LA-UR-14-24630

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Low Enriched Uranium Control

Applicable to a Range of Potential ^{99}Mo Production Processes

I. May

2014 Mo-99 Topical Meeting,
June 24-27, Washington D.C.

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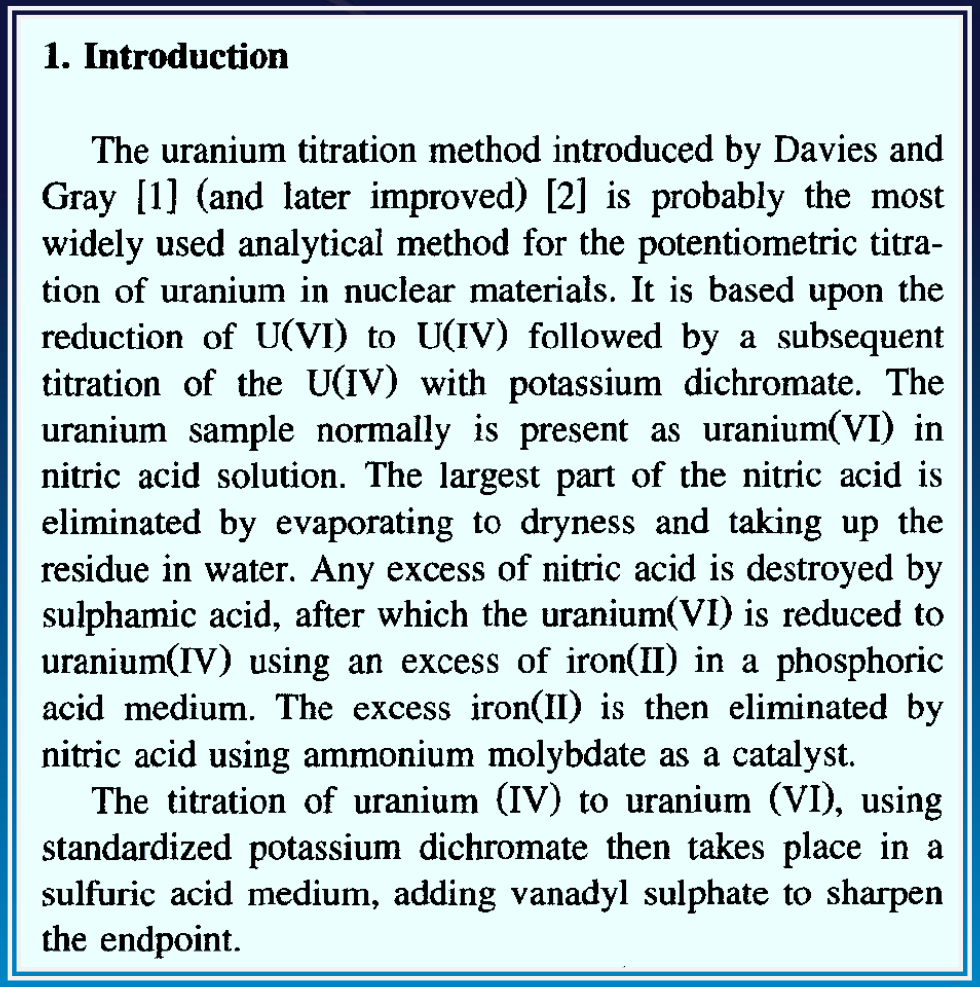
NRC Regulations, Title 10 – Nuclear Material Accountancy Requirements

- >10,000 g of ^{235}U containing materials enriched up to 20.00 % is deemed to be special nuclear material of moderate strategic significance.
  - http://www.nrc.gov/reading-rm/doc-collections/cfr/part074/part074-0041.html

- *Establish and maintain a measurement control program so that for each inventory period the SEID (Standard Error of Inventory Difference) is less than 0.125 percent of the active inventory*
  - http://www.nrc.gov/reading-rm/doc-collections/cfr/part074/part074-0045.html

Davis and Gray Titration

- Destructive analysis method for quantitative uranium measurement
- Titration method used extensively for the analysis of uranium in nuclear materials
- M. Bickel, J. Nucl. Mater., 246 (1997), 30-36
- W. Davies and W. Gray, Talanta, 11 (1964), 1203



1. Introduction

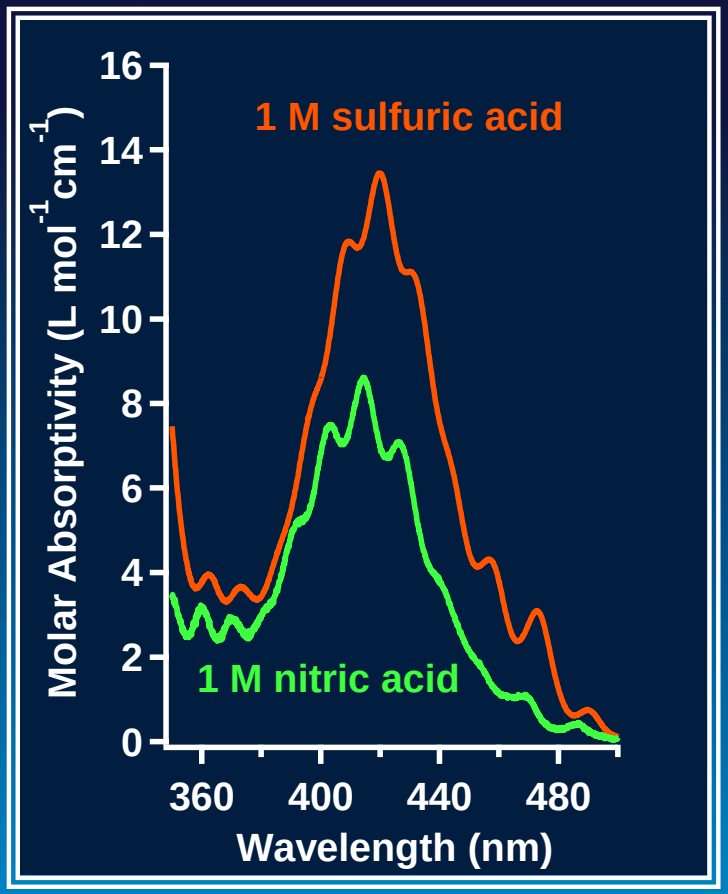
The uranium titration method introduced by Davies and Gray [1] (and later improved) [2] is probably the most widely used analytical method for the potentiometric titration of uranium in nuclear materials. It is based upon the reduction of U(VI) to U(IV) followed by a subsequent titration of the U(IV) with potassium dichromate. The uranium sample normally is present as uranium(VI) in nitric acid solution. The largest part of the nitric acid is eliminated by evaporating to dryness and taking up the residue in water. Any excess of nitric acid is destroyed by sulphamic acid, after which the uranium(VI) is reduced to uranium(IV) using an excess of iron(II) in a phosphoric acid medium. The excess iron(II) is then eliminated by nitric acid using ammonium molybdate as a catalyst.

The titration of uranium (IV) to uranium (VI), using standardized potