

Beryllium: Necessity for Monitoring

UGM05 - 09/12/05 - Manchester

Outline

- **Beryllium, uses and properties**
- **Beryllium: associated problems**
- **Necessity for monitoring**
- **Problem encountered**
- **Dipex resin**
- **Effects of large quantities of Uranium**
- **Summary**

Beryllium: uses and properties

- **Discovered in 1798**
 - Not widely used in Industry until 1940s and 50s
- **Lighter than Aluminum, Stiffer than Steel**
 - 2nd lightest metal
 - 6 times stiffer than steel
- **High heat absorption**
 - One pound absorbs as much heat as 5 pounds of copper
- **Be Metals, Alloys, Salts and Oxides are used for a wide variety of Industries**
 - Structures in high-speed aircraft (space shuttle)
 - Satellite mirrors and space telescopes
 - Golf clubs and bicycle frames
 - Neutron moderators or reflectors in nuclear reactors

Beryllium: associated problems

- **Physical Problems**
 - Expensive
 - Brittleness
 - Increases toxicity
- **Health Hazard**
 - Most Significant disadvantage for industrial use
 - Causes Chronic Beryllium Disease (CBD)
 - No known cure, can only be treated
 - Produces scarring of lung tissue
 - Chronic, may take years to develop
 - Average latency period is 10-15 years
 - 2-5 % of population Be sensitive
 - Exemple: Over 100 current and former DOE employees have CBD

Necessity for monitoring

- **Workers safety**
 - Air and surfaces monitoring
- **Currently**
 - ICP-AES or GFAA on microwave digested samples
 - sensitive to certain interferences

Problems encountered

Interfering elements in the AES spectrum of Beryllium

Table 1. Potential Spectral Interferences for Be determination by ICP-AES^a

Analyte	Peak (nm)	Intensity	Analyte	Peak (nm)	Intensity
Cr	312.870	15.0	Nb	313.079	2200.0
U	312.879	6.0	Ti	313.080	6.0
Zr	312.918	400.0	Ce	313.087	65.0
Nb	312.964	22.0	Th	313.107	27.0
U	312.973	15.0	Be^b	313.107	41000.0
Zr	312.976	550.0	Tm	313.126	2300.0
Th	312.997	10.0	U	313.132	8.0
V	313.027	1020.0	Hf	313.181	20.0
OH	313.028	0.0	U	313.199	15.0
Ce	313.033	50.0	Cr	313.206	1000.0
Be^b	313.042	64000.0	Zr	313.207	7.0
U	313.056	6.0	Th	313.226	5.0
OH	313.057	0.0	Mo	313.259	1800.0
U	313.073	0.0	Ce	313.259	30.0

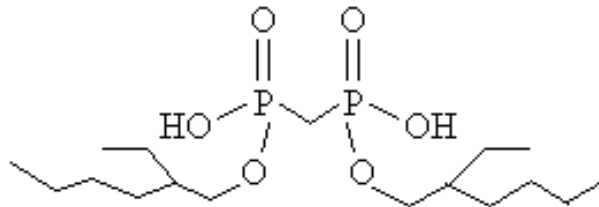
^aAs listed in Varian Plasma96 software version 1.12

