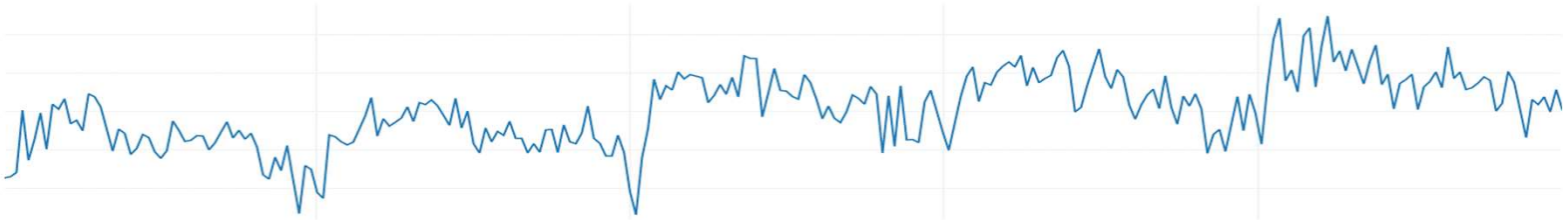
- If using an HF resistant nebulizer and spray chamber
  - Can go up to 2-3%
  - >3% HF will degrade the coating

Specialty Rinse Solutions

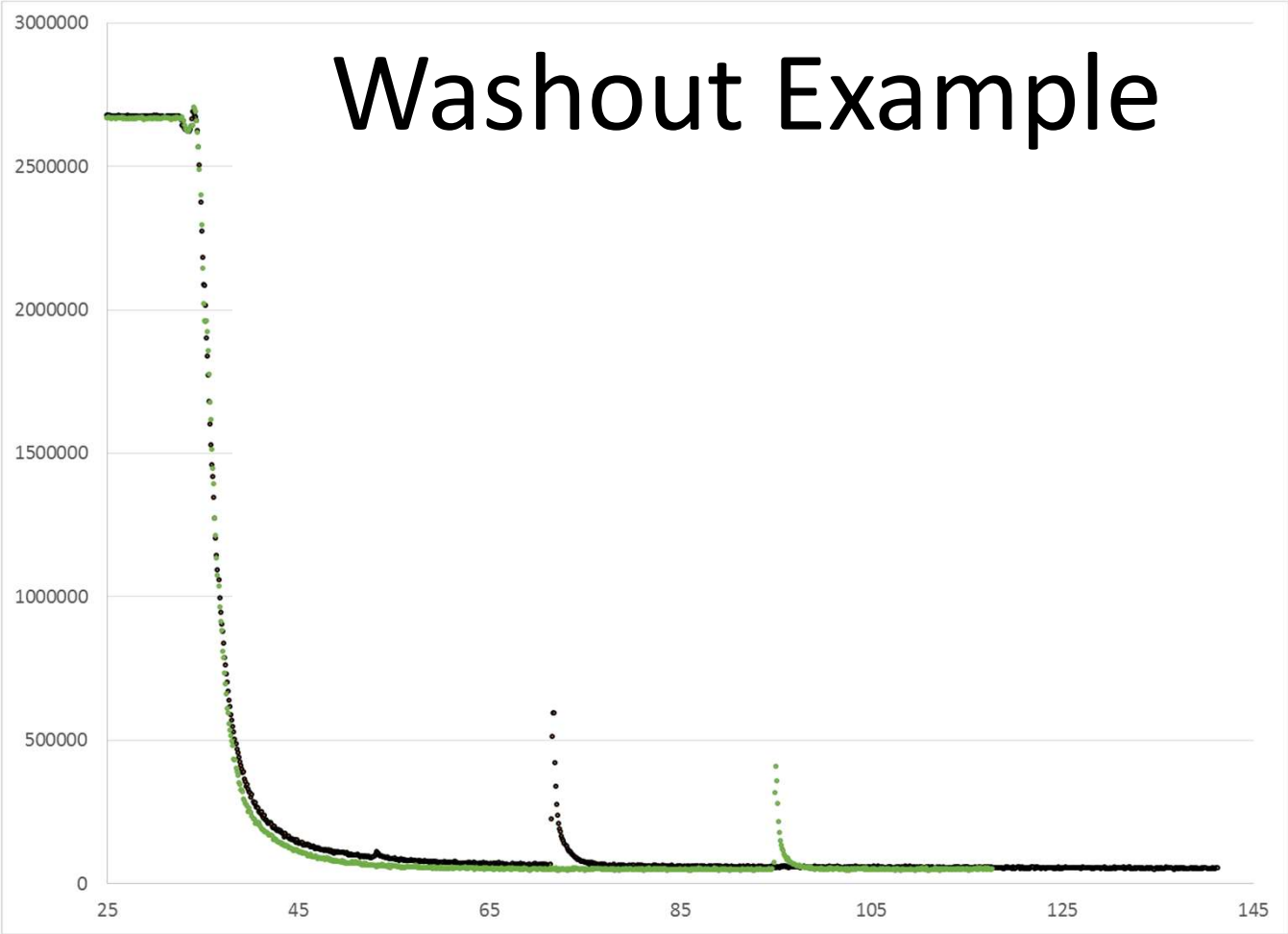
- NH_4OH
  - 1-5% for OES or MS
  - Use for B, Br, I, Hg
- HCl / Thiourea
  - 1-10% HCl
  - 0.5% Thiourea
  - Use for Hg, Au, Os
- HCl / Hydroxylamine·HCl
  - 10% HCl
  - 0.5% NH_2OH·HCl
  - Use for Os

