New Method for Removal of Spectral Interferences for Be Assay

Sherrod L. Maxwell
Washington Savannah River Co.
53rd Radiobioassay and Radiochemical Measurements Conference
Eichrom Workshop

October 30, 2007

Requirements

- DOE - Chronic Beryllium Disease (CBD) prevention program in 1999 (10CFR Part 850)
  - to protect DOE workers from Be-contaminated dust
- Requires frequent monitoring of air and possible contaminated surfaces to identify potential health risks
- Samples (filters and smears) are digested and analyzed
  - inductively coupled plasma atomic emission spectrometry (ICP-AES) or alternate method (molecular fluorescence/ ICP-MS).

Spectral Interferences

- Other elements can interfere spectrally with the beryllium measurement by ICP-AES.
- Interference correction software is used at the ICP-AES
  - but at higher levels the spectral interferences cannot be handled adequately
- A rapid separation method to remove spectral interferences is needed
  - to allow accurate measurement of Be at low levels using ICP-AES to meet requirements

Current Separation Methods

- PG Research Foundation developed a Be separation method for Eichrom using Be Resin® to remove spectral interferences
  - E. Philip Horwitz et al, "A Method For The Separation Of Beryllium From Spectral Interfering Elements In Inductively-Coupled Plasma-Atomic Emission Spectroscopic Analysis," Talanta, Vol. 67, 873 (2005)
- One or more guard columns may be needed prior to Be Resin to remove large amounts of interferences
  - this method can be affected by large amounts of interferences that can reduce Be retention on the resin

Current Separation Methods

- Fluoride, if present, must be complexed with boric acid to prevent Be losses using the Be Resin method.
  - An adjustment of each sample to pH >1 using an indicator is also required
- DOE Y-12 facility uses a pass through approach using LN-3 Resin to remove spectral interferences
  - bis (2,4,4-trimethylpentyl) phosphinic acid extractant

Current Separation Methods

- LN-3 Resin will retain U, Nb and Mo under the conditions used (dilute sulfuric-nitric acid mixture) while allowing Be to pass through.
  - Vanadium, however, is not retained using this method.
- If vanadium is present, Be Resin method can be used after LN-3 resin to remove V

New SRS Method

- New SRS method uses stacked column (5 ml of Diphonix Resin and 2 ml of TEVA Resin)
  - Single column pass-through approach for Be
  - Reduces the levels of the spectral interferences significantly
  - Removes uranium (U), thorium (Th), niobium (Nb), vanadium (V), molybdenum (Mo), zirconium (Zr), tungsten (W), iron (Fe), chromium (Cr), cerium (Ce), erbium (Er) and titanium (Ti)

Why this way?

- Separate interferences without multiple guard columns
  - Pass-through approach has less risk of Be loss
- Utilizes fluoride complexing
  - SRS digestion already uses HF
- Cation/Anion exchange using HF well-documented
  - Diphonix is powerful resin even with HF
    - SRS fecal method
  - TEVA cartridge can be conveniently attached to Diphonix column

References

- J.P. Faris, “Adsorption of the Elements from Hydrofluoric Acid by Anion Exchange”, Analytical Chemistry, Vol.32, 520 (1960)
- L. Danielson, “Adsorption of a Number of Elements from HNO3-HF and H2SO4-HF Solutions by Cation and Anion Exchange” , Acta Chemica Scandinavia, Vol. 19, 5 (1965)
- K.A Kraus et al, “Anion- exchange studies. XVII. Molydenum (VI), Tungsten (VI) and Uranium (VI) in HCL and HCl-HF Solutions”, Journal of Am. Chem. Soc., Vol.77, 3972, (1955)
- K.A Kraus et al, “Absorbability of a Number of Elements in HCl-HF Solutions”, Journal of Am. Chem. Soc., Vol. 82, 339, (1960)

Blend of Old and New

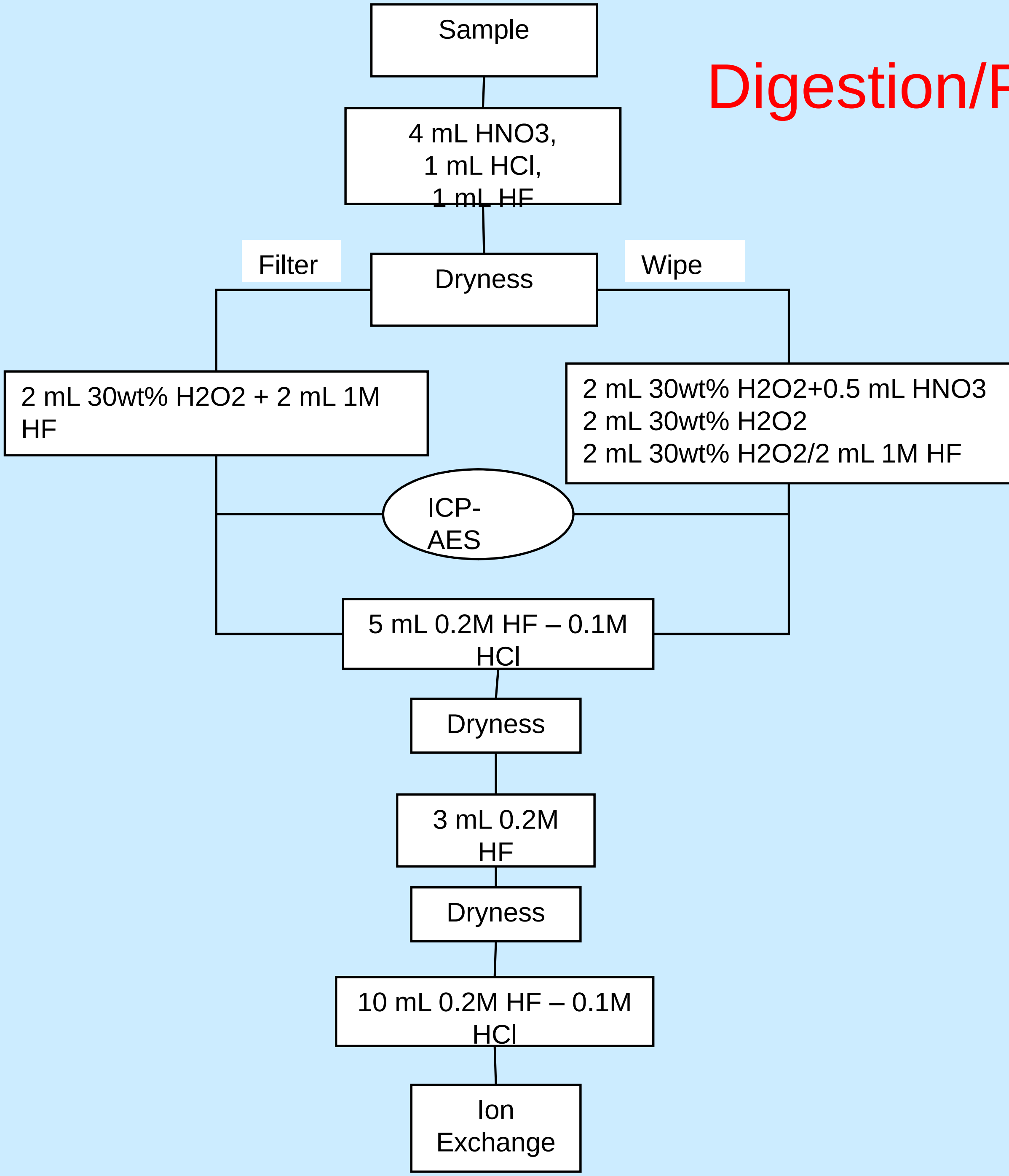
- Diphonix Resin
  - Much higher retention than typical cation resin with sulfonic acid groups
  - Diphonix Resin has a very high retention for U, Th, V, Fe, Er and Ce even in dilute HF
  - Relatively inexpensive (<$7 for 5 ml resin)
- TEVA Resin
  - Efficient anion exchanger (Aliquat 336 extractant)
  - retains Nb, Ti, Mo, Zr, and W from dilute hydrofluoric acid-hydrochloric acid solutions

Additional Cr Removal

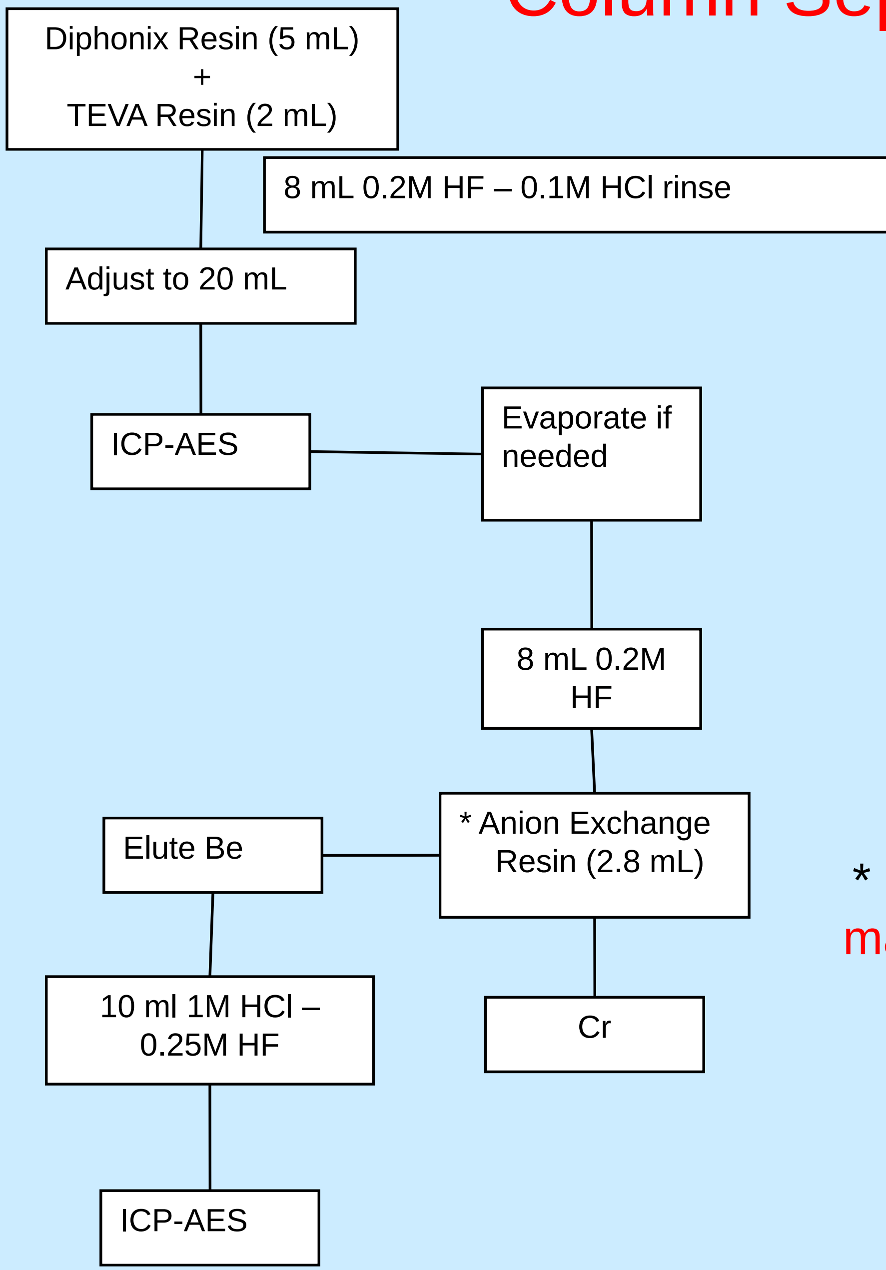
- An optional anion resin column separation can also be used to remove additional chromium if needed.
  - Anion Resin (2.8 ml) 100-200 mesh chloride form
  - Dilute HF
  - Will also lower other interferences (Zr, Nb, W, Ti, Mo) as well