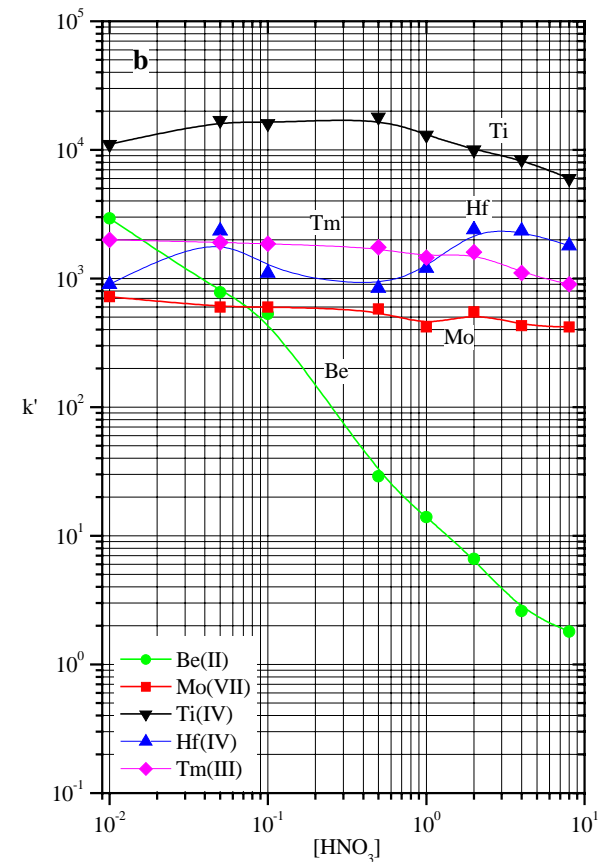
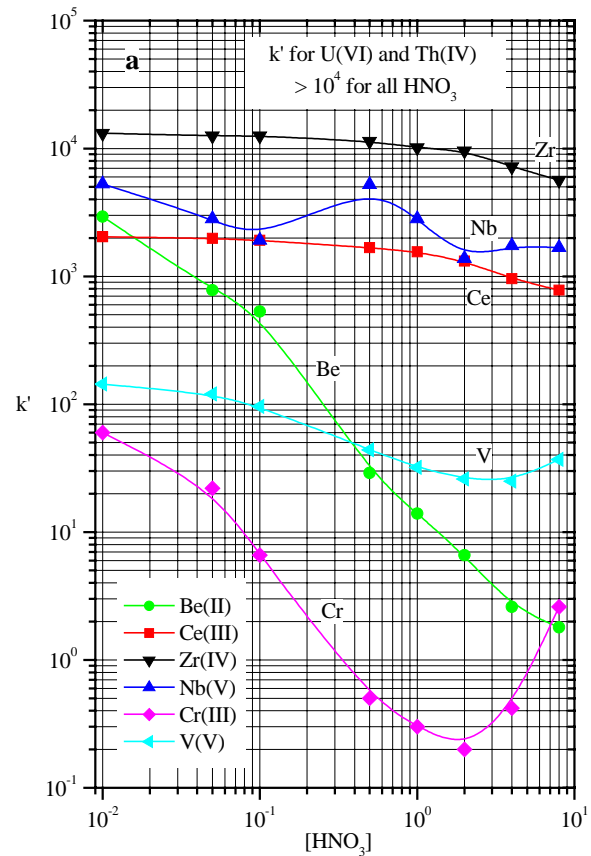
^bCommonly used peaks for beryllium determination by ICP-AES

- Beryllium lines very intense → method is very sensitive for the determination of beryllium
- Interfering lines from other elements could lead to false positives
- Positive determination of beryllium leads to shut down of operation until cleanup

Problems encountered

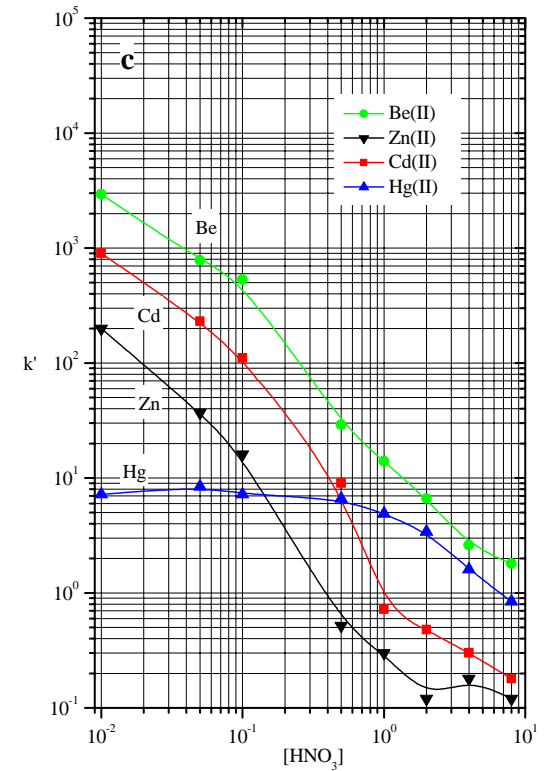
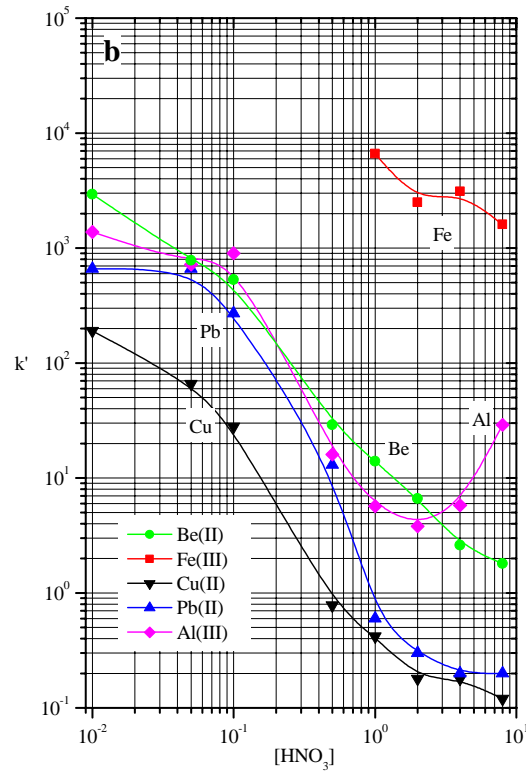
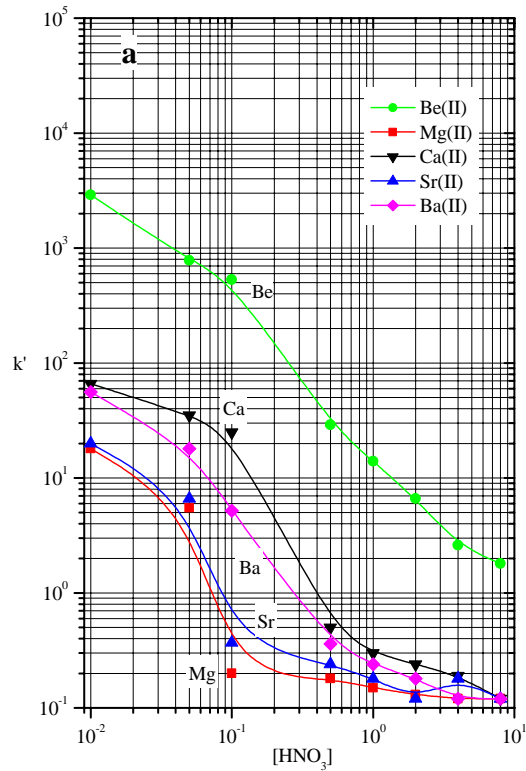
- Currently Interfering lines are corrected using inter element correction (IEC)
- Uranium is particularly spectrally rich
- Spectrum shifts depending on the degree of enrichment of the Uranium
- Method for removing AES interfering elements from samples desired, Uranium in particular
- Several EXC Resins evaluated for their ability to purify Be samples



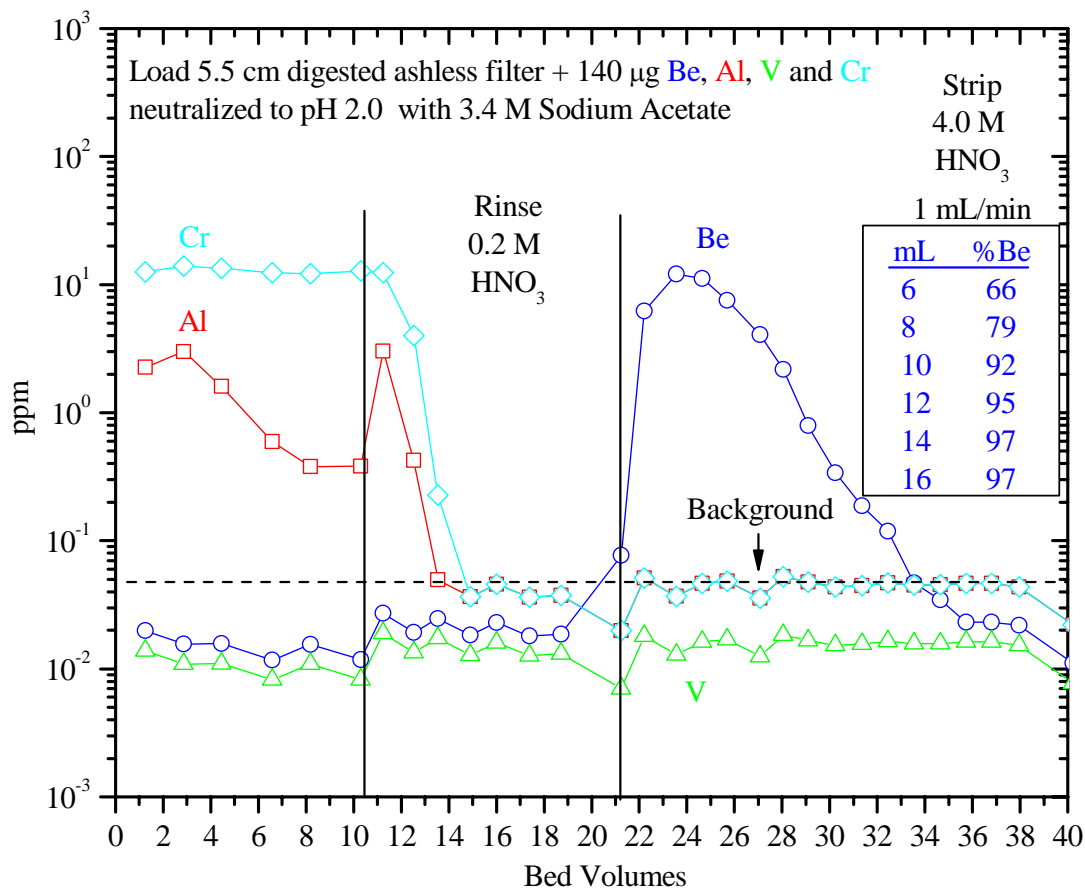


- Be retained at low acid and stripped at high acid
- Most interferences strongly retained over entire range
- Cr weakly retained over entire range
- Single column should purify Be from all interferences
- Uranium very strongly retained

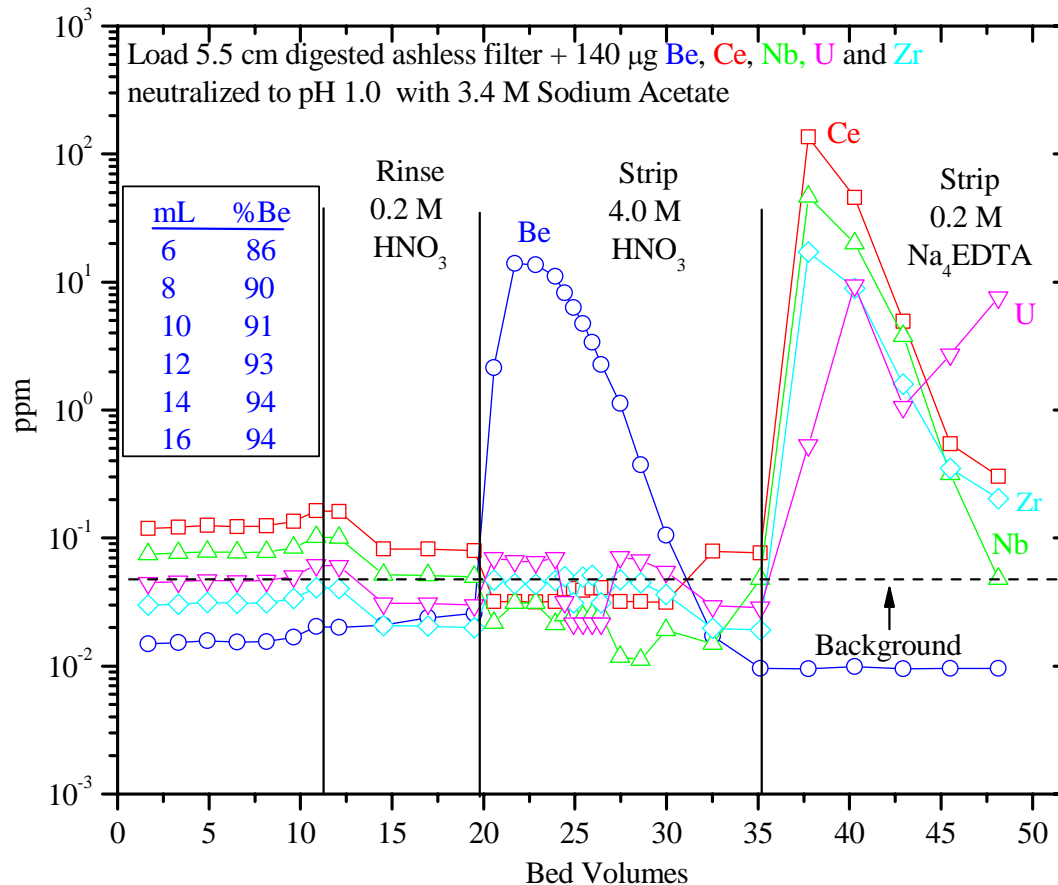
Uptake of Selected Elements on Dipex Resin