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



Washout Example



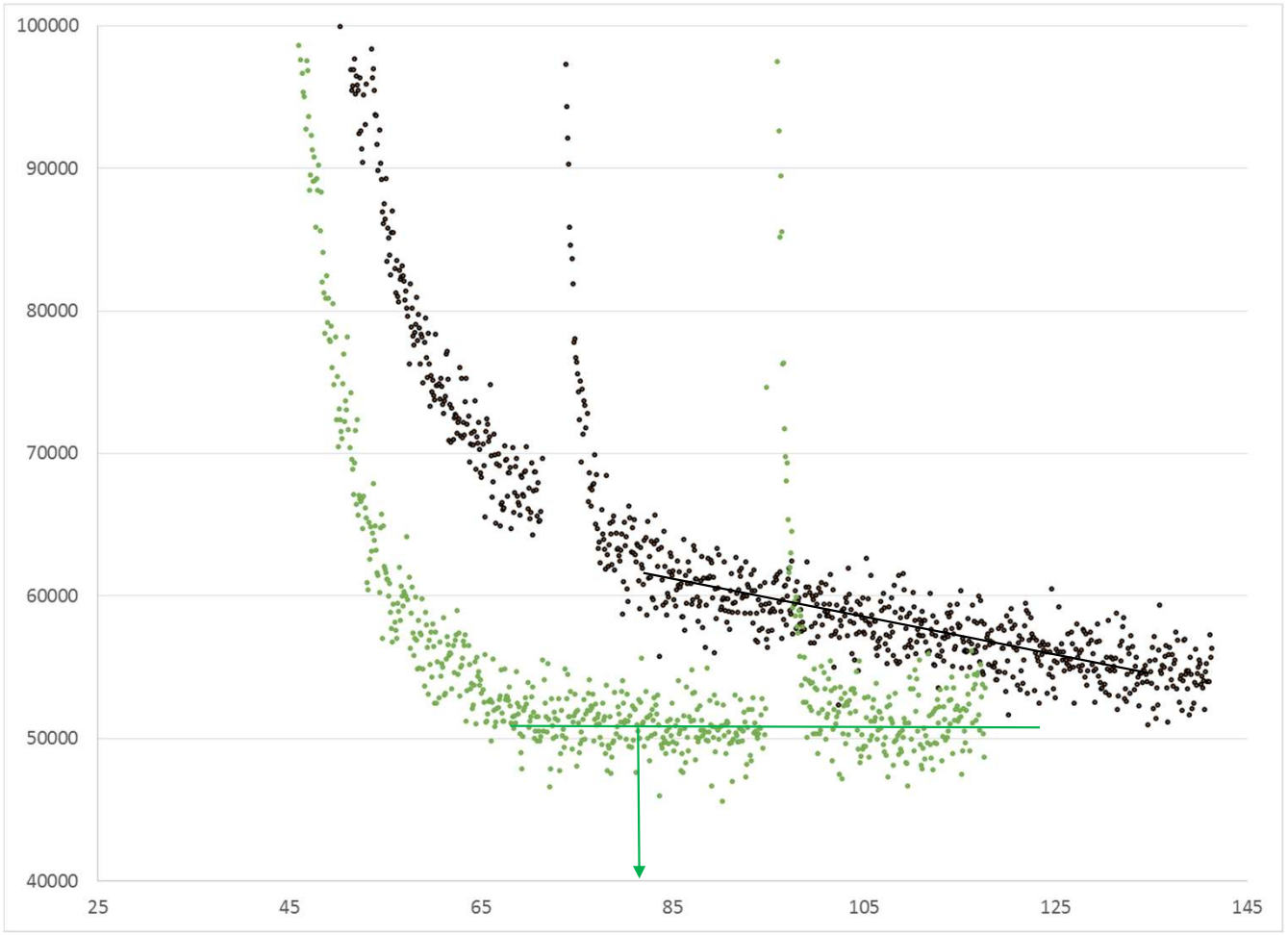
100ppm Boron in 0.1% v/v HNO_3

Monitoring Washout on B 208.959nm

Rinse w/ 5% HNO_3

Rinse w/ 5% NH_4OH

No obvious difference in washout at first glance.



Monitoring Washout on B 208.959nm

Rinse w/ 5% HNO_3

Rinse w/ 5% NH_4OH

5% HNO_3 doesn't go to baseline even within 2 minutes.

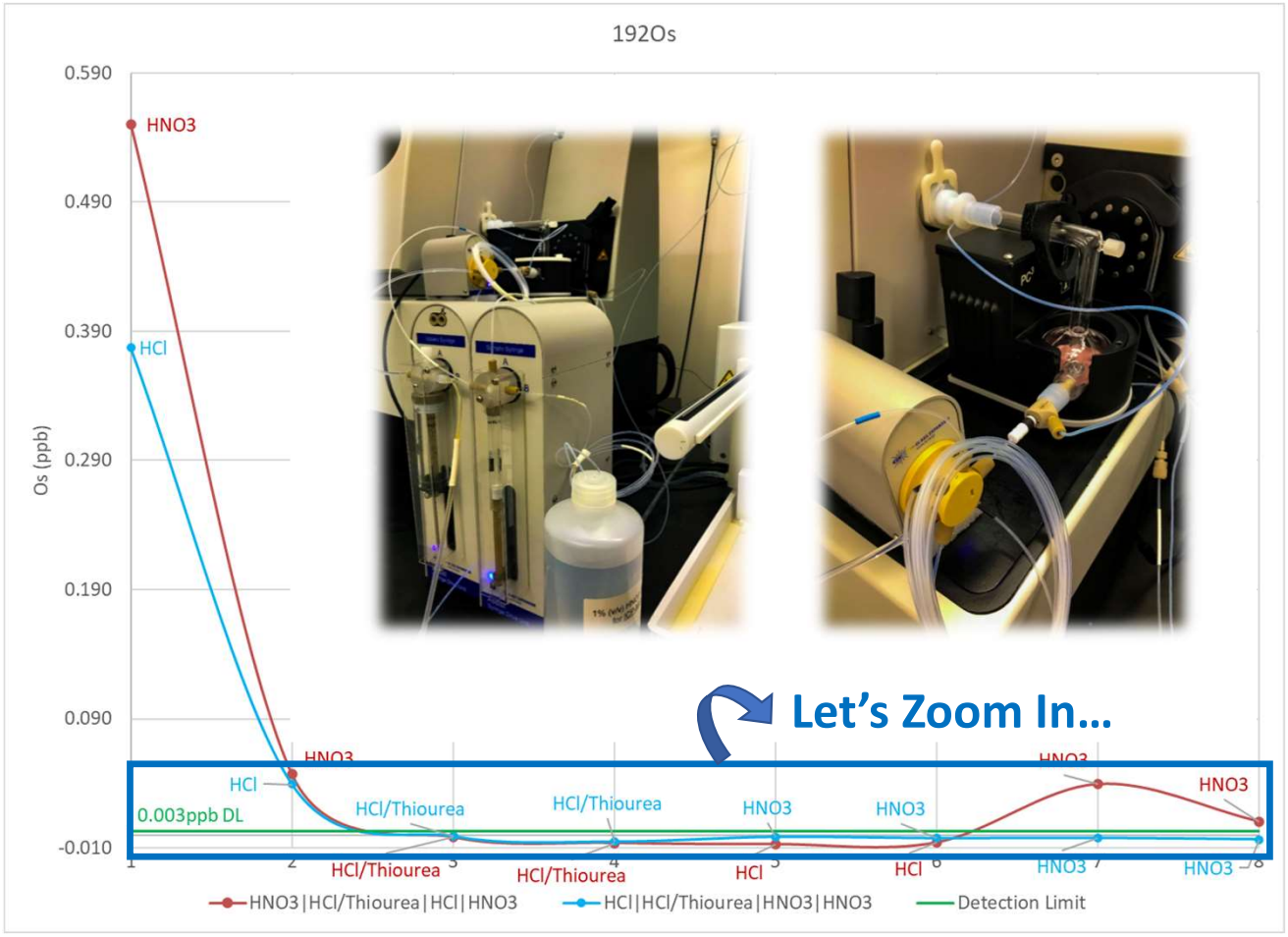
5% NH_4OH rinses it out within 80 seconds.

Washout Considerations

- Boron took much longer to washout when rinsing with the typical 5% v/v HNO_3 rinse.
- Washout time was significantly reduced using NH_4OH.
- Time graph only tells part of the story.
  - A very small peak is still present when viewing in spectra mode.
  - Time graph can help determine estimated washout.
  - Verify absence of an element by viewing the spectra.

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 HNO_3 to prevent $^{40}Ar^{35}Cl^+$ & $^{40}Ar^{37}Cl^+$ from interfering on ^{75}As & ^{77}Se.
- Running rinses as samples in varying order can help determine which types of rinses are more effective for certain elements and intro-system setups.

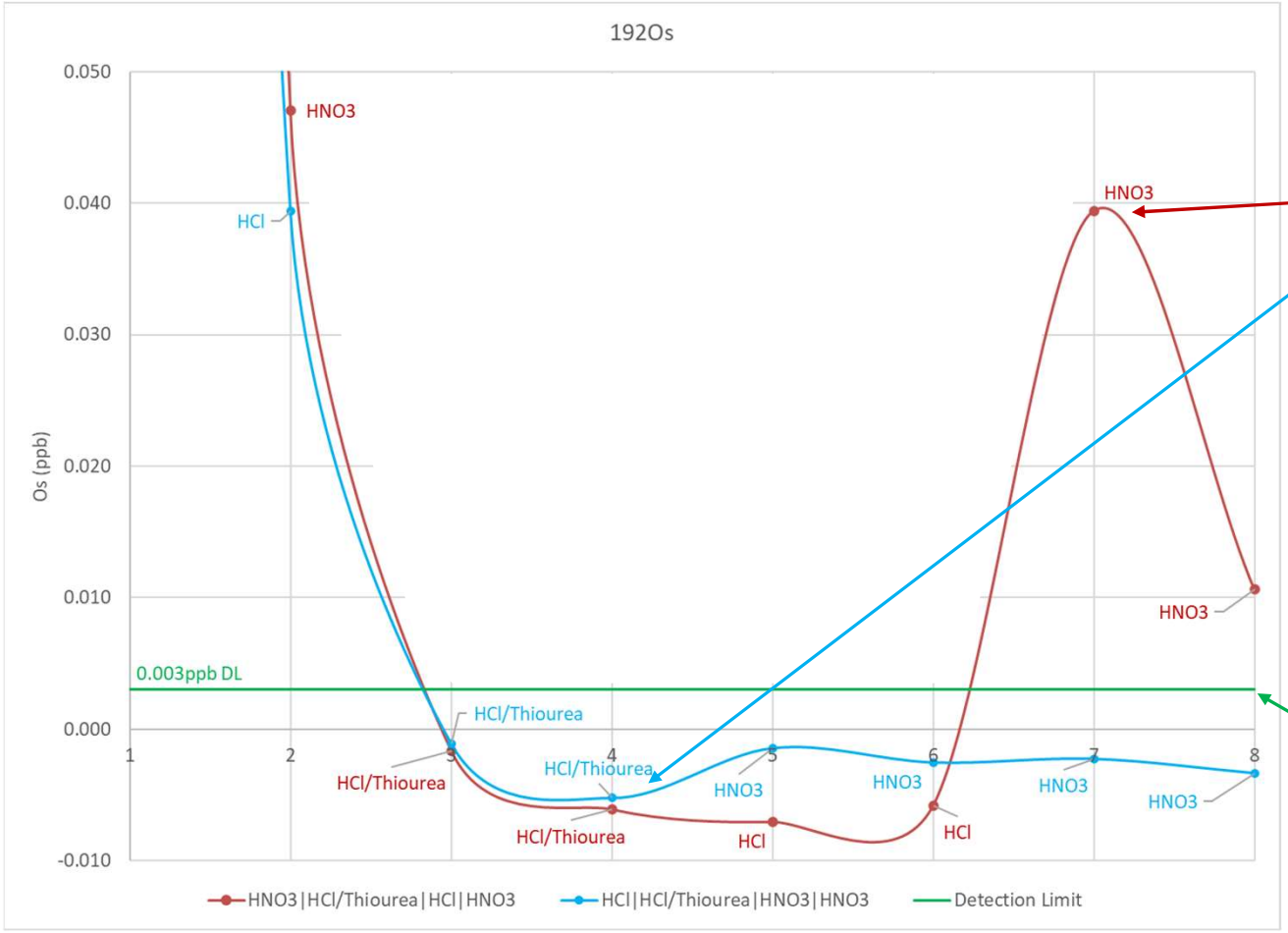


50ppb Os run followed by 8 rinses run as samples (Rinses shown)

2 Rinse strategies were performed in pairs

Carrier solution & rinse station contained 1% HNO_3.

Assist system from GE used with glass double pass spray chamber and Duramist Nebulizer



When HNO_3 is run first, some Os appears to stick around even after HCl & Thiourea rinses (likely tubing or valve).

When HCl and Thiourea are run first, most Osmium is rinsed out by rinse number 4.

HNO_3 causes some residual osmium to give a higher signal due to OsO_x changing the nebulization efficiency.

The HCl/Thiourea rinses appeared to rinse out the osmium beyond the originally calculated detection limit.

Question 5

- What solution do you use in your auto-sampler rinse station?

A. Deionized Water
B. Dilute HNO_3
C. Dilute HCl
D. Dilute HNO_3/HCl
E. Something Else

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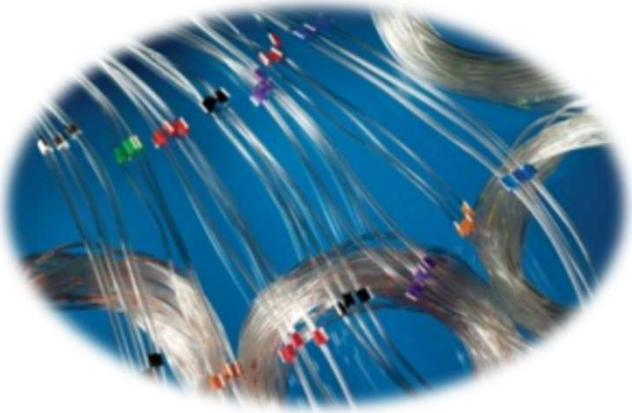
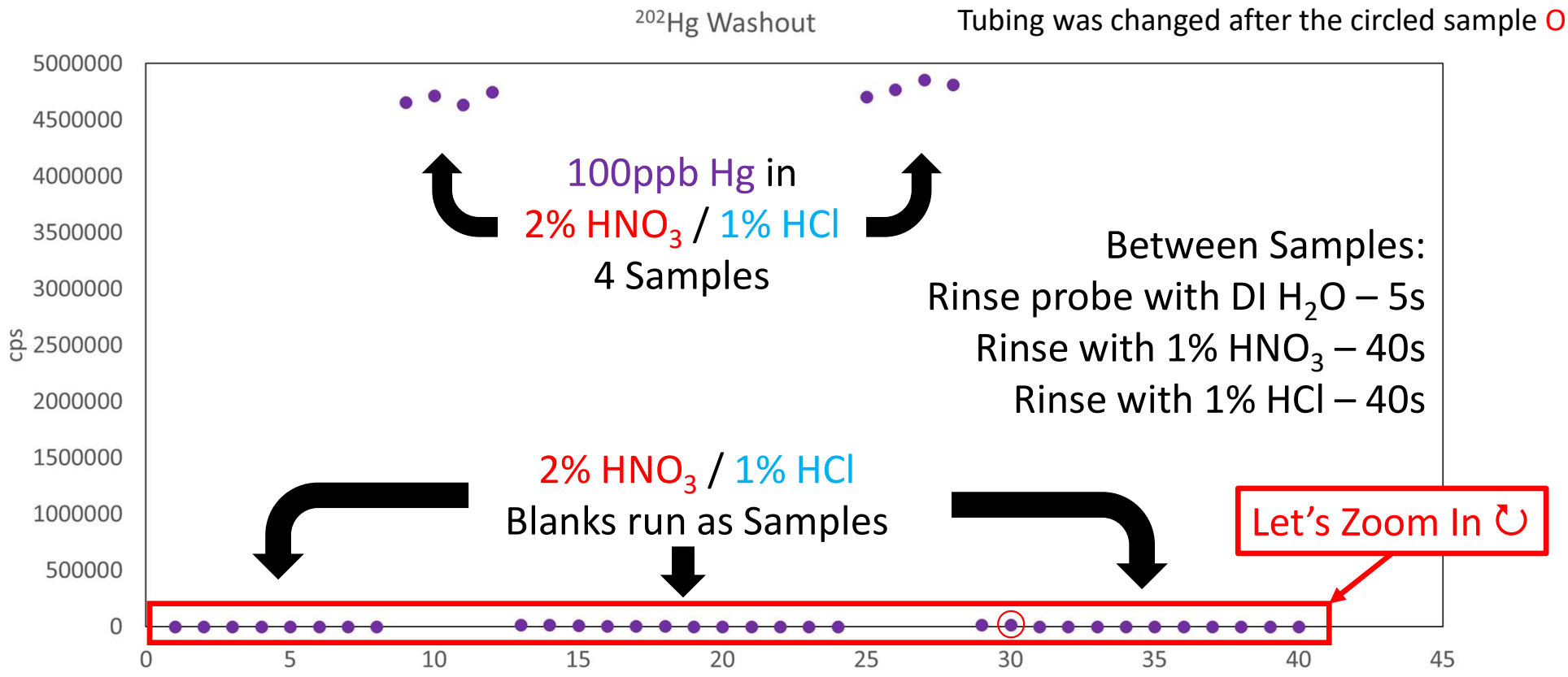
Peristaltic Pump Tubing

