Effects of Flow Rate on Extraction Efficiency

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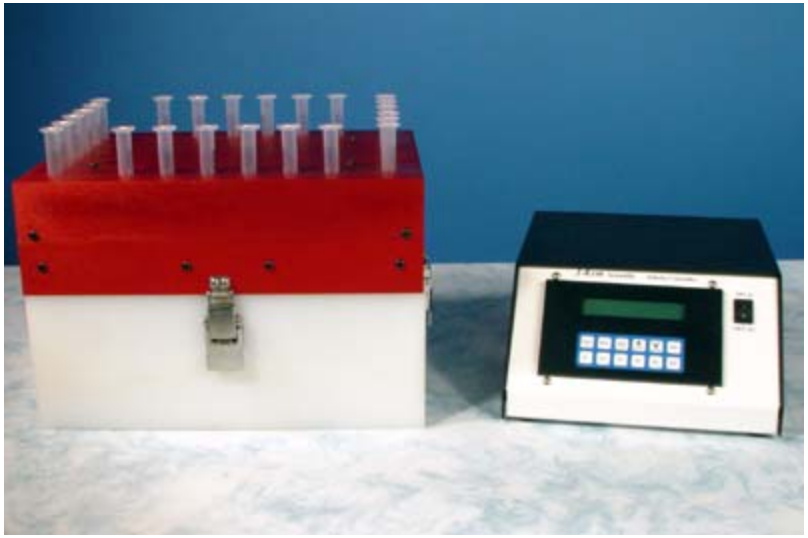
Overview

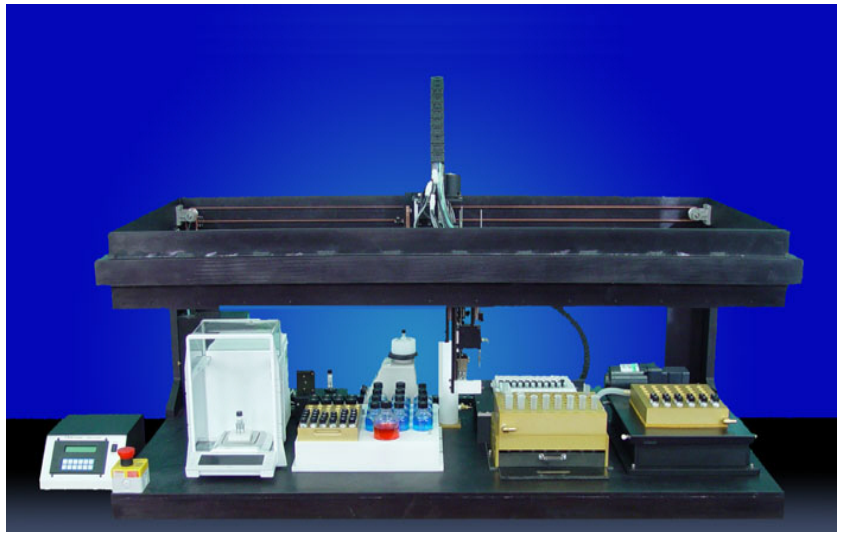
- Research project goals
- Experimental design and objectives
- Results
- Future work

Project Goals

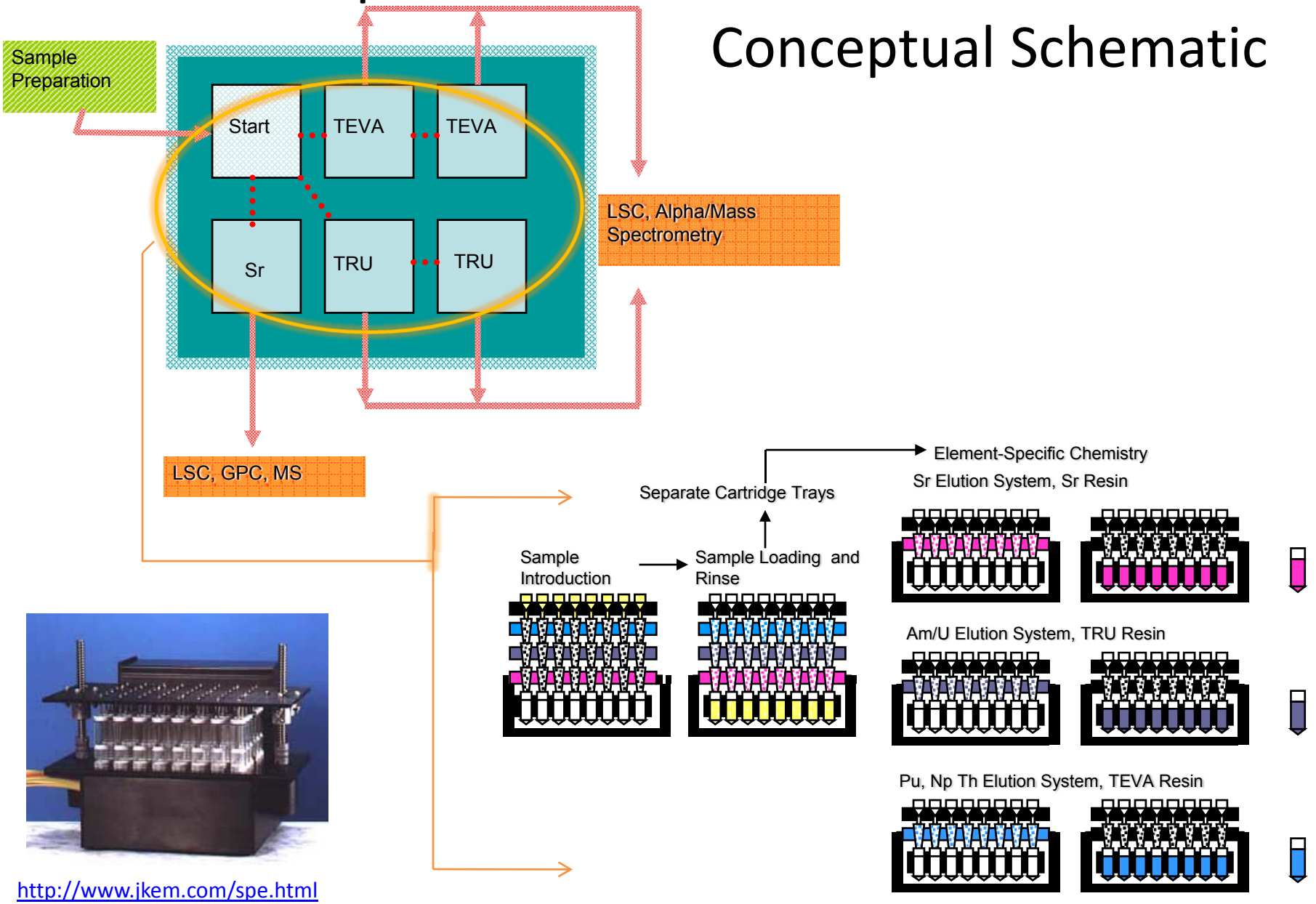
- Evaluate current rapid chromatography techniques for actinides and strontium in aqueous samples
- Determine suitability for automation, determine method parameterization
- Evaluate commercially available robotic platform technology for automation



http://www.jkem.com/spe.html



Sequential Extraction Robotic Platform: Conceptual Schematic



http://www.jkem.com/spe.html

Experimental Design

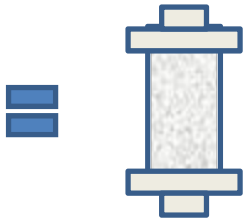
- **Phase 1A and 1B:** Examine flow rate characteristics for single and multiple systems in aqueous solutions
- **Phase 1C:** Determine optimal flow rate characteristics for laboratory solutions

- **Phase 1D and 1E:** Examine protocol with various aqueous samples containing other potential interferences (single system and multiple systems)

- **Phase 1F:** Determine if optimized method can be automated

Parameter Evaluation

- Column efficiency governed by
  - Flow phenomena
  - Diffusion
  - Extraction Kinetics
- Influenced by
  - Operating Temperature
  - Matrix constituents
  - Extractant loading and mobile phase velocities
  - Column Length
  - Bead size



Pre-packed 2 mL Column

Horwitz, E. P.; Bloomquist, C. A. *Preparation , performance , and factors affecting band spreading of high-efficiency extraction chromatographic columns for actinide separations.* Journal of Inorganic and Nuclear Chemistry (1972), 34(12), 3851-71.