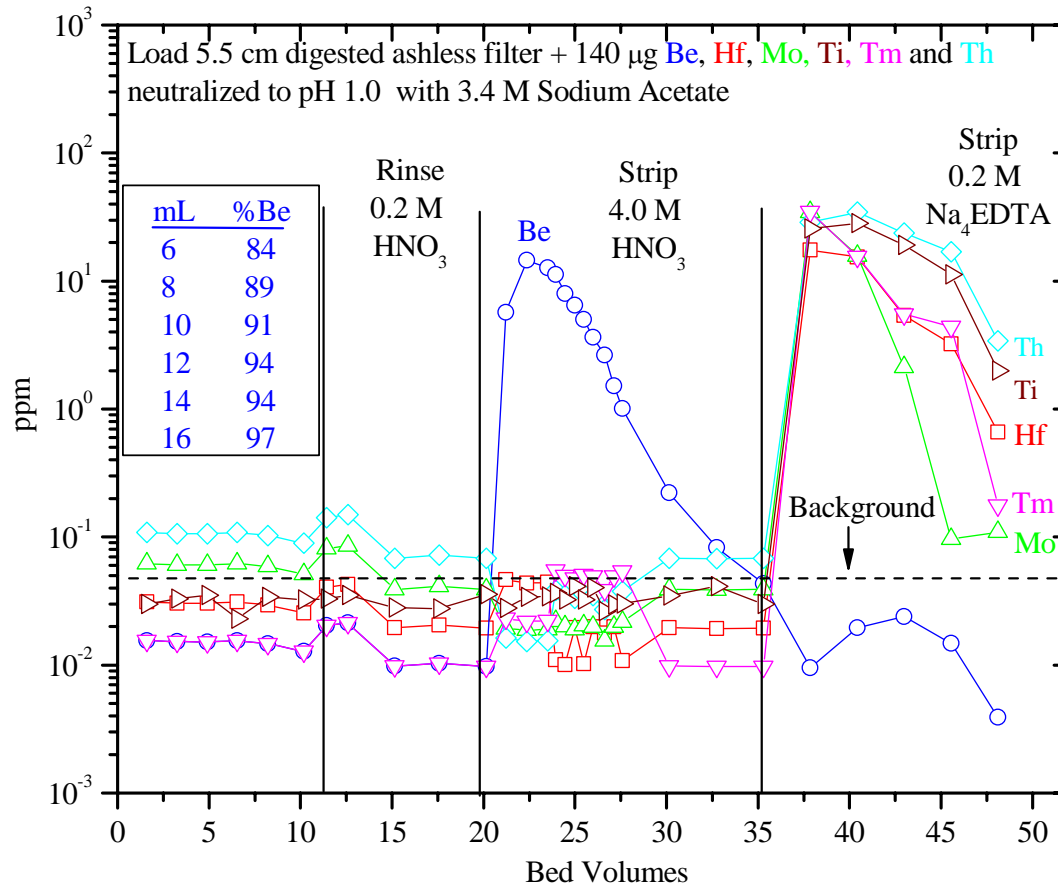
Elution of Be and Selected Elements on Dipex Resin



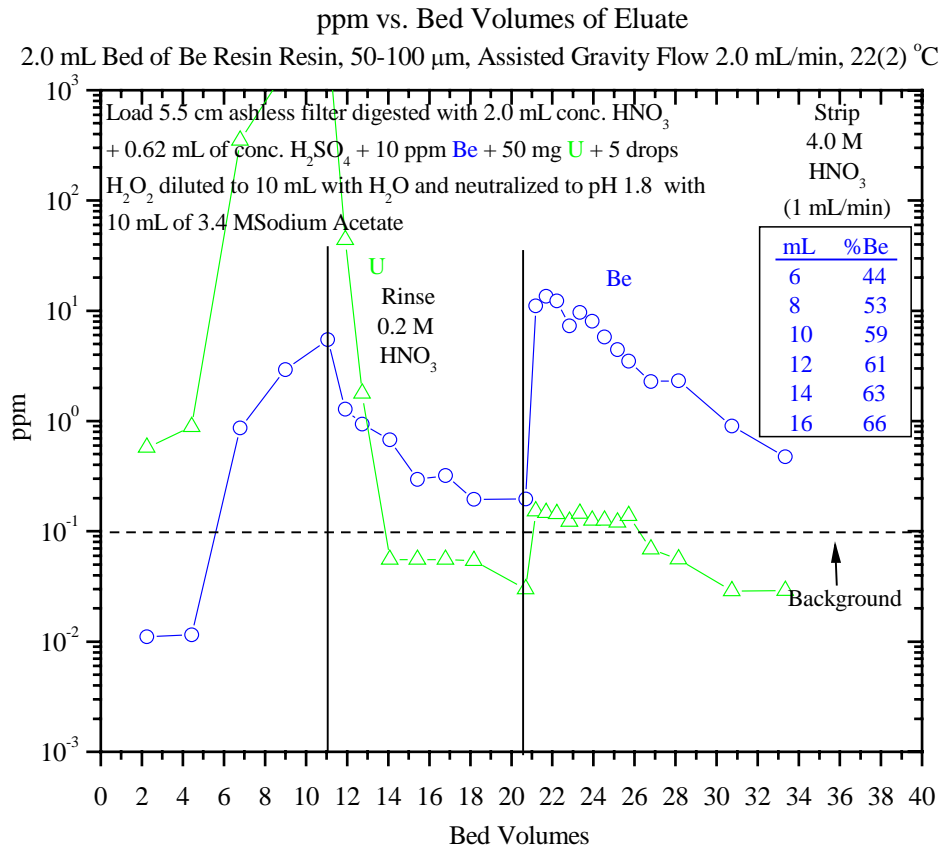
Elution of Be and Selected Elements on Dipex Resin



