Prepared for Submission to SXIX 3/05

THE SEPARATION OF BERYLLIUM FROM SELECTED ELEMENTS USING THE DIPEX® EXTRACTION CHROMATOGRAPHIC RESIN

E. Philip Horwitz* and Daniel R. McAlister

PG Research Foundation, Inc., 8205 S. Cass Ave., Suite 106, Darien, IL 60561

ABSTRACT

An extraction chromatographic resin containing the acidic chelating organophosphorus extractant, Dipex® sorbed onto an inert polymeric substrate has been evaluated for the separation of beryllium from a wide range of elements. The elements selected comprise elements which can interfere with the determination of beryllium by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) and matrix elements which commonly occur in environmental and industrial samples. Based on batch uptake measurements, a method that separates beryllium from all potential ICP-AES spectral interfering elements using a single extraction chromatographic column is outlined. The chromatographic parameters of the separation method have been optimized using simulated samples generated using the digestion process employed in beryllium analyses by the Y-12 National Security Complex and simulated ground water samples.

Key words: Chronic Beryllium Disease (CBD), Extraction Chromatography, ICP-AES, Dipex®

INTRODUCTION

Beryllium possesses many unique physical properties and is, therefore, an important industrial metal. It is light weight, six times stiffer than steel, nonmagnetic and corrosion resistant. Beryllium is particularly valuable in specific areas of nuclear technology. Its ability to reflect neutrons and its efficiency in the production of neutrons when exposed to alpha emitters has led to its use in nuclear reactors and nuclear weapons (1). However, the use of Be carries with it some serious health hazards, including cancer and chronic beryllium disease (CBD). Chronic beryllium disease is caused by the inhalation of beryllium compounds, particularly the oxide, and produces scarring of the lung tissue. The lung condition may take years (average

*Address correspondence to E. P. Horwitz, PG Research Foundation, Inc. 8205 S Cass Ave., Suite 106 Darien, IL 60561, USA

10 to 15) to develop symptoms (2-4). The disease has no known cure and usually results in death. Over 100 current and former DOE employees have CBD (5). Because of the seriousness of CBD, the United States Department of Energy promulgated in 1999 the CBD prevention program, 10CFR Part 850, to protect DOE workers from exposure to Be contaminated dust. This program requires frequent monitoring of air and possible contaminated surfaces to identify potential health risks.

While the clearest correlation of beryllium exposure and disease has been linked to its inhalation by workers involved in the machining of beryllium, beryllium has been linked to a number of other health effects resulting from interference of enzyme function, DNA synthesis, protein phosphorylation and cell division. The potential for exposure to the general population is primarily due to the release of beryllium during coal incineration. An estimated 10-20 million pounds per year of beryllium are emitted during coal and refuse incineration, which can contaminate air, drinking water, soil and agricultural products (1).

Due to the high toxicity of beryllium, there is a need to analyze large numbers of environmental and industrial samples for beryllium contamination. The current analytical method of choice is inductively coupled plasma-atomic emission spectroscopy (ICP-AES) (1,6), however, several other methods, including precipitation, ion-exchange, colorimetry and fluorimetry have been used to concentrate and/or determine beryllium in industrial and environmental samples (1). In DOE facilities, samples, including air filters and surface smears, are digested using combinations of hydrochloric, hydrofluoric, nitric and/or sulfuric acid and hydrogen peroxide at elevated temperature to ensure that beryllium oxide or metallic beryllium is in an aqueous soluble state (7). Beryllium is then determined by ICP-AES using the 313.107 and 313.034 nm lines in the atomic emission spectrum of beryllium. Although ICP-AES is an excellent method for the detection beryllium because of the low detection limits, a number of elements can cause spectral interferences (Table 1). Therefore, there is a need to separate beryllium from such elements. Because of the large number of samples that need to be analyzed, any separation must be simple, fast, and reliable.

Extraction chromatography has been demonstrated to be a fast and reliable method for the separation and preconcentration of a number of radionuclides and metal ions from a wide range of matrices (8). The objective of this study was to evaluate the separation and preconcentration of beryllium from simulated industrial and environmental samples using an extraction chromatographic (EXC) resin called Dipex® (9). Dipex® contains a chelating diphosphonic acid extractant, bis (2-ethylhexyl) methanediphosphonic acid, sorbed onto Amberchrom CG-71ms acrylic ester beads.

EXPERIMENTAL

Reagents

The Dipex® extraction chromatographic resin containing bis (2-ethylhexyl) methanediphosphonic acid, sorbed onto Amberchrom CG-71ms acrylic ester beads was obtained from Eichrom Technologies, Inc. (Darien, IL). Nitric and sulfuric acid solutions were prepared from Trace Metal Grade acids (Fisher Scientific) using deionized water obtained from a Milli-Q2 water purification system. Sodium acetate, sodium citrate, tetrasodium-EDTA, and 35% H_2O_2 were ACS grade (Aldrich). Metal ion solutions were prepared using single element atomic absorption standard solutions of 1,000 or 10,000 parts per million metal ion in water (Be, Nb, Cr, Mo), dilute nitric acid (U, Sr, Ba, Ca, Mg, Pb, Cu, Fe, Hg, Zn, Cd, Zr, Ce, Tm) or dilute hydrochloric acid (V, Al, Ti, Hf) (Fisher Scientific).

Procedures

Determination of weight distribution ratios and column capacity factors

The uptake of metal ions by Dipex® resin from acidic solutions was measured by contacting a known volume of solution (5.0 to 7.5 mL) with a known mass of resin (100-300 mg) in a borosilicate glass culture tube. Unless otherwise noted, all experiments were performed at 22(2)°C using 50-100 μm particle size resin beads.

The exact ratio of resin to aqueous phase and the concentration of metal ions was varied to produce a measurable difference in the initial and final concentrations of metal ion in the aqueous phase and to ensure that the molar ratio of extractant to metal ion was at least 50:1. The mixing of resin and the aqueous phase was performed by intermittent agitation on a vortex mixer and by using a small magnetic stir bar rotated at a speed sufficient to keep the resin beads suspended in the aqueous phase. Following equilibration with the resin, the aqueous phase was filtered with a 0.45 μm PTFE filter to remove any resin particles. Metal ion concentrations were determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES) on a Varian Liberty Series II sequential inductively coupled plasma atomic emission spectrometer using the parameters listed in Table 2. Beryllium was determined using the 234.861 nm peak of its atomic emission spectrum, rather than the 313.042 nm and 313.107 nm peaks more commonly used for the determination of beryllium. While the 234.861 nm peak is less intense than the 313.042 nm and 313.107 nm peaks, the 234.861 nm peak is considerably more free of spectral interferences (6), and the intensity of the 234.861 nm peak is still sufficient for the concentrations of beryllium employed in this study. Preliminary experiments showed that the uptake of beryllium approached equilibrium after 40 minutes. An equilibration time of one hour was used in all determinations of weight distribution ratios.

Weight distribution ratios (D_w) were calculated using the following equation:

$$D_w = ((A_o - A_s)/w)/(A_s/V) \qquad (1)$$

where A_o and A_s are the aqueous phase metal ion concentrations (parts per million) before and after equilibration, w is the weight of the resin in grams and V is the volume of aqueous phase in milliliters. Duplicate experiments showed that the reproducibility of the D_w measurements was generally within 10%, although the uncertainty was somewhat higher for the highest D_w values ($>10^3$). The weight distribution ratios were converted to the number of free column volumes to peak maximum, k′ (the resin capacity factor), by first calculating the volume distribution ratio (D_v, a value calculated from equation 1 in which the weight of the resin, w, is replaced by the volume of extractant) using the following equation:

$$D_v = D_w \text{ x } d_{extr}/0.4 \qquad (2)$$

where d_{extr} is the density of the extractant and 0.4 is the extractant loading in grams of extractant per gram of resin. The D_v values were then converted to k′ by using the following equation:

$$k' = D_v \text{ x } (v_s/v_m) \qquad (3)$$

where v_s and v_m are the volumes of stationary phase (extractant) and mobile phase, respectively, for a dry packed column of Dipex® Resin. The physical constants necessary to convert D_w to k′ for dry packed columns of 50-100 μm particle size Dipex® Resin are listed in Table 3. By combining equations (2) and (3) and using the values reported in Table 3 for d_{extr} and v_s/v_m, one obtains:

$$k' = D_w \text{ x } 0.60 \qquad (4)$$

Thus, for each weight distribution ratio measured on Dipex® Resin, the corresponding k′ value can be obtained by multiplying the D_w value by 0.60.