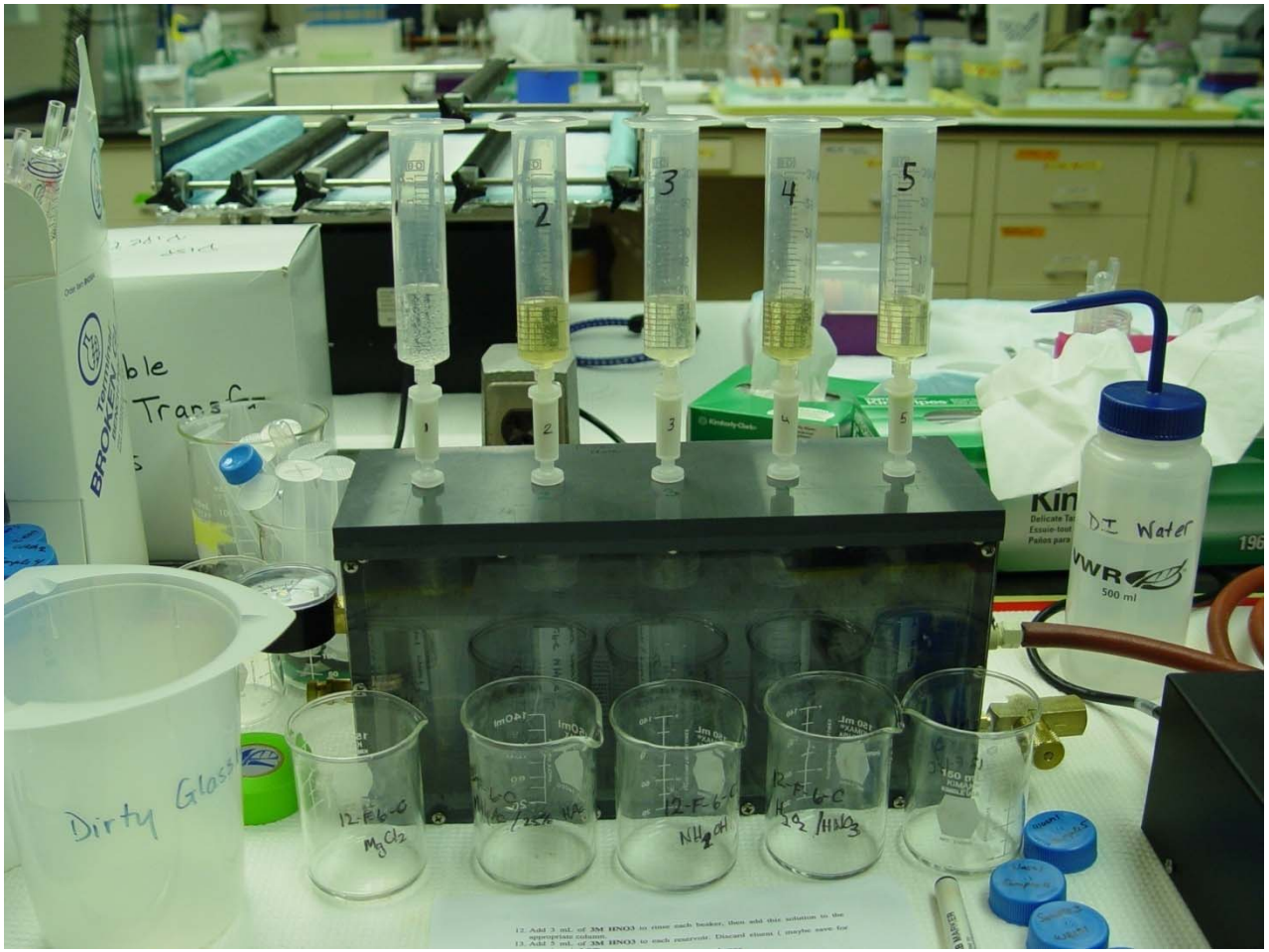
Objectives

- Evaluate vacuum-assisted extraction chromatography from an automation perspective
- Determine the influence of flow rate on the loading and unloading efficiency of the system
- Determine if extraction efficiency is reproducible at a given flow rate

Vacuum Box Characterization

No Activity Present, Evaluation of Digital Vacuum Regulator (DVR)

Experimental Set Up

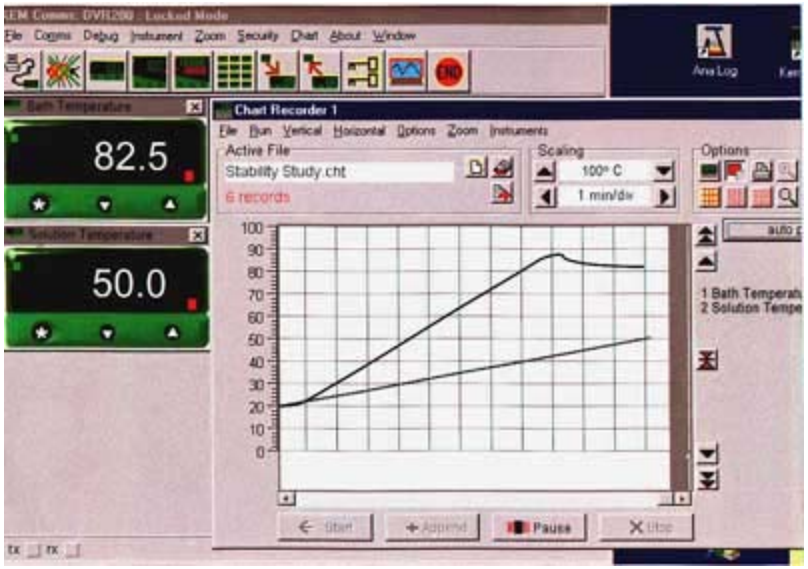


Modified vacuum box, 2mL resin cartridges pass through the box lid for increased stability.

Digital Vacuum Regulator

- Digital Vacuum Regulator with High Precision Needle Valve
- Finer control over lower vacuum pressures

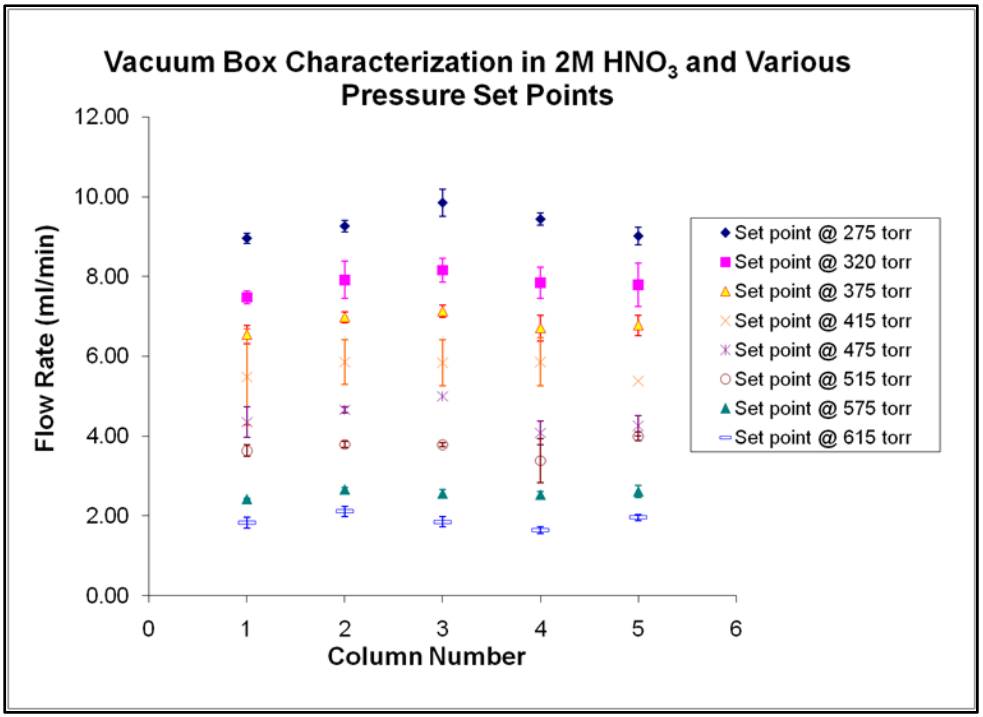
J-Kem Digital Vacuum Regulator. Item No. DVR-200 Includes built-in stainless steel vacuum sensor and stainless steel vacuum solenoid valve.

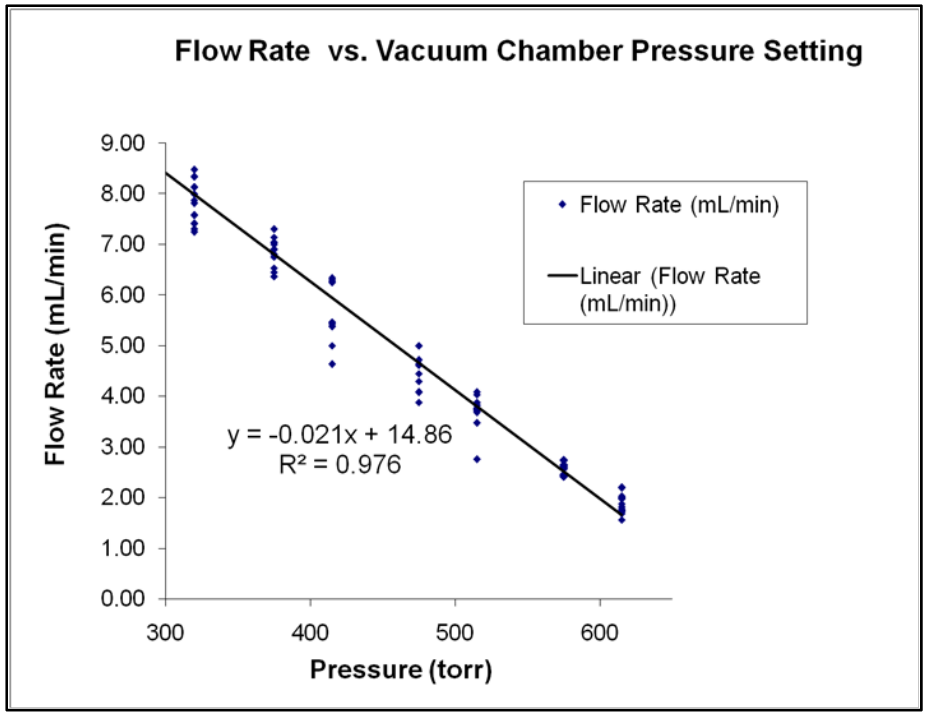


- Evaluate ramp-to-set point conditions for column flow rate and efficiency

J-Kem Software. Used to manipulate the evacuation rates with ramp-to-set point features

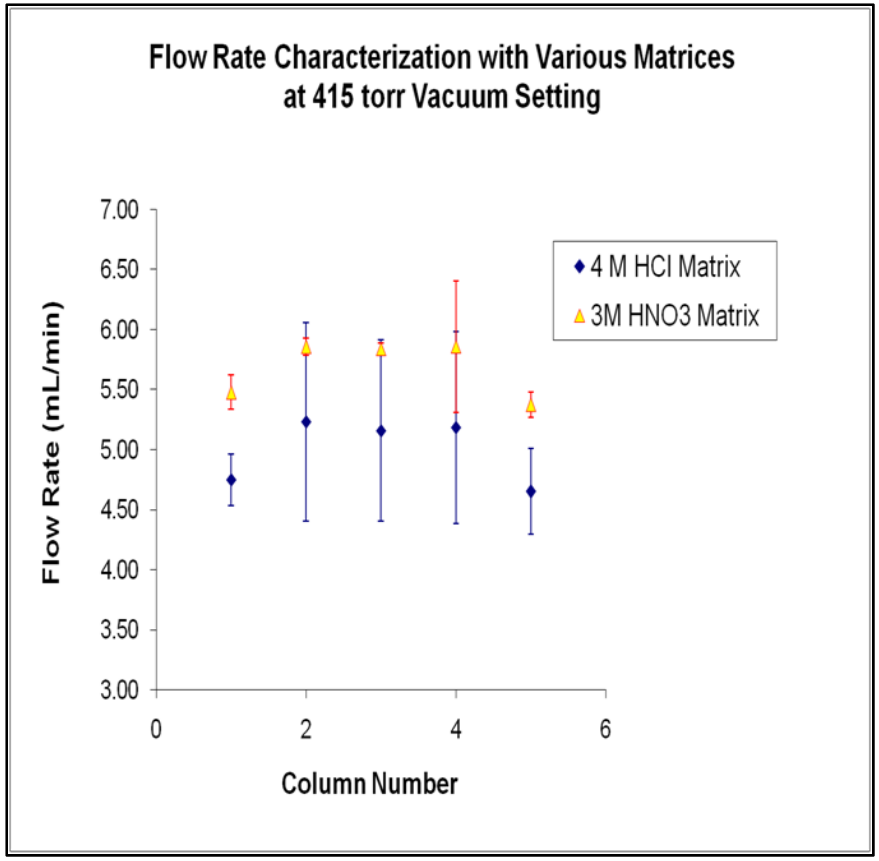
Vacuum Box Characterization with Digital Regulator (No Activity)