- Not required if Cr is low or if 234.861 nm line can be used

Digestion/Preparation



Column Separation



* Extra Cr removal may not be needed

Spectral Interference Removal

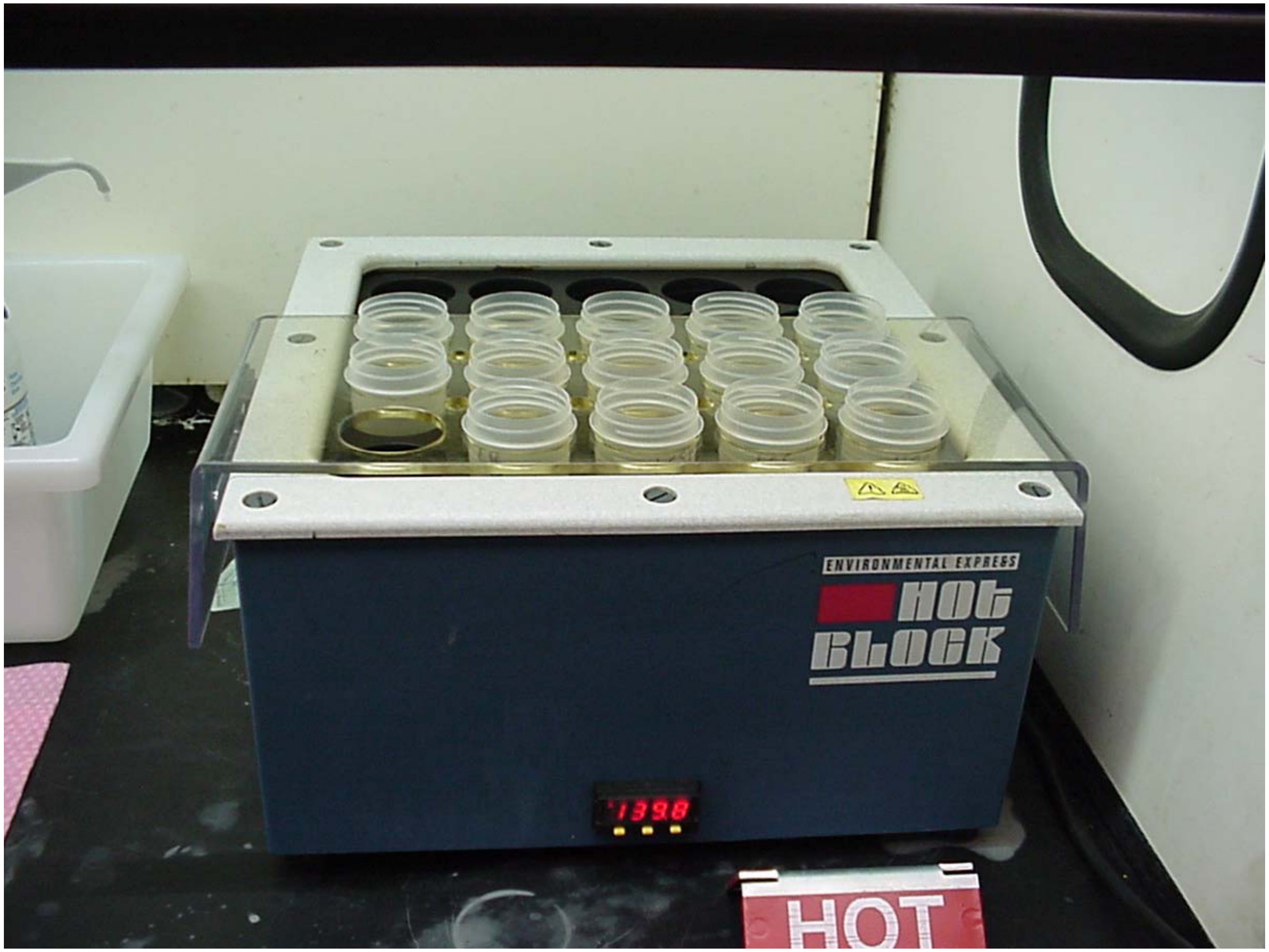
Interference	Added (ppm)	Measured (ppm)	Removal (%)
Iron**	1000	0.039	99.996
Uranium	300	0.112	99.963
Niobium	100	ND	~100
Molybdenum	100	0.002	99.998
Vanadium	100	0.003	99.997
Zirconium	100	0.082	99.918
Tungsten	100	0.010	99.990
Thorium	50	ND	~100
Titanium	100	0.736	99.964
Cerium	50	ND	~100
Erbium	100	ND	~100
Chromium	100	50.01	49.99
Chromium*	100	8.98	91.02