Determination of metal ion elution curves

A volume (20-100 mL) of solution containing 0.1 -10,000 ppm of various metal ions, selected as possible spectral interferences in the determination of beryllium by ICP-AES or as possible matrix interferences in the uptake of beryllium on Dipex® Resin, was loaded onto a 2 mL dry packed cartridge of Dipex® resin (50-100 μm particle size, 9 mm inner diameter, 30 mm column height). The column was then rinsed with dilute nitric acid and stripped with 3-5 M nitric acid to remove beryllium or 0.2 M tetrasodium-EDTA or 0.2 M sodium citrate to remove more strongly absorbed metal ions. Unless otherwise noted, all experiments were performed at 22(2)°C using 2 mL/min flow rates. Fractions of the eluate were collected into tared 15 mL polypropylene centrifuge tubes and diluted to 5 mL with deionized water. Metal ion concentrations in the diluted eluate solutions were then determined by ICP-AES using atomic emission lines of the highest intensity and/or having the fewest spectral interferences. The concentration of beryllium determined by ICP-AES was found to vary as the matrix of the beryllium containing solution was changed. This phenomenon is frequently observed in ICP-AES (10,11). The beryllium concentrations determined by ICP-AES were, therefore, normalized to the 4.0 M HNO_3 matrix used for the ICP-AES calibration standards by using the data in Table 4.

Preparation of digested samples

Circles of ashless filter paper (5.5 cm in diameter) were spiked with 1.4 to 140 μg of various metal ions and digested using 3 mL of concentrated nitric acid (70%) and 0.6 mL of concentrated sulfuric acid (98%) on a hotplate set at $150^{o}C$. The digestion evolved a reddish brown gas (likely NO_x). After 10-20 minutes of heating, no traces of the filter paper remained and the evolution of the reddish brown gas ceased. The resulting solution was pale yellow and became black if heated at $150^{o}C$ for longer than 20 minutes. Dropwise addition of 10-20 drops of 35% H_2O_2 removed all color from the solution and the sample was heated at $150^{o}C$ for an additional ten minutes. The resultant solution was cooled, transferred to a 50 mL polypropylene centrifuge tube, neutralized to pH 1 to 4.5 with sodium acetate (pH meter) and diluted to 20 mL with deionized water. Weakly basic sodium acetate, rather than a strong base, such as sodium hydroxide, was chosen to neutralize the load solution because the buffering capacity of sodium acetate prevents the pH of the solution from exceeding pH 4.5, reducing the likelihood of precipitation of hydrolyzed metal species (12,13). The addition of an excess sodium acetate will result in a mildly acidic solution, rather than the highly basic solution possible if a strong base were used to neutralize the load solution.

Preparation of simulated ground water samples

Stock solutions A and B were prepared, combined in equal parts, diluted 20:1 with deionized water and the pH of the solution adjusted to 8.0 using 0.1 M HCl or 0.1 M NaOH (14). Stock solution A consisted of 75 mg $Al(NO_3)_3$, 1.07 g KCl, 228 mL of 0.1 M $CaCl_2$ and 201 mL of 2 M HCl diluted to 1 liter with deionized water. Stock solution B consisted of 30.36 g $Na_2SiO_2 \cdot 9H_2O$, 6.35 g Na_2CO_3, 3.09 g NaF, 10.06 g of Na_2SO_4 and 3 g NaOH diluted to 1 liter with deionized water. The groundwater stimulant was spiked with 140 μg of selected metal ions and adjusted to pH 2 with concentrated and 0.1 M HNO_3.

RESULTS AND DISCUSSION

Kinetics of Be(II) uptake

Figure 1 depicts the kinetics of uptake of Be(II) on Dipex® resin from a simulated digested filter solution neutralized to pH 1 with sodium acetate. Equilibrium was approached after 40 minutes. The uptake of Be(II) on Dipex® resin is slower than that observed for other extraction chromatographic materials employing organophosphorus extractants (9), which typically reach equilibrium metal ion uptake in 10 minutes. However, the Be(II) uptake is similar to previous observations for Dipex® resin with Am(III) and Fe(III) radiotracers, which reached equilibrium in 20 minutes (9).

Uptake of Be(II) and ICP-AES spectral interferences on Dipex® resin

Figure 2 depicts the uptake on Dipex® resin vs. HNO_3 of Be(II) and metal ions identified as potential spectral interferences in the determination of beryllium by ICP-AES (Table 1). Be(II) is strongly retained from 0.01-0.1 M HNO_3 and the plot of k' vs. HNO_3 exhibits a slope of -1.5, close to -2 expected for the plot of the uptake of a divalent metal ion by an acidic extractant. Several of the potential spectral interferences (Mo, Zr, Nb, Ce, Tm, Hf, Ti, U and Th) are strongly retained over the entire range of HNO_3 concentrations, and Cr is weakly retained over the entire range of HNO_3 concentrations.

Based on the data in Figure 2, a separation of Be(II) from all of the potential ICP-AES interferences should be possible by loading a Dipex® resin column with a solution of pH 1-2, rinsing the column with a small volume of dilute nitric acid (0.1-0.2 M HNO_3) and then stripping Be(II) with 3-5 M HNO_3. Any Cr present in the load solution will elute from the Dipex® resin during the load and rinse, while Be(II) and the other potential spectral interferences are retained on the Dipex® resin. The Be(II) will elute with 3-5 M HNO_3, while any Mo, Zr, Nb, Ce, Tm, Hf, Ti, Th and U will be strongly retained on the Dipex® resin column. Therefore, Be(II) should be efficiently separated from all of the potential ICP-AES spectral interferences using a single extraction chromatographic column.

Uptake of Be(II) and potential matrix interferences on Dipex® resin

Figure 3 depicts the uptake on Dipex® resin versus HNO_3 of Be(II) and potential matrix interferences. Figure 3a shows that Dipex® resin exhibits high selectivity for Be(II) over the other alkaline earth metal ions. Therefore, the presence of Ca(II), a common impurity in water and soil samples, should not adversely affect the retention of Be(II) on Dipex® resin.

Figures 3b and 3c show that Cu(II), Zn(II), Cd(II), Mn(II) and Hg(II) are more weakly retained than Be(II) by Dipex® resin, while Fe(III) is strongly retained over the entire range of HNO_3, and Pb(II) and Al(III) exhibit retention profiles similar to that of Be(II). While Fe(III), Cd(II), Mn(II), Pb(II) and Al(III) are not spectral interferences in the measurement of beryllium by ICP-AES, large amounts of these metal ions in the sample matrix could interfere with the uptake of Be(II) on Dipex® resin. Also, based on the data in Figure 3b, it appears that a separation of Be(II) and Al(III) is possible at high nitric acid concentrations (4-8 M HNO_3). The uptake of Al(III) at high HNO_3 concentrations is likely due to the retention of Al(III)-nitrate salts by the fully protonated organophosphorus extractant.

Elution curves for Be(II) and spectral and matrix interferences on Dipex® resin

Effect of the pH of the load solution

Figures 4-7 depict the elution curves for Be(II), Cr(III), Al(III) and V(V) on Dipex® resin as a function of the pH of the load solution. Data has been collected for the elution of the entire series of ICP-AES spectral and matrix interferences (15), but only Be(II) and selected interferences are shown here for brevity. In Figures 4-7, Cr(III) and Al(III) elute during the load, while Be(II) is retained on the Dipex® resin column. The elution of Al(III) during the load is unexpected based on the data in Figure 3b for the uptake of Be(II) and Al(III) on Dipex® resin versus nitric acid, where the Al(III) and Be(II) data overlap at low acidity. The Al(III) elution from the load solution is likely due to the increased complexation of Al(III) by sulfate and acetate relative to Be(II). The formation constants for Al(III) sulfate and acetate species are an order of magnitude larger than those for Be(II) (16).

The elution of vanadium during the load at pH 3.4 and 4.5 was not observed for load solutions of pH 1 and 2. This difference is likely due the formation of large anionic aggregates of vanadium. At pH 1-2 vanadium exists primarily as VO_2^+, while at pH 3-5 species such as $V_{10}O_{26}(OH)_2^{4-}$ and $V_{10}O_{27}(OH)^{5-}$ become prevalent (12).

The Cr(III), Al(III), V(V) elution curves decrease to background after rinsing with several bed volumes of 0.2 M HNO_3, while the Be(II) is retained on the Dipex® resin. Stripping the column with 4 M HNO_3 produces >95% of the beryllium in 12 mL of solution. The most favorable stripping behavior of beryllium was obtained with 4 M HNO_3 using a flow rate of 1 mL/min (vide infra).