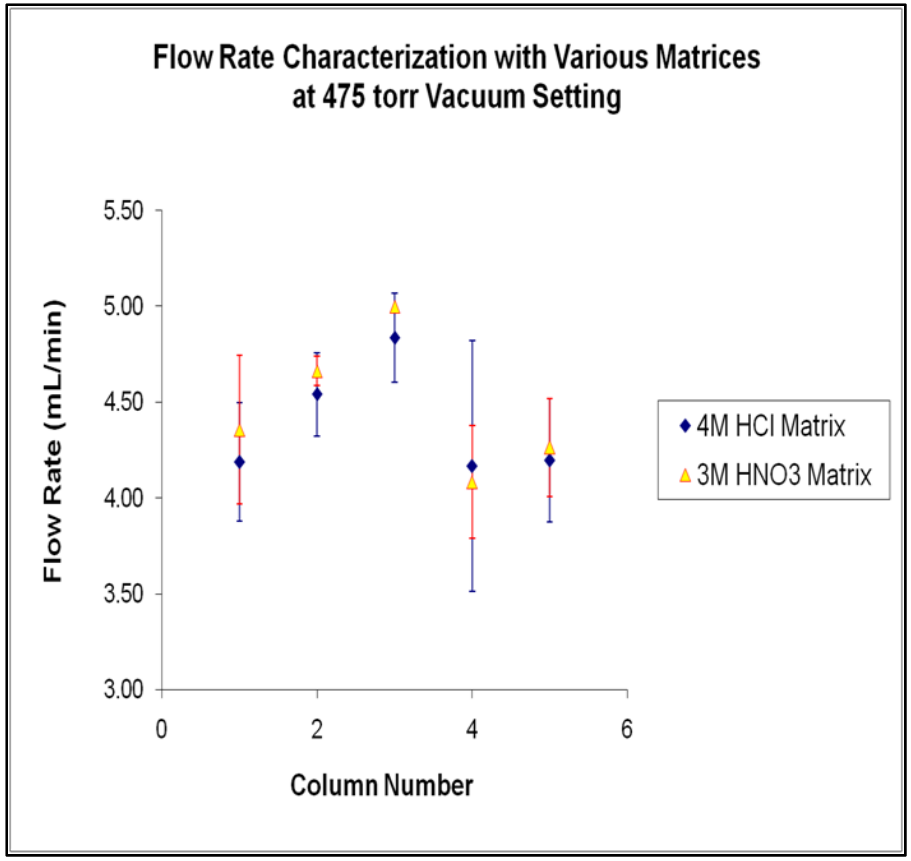




Each data point represents the average flow rate over five trials with TRU Resin.

Vacuum Box Characterization Various Acid Matrices (No Activity)



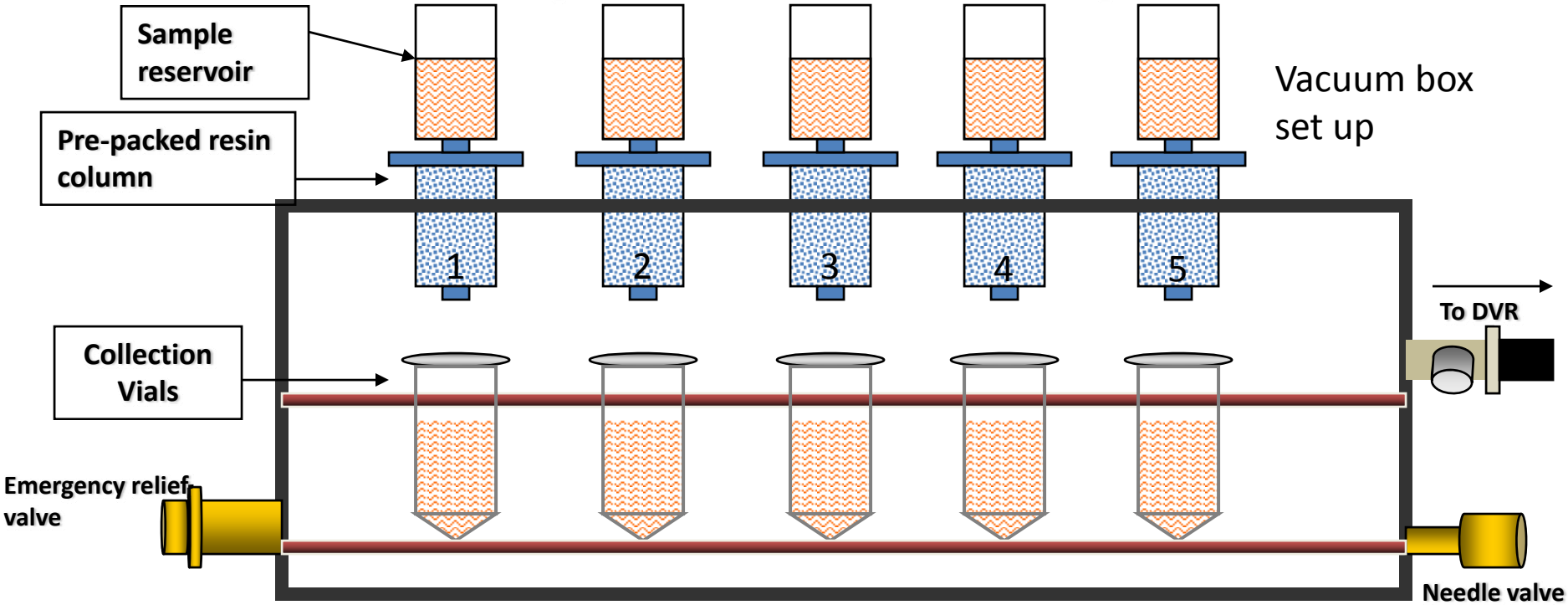


Each column was used for 4 trials, alternating between the HNO_3 and HCl matrices.

Vacuum Box Characterization

No Activity Present, Evaluation of
TRU Pre-packed 2mL Columns

Experimental Set Up



Flow Rate Characterization Procedure

- Vacuum set point programmed into DVR, sample reservoirs loaded with solution/fraction
- Start vacuum pump and timer.
- Record time at which reservoirs empty.
- Close valve, allow box to return to ambient pressure
- Reset box, load next fraction, and start vacuum.

TRU Solution Matrices:

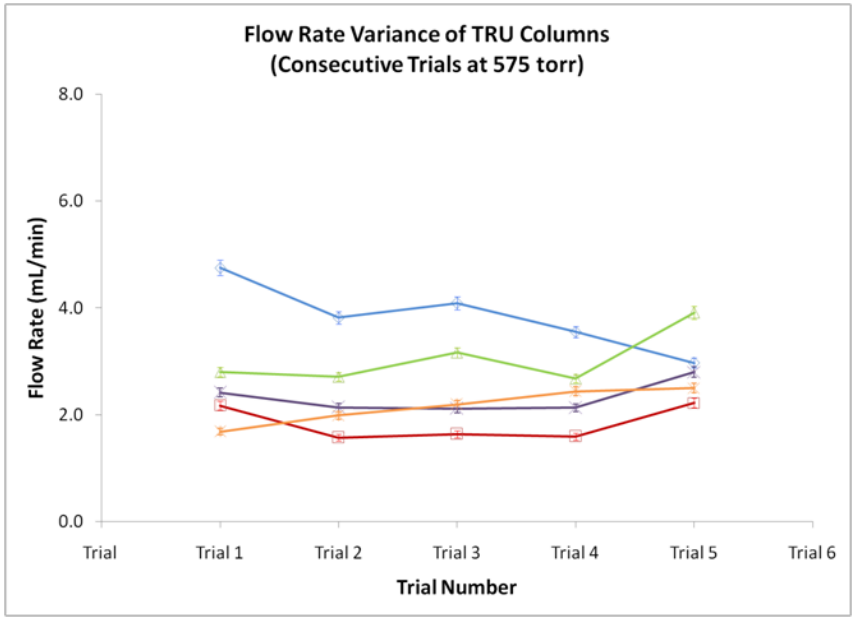
Column Preparation: 3M HNO_3 (Volume: 5 mL)

Sample: 3M HNO_3 – 1 M $Al(NO_3)_3$ (Volume: 9.5 mL)

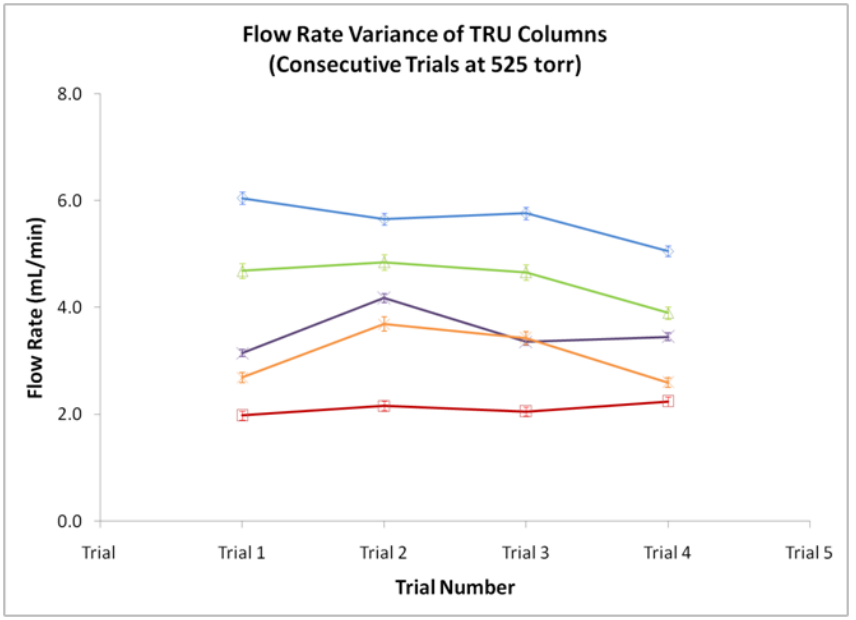
Rinse: 3M HNO_3 (Volume: 8 mL)

Elutions: 4M HCl (Volume: 15 mL)

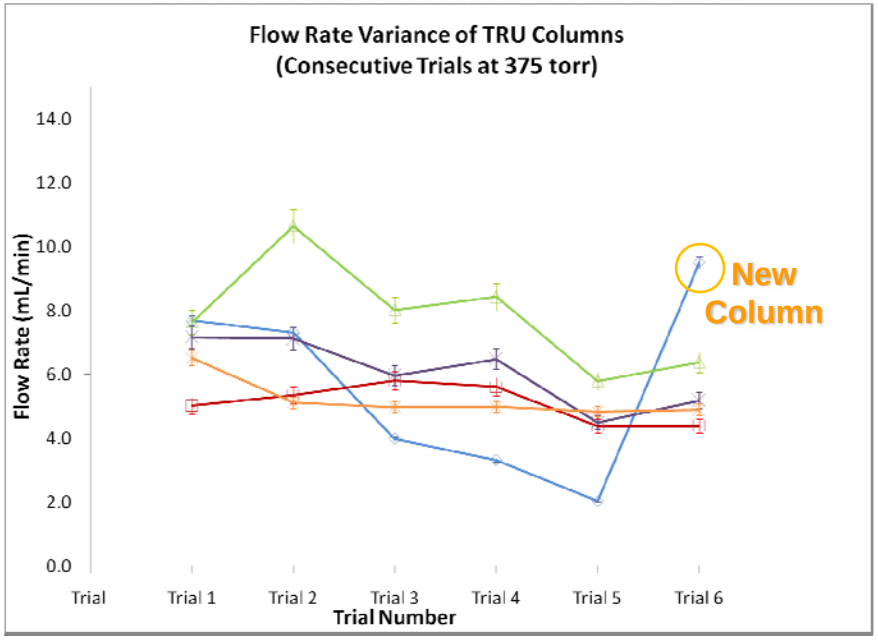
Flow Rate Variance at 575 torr



Flow Rate Variance at 525 torr



Flow Rate Variance at 375 torr



Fraction Matrices:

- Column Preparation: 3M HNO3, 5 mL
- Sample Loading: 3M HNO_3/1M $Al(NO_3)_3$, 9.5 mL
- Column Rinse: 3M HNO3, 8 mL
- Elution 1: 4M HCl, 15 mL
- Elution 2: 4M HCl, 15 mL

➢ *Each data point represents the average flow rate for all 5 columns.*

Vacuum Box Characterization

Flow rate evaluation using ^{241}Am and TRU columns

TRU Resin Extractant

Tru Resin Extractant: Octylphenyl-N,N-di-isobutyl carbamoylphosphine oxide

Figure 1

CMPO

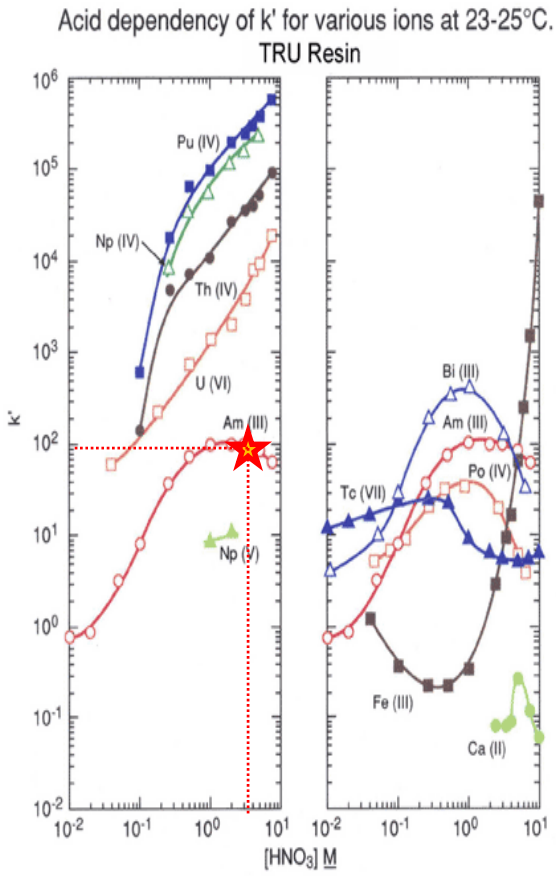
Extraction Equilibria:

$Am^{3+} + 3NO_3^- + 3E \leftrightarrow Am(NO_3)_3 \cdot E_3$

$Pu^{4+} + 4NO_3^- + 2E \leftrightarrow Pu(NO_3)_4 \cdot E_2$

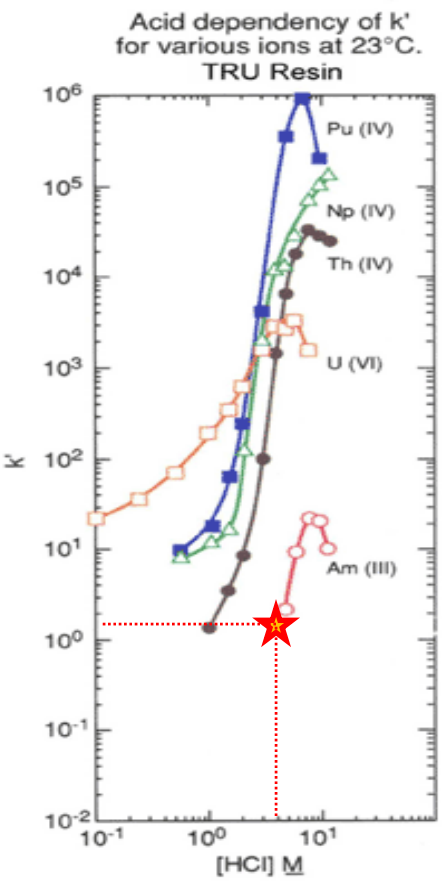
$UO_2^{2+} + 2NO_3^- + 2E \leftrightarrow UO_2(NO_3)2 \cdot E_2$

Figure 2



Horwitz, et al. (HP193)

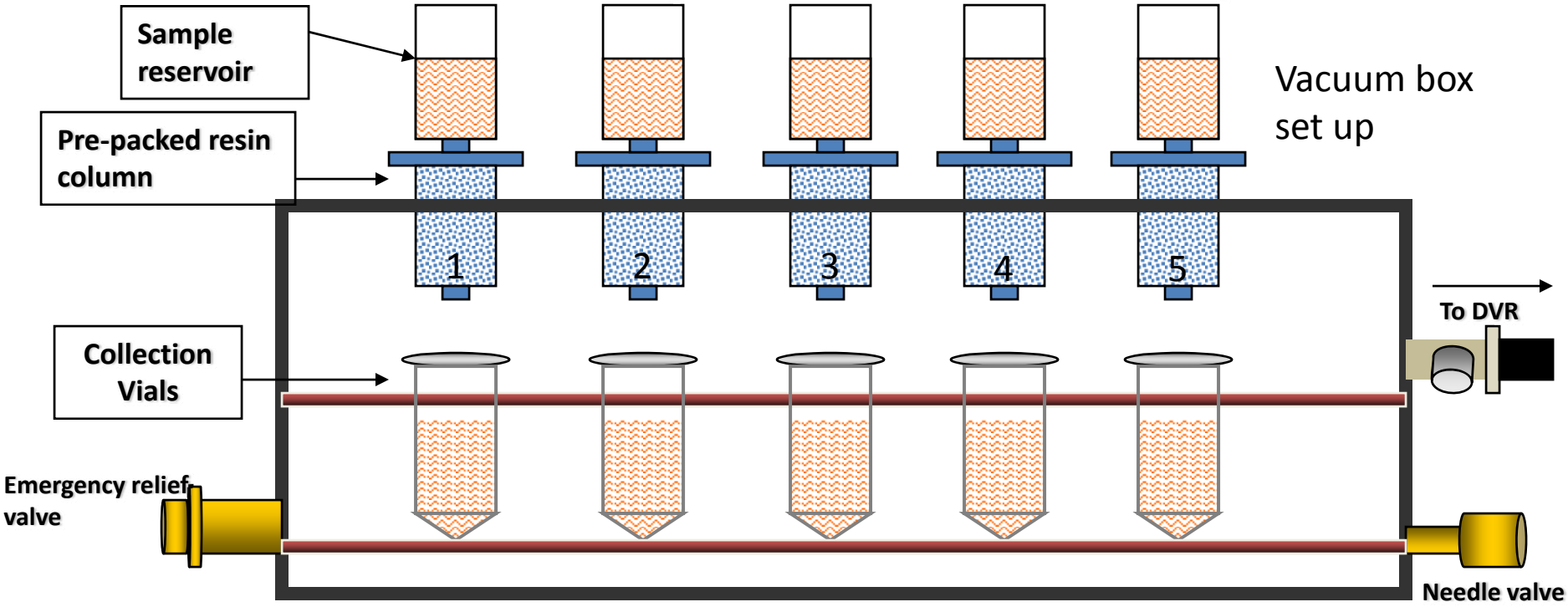
Figure 3



Horwitz, et al. (HP193)

E. P. Horwitz, R. Chiarizia, M. L. Dietz, H. Diamond, and D. Nelson, *Separation and Preconcentration of Actinides from Acidic Media by Extraction Chromatography*, Analytica Chimica Acta, 281 (1993) 361-372.

Phase 1: Experimental Set Up



Flow Rate Characterization Procedure

- Vacuum set point programmed into DVR, sample reservoirs loaded with 10 mL of solution
- Start vacuum pump and timer.
- Record time at which reservoirs empty.
- Close valve, allow box to return to ambient pressure
- Reset box, load next 10 mL fraction, and start vacuum.
- Take aliquots of each fraction to determine chemical yield. Counting method: LSC

TRU Solution Matrices:

Column Preparation: 3M HNO_3

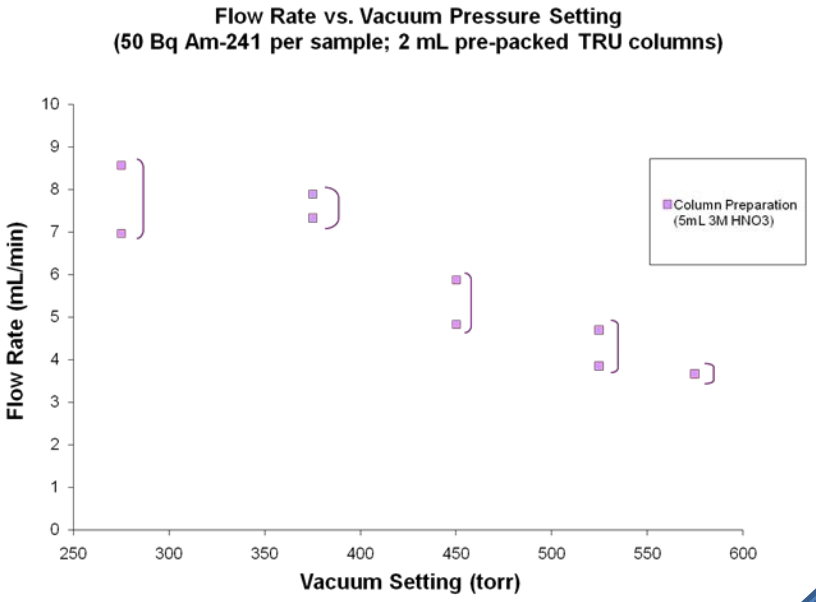
Sample: 3M HNO_3 – 1 M $Al(NO_3)_3$

Elution: 4M HCl

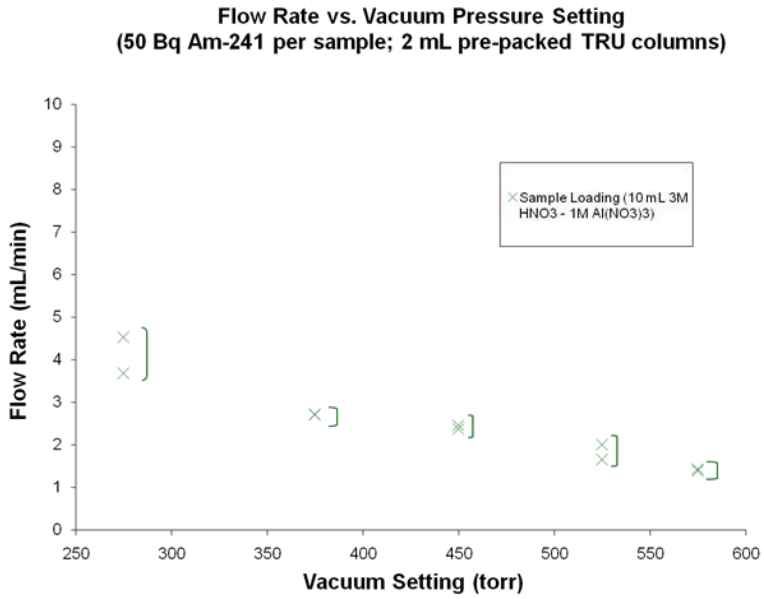
Radionuclide: ^{241}Am

Activity Levels: 50, 100, 500 and 1000 Bq per sample

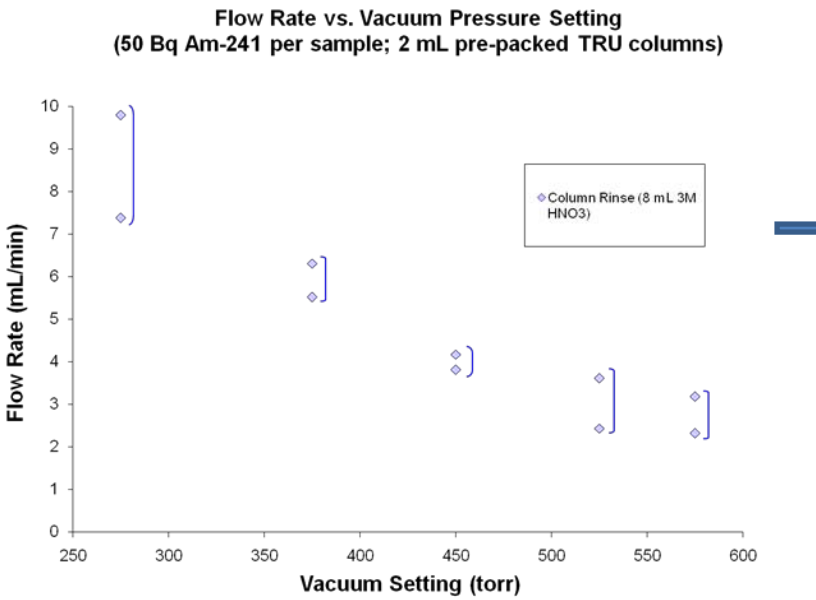
Fraction 1: Column Preparation



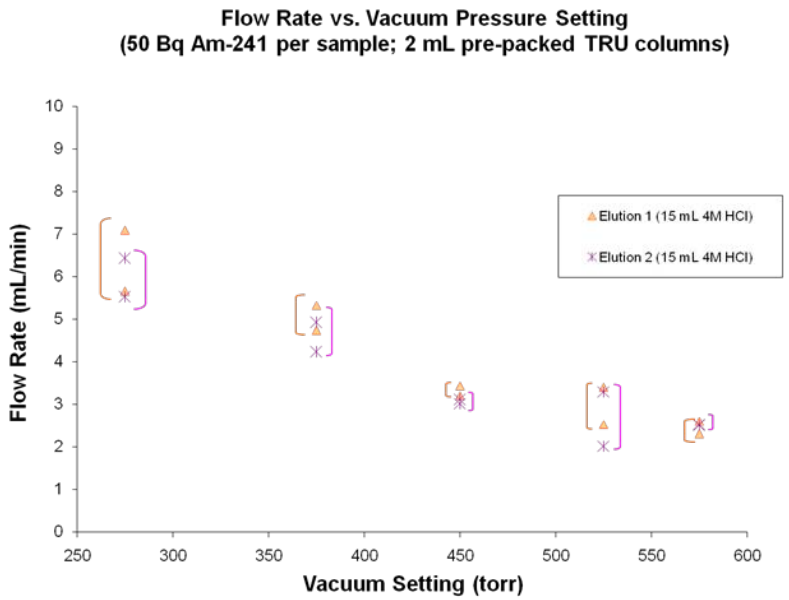
Fraction 2: Sample Loading

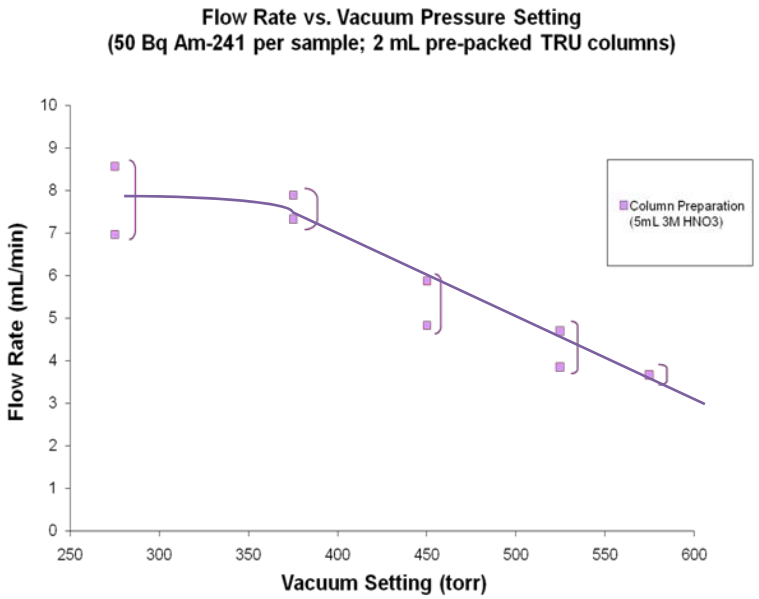


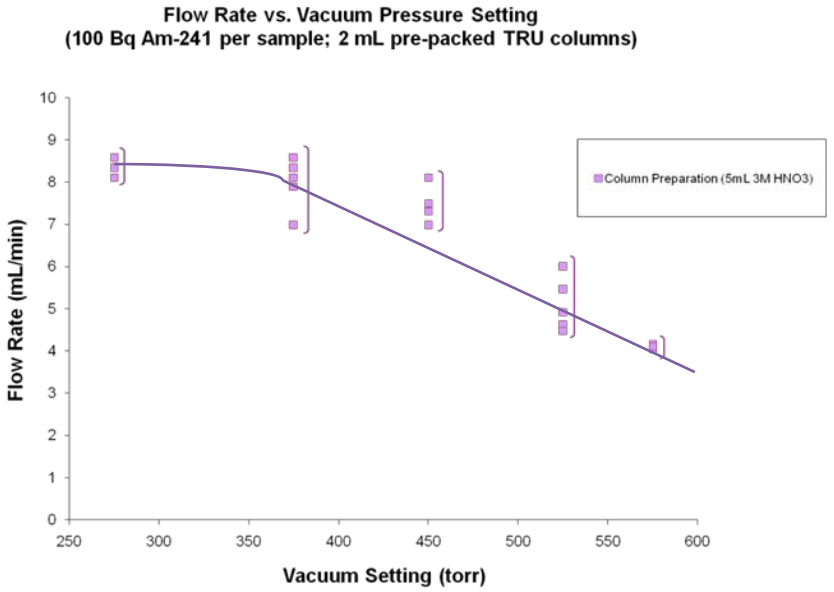
Fraction 3: Column Rinse

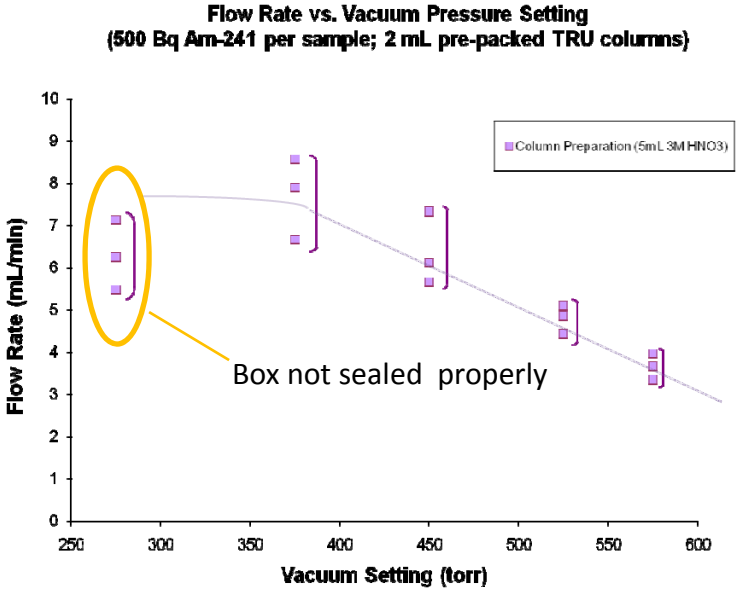


Fractions 4 and 5: Elutions 1 and 2

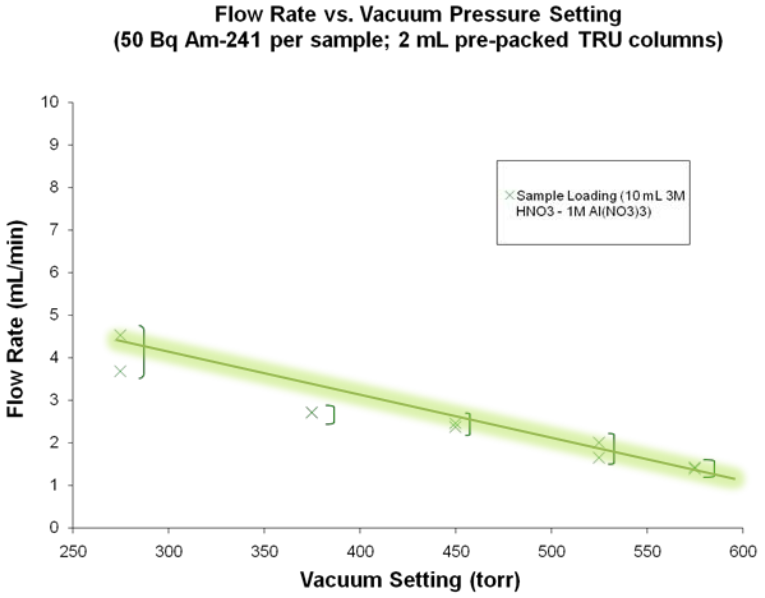


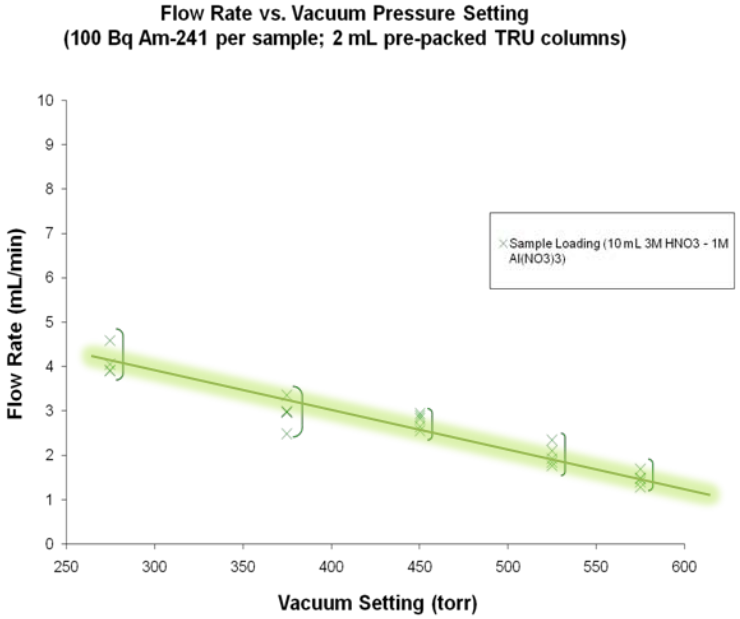


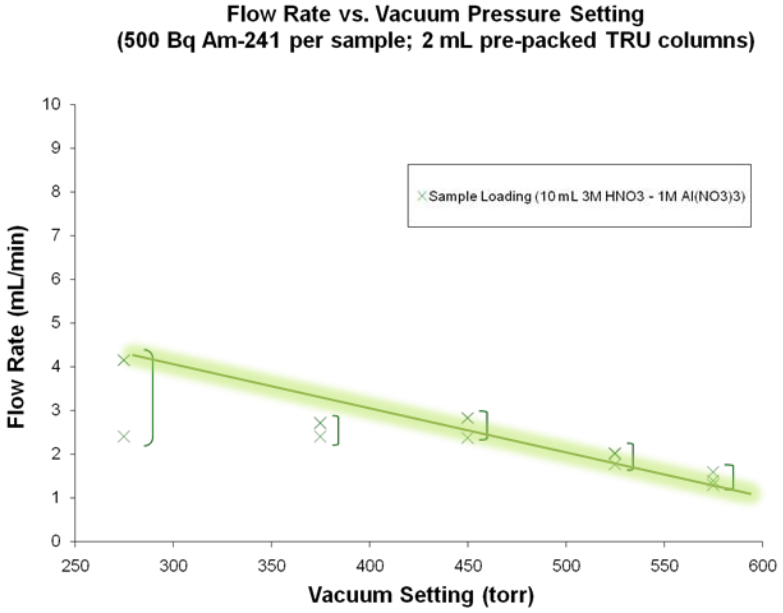




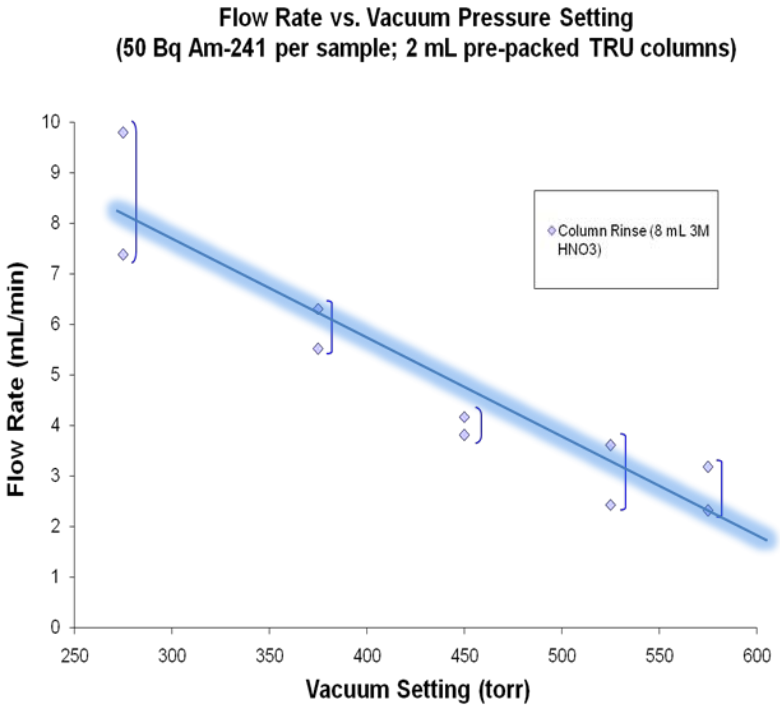
- Expect the column preparation flow rate to behave similarly
- System behaves linearly over a wide range of vacuum settings
- Reach a physical limit of the volume that can move through the column at 275 torr (*under the current system conditions)*

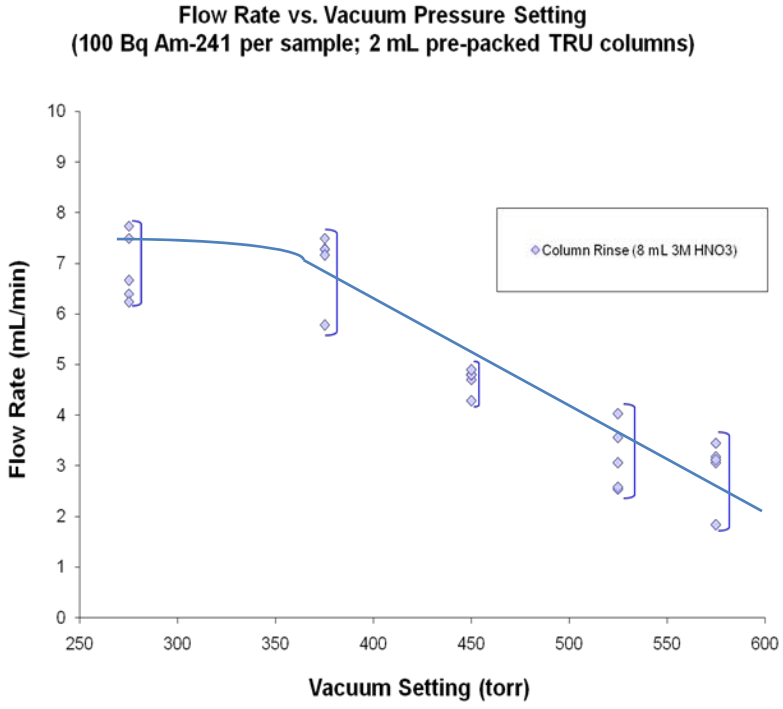


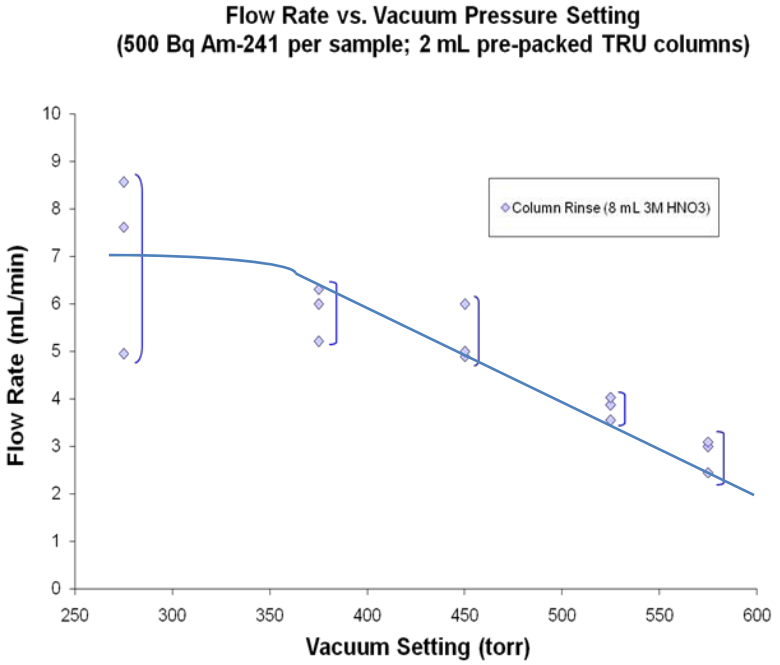




- Linear relationship between flow rate and vacuum setting
- Higher viscosity/ ionic strength influences flow rate
- No variance due to activity present