Elution of Be and Selected Elements on Dipex Resin

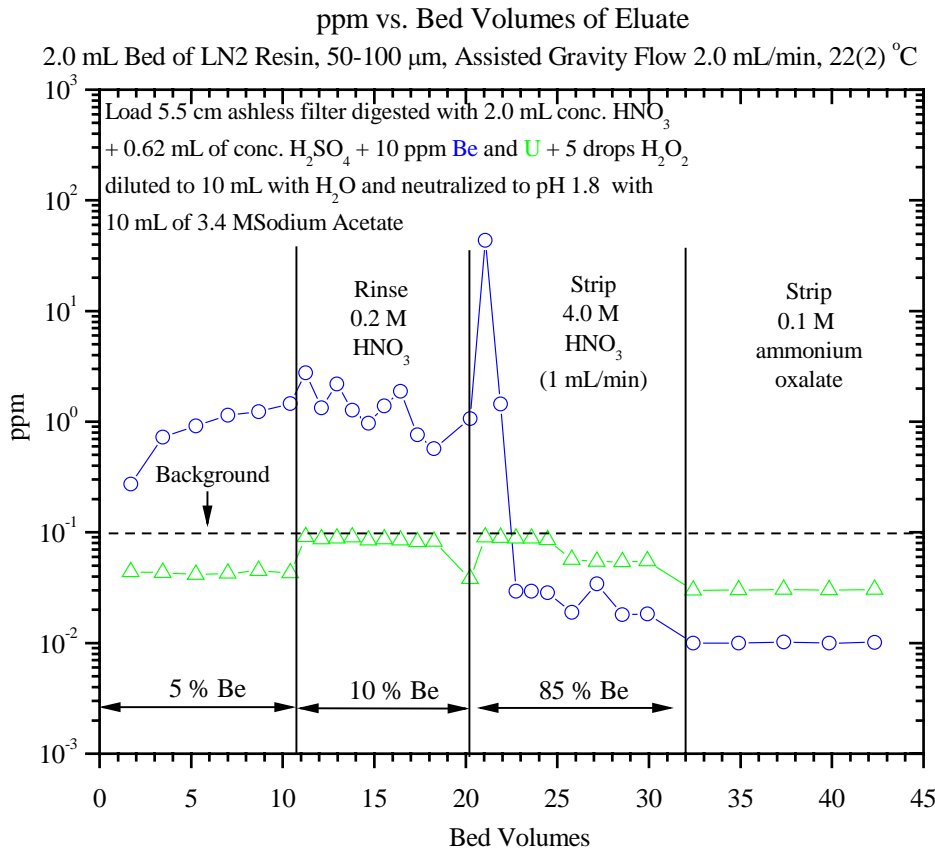


Effect of Large Quantities of Uranium

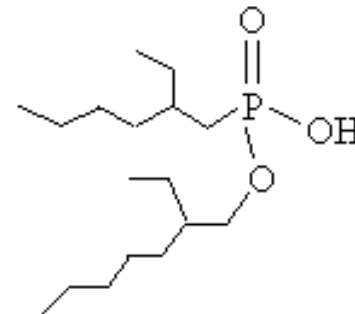


- Uranium uptake on Dipex Resin is very high
- Large amounts of Uranium could consume resin capacity and reduce Beryllium yields
- 50 mg of U reduces Beryllium yield to ~60%
- 100 mg of U reduces Beryllium yield to 29% and leads to U in Beryllium fraction

