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New Method for Removal of Spectral Interferences for Be Assay

M. Bernard and S. Maxwell
Savannah River Nuclear Solutions, LLC
Aiken, SC
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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)

New Method for Removal of Spectral Interferences for Beryllium Assay using Inductively-Coupled Plasma Atomic Emission Spectrometry", S.L. Maxwell, M. Bernard, Talanta 76 (2008), 432-440

Potential spectral interferences for Be determination by ICP-AES [a]

Analyte	Peak (nm)	Intensity	Analyte	Peak (nm)	Intensity	Analyte	Peak (nm)	Intensity
U	312.879	6.0	U	313.056	6.0	Hf	313.181	20.0
Zr	312.917	400.0	U	313.073	0.0	U	313.199	15.0
Nb	312.964	22.0	Nb	313.079	2200.0	Cr	313.206	1000.0
U	312.973	15.0	Ti	313.079	150.0	Zr	313.207	7.0
Zr	312.976	550.0	Ce	313.087	65.0	Th	313.226	5.0
Th	312.997	10.0	Th	313.107	27.0	Mo	313.259	1800.0
V	313.027	1020.0	Be[b]	313.107	41000.0	Ce	313.259	30.0
Ce	313.033	50.0	Tm	313.126	Not listed			
Be[b]	313.042	64000.0	U	313.132	8.0			

a As listed in Perkin Elmer WinLab32 software v.2.0
b Commonly used peaks for determining beryllium by ICP-AES

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 HCI-HF Solutions”, Journal of Am. Chem. Soc., Vol.77, 3972, (1955)
- K.A Kraus et al, “Absorbability of a Number of Elements in HCI-HF Solutions”, Journal of Am. Chem. Soc., Vol. 82, 339, (1960)

Blend of Old and New

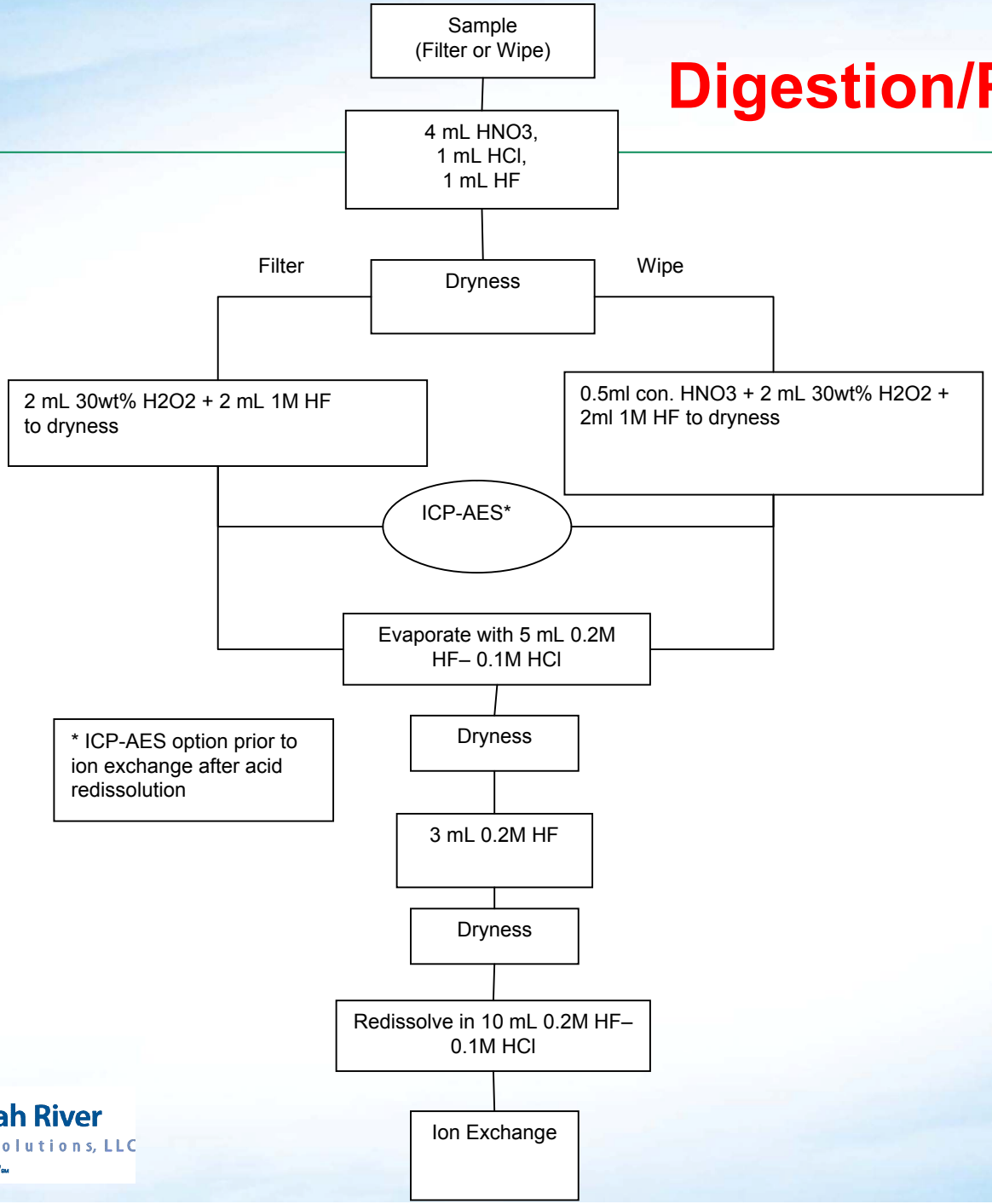
- **Diphonix Resin**
  - Much higher retention than typical cation resin with sulfonic acid groups
  - Diphonix Resin has a very high retention for U, Th, V, Fe, Er and Ce even in dilute HF
  - Relatively inexpensive (<$7 for 5 ml resin)
- **TEVA Resin**
  - Efficient anion exchanger (Aliquat 336 extractant)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



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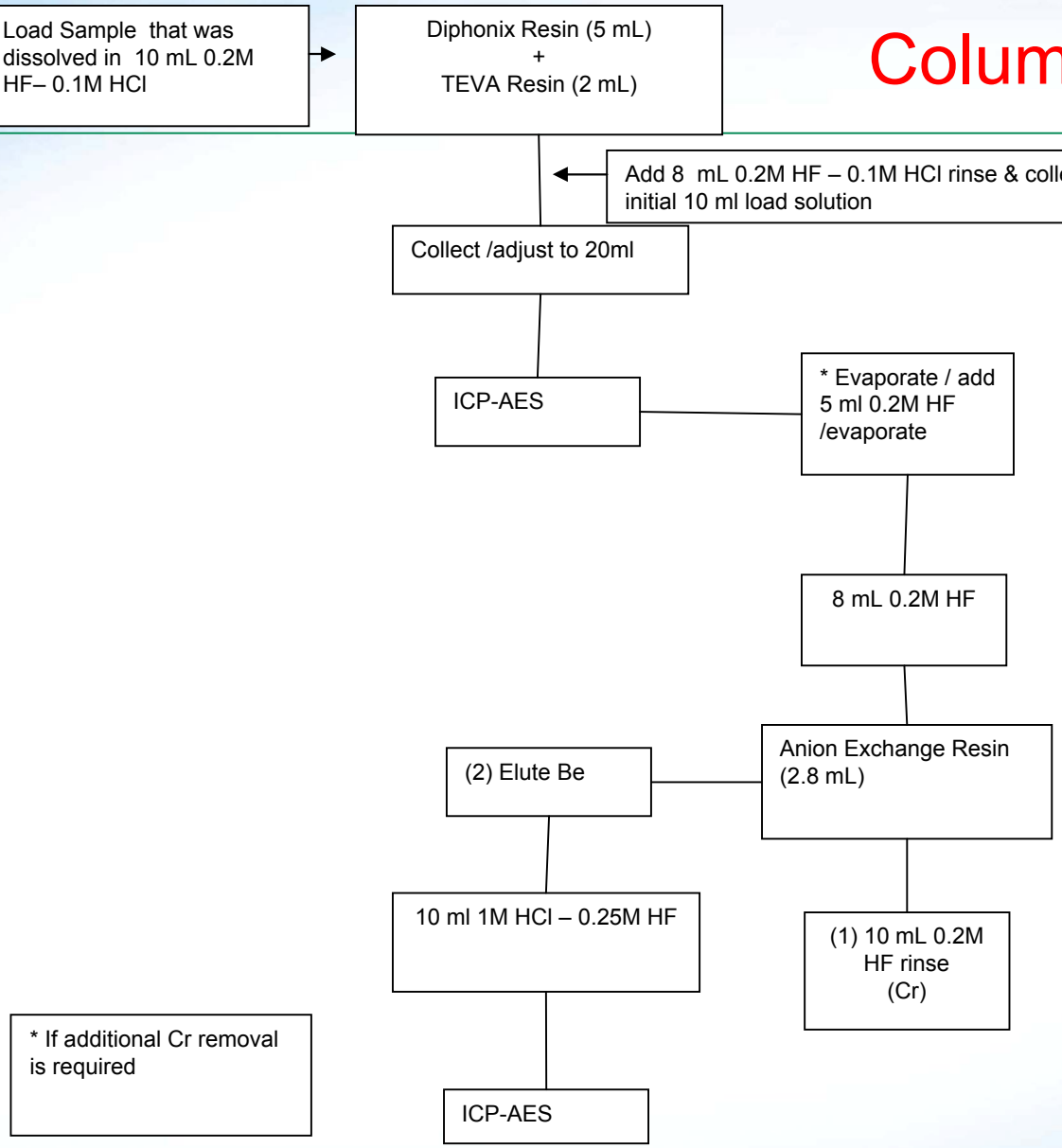
Column Separation



Spectral Interference Removal

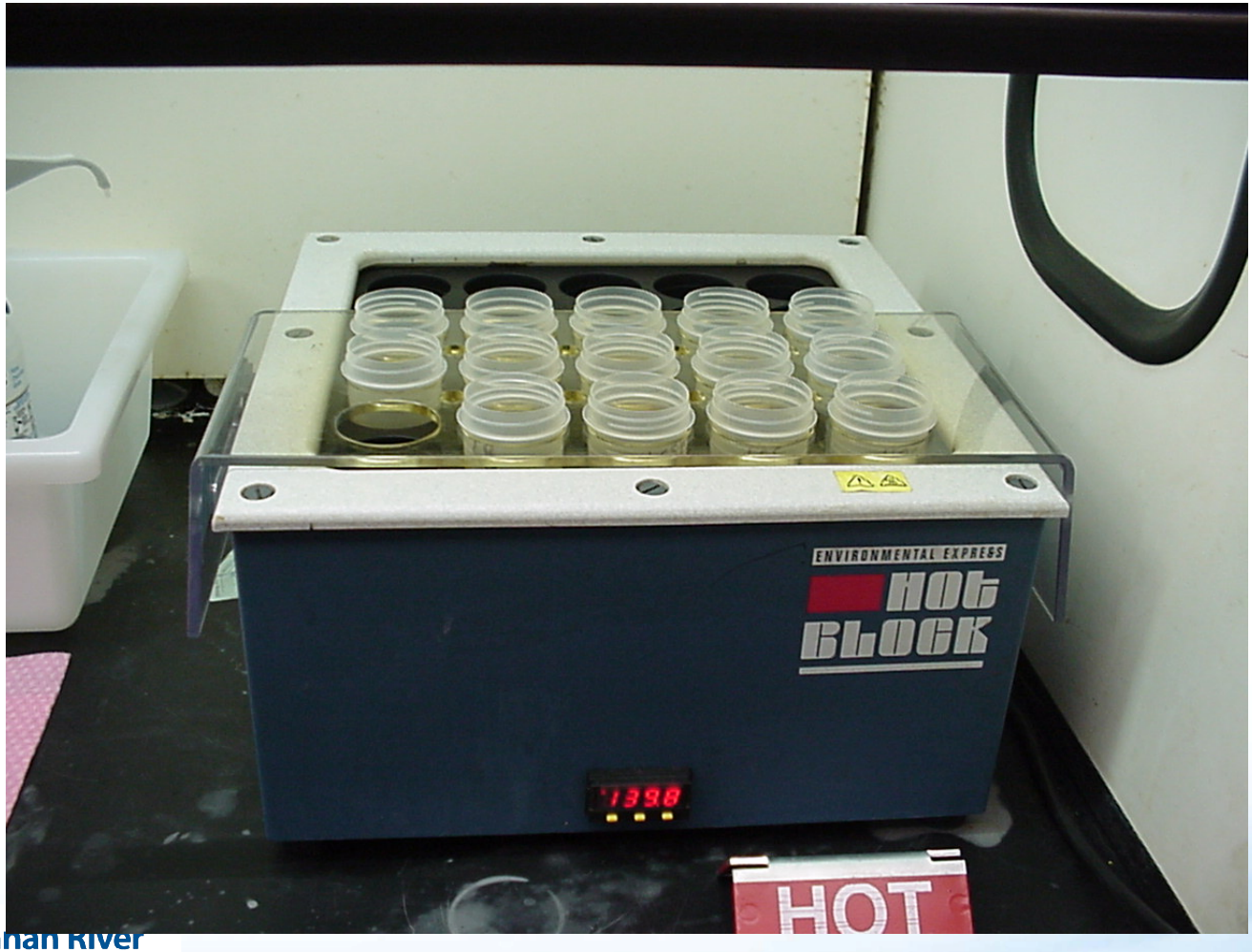
Interference	Added (ppm)	Measured Removal (ppm)	(%)
Iron**	1000	0.039	99.996
Uranium	300	0.112	99.963
Niobium	100	ND	~100
Molybdenum	100	0.002	99.998
Vanadium	100	0.003	99.997
Zirconium	100	0.082	99.918
Tungsten	100	0.010	99.990
Thorium	50	ND	~100
Titanium	100	0.736	99.964
Cerium	50	ND	~100
Erbium	100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