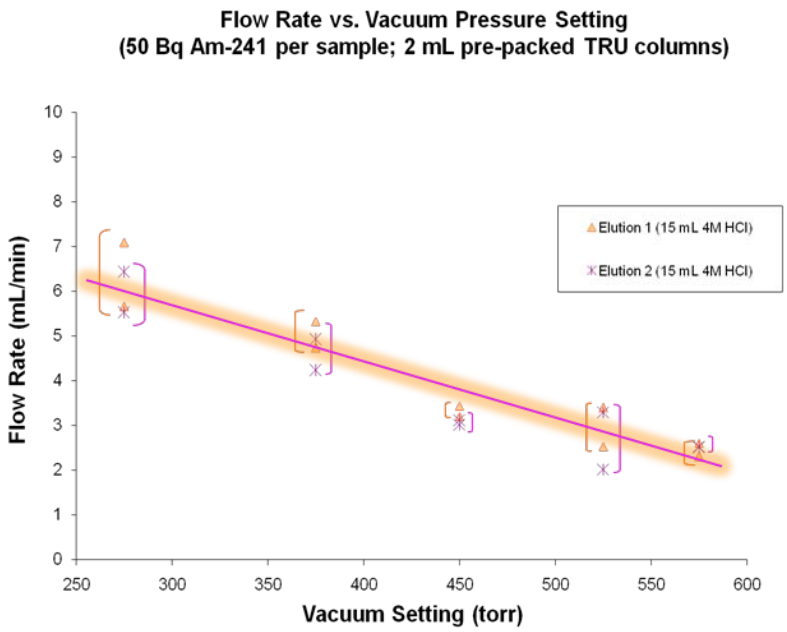


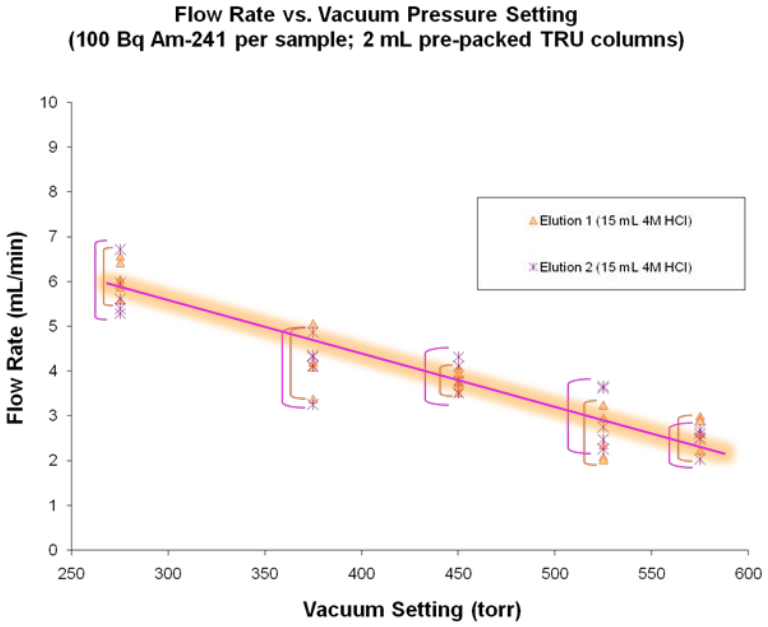


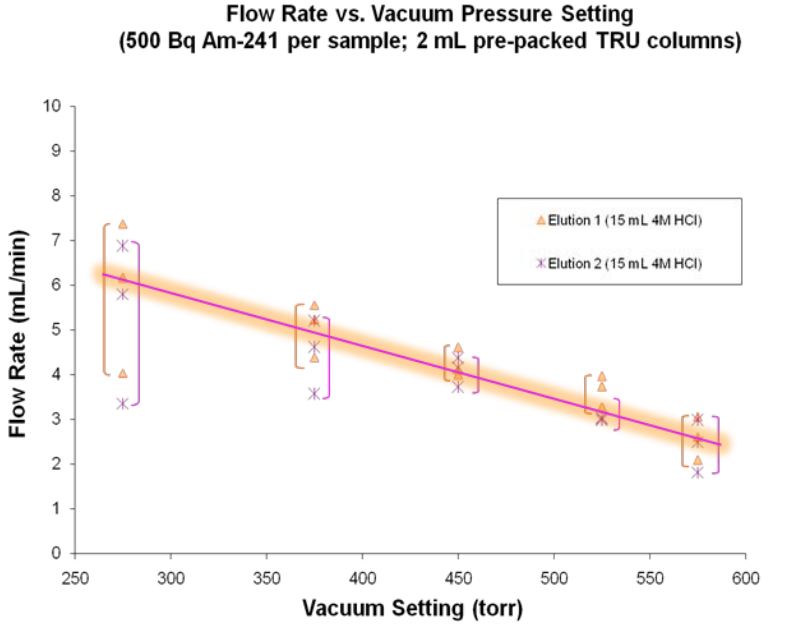
- System behaves linearly over a wide range of vacuum settings

- Physical limitations of the volume that can move through the column at lower vacuum settings (*under the current system conditions)*

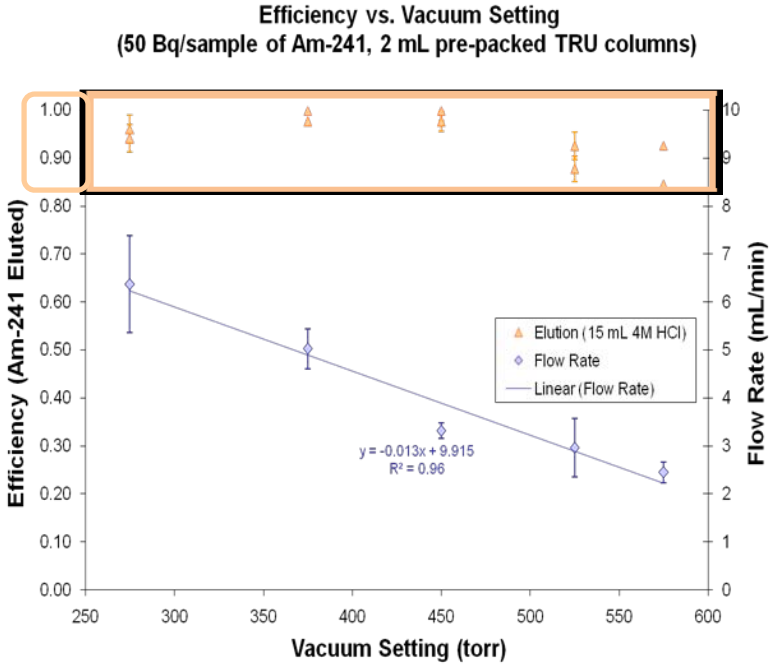
- *Data correlates with column preparation fraction data (same matrix = reproducible flow rate)*

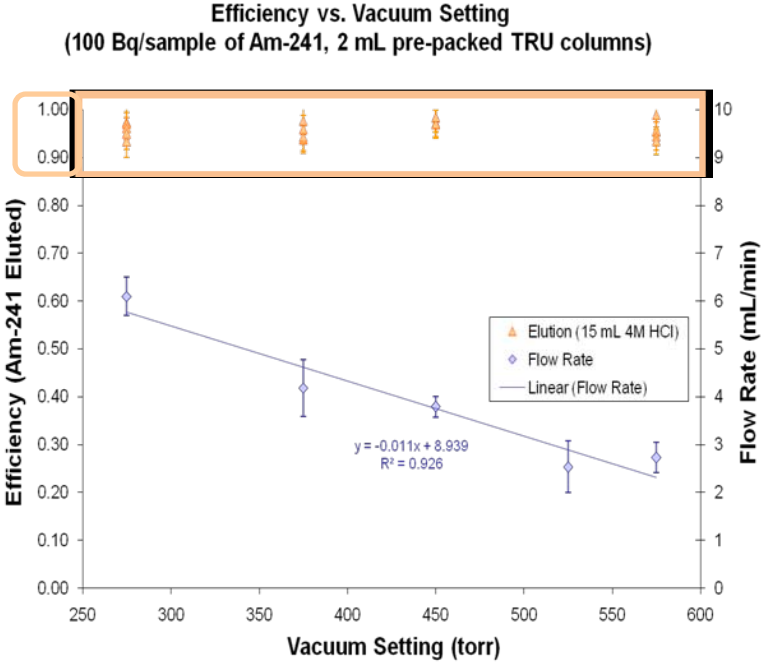


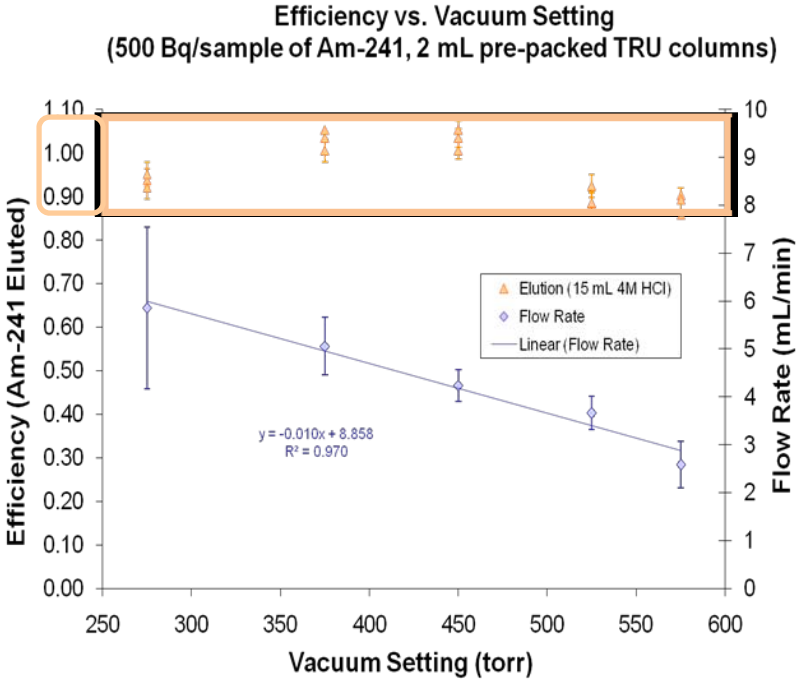




- Linear relationship between flow rate and vacuum setting
- Higher ionic strength influences flow rate
- No variance due to activity present







- Column efficiency is >90% over all of the flow rates evaluated

- Column kinetics are sufficient to run at higher flow rates (with no matrix interferences present)

TRU Procedure Results

- Reproducible, linear relationship between flow rate and the DVR vacuum setting
- Inter-column flow rate variance 0.5-1.5 mL/min
- Physical limitation of the volume that can be pulled through the column (*in the current set up*), effecting high flow rates
- Flow rate does not affect the loading and unloading efficiencies

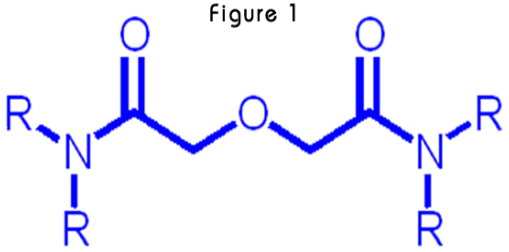
Vacuum Box Characterization

Flow rate evaluation using ^{241}Am and DGA columns

DGA Resin Extractant

DGA Resin Extractant:
N,N,N',N'-tetra-n-octyldiglycolamide
(DGA Resin, Normal)