Optimization of the Be(II) stripping conditions

Figure 8 depicts data obtained in an effort to optimize the efficiency of stripping Be(II) from Dipex® resin. Be(II) was loaded onto a Dipex® resin column from a solution of 10% HNO_3 6% H_2SO_4 that was neutralized to pH 1 with sodium acetate. Following a rinse with 0.2 M HNO_3, the beryllium was stripped under various conditions. The most efficient stripping of beryllium was observed for 4 M HNO_3 at a flow rate of 1 mL/min. The improved yield observed for the slower flow rate is likely due to similar kinetic issues as those observed for the batch uptake for Be(II) on Dipex® resin in Figure 1. Stripping with 3 M HNO_3 was attempted in an effort to reduce the damage done to the ICP-AES instrument due to the corrosive nature of nitric acid solutions. However, the decreased yield of Be(II) observed for 3 M HNO_3 may outweigh the potential benefit of using lower acid concentrations on the life expectancy of the ICP-AES instrument components. In extraction chromatography, the use of elevated temperature often yields sharper elution curves. However, in this case, elution with 4 M HNO_3 at 50^oC yields only a very modest increase in the beryllium yield and is therefore not recommended.

Effect of beryllium mass on recovery

To assess the effect of the mass of beryllium loaded onto the Dipex® resin on the recovery of beryllium, a series of experiments was performed in which 2 mL Dipex® resin cartridges were loaded with 20 mL of pH 1.0 solutions containing 140 ppm, 14 ppm and 1.4 μg beryllium. The cartridges were rinsed with 0.2 M HNO_3 and then stripped with 4.0 M HNO_3. The results of these experiments are depicted in Figure 9. No significant difference in the percent recovery beryllium was observed for the three different beryllium concentrations, with nearly 90% of the beryllium recovered in 10 mL in each case.

Simulated Groundwater samples

Figure 10 depicts the concentration and separation of beryllium from a 500 mL simulated ground water sample spiked with 100 μg of Be, Pb, U, Fe and Ti using a 2 mL cartridge of the Dipex® resin. The beryllium is concentrated 50:1 and is recovered free of any of the ICP-AES interfering elements. Lead elutes with the beryllium during the 4.0 M HNO_3 strip, but is not an interfering element in the determination of beryllium by ICP-AES. The sample was loaded using a flow rate of 4 mL/min, and the entire time to perform the separation was 2.5 hours.

Elution of Be(II) and Al(III) on Dipex® resin from HNO_3

The batch uptake data in Figure 3b suggest the possibility of separating Be(II) and Al(III) at high concentrations of HNO_3. Figure 11 depicts the results of an experiment in which 20 mL of 0.1 M HNO_3 spiked with 10 ppm of Be(II) and Al(III) is passed through a 2 mL cartridge of Dipex® resin. Very little of the Be(II) and Al(III) (< 1%) elute during the load and 0.2 M HNO_3 rinse. This supports the conclusion that the elution of Al(III) from Dipex resin observed during the load fractions in Figures 4-7 is due to the formation of sulfate and/or acetate complexes. Stripping the cartridge with 4.0 M HNO_3 produces 94% of the beryllium in 12 mL, while the aluminum is retained. Stripping with 2.0 M HNO_3 does not elute the Al(III) as suggested by the batch uptake data in Figure 3b (We have no explanation for this behavior). However, stripping with 0.2 M sodium citrate does verify the presence of aluminum.

SUMMARY AND CONCLUSIONS

An extraction chromatographic resin containing the acidic chelating organophosphorus extractant Dipex sorbed onto Amberchrom CG-71 has been shown to retain beryllium under conditions which enable one to separate beryllium from a wide range of elements. The resin is particularly useful in the removal of several elements that interfere with the determination of beryllium by ICP-AES.

Optimal performance of the beryllium separation method is obtained when loading from a solution of pH 1-4.5, rinsing with 0.2 M HNO_3 and stripping with 4 M HNO_3. The method has been shown to effectively concentrate and isolate beryllium from simulated air filter and groundwater samples.

ACKNOWLEDGEMENT

The authors wish to thank Darrin K. Mann of the Y-12 National Security Complex, Oak Ridge, TN for making us aware of the beryllium problem and for many helpful discussions.

REFERENCES

1. Taylor, T. P.; Ding, M.; Ehler, D. S.; Foreman, T. M.; Kaszuba, J. P.; Sauer, N. N. Beryllium in the Environment: A Review, J. Environ. Sci. Health A. Environ. Sci. Eng. Toxic Hazard. Subst. Control, 2003, A38, 439-469.

2. Meyer, K. C. Beryllium and Lung Disease, Chest, 1994, 106, 942-946.

3. Newman, L. Beryllium, in Hazardous Materials Toxicology: Clinical Principles of Environmental Health, Sullivan, J. B.; Krieger, G. R.; Editors, Williams and Wilkins, Baltimore, MD, 1992, 882-890.

4. Williams, W. J. Beryllium Disease, in Occupational Lung Disorders, 3rd ed., Parkes, W. R.; Editor, Butterworth-Heinemann, Oxford, 1994, 571-592.

5. Mann, D. K.; Bowman, B.; Oatts, T. J.; Belt, V. F. The Determination of Beryllium in an Enriched Uranium Matrix, Eichrom Technologies, Inc. Users Meeting, Charleston, SC, May 4, 2004, www.eichrom.com/analytical/radio/meet/2004/ powerpoint/v10_auto.ppt.

6. Jurgensen, A. R.; Hart, J. C.; Farrow, L. L. Beryllium Limits of Detection and Spectral Interferences in 2% Nitric Acid, Digested Air Filter Paper, and GHOSTWIPE™ Matrices by Inductively Coupled Plasma Emission Spectrometry, Westinghouse Savannah River Company, WSRC-TR-2003-0493, Rev. 0, 2003.

7. Coleman, C. J.; Jurgensen, A. R.; Click, D. R.; Hart, J. C.; Rutherford, R. L.; Smith, W. M.; White, T. L.; Burch, B. H.; Missimer, D. M. Evaluation of High-Fired Beryllium Oxide Digestion Methods to Measure Beryllium in Industrial Hygiene Samples by Inductively Coupled Plasma-Atomic Emission Spectroscopy, Westinghouse Savannah River Company WSRC-TR-2004-00395, Rev. 1, 2004.

8. Horwitz, E. P. Extraction Chromatography of Actinides and Selected Fission Products, in Proceedings of the International Workshop on the Application of Extraction Chromatography in Radionuclide Measurement (IRMM), Geel, Belgium, November 9-10, 1998, 27-37.

9. Horwitz, E. P.; Chiarizia, R.; Dietz, M. L. Dipex: A New Extraction Chromatographic Material for the Separation and Preconcentration of Actinides from Aqueous Solution, React. Funct. Polym., 1997, 33, 25-36.

10. Greenfield, S.; McGeachin, H. M.; Smith, P. B. Nebulization Effects with Acid Solutions in I.C.P. Spectrometry, Anal. Chim. Acta, 1976, 84, 67-78.

11. Canals, A.; Gras, L.; Contreras, H. Elimination of Nitric Acid Interference in ICP-AES by Using a Cyclonic Spray Chamber/Nafion Membrane-Based Desolvation System, J. Anal. At. Spectrom., 2002, 17, 219-226.

12. Baes Jr., C.F.; Messmer, R. E. The Hydrolysis of Cations, John Wiley and Sons, New York, 1976, 200-205.

13. Lide, D. R. CRC Handbook of Chemistry and Physics, 83rd ed., CRC Press, New York, 2002, 8-16 to 8-18.

14. Coates, J. T.; Fjeld, R. A.; Paulenova, A.; Devol, T. Evaluation of a Rapid Technique for Measuring Actinide Oxidation States in a Ground Water Stimulant, J. Radioanal. Nucl. Chem., 2001, 248, 501-506.

15. McAlister, D. R.; Horwitz, E. P. A method for the Separation of Beryllium from Spectral Interfering Elements in Inductively Coupled Plasma – Atomic Emission Spectroscopic Analysis, Talanta, 2005, in press.

16. Martell, A. E.; Smith, R. M. NIST Critically Selected Stability Constants of Metal Complexes, NIST Standard Reference Database 46, version 6.0.

Figure Captions

Figure 1. k′ for beryllium on Dipex® resin from 10% HNO_3 6% H_2SO_4 neutralized to pH 1 with sodium acetate vs equilibration time, 22(1)°C, 50-100 μm particle size.

Figure 2. k' for beryllium and potential ICP-AES spectral interferences on Dipex® resin vs. HNO_3, 1 h equilibration time, 22(1)°C, 50-100 μm particle size.

Figure 3. k' for beryllium and potential matrix interferences on Dipex® resin vs. HNO_3, 1 h equilibration time, 22(1)°C, 50-100 μm particle size.

Figure 4. Elution of Al, Be, Cr, and V on a 2 mL dry packed cartridge of Dipex® resin, 50-100 μm particle size, flow rate 2 mL/min, 22(1)°C, Load: 5.5 cm ashless filter spiked with 140 μg Al, Be, Cr, and V, digested with H_2SO_4 and H_2O_2, diluted to 10 mL with HNO_3 and neutralized to pH 1.0 with 3.4 M sodium acetate.

Figure 5. Elution of Al, Be, Cr, and V on a 2 mL dry packed cartridge of Dipex® resin, 50-100 μm particle size, flow rate 2 mL/min, 22(1)°C, Load: 5.5 cm ashless filter spiked with 140 μg Al, Be, Cr, and V, digested with H_2SO_4 and H_2O_2, diluted to 10 mL with HNO_3 and neutralized to pH 2.0 with 3.4 M sodium acetate.

Figure 6. Elution of Al, Be, Cr, and V on a 2 mL dry packed cartridge of Dipex® resin, 50-100 μm particle size, flow rate 2 mL/min, 22(1)°C, Load: 5.5 cm ashless filter spiked with 140 μg Al, Be, Cr, and V, digested with H_2SO_4 and H_2O_2, diluted to 10 mL with HNO_3 and neutralized to pH 3.4 with 3.4 M sodium acetate.

Figure 7. Elution of Al, Be, Cr, and V on a 2 mL dry packed cartridge of Dipex® resin, 50-100 μm particle size, flow rate 2 mL/min, 22(1)°C, Load: 5.5 cm ashless filter spiked with 140 μg Al, Be, Cr, and V, digested with H_2SO_4 and H_2O_2, diluted to 10 mL with HNO_3 and neutralized to pH 1.0 with 4.5 M sodium acetate.

Figure 8. Optimization of beryllium stripping from a 2 mL dry packed cartridge of Dipex® resin, 50-100 μm particle size, Load: 5.5 cm ashless filter spiked with 140 μg Be, digested with H_2SO_4 and H_2O_2, diluted to 10 mL with HNO_3 and neutralized to pH 2.0 with 3.4 M sodium acetate, Rinse: 20 mL of 0.2 M HNO_3.

Figure 9. Effect of beryllium mass on stripping from a 2 mL dry packed cartridge of Dipex® resin, 50-100 μm particle size, Load: 5.5 cm ashless filter spiked with 1.4 to 140 μg Be, digested with H_2SO_4 and H_2O_2, diluted to 10 mL with HNO_3 and neutralized to pH 2.0 with 3.4 M sodium acetate, Rinse: 20 mL of 0.2 M HNO_3.

Figure 10. Elution of Be, Fe, Pb, Ti and U on a 2 mL dry packed cartridge of Dipex® resin, 50-100 μm particle size, flow rate 4 mL/min during load and rinse, 1mL/min

during strip, 22(1)°C, Load: 500 mL simulated ground water spiked with 100 μg Be, Fe, Pb, Ti and U, pH adjusted to 2.0 with HNO_3.

Figure 11. Elution of Al and Be on a 2 mL dry packed cartridge of Dipex® resin, 50-100 μm particle size, flow rate 2 mL/min, 22(1)°C, Load: 20 mL of 0.1 M HNO3 spiked with 140 μg Al and Be.

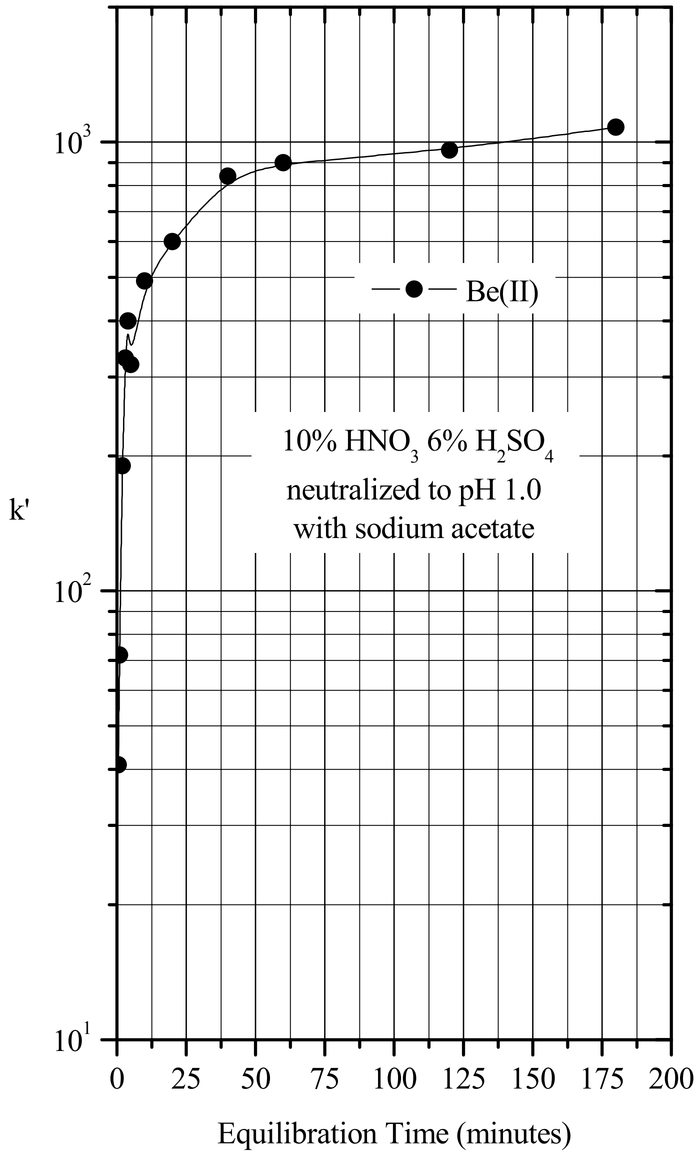

Figure 1. k′ for beryllium on Dipex® resin from 10% HNO_3 6% H_2SO_4 neutralized to pH 1 with sodium acetate vs equilibration time, 22(1)°C, 50-100 μm particle size.

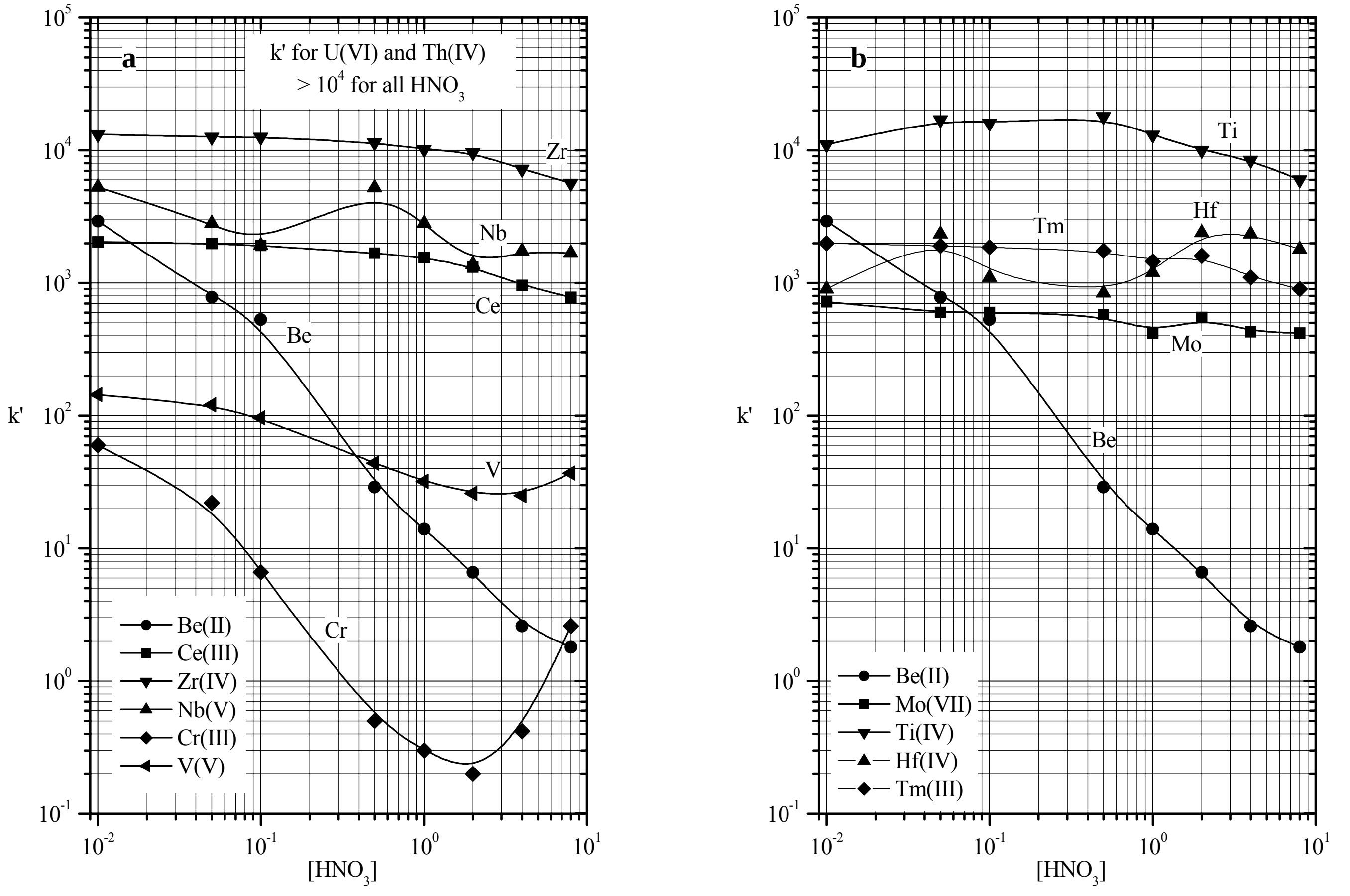

Figure 2. k′ for beryllium and potential ICP-AES spectral interferences on Dipex® resin vs. HNO_3, 1 h equilibration time, 22(2)°C, 50-100 μm particle size

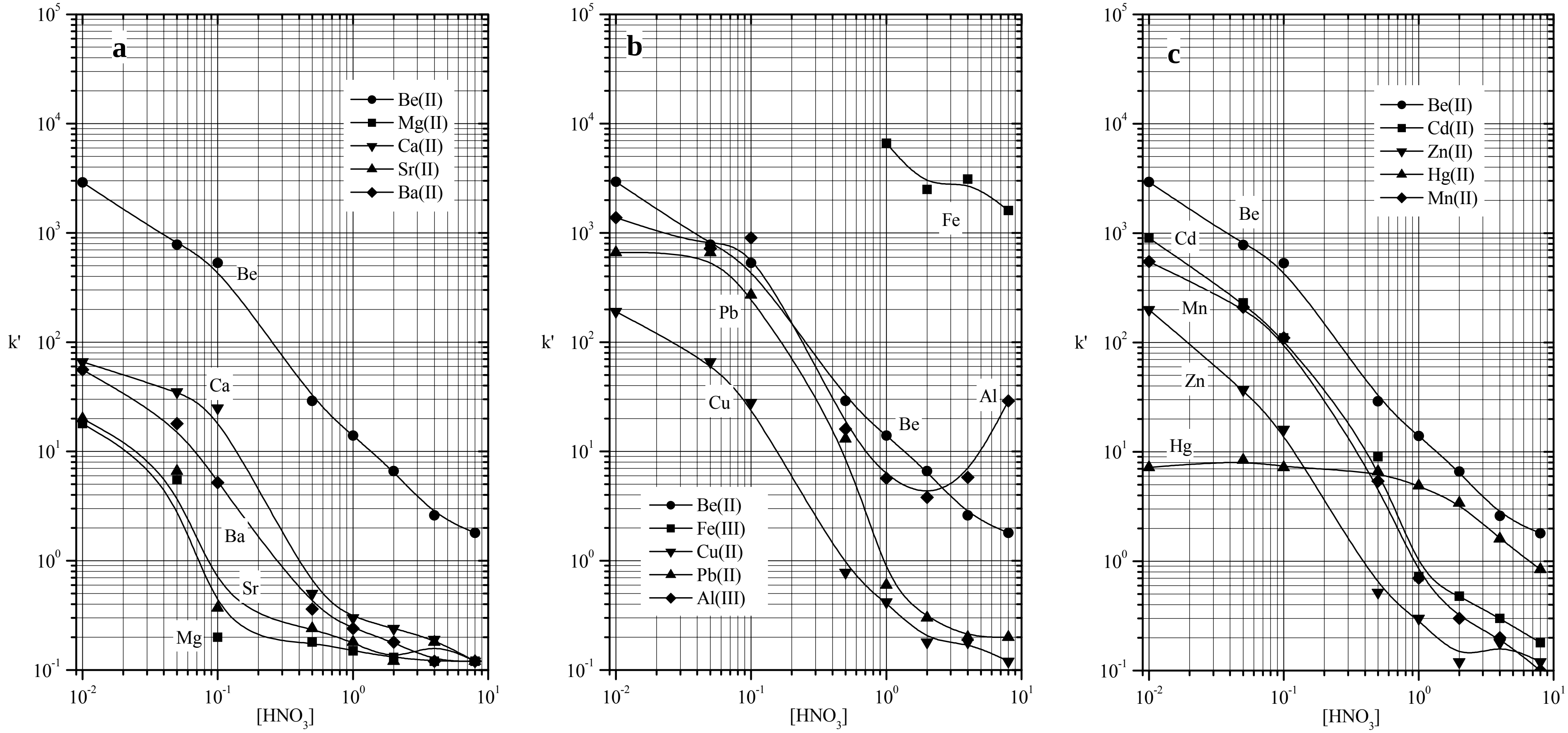

Figure 3. k′ for beryllium and potential matrix interferences on Dipex® resin vs. HNO$_3$, 1 h equilibration time, 22(2)°C, 50-100 μm particle size

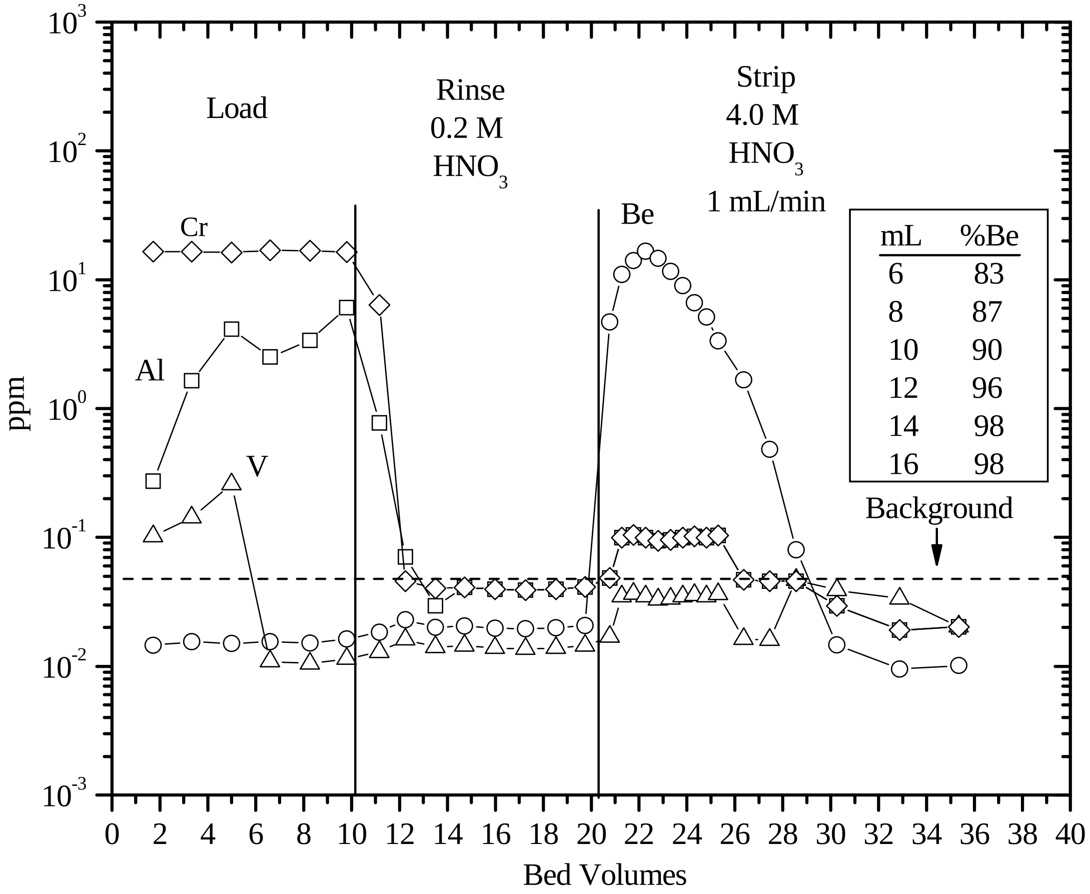

Figure 4. Elution of Al, Be, Cr, and V on a 2 mL dry packed cartridge of Dipex® resin, 50-100 µm particle size, flow rate 2 mL/min, 22(1)°C, Load: 5.5 cm ashless filter spiked with 140 µg Al, Be, Cr, and V, digested with H_2SO_4 and H_2O_2, diluted to 10 mL with HNO_3 and neutralized to pH 1.0 with 3.4 M sodium acetate.