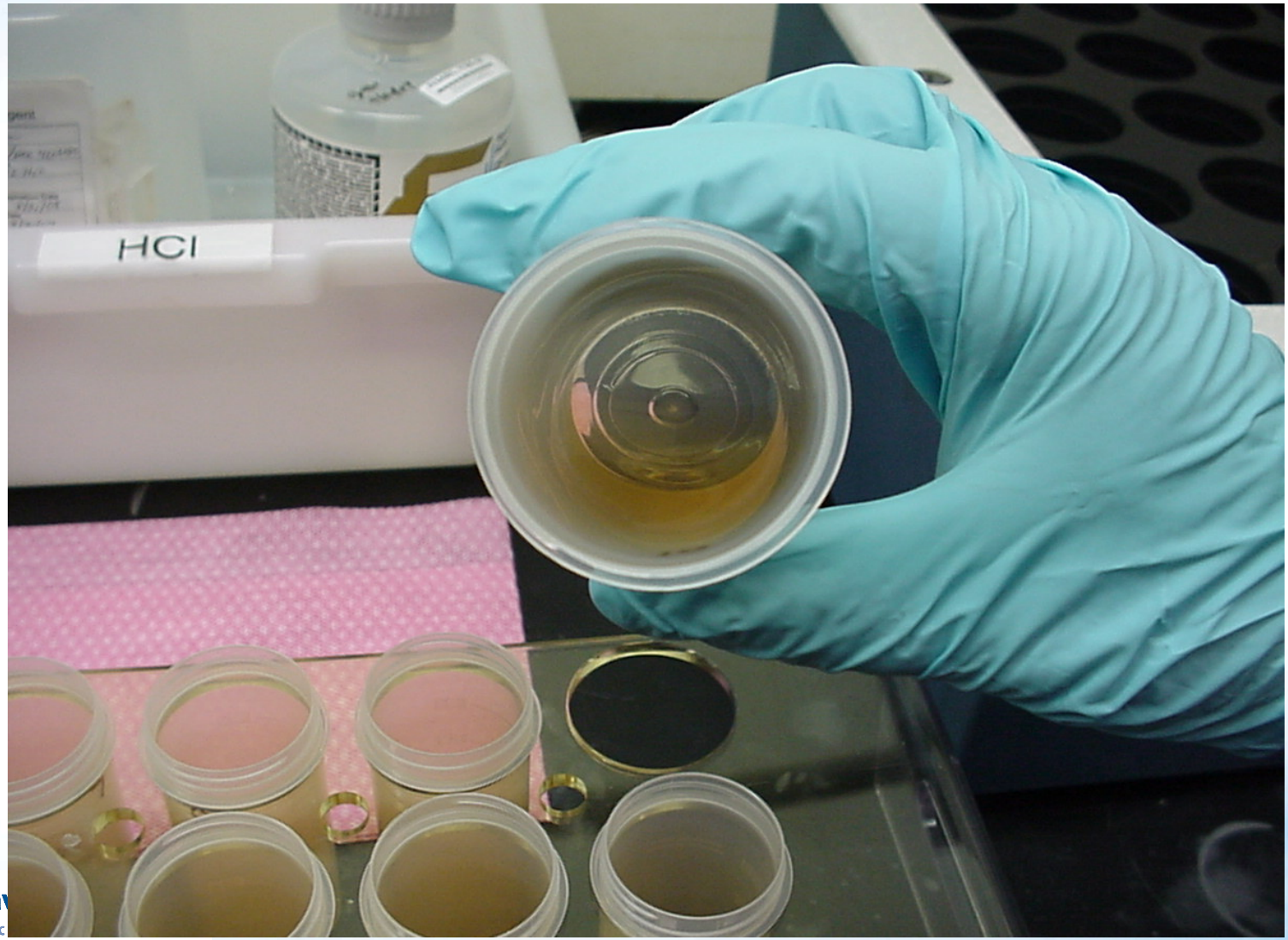
**Fe has similar removal at 2500 ppm

Hot Block Digestion



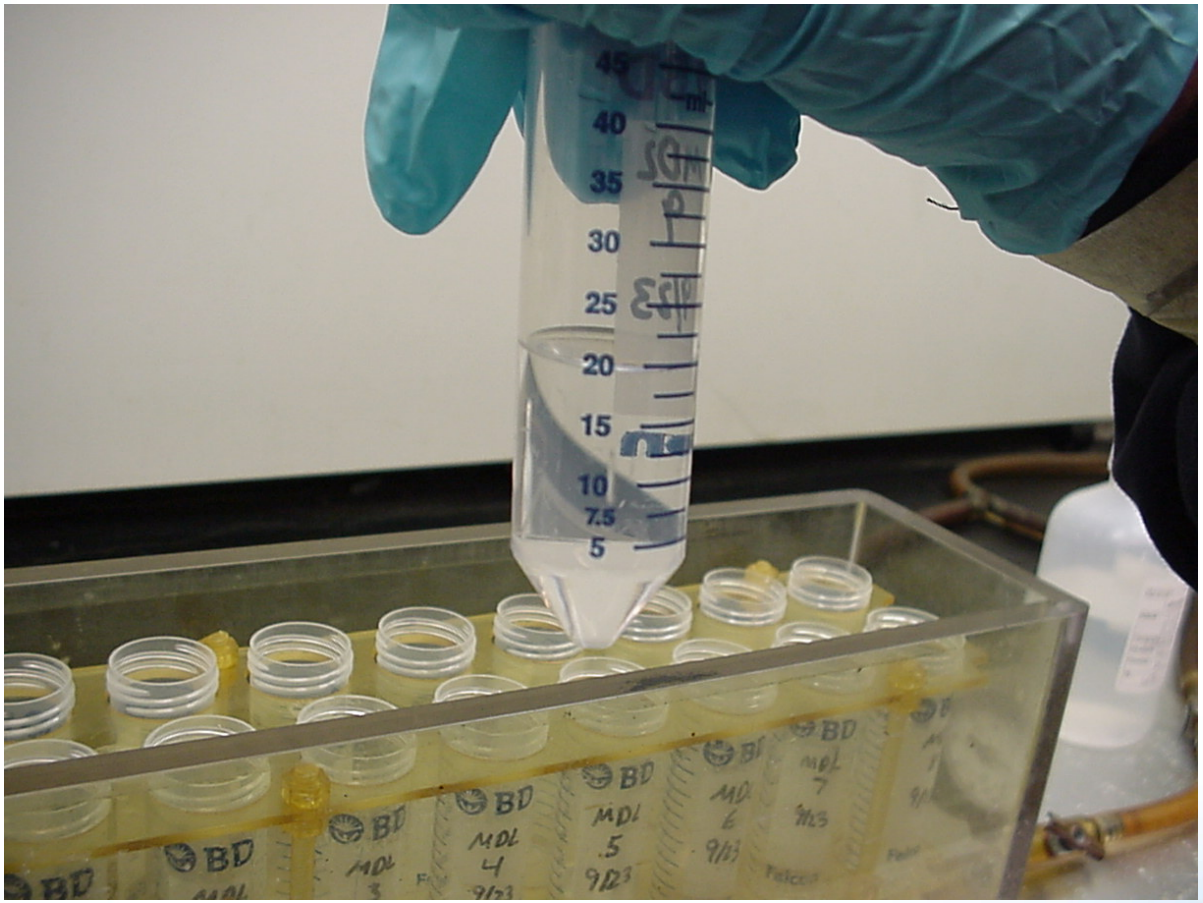
Hot Block Digestion

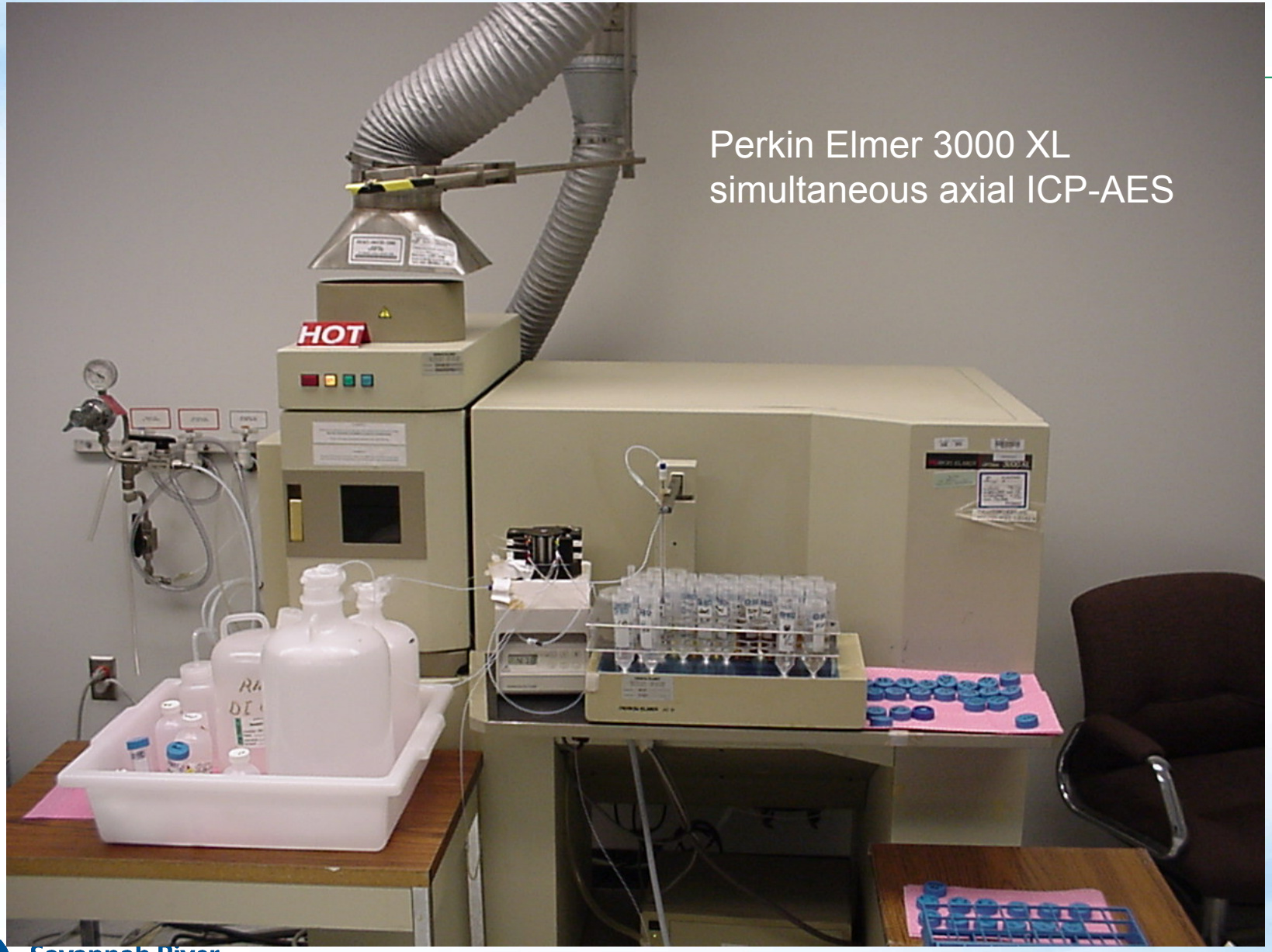
Digested Filter



Diphonix Resin+ TEVA

Ready for ICP-AES





Perkin Elmer 3000 XL
simultaneous axial ICP-AES

Instrument Operating Conditions and Parameters for Perkin Elmer Optima 3000XL

RF Power	**1400 watts**
Nebulizer Flow	**0.75 L/min**
Auxillary Flow	**0.5 L/min**
Plasma Flow	**15 L/min**
Sample Pump Flow	**1.5 mL/min**
Plasma Viewing	**Axial**
Processing Mode	**Area**
Auto Integration (min-max)	**5-20 s**
Read Delay	**30 s**
Rinse	**90 s**
Replicates	**3**