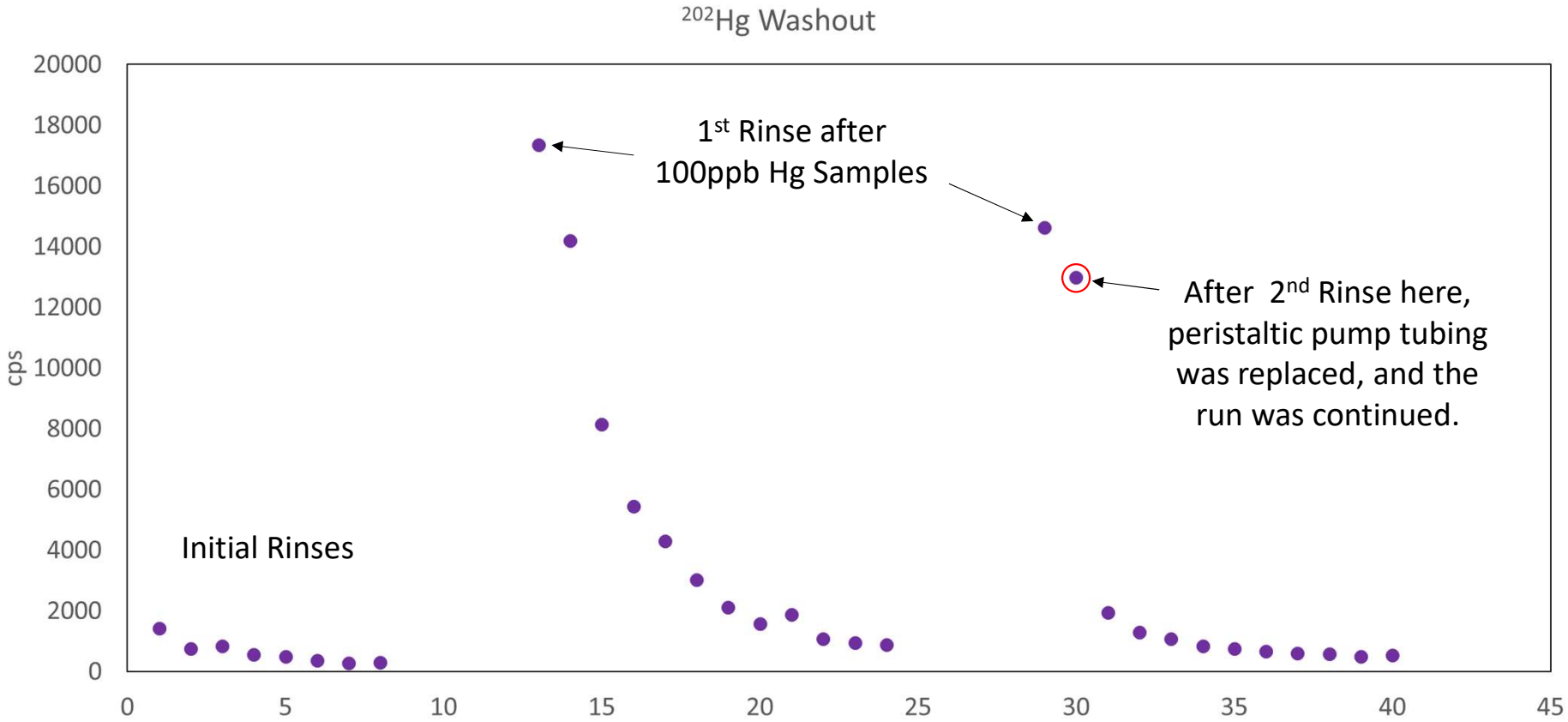
- If using peristaltic pump tubing for sample delivery…
  - Consider changing the tubing daily
  - Or directly after a run with “sticky” elements



Example of effect of changing tubing

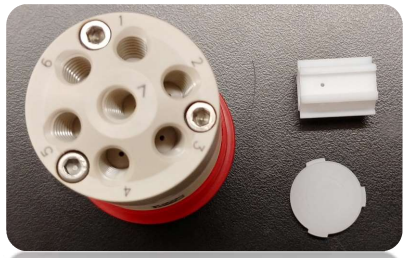


Example of effect of changing tubing



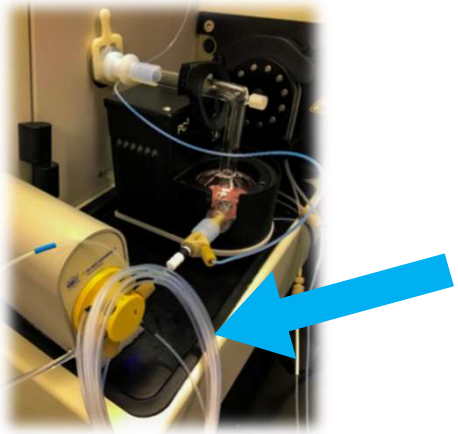
Switching Valve Systems

- 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.

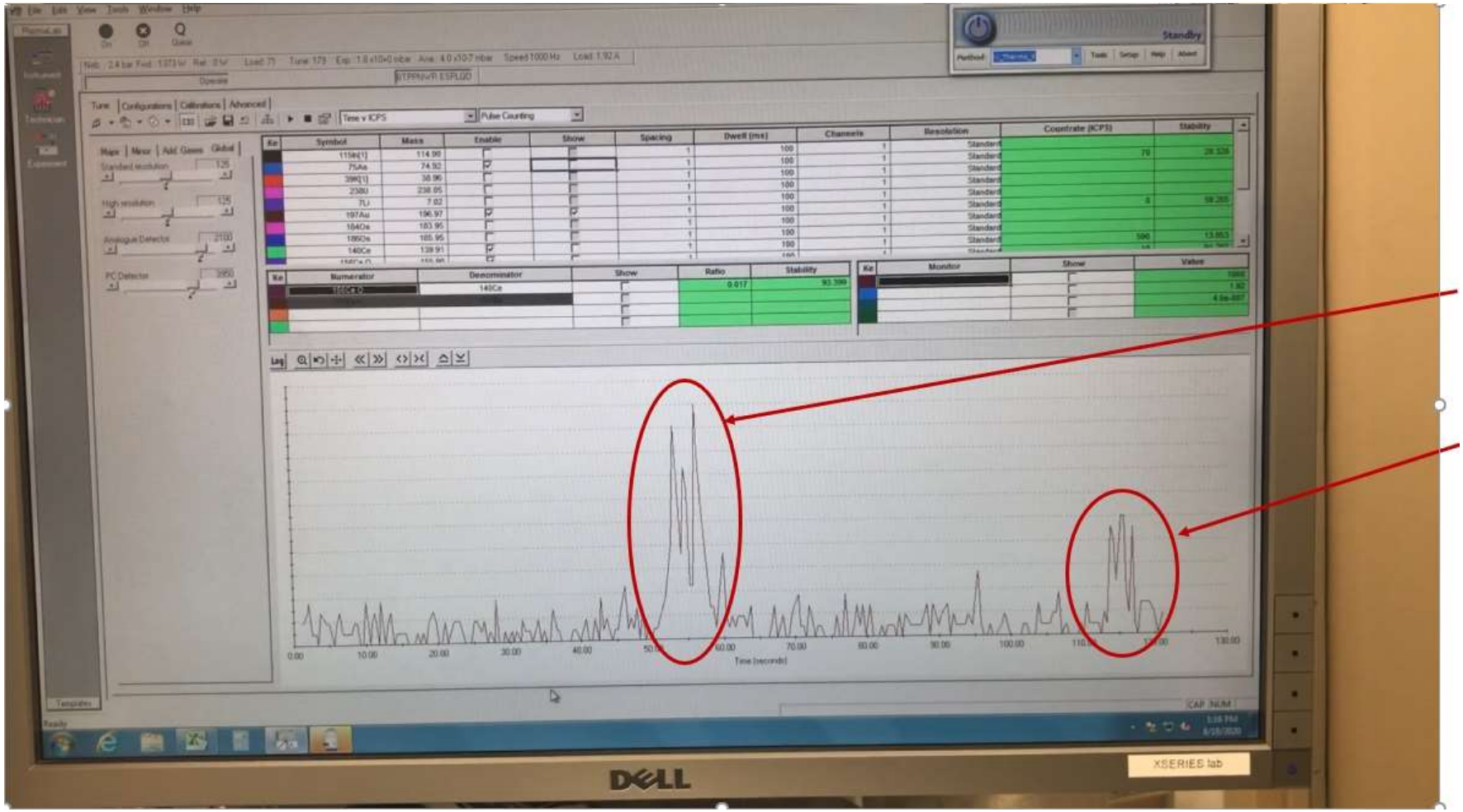


Switching Valve Systems

- 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



Sample Loop Connections



1st time shaking the loop.

2nd time shaking the loop.

Less contaminant remains, element likely getting stuck in the connector to the valve.