n=10; ppm added to have this level interference in 20 ml at ICP-AES

*additional anion exchange to remove more Cr

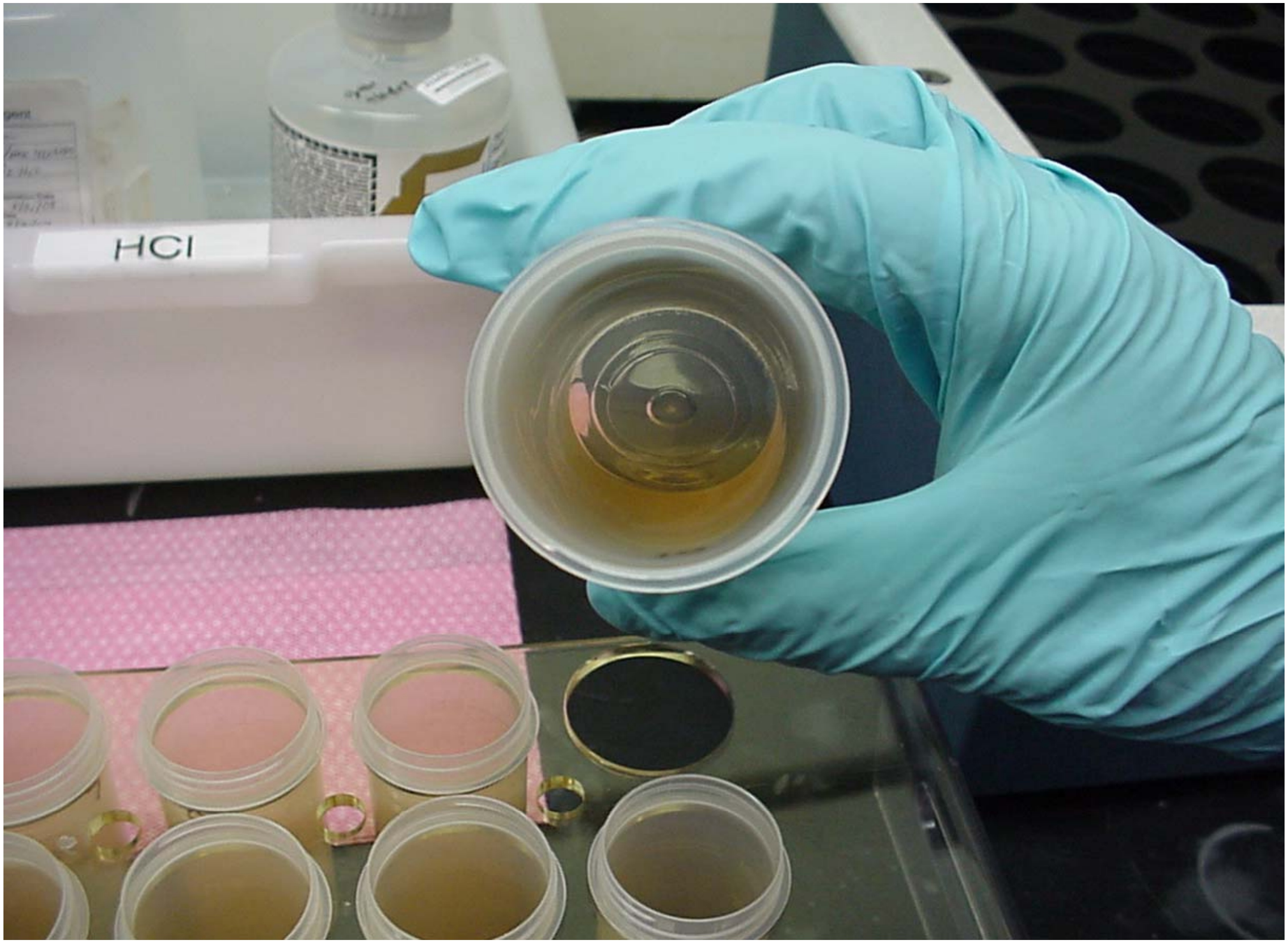
**Fe has similar removal at 2500 ppm

Hot Block Digestion



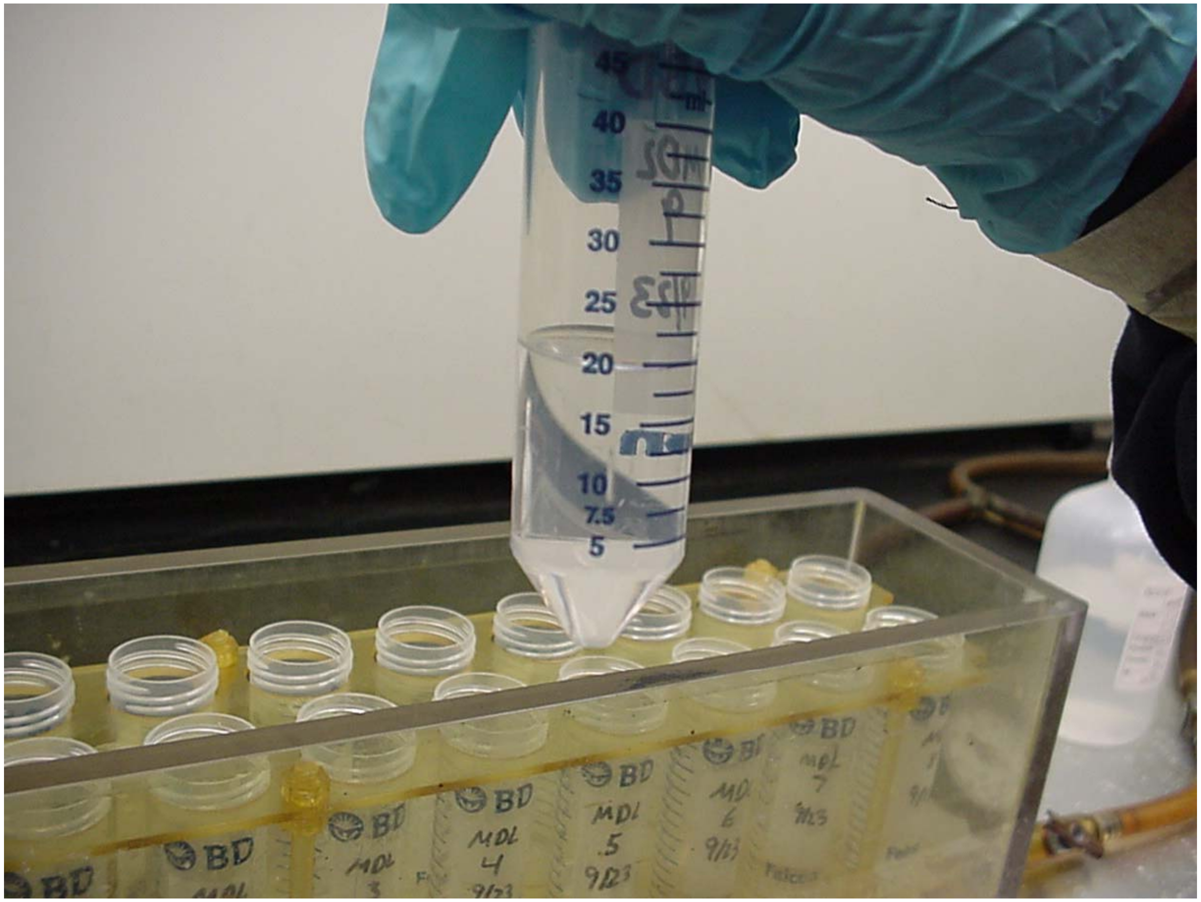
Hot Block Digestion

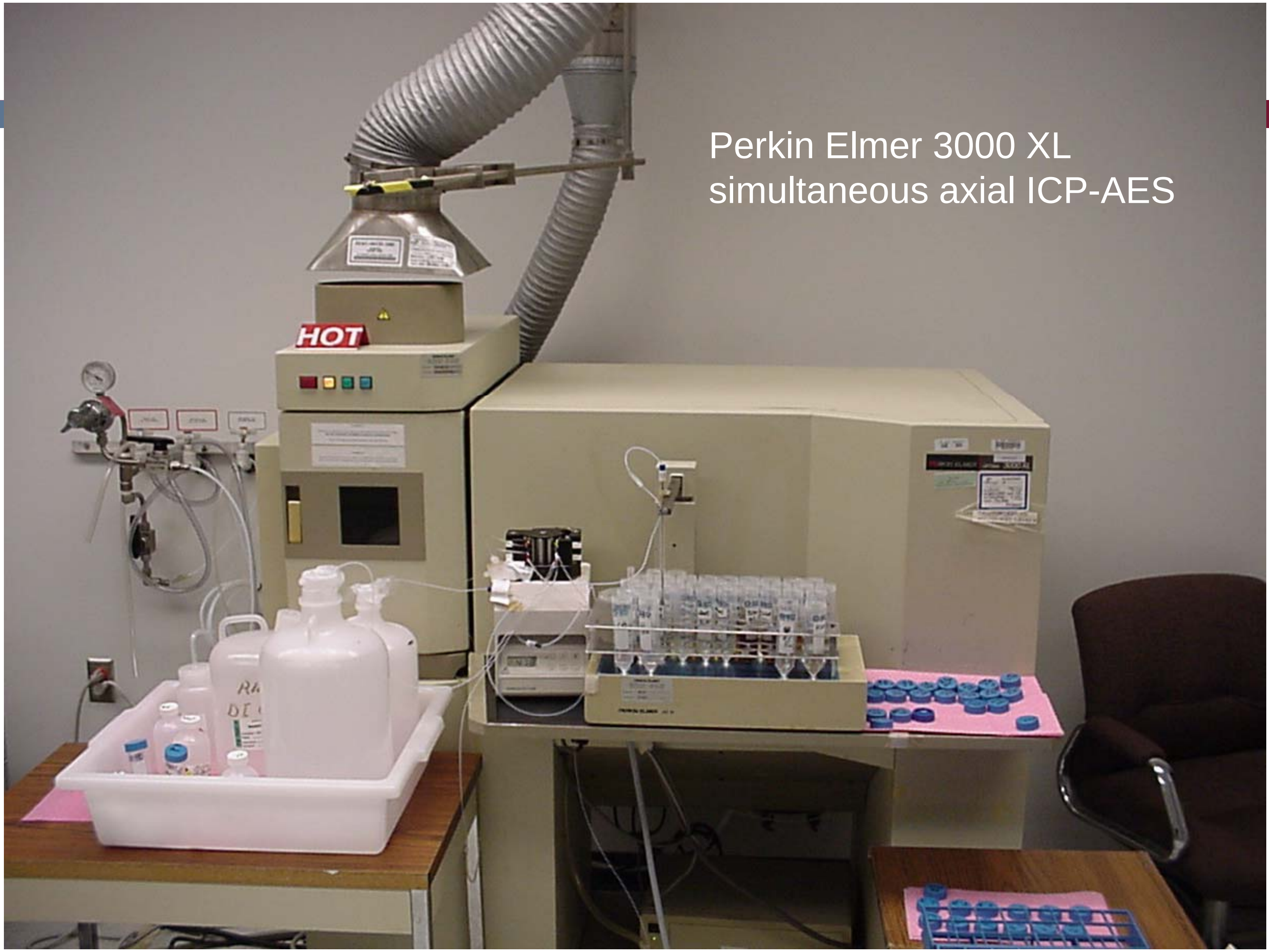
Digested Filter



Diphonix Resin+ TEVA

Ready for ICP-AES




Perkin Elmer 3000 XL
simultaneous axial ICP-AES
HOT

Be Test Results- 234.861 nm line

Sample	Be (Ref) (ppb)	Be Measured after IEX (ppb) (234.861 nm)	Recovery (%)	Bias (%)
wipe	1	1.128	112.8	12.8
wipe	1	1.151	115.1	15.1
wipe	1	1.10	110.0	10.0
wipe	1	1.08	108.0	8.0
wipe	1	1.096	109.6	9.6
wipe	1	1.14	114.0	14.0
Be filter	5	4.916	98.3	-1.68
Be filter	5	4.926	98.5	-1.48
BeO filter	25	22.8	91.2	-8.8