Background Correction	**1-2 points**
Nebulizer GemCone ™	**Low-flow**
Nebulizer Chamber	**Cyclonic**
Injector	**Alumina, 2 mm**

Be Average Recovery Results (Wipes) - Interferences Added

Emission Line	Be Added (ppb)	Be Measured after IEX (ppb)	Recovery (%)	Bias (%)	RSD (%)	After Anion IEX	Recovery (%)	Bias (%)	RSD (%)
234.861 nm	1.00	1.07	107.29	7.29	7.28	N/A	N/A	N/A	N/A
313.042 nm	1.00	1.60	159.75	59.75	14.79	1.06	105.50	5.50	13.54
313.107 nm	1.00	1.61	161.25	61.25	18.85	1.18	117.61	17.61	10.86

N=12

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Be Average Recovery Results (Air Filters) - Interferences Added

Emission Line	Be Added (ppb)	Be Measured after IEX (ppb)	Recovery (%)	Bias (%)	RSD (%)	After Anion IEX	Recovery (%)	Bias (%)	RSD (%)
234.861 nm	5.00	4.76	95.11	-4.89	3.97	N/A	N/A	N/A	N/A
313.042 nm	5.00	5.30	105.97	5.97	5.99	4.91	98.13	-1.87	3.85
313.107 nm	5.00	5.18	103.53	3.53	4.72	4.94	98.87	-1.13	3.86

N=6

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BeO Filter Recovery Results - Interferences Added

		Be Added (ppb)	Be Measured after IEX (ppb) 234.861 nm	Recovery (%)	Bias (%)
1	BeO filter	10	8.35	83.50	-16.50
2	BeO filter	10	8.37	83.70	-16.30
3	BeO filter	10	8.44	84.40	-15.60
4	BeO filter	10	8.27	82.7	-17.30
			Avg.	83.58	-16.42
			%RSD	0.84	
	BeO bias-No IEX		SRS F/H lab		-21.87
	BeO bias-No IEX		SRS EBL Lab		-14.80