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_2O.

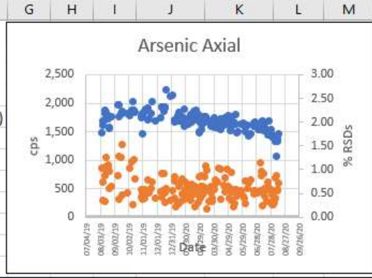
More tips and tricks for washout issues

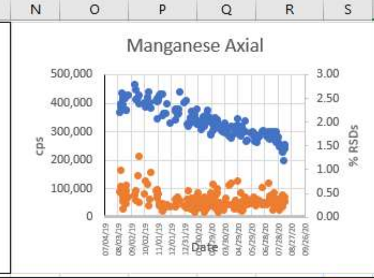
- Keep up with routine instrument maintenance to prevent other washout issues.
  - Torch parts, cones/interface, tubing, autosampler probe, rinse station reservoirs
  - Keep a detailed log of maintenance steps and record performance report data

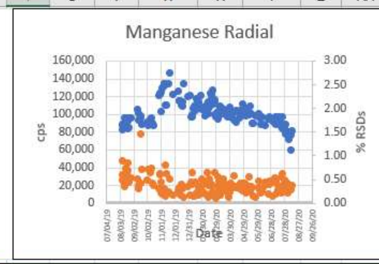
Example of a Daily Maintenance Log

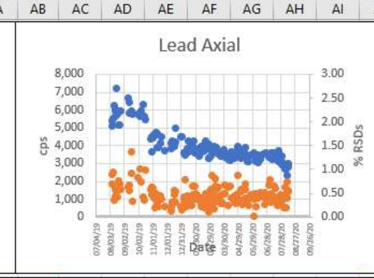
Agilent 5110 ICP-OES Maintenance Log

Total Plasma On Time 1132876:54 (h:m)