BeO filter	25	21.6	86.4	-13.6
		Avg.	**104.394**	**4.394**

Be Test Results- 313.042 nm line

	Be (ppb)	Be Measured after IEX (ppb) 313.042 nm	Recovery (%)	Bias (%)
wipe	1	1.41	141.0	41.0
wipe	1	1.23	123.0	23.0
wipe	1	1.47	147.0	47.0
wipe	1	1.76	176.0	76.0
wipe	1	1.57	157.0	57.0
wipe	1	1.72	172.0	72.0
Be filter	5	4.88	97.6	-2.4
Be filter	5	5.4	108.0	8.0
BeO filter	25	22.42	89.7	-10.3
BeO filter	25	21.25	85	-15.0
		Avg.	**129.628**	**29.6**

After Anion IEX (Cr)- Be 313.042 nm line

		Be Added (ppb)	After Anion exchange 313.042 nm	Rec (%)	Bias (%)
1	wipe	1	1.01	101	1
2	wipe	1	1.13	113	13
3	wipe	1	0.95	95	-5
4	wipe	1	0.94	94	-6
5	wipe	1	0.98	98	-2
6	wipe	1	0.98	98	-2
7	Be filter	5	4.84	96.8	-3.2
8	Be filter	5	4.74	94.8	-5.2
9	BeO filter	25	22.75	91	-9
10	BeO filter	25	21.07	84.28	-15.72
			Avg	**96.59**	**-3.41**

Be Test Results- 313.107 nm line

	Be (Ref) (ppb)	Be Measured after IEX (ppb) 313.107 nm	Recovery (%)	Bias (%)
wipe	1	1.77	177.0	77.0
wipe	1	1.23	123.0	23.0
wipe	1	1.74	174.0	74.0
wipe	1	1.76	176.0	76.0
wipe	1	1.79	179.0	79.0
wipe	1	1.83	183.0	83.0
Be filter	5	4.89	97.8	-2.2
Be filter	5	5.44	108.8	8.8
BeO filter	25	22.62	90.48	-9.5
BeO filter	25	21.36	85.44	-14.6
		Avg.	**139.45**	**39.45**

After Anion IEX (Cr)- Be 313.107 nm line

	Be Added (ppb) 313.107 nm	After Anion exchange	Recovery (%)	Bias (%)
wipe	1	1.314	131.4	31.4
wipe	1	1.289	128.9	28.9
wipe	1	1.14	114	14
wipe	1	1.18	118	18
wipe	1	1.19	119	19
wipe	1	1.15	115	15
Be filter	5	5.02	100.4	0.4
Be filter	5	5.04	100.8	0.8
BeO filter	25	22.7	90.8	-9.2
BeO filter	25	21.1	84.4	-15.6
		Avg	**110.27**	**10.27**

Be Test Results- 234.861 nm line

Sample	Be (Ref) (ppb)	Be Measured after IEX (ppb) (234.861 nm)	Recovery (%)	Bias (%)
wipe	1	1.16	116.00	16.0
wipe	1	1.12	112.00	12.0
wipe	1	1.02	102.00	2.0
wipe	1	1.03	103.00	3.0
wipe	1	0.92	92.00	-8.0
wipe	1	0.93	93.00	-7.0
Be filter	5	4.80	96.00	-4.0
Be filter	5	4.90	98.00	-2.0
Be filter	5	4.50	90.00	-10.0
Be filter	5	4.49	89.80	-10.2
		Avg.	**99.18**	**-0.82**
		% rsd	**9.16**	

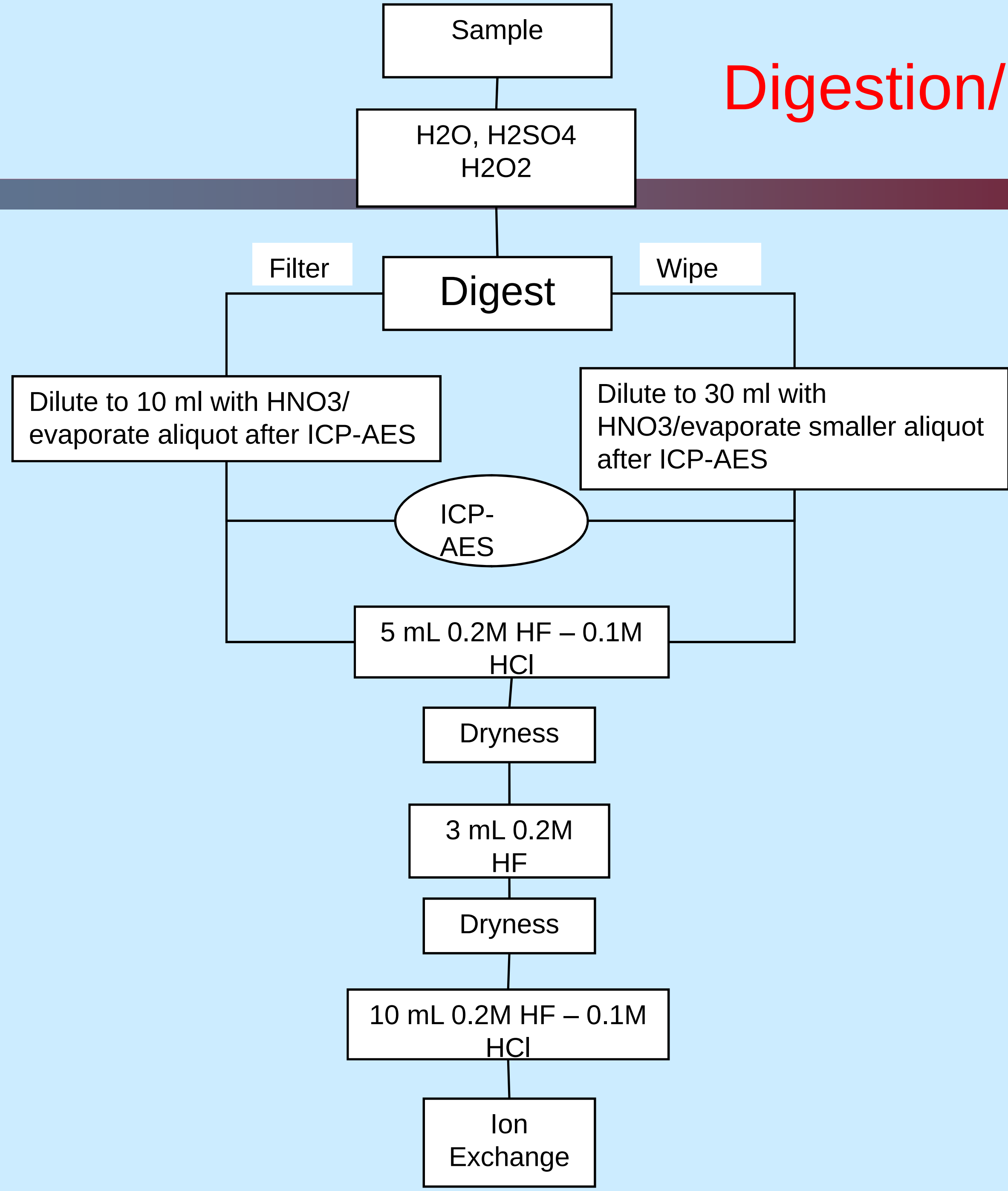
Method Report Limit

	Be 234.861	Be 313.042	Be 313.107
1	1.086	1.043	0.978
2	1.082	1.053	1.017
3	1.113	1.005	0.947
4	1.178	1.114	1.064
5	1.133	1.102	1.056
6	1.099	1.101	1.004
7	1.128	1.114	1.052
8	1.136	1.099	1.041
9	1.102	1.123	1.035
10	1.164	1.073	1.031
AVERAGE	**1.122**	**1.083**	**1.022**
STD DEV	**0.0318**	**0.0384**	**0.0368**
%Recovery/Bias	**112.206**	**108.272**	**102.233**
Report Limit [ug/filter]	**0.009**	**0.011**	**0.010**

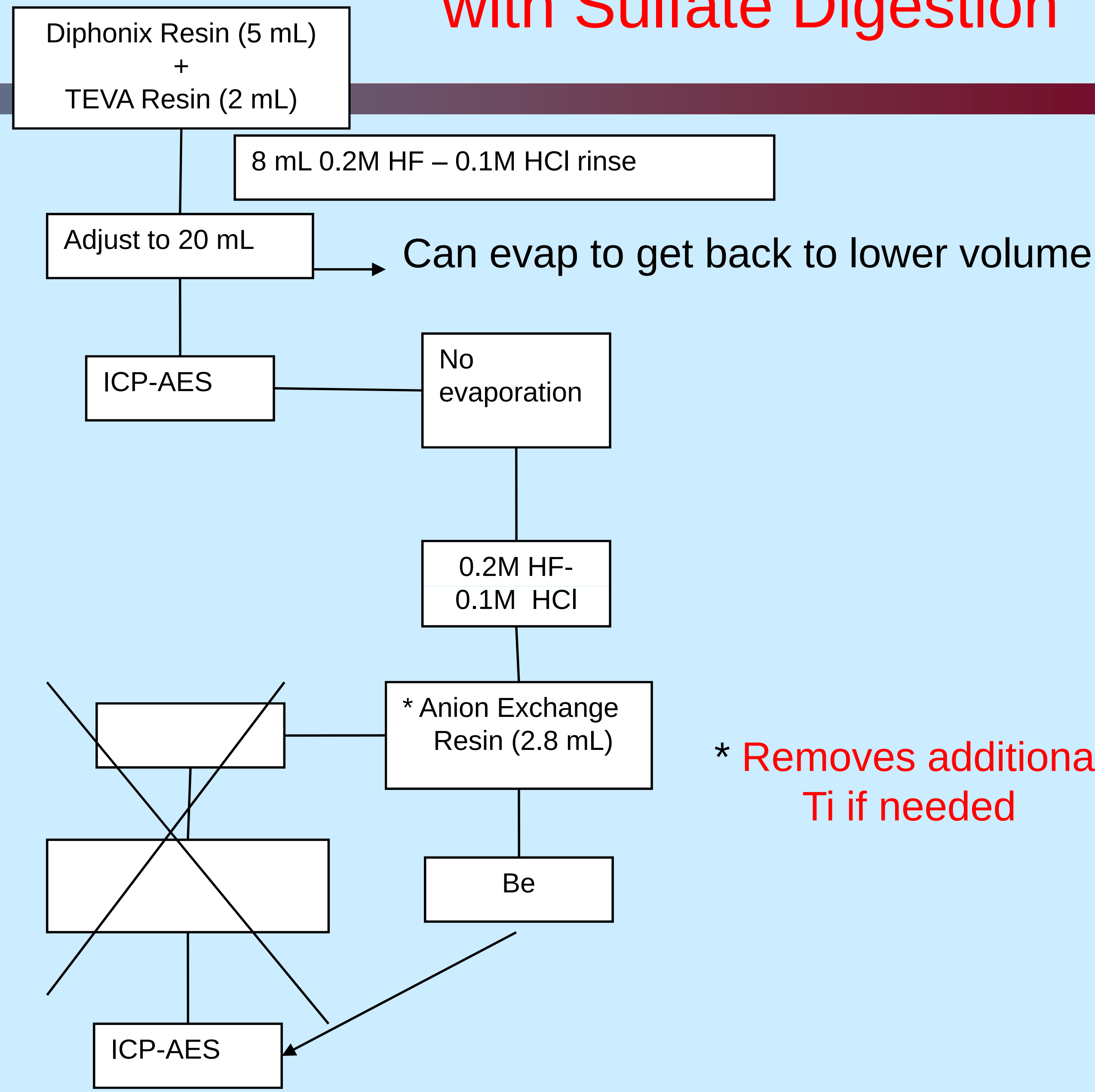
Other digestion methods

- Will it work with H_2SO_4 digestion?
- Yes!
  - Less retention of Ti on Diphonix-TEVA (~75% removed at 100 ppm level instead of 99%+) - sulfate effect
  - Everything else removed but Cr is still partial
  - Anion resin method can be modified to remove rest of Ti, but not Cr due to sulfate interference on Be retention
    - Simply pass 0.2M HF-0.1M HCl through 2.8 ml anion resin/no rinsing to remove additional Ti, etc.

Digestion/Preparation



Column Separation with Sulfate Digestion



* Removes additional Ti if needed

Spectral Interference Removal-Sulfate Digestion

Interference	Added (ppm)	Measured (ppm)	Removal (%)
Iron	1000	0.021	99.998
Uranium	100	0.262	99.74
Niobium	100	ND	~100
Molybdenum	100	0.027	99.973
Vanadium	100	ND	~100
Zirconium	100	3.795	96.205
Zirconium*	100	ND	~100
Tungsten	100	0.0.006	99.994
Thorium	50	ND	~100
Titanium	100	13.86	86.14
Titanium*	100	0.030	99.97
Cerium	50	ND	~100
Chromium	100	69.18	30.82

n=4; ppm added to have this level interference in 20 ml at ICP-AES
*additional anion exchange

Summary

- New rapid ion exchange method to remove spectral interferences developed at SRS
  - Simple, single* pass with excellent removal of interferences
  - Good accuracy and precision
  - Less expensive than LN-3 + Be Resin
- Can be used with other digestion methods
- Makes low level Be work by ICP-AES more feasible even with high levels of impurities
- May have application to “protect” ICP-MS from high levels of impurities (that may also be analytes)

* if 234 nm line used or low Cr

Acknowledgements

- Chemists
  - Maureen Bernard, Linda Youmans, Matthew Nelson
- Lab Technicians
  - Phil Baker, Roslyn Cooke