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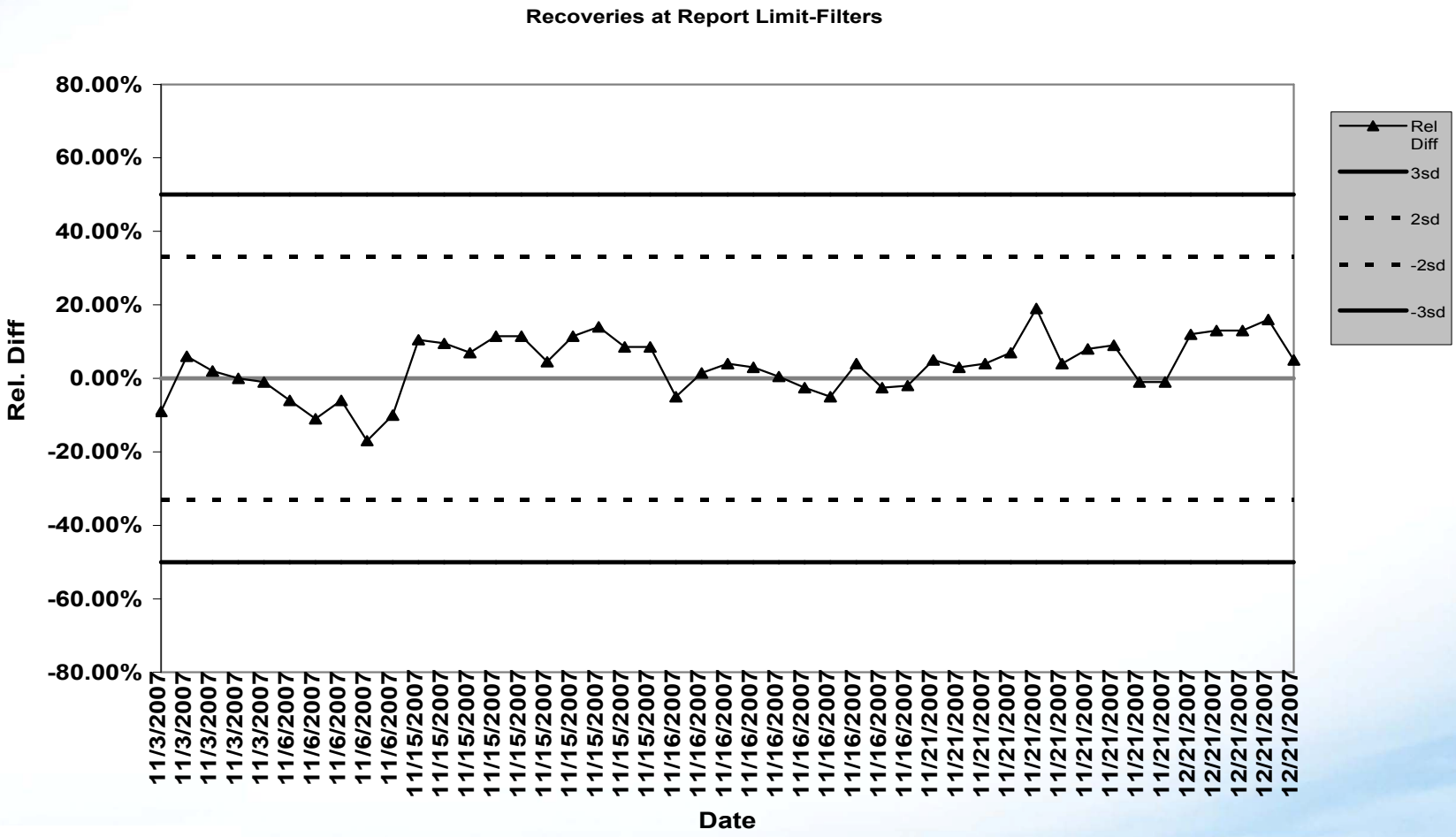
Be Recovery Results at Report Limit - Filters