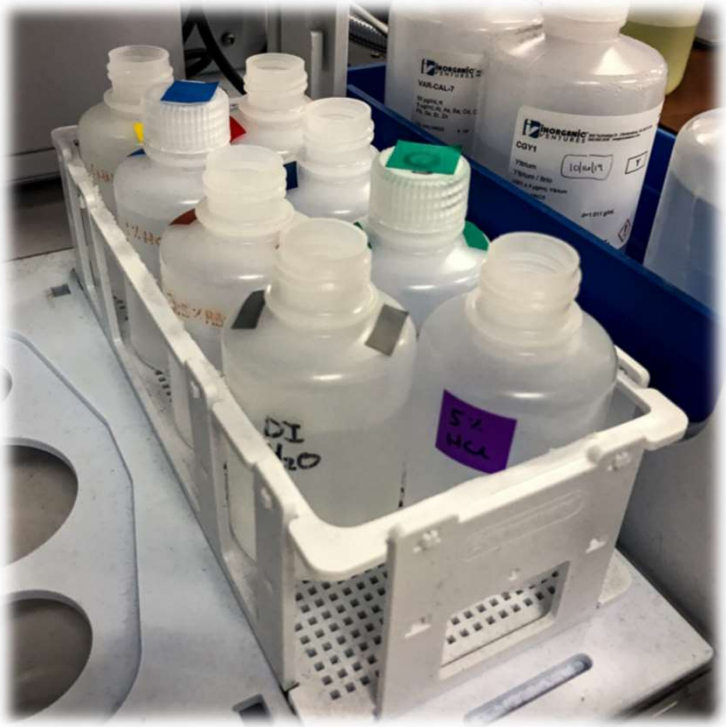




13			Daily Tasks							Plasma On & Off Times				Introduction System Parts					Weekly	Daily Initial Cleaning / Performance Reporting Method									Tasks done "as needed" (appx weekly)												
14	Day	Date	✓ Inspect Torch	✓ Inspect Interface	✓ Inspect Pump Tubing	✓ Inspect Spray Chamber	✓ Inspect Nebulizer	✓ Chk Rinse Sta 1% HNO3 Level	✓ Check Waste Level	✓ Turn on Instrument (Time)	✓ Instrument Off (Time)	✓ Unclamp Tubing and Turn off Chiller	✓ Plasma On Duration (hours:minutes)	✓ Spray Chamber Used (Glass or PTFE)	✓ Nebulizer Used (SeaSpray or DuraMist)	Torch Type (Full or D-Torch)	✓ Torch Outer Tube Used (Quartz or Ceramic)	✓ Torch Injector Used (Quartz or Alumina)	✓ WaveCal Performed	✓ Initial Cleaning/Performance Method Run	✓ As 188.980nm Axial Counts	✓ As 188.980nm Axial RSDs	✓ Mn 257.610nm Axial Counts	✓ Mn 257.610nm Axial RSDs	✓ Mn 257.610nm Radial Counts	✓ Mn 257.610nm Radial RSDs	✓ Pb 220.353nm Axial Counts	✓ Pb 220.353nm Axial RSDs	✓ Clean or Change Torch	✓ Clean Interface	✓ Change Pump Tubing	✓ Clean and/or Change Spray Chamber	✓ Clean and/or Change Nebulizer	✓ Refill Rinse Station Solution (1% HNO3)	✓ Dump Waste Container Cubi	✓ Clean or Change Air Filter (Top of ICP)	✓ Clean or Change Air Filter (Chiller)	✓ Check Water Level (Chiller)	✓ Preventive Mainten	✓ *Other Majo	✓ *Not
15		mm/dd/	Initi	Initi	Initi	Initi	Initi	Initi	Initi	hh:mm	hh:mm	Init or		Typ	Type	Type	Typ	Type	Initi	Initi	cp	%R	cps	%R	cps	%R	cp	%R	Initi	Initi	Initi	Initi	Initi	Initi	Initi						
194	Tue	07/28/20	GS	GS	GS	GS	GS	GS	GS	10:42 AM				PTFE	DuraMist	D-Torch	Ceramic	Alumina		GS	1,465	0.32	263,100	0.20	84,160	0.34	3,160	0.47													
195	Wed	07/29/20	BB	BB	BB	BB	BB	BB	BB	11:21 AM				PTFE	DuraMist	D-Torch	Ceramic	Alumina		BB	1,547	0.59	281,900	0.27	89,270	0.44	3,421	0.36						BB							
196	Thu	07/30/20	BB	BB	BB	BB	BB	BB	BB	1:01 PM				PTFE	DuraMist	D-Torch	Ceramic	Alumina		BB	1,434	0.47	254,800	0.16	81,830	0.39	3,064	0.33		BB											
197	Fri	07/31/20	BB	BB	BB	BB	BB	BB	BB					PTFE	DuraMist	D-Torch	Ceramic	Alumina		BB	1,407	0.27	247,700	0.32	78,550	0.46	2,964	0.41													
198	Mon	08/03/20	BB	BB	BB	BB	BB	BB	BB	10:56 AM				PTFE	DuraMist	D-Torch	Ceramic	Alumina	BB	BB	1,434	0.26	249,800	0.20	79,600	0.21	3,007	0.20	BB	BB	BB	BB	BB	BB	BB						
199	Tue	08/04/20	ACG	ACG	ACG	ACG	ACG	ACG	ACG	10:50 AM				PTFE	DuraMist	D-Torch	Ceramic	Alumina		ACG	1,381	0.31	242,900	0.35	78,350	0.33	2,896	0.41													
200	Wed	08/05/20	ACG	ACG	ACG	ACG	ACG	ACG	ACG	11:20 AM				PTFE	DuraMist	D-Torch	Ceramic	Alumina		ACG	1,411	0.41	247,700	0.34	79,860	0.41	2,943	0.47													
201	Thu	08/06/20	BB	BB	BB	BB	BB	BB	BB	9:04 AM				PTFE	DuraMist	D-Torch	Ceramic	Alumina		BB	1,323	0.83	227,100	0.47	72,100	0.27	2,675	0.63		BB				BB							
202	Fri	08/07/20	BB	BB	BB	BB	BB	BB	BB	7:11 AM				PTFE	DuraMist	D-Torch	Ceramic	Alumina		BB	1,327	0.41	227,200	0.22	72,900	0.37	2,675	0.19													
203	Mon	08/10/20	BB	BB	BB	BB	BB	BB	BB	10:06 AM				PTFE	DuraMist	D-Torch	Ceramic	Alumina	BB	BB	1,076	0.88	197,200	0.33	60,220	0.30	2,304	0.75	BB	BB	BB	BB	BB	BB	BB						Air flow e
204	Tue	08/11/20	BB	BB	BB	BB	BB	BB	BB	8:15 AM				PTFE	DuraMist	D-Torch	Ceramic	Alumina		BB	1,379	0.56	247,900	0.34	78,630	0.35	2,897	0.41													
205	Wed	08/12/20	BB	BB	BB	BB	BB	BB	BB	8:05 AM				PTFE	DuraMist	D-Torch	Ceramic	Alumina		BB	1,340	0.59	240,400	0.33	76,550	0.29	2,792	0.55													
206	Thu	08/13/20	BB	BB	BB	BB	BB	BB	BB	8:52 AM				PTFE	DuraMist	D-Torch	Ceramic	Alumina		BB	1,462	0.72	255,100	0.43	81,420	0.38	2,988	0.54		BB											
207	Fri	08/14/20	BB	BB	BB	BB	BB	BB	BB	7:06 AM				PTFE	DuraMist	D-Torch	Ceramic	Alumina																							Instrumer

More tips and tricks for washout issues

- Keep several different rinse solutions on hand to washout high TDS samples more effectively
  - This will keep your lab running smoothly to get more done!

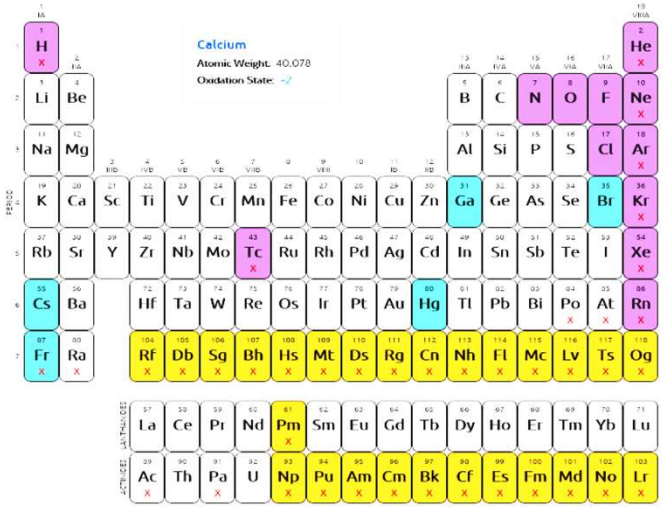


Final Thoughts

- 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



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.