Figure 1



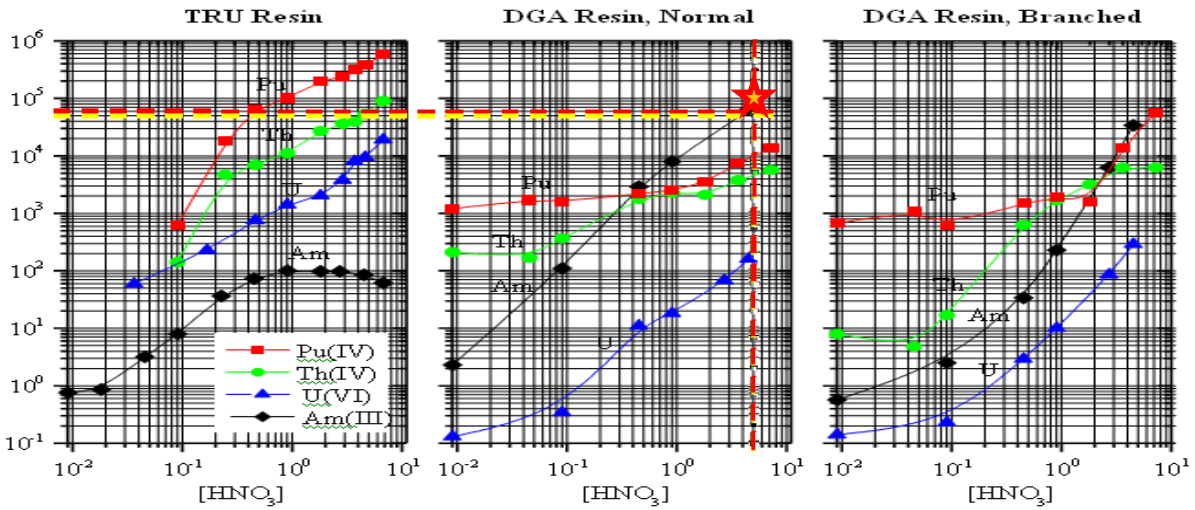


Figure 2

Extraction equilibrium:

$Am^{3+} + 3NO_3^- + 3E \leftrightarrow Am(NO_3)_3 \cdot E_3$

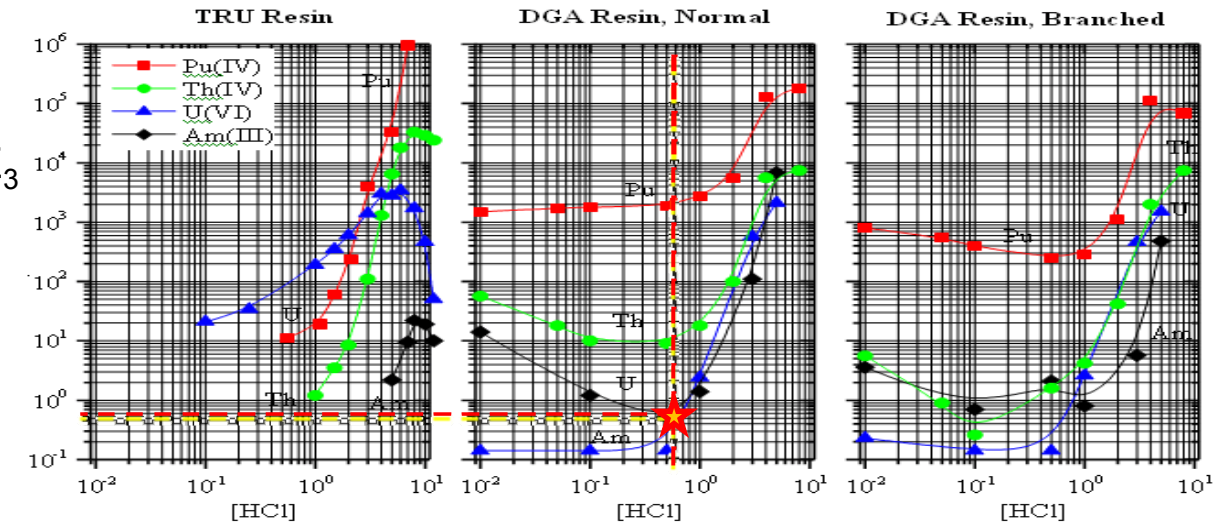
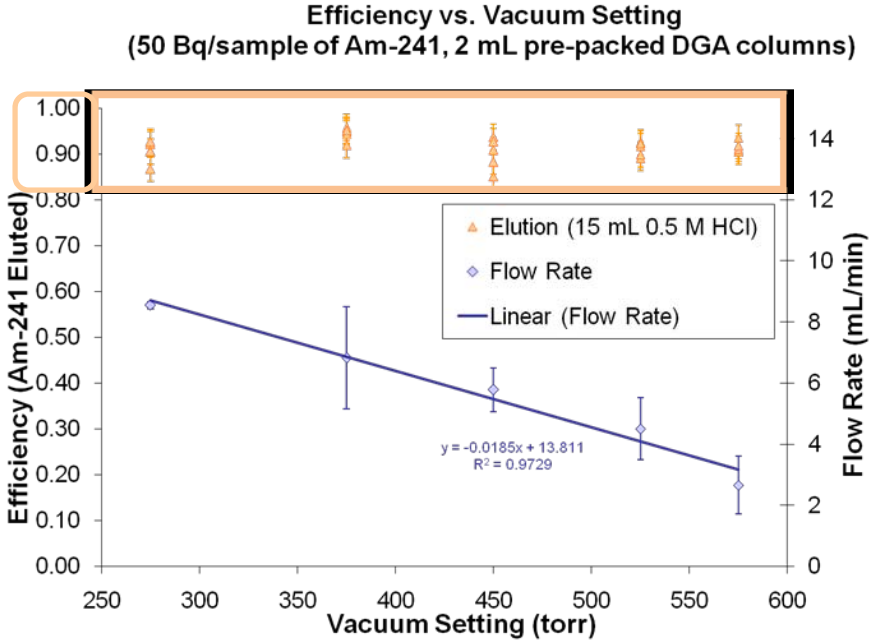
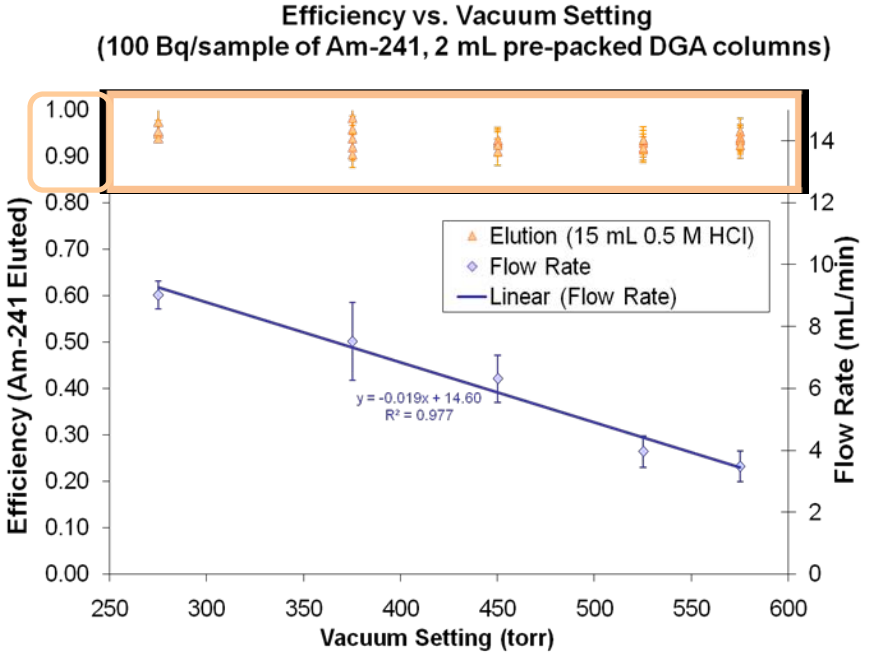
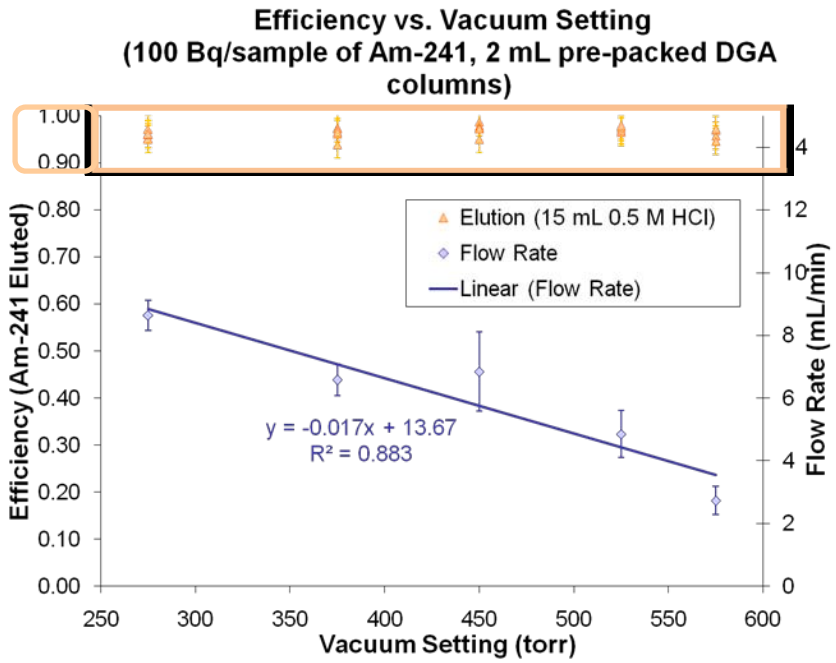


Figure 3







- Column efficiency is >85% over all of the flow rates evaluated

- Column kinetics are sufficient to run at higher flow rates (with no matrix interferences present)

DGA Procedure Results

- Reproducible, linear relationship between flow rate and the DVR vacuum setting
- Inter-column flow rate varies more for the DGA procedure than the TRU Procedure
- Physical limitation of the volume that can be pulled through the column (*in the current set up*), effecting high flow rates
- Flow rate does not effect the loading and unloading efficiencies

Future Work

- Determine the effects of matrix interferences on the system
  - Fe/Mn Oxides, Silicates, Al, etc.
- Examine flow rate characteristics for multiple radionuclide systems (U, Pu and Am)
- Evaluate soil samples from BOMARC project
- Continue automation protocol development

Acknowledgements

- Ken Czerwinski
- Ralf Sudowe
- Rich Gostic
- Ashlee Crable
- Christina Barnes
- Tom O’dou
- Trevor Low

Questions?