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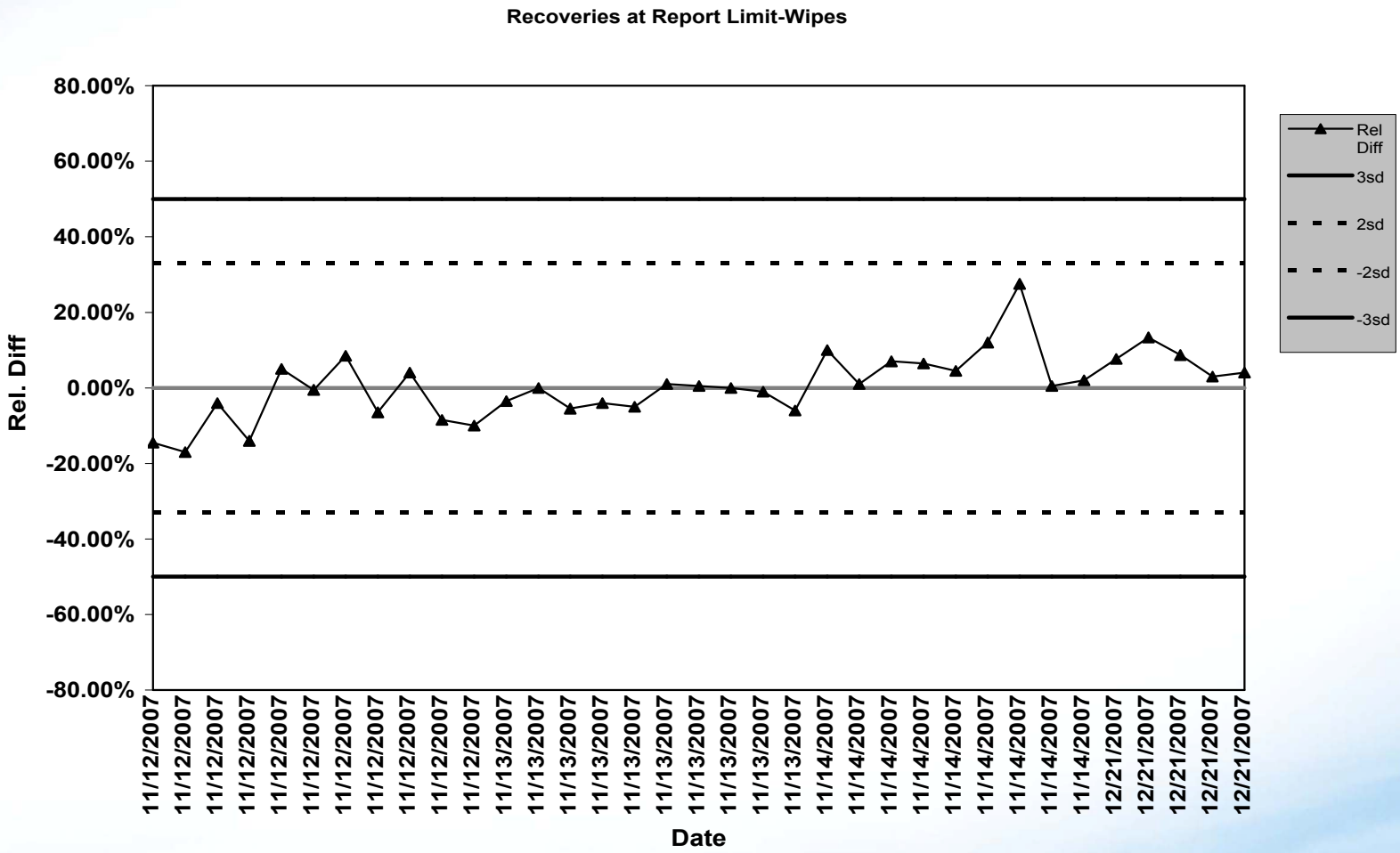
Be Recovery Results at Report Limit - Wipes



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Summary of MDL and RL Results for Be Filter Method

Analyzed:	10/17/2007	10/17/2007	10/17/2007	11/15/2007	11/15/2007	11/15/2007	11/16/2007	11/16/2007	11/16/2007
ppb	1	1	1	1	1	1	1	1	1
	Be 234.861	Be 313.042	Be 313.107	Be 234.861	Be 313.042	Be 313.107	Be 234.861	Be 313.042	Be 313.107
AVERAGE	1.12206	1.07341	1.02602	1.46648	0.80707	1.09679	1.12479	0.99870	0.99605
STD DEV	0.031843	0.038831	0.036713	0.049504	0.040893	0.026412	0.031859	0.046317	0.034562
MDL, ppb Be	0.090	0.110	0.104	0.140	0.115	0.075	0.090	0.131	0.097
Report Limit [MDL*5] , ppb Be	0.449	0.548	0.518	0.698	0.577	0.373	0.449	0.653	0.487
Report Limit [MDL*5*0.020L] , ug Be /filter	0.009	0.011	0.010	0.014	0.012	0.007	0.009	0.013	0.010
N=10									

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Summary of MDL and RL Results for Be Wipes Method

Analyzed:	11/13/2007	11/13/2007	11/13/2007	11/14/2007	11/14/2007	11/14/2007
ppb	1	1	1	1	1	1
	Be 234.861	Be 313.042	Be 313.107	Be 234.861	Be 313.042	Be 313.107
AVERAGE	0.96218	1.02472	0.97656	1.05410	1.05407	1.07881
STD DEV	0.033457	0.029333	0.026731	0.095662	0.094815	0.083318
%Recovery	96.218	102.472	97.656	105.41	105.41	107.88
MDL, ppb Be	0.094	0.083	0.075	0.277	0.275	0.241
Report Limit [MDL*5] , ppb Be	0.472	0.414	0.377	1.385	1.373	1.206
Report Limit [MDL*5*0.020L] , ug Be /wipe	0.009	0.008	0.008	0.028	0.027	0.024

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.

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
- **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

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  - Linda Youmans-McDonald, Matthew Nelson
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