Effect of Large Quantities of Uranium

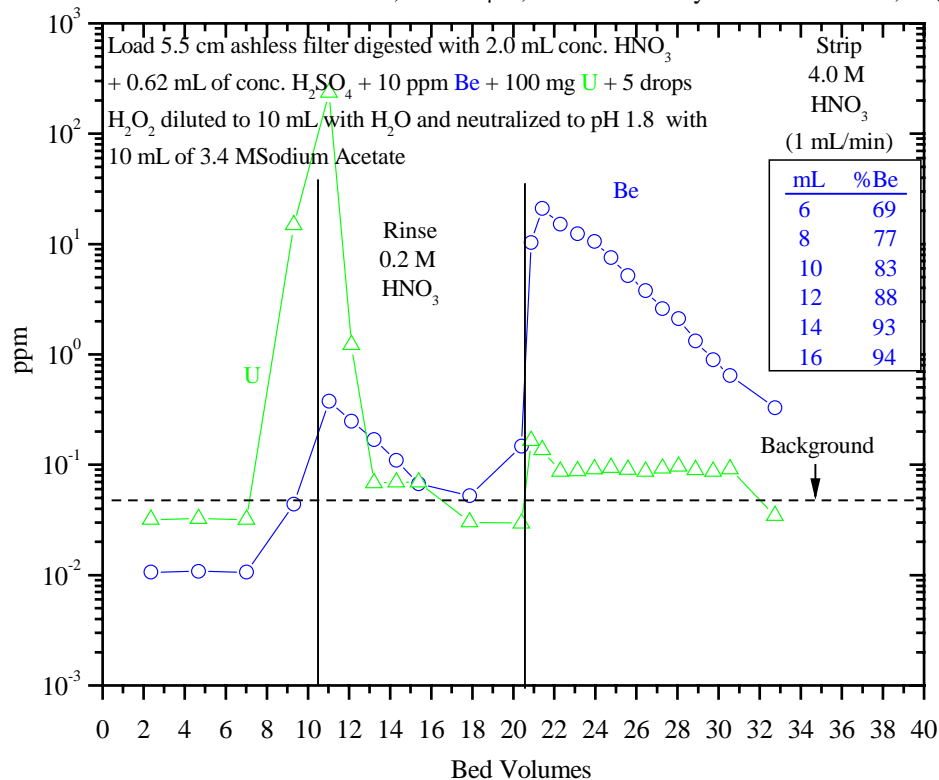


- An LN2 Resin guard column effectively separates U from Be
- LN2 resin contains a substituted phosphonic acid



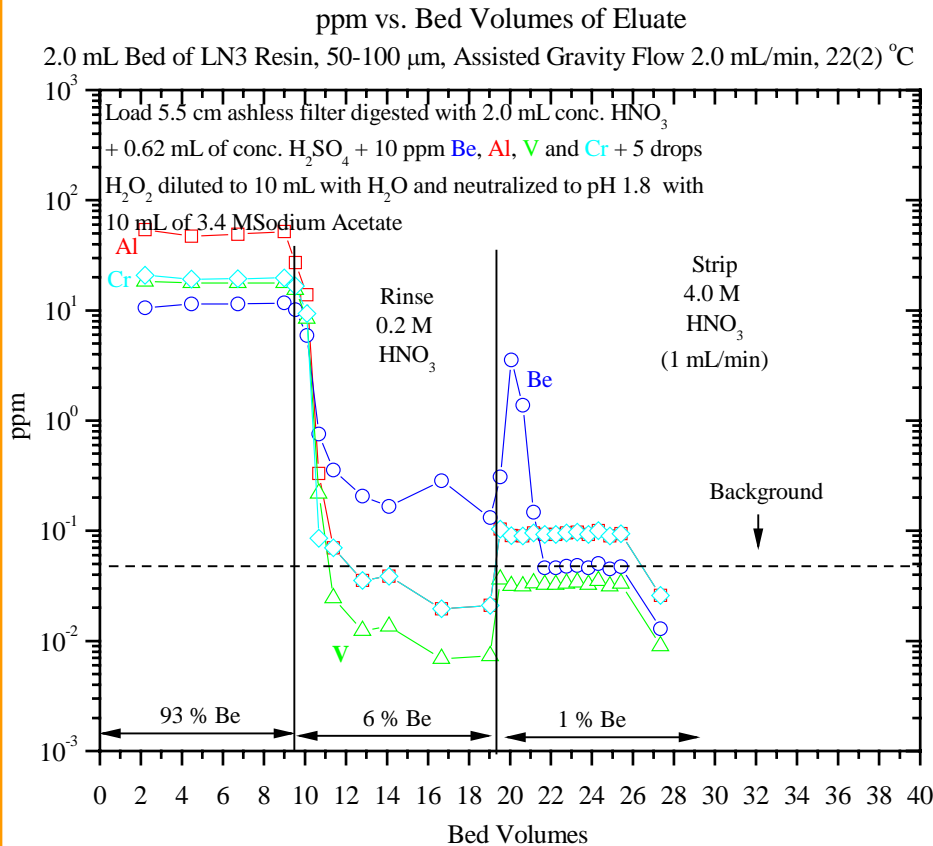
Effect of Large Quantities of Uranium

ppm vs. Bed Volumes of Eluate
 2.0 mL Beds of Be Resin and LN2 Resin, 50-100 μm , Assisted Gravity Flow 2.0 mL/min, 22(2) $^{\circ}\text{C}$

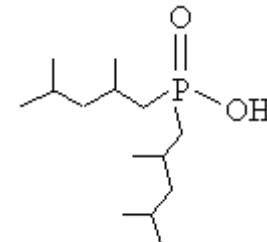


- Coupling an LN2 Resin guard column increases Uranium capacity without decreasing Beryllium yields or changing chemistry
- Over 100 mg of Uranium does not decrease Beryllium yield or produce Uranium in Beryllium fraction
- GC attached through load, rinse and strip