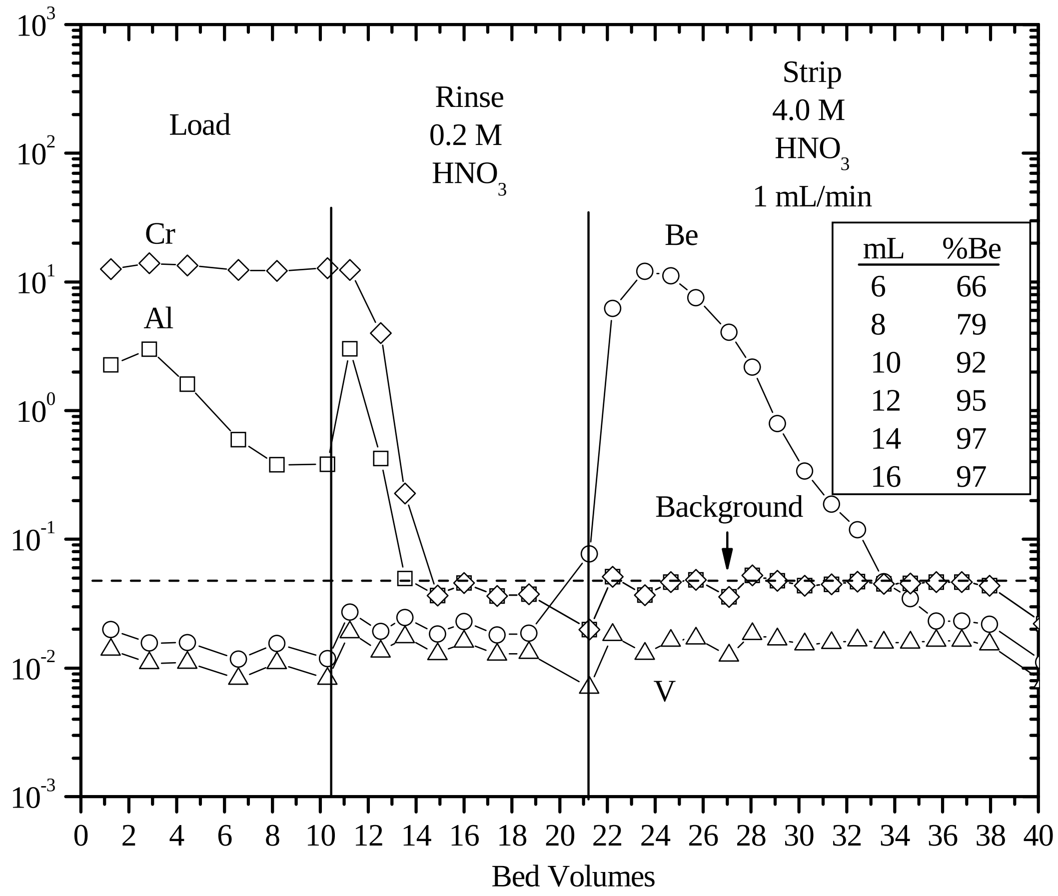

Figure 5. Elution of Al, Be, Cr, and V on a 2 mL dry packed cartridge of Dipex® resin, 50-100 µm particle size, flow rate 2 mL/min, 22(1)°C, Load: 5.5 cm ashless filter spiked with 140 µg Al, Be, Cr, and V, digested with H_2SO_4 and H_2O_2, diluted to 10 mL with HNO_3 and neutralized to pH 2.0 with 3.4 M sodium acetate.

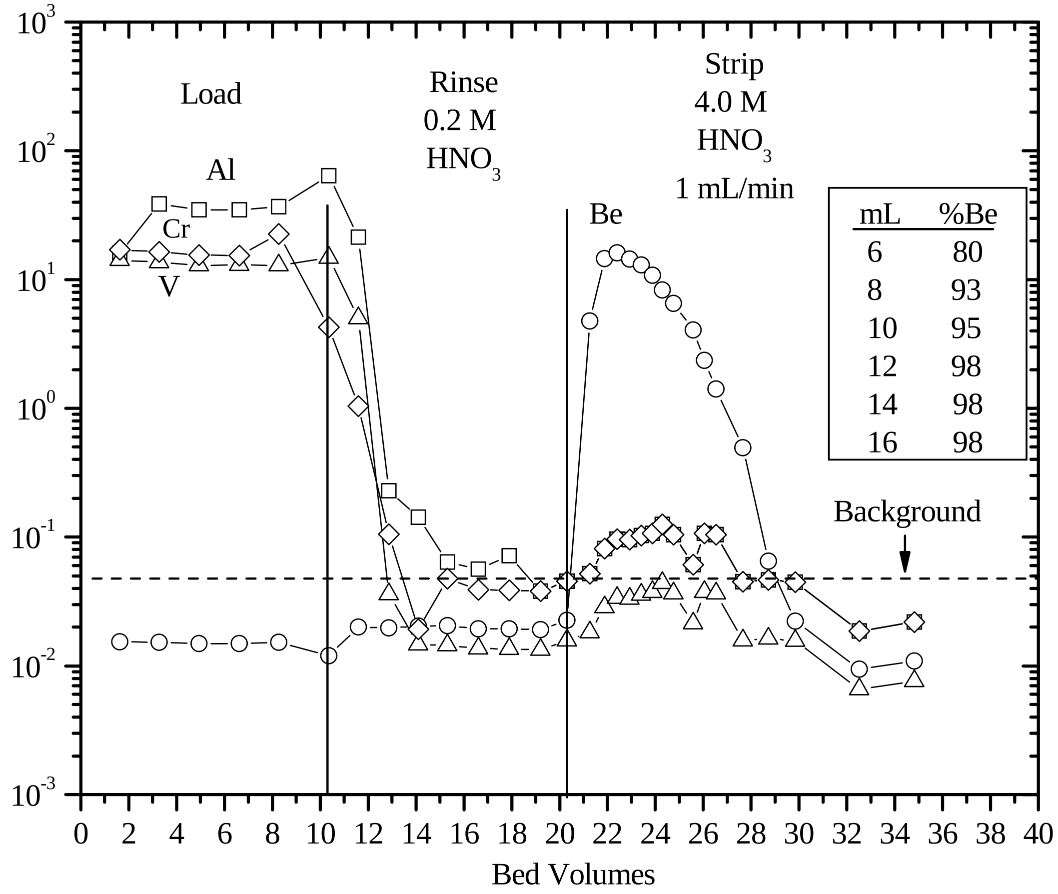

Figure 6. Elution of Al, Be, Cr, and V on a 2 mL dry packed cartridge of Dipex® resin, 50-100 µm particle size, flow rate 2 mL/min, 22(1)°C, Load: 5.5 cm ashless filter spiked with 140 µg Al, Be, Cr, and V, digested with H_2SO_4 and H_2O_2, diluted to 10 mL with HNO_3 and neutralized to pH 3.4 with 3.4 M sodium acetate.