Effect of Large Quantities of Uranium



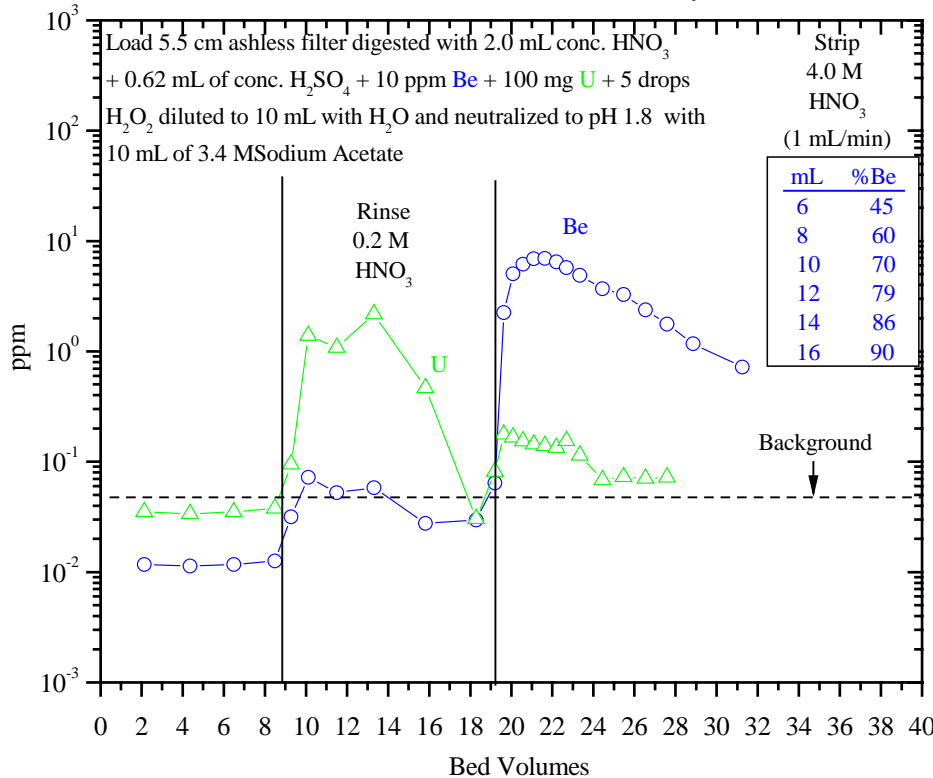
- An LN3 Resin guard column also removes U from Be and retains Be less than LN2
- LN3 resin contains a substituted phosphinic acid



Effect of Large Quantities of Uranium

ppm vs. Bed Volumes of Eluate

2.0 mL Beds of Be Resin and LN3 Resin, 50-100 μm , Assisted Gravity Flow 2.0 mL/min, 22(2) $^{\circ}\text{C}$



- Coupling an LN3 Resin guard column increases Uranium capacity without decreasing Beryllium yields or changing chemistry
- Over 100 mg of Uranium does not decrease Beryllium yield or produce Uranium in Beryllium fraction
- GC can be removed following rinse

Effect of Large Quantities of Uranium

Beryllium Yields and Uranium Impurity vs mg Uranium in Load Solution^a

mg U	2 mL Beryllium Resin		2 mL Beryllium Resin + 2 mL LN2		2 mL Beryllium Resin + 2 mL LN3	
	% Be	µg U in	% Be	µg U in	% Be	µg U in
	in 12 mL ^b	Be fraction	in 12 mL ^b	Be fraction	in 12 mL ^b	Be fraction
0.14	90	< 1.5 ^c	85	< 1.5	N/A	N/A
10	92	< 1.5	N/A	N/A	N/A	N/A
25	86	< 1.5	87	< 1.5	97	< 1.5
50	61	< 1.5	88	< 1.5	97	< 1.5
75	N/A	N/A	81	< 1.5	93	< 1.5
100	29	580	88	< 1.5	79	< 1.5

^aWhatman filter paper spiked with 0.14 mg Be, digested with H₂SO₄/H₂O₂, and neutralized with sodium acetate to pH 1.8

^bBeryllium Resin Strip Solution 4.0 M HNO₃

^cDetection limit for Uranium by ICP-AES under the experimental conditions

- LN2 and LN3 Resins effectively increase the capacity for Uranium
- With LN2, the GC remains connected through the load, rinse and strip
- With LN3, the GC can be removed following the rinse

Summary

- Efficient, reliable method for purifying Be from all ICP-AES spectral interfering elements has been found using a single column
- Method is compatible with current monitoring and sample digestion methods
- Method is robust and performs over a wide pH range
 - pH can be monitored with indicator to ensure optimal performance
- Inserting a LN2 or LN3 Resin guard column increases U capacity without changing the chemistry or significantly decreasing Be yields
- Dipex Resin currently available from Eichrom as Beryllium Resin