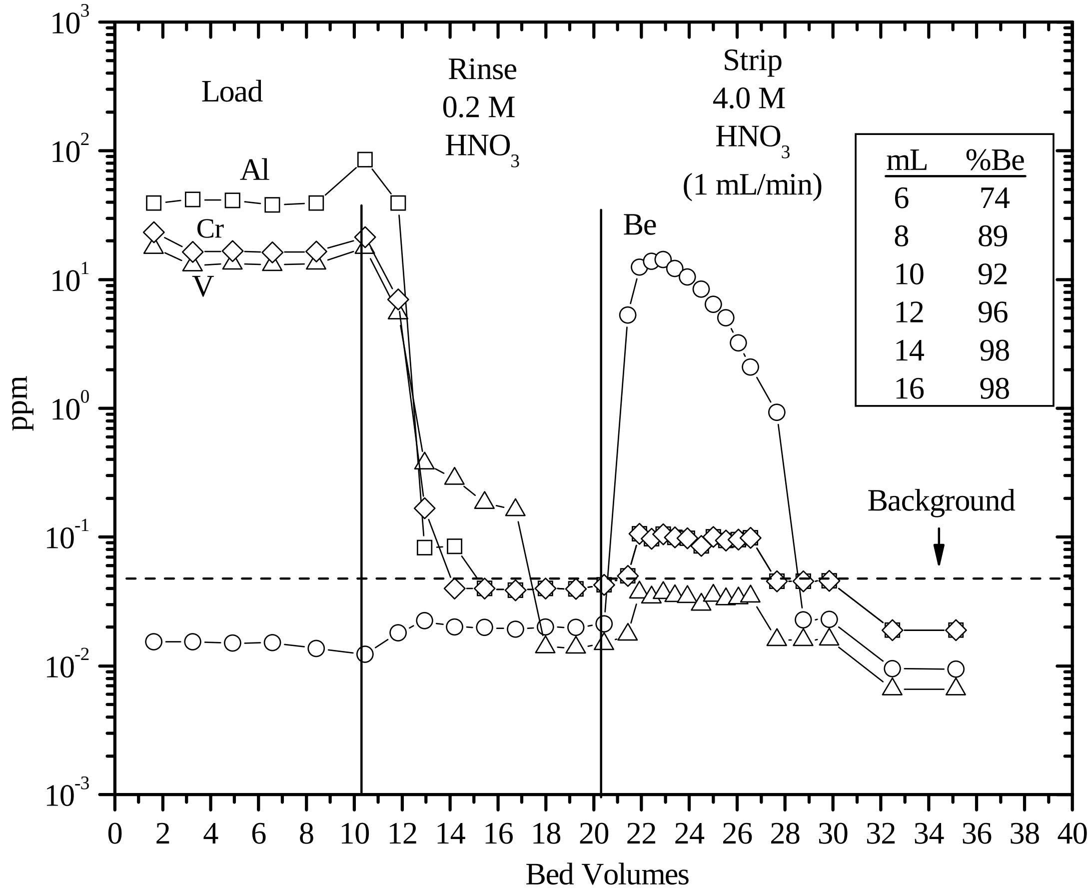

Figure 7. Elution of Al, Be, Cr, and V on a 2 mL dry packed cartridge of Dipex® resin, 50-100 µm particle size, flow rate 2 mL/min, 22(1)°C, Load: 5.5 cm ashless filter spiked with 140 µg Al, Be, Cr, and V, digested with H_2SO_4 and H_2O_2, diluted to 10 mL with HNO_3 and neutralized to pH 4.5 with 3.4 M sodium acetate.

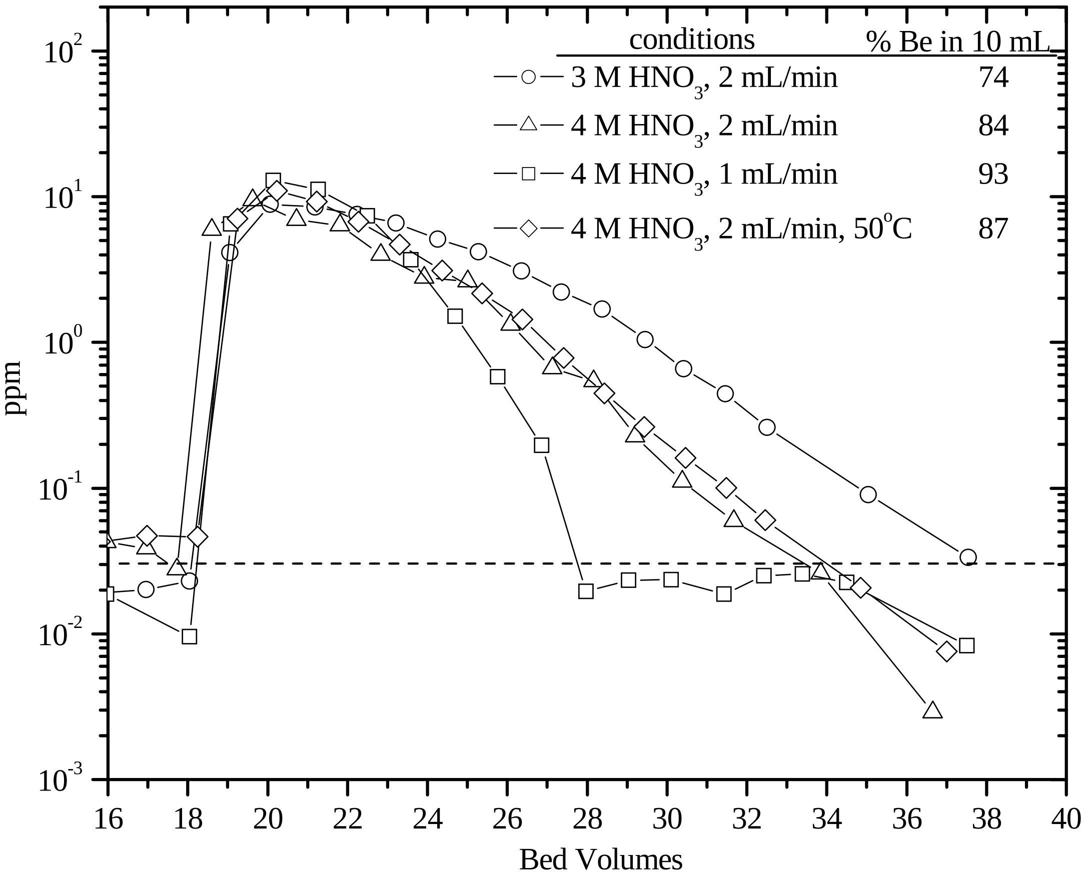

Figure 8. Optimization of beryllium stripping from a 2 mL dry packed cartridge of Dipex® resin, 50-100 μm particle size, Load: 5.5 cm ashless filter spiked with 140 μg Be, digested with H_2SO_4 and H_2O_2, diluted to 10 mL with HNO_3 and neutralized to pH 2.0 with 3.4 M sodium acetate, Rinse: 20 mL of 0.2 M HNO_3.

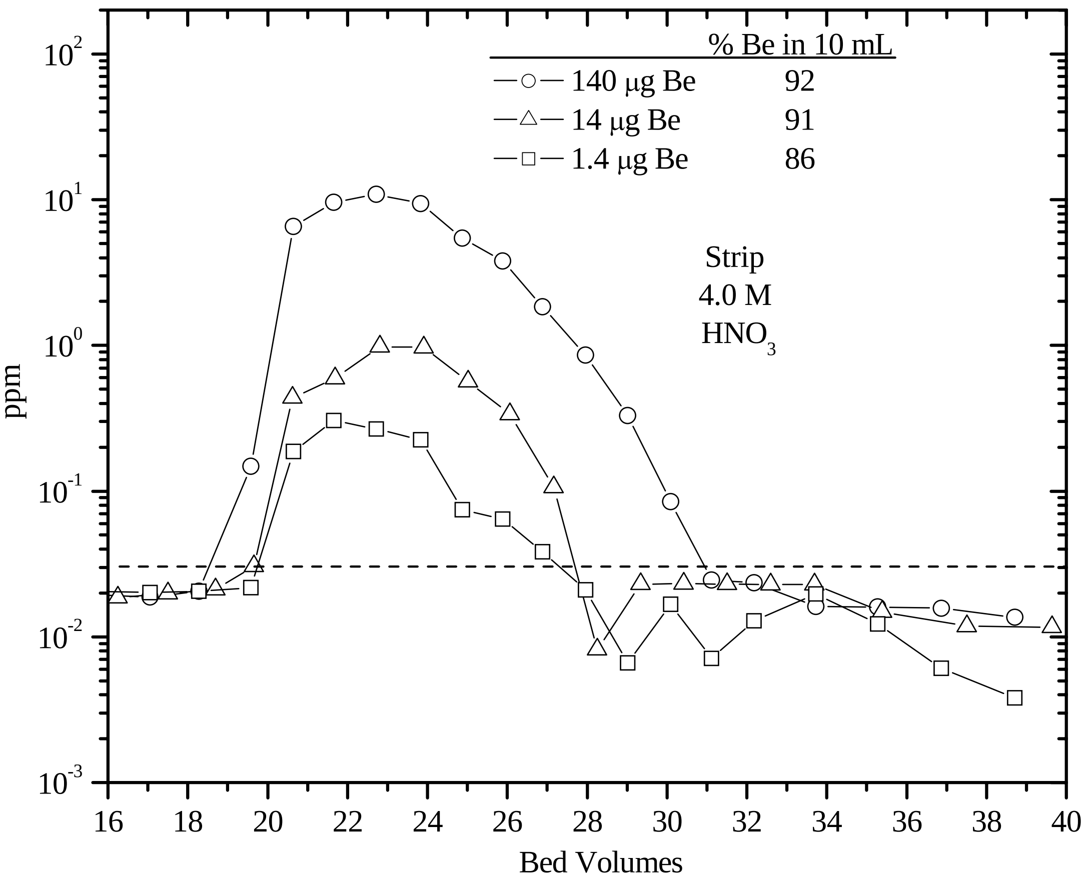

Figure 9. Effect of beryllium mass on stripping from a 2 mL dry packed cartridge of Dipex® resin, 50-100 μm particle size, Load: 5.5 cm ashless filter spiked with 1.4 to 140 μg Be, digested with H_2SO_4 and H_2O_2, diluted to 10 mL with HNO_3 and neutralized to pH 2.0 with 3.4 M sodium acetate, Rinse: 20 mL of 0.2 M HNO_3.

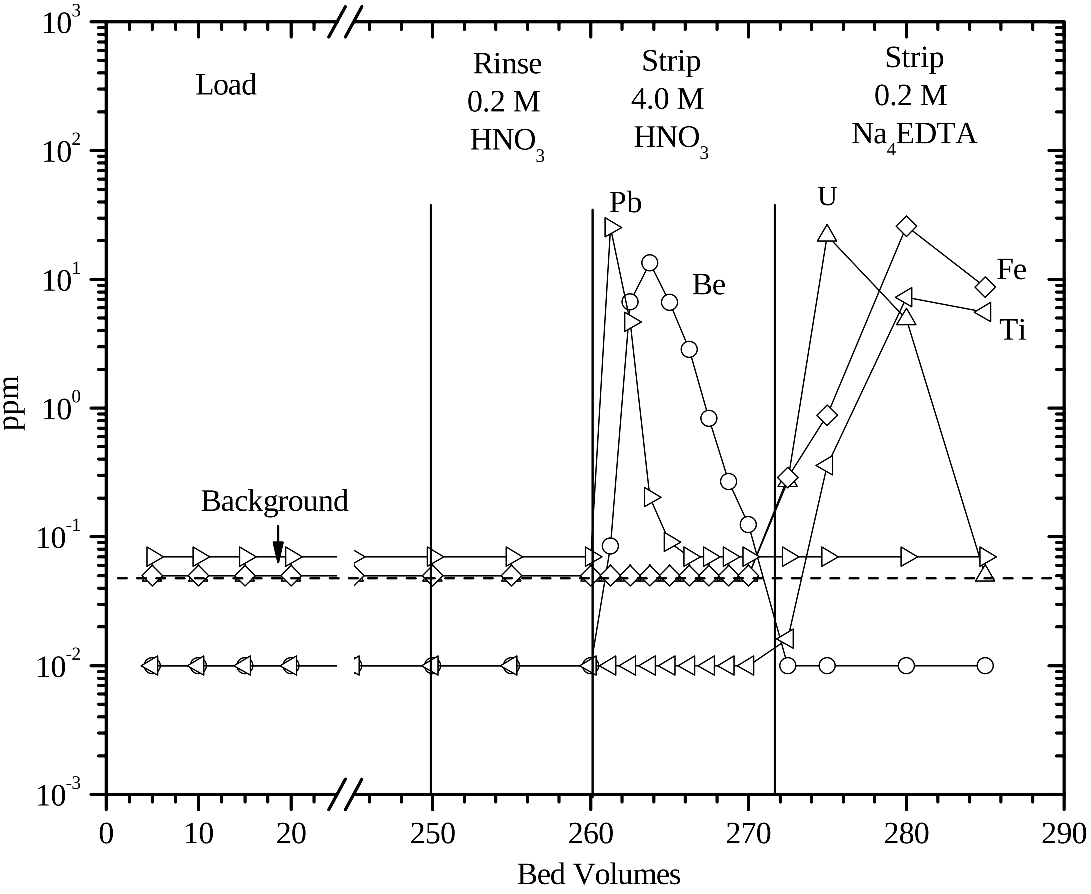

Figure 10. Elution of Be, Fe, Pb, Ti and U on a 2 mL dry packed cartridge of Dipex® resin, 50-100 μm particle size, flow rate 4 mL/min during load and rinse, 1mL/min during strip, 22(1)°C, Load: 500 mL simulated ground water spiked with 100 μg Be, Fe, Pb, Ti and U, pH adjusted to 2.0 with HNO_3.

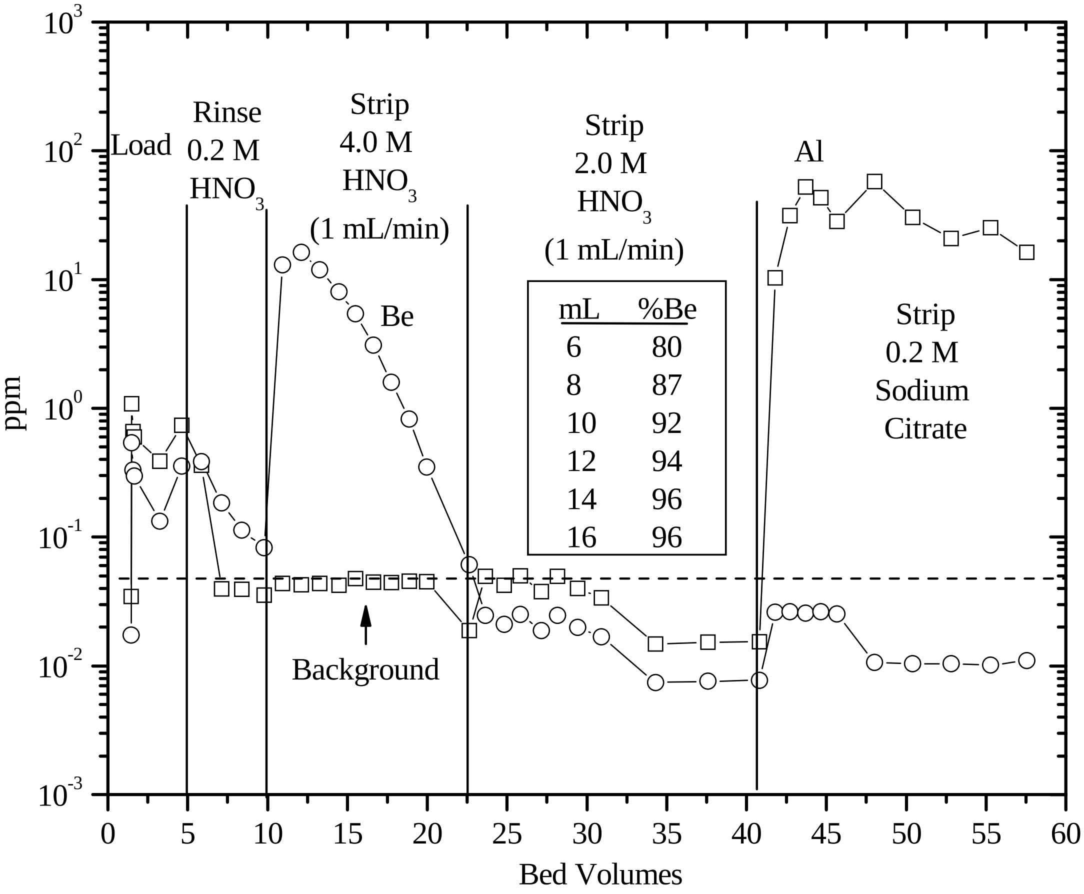

Figure 11. Elution of Al and Be on a 2 mL dry packed cartridge of Dipex® resin, 50-100 μm particle size, flow rate 2 mL/min, 22(1)°C, Load: 20 mL of 0.1 M HNO_3 spiked with 140 μg Al and Be.

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

[a] As listed in Varian Plasma96 software version 1.12

[b] Commonly used peaks for beryllium determination by ICP-AES

Table 2. Parameters employed for metal ion determination by ICP-AES

Analyte	Peak (nm)	Window (nm)	Analyte	Peak (nm)	Window (nm)
Al	396.152	0.080	Mo	281.615	0.040
Ba	455.403	0.080	Nb	316.340	0.040
Be	234.861	0.040	Pb	220.353	0.027
Ca	393.366	0.080	Sr	407.771	0.080
Cd	228.802	0.027	Th	283.730	0.040
Ce	413.765	0.080	Ti	334.941	0.080
Cr	267.716	0.040	Tm	313.126	0.040
Cu	324.754	0.040	U	385.958	0.080
Fe	259.940	0.040	V	292.402	0.040
Hf	277.336	0.040	Zn	213.856	0.027
Hg	253.652	0.040	Zr	343.823	0.040
Mg	279.553	0.040			

Integration time:	3.00 seconds	Sample uptake delay:	20 seconds
Replicates:	3	Pump rate:	15 rpm
Power:	1 kW	Instrument stabilization:	15 seconds
Viewing height:	10 mm	Rinse time:	30 seconds

Table 3. Physical Characteristics of Dipex® Resin

Particle Size (μm)	50-100
Extractant Density (g/mL)	1.05
Bed Density (g/mL)	0.39
Resin Density (g/mL)	1.15
v_s	0.15
v_m	0.66
v_s/v_m	0.23
D_v conversion factor (C_1)[a]	2.62
k' conversion factor (C_2)[b]	0.60

[a] $D_v = D_w \times C_1$

[b] $k' = D_w \times C_2$

Table 4. Effect of Matrix on Be Concentration by ICP-AES

Matrix	Real Be Concentration (ppm)	Be Concentration by ICP-AES (ppm)
Digest Solution[a]	10.0	13.7
0.1 M HNO_3	10.0	10.0
0.2 M HNO_3	10.0	8.80
3.0 M HNO_3	10.0	7.39
4.0 M HNO_3[b]	10.0	7.32
5.0 M HNO_3	10.0	6.91

[a] 10% HNO_3 6% H_2SO_4 neutralized to pH 1.0 with sodium acetate

[b] Matrix used for ICP-AES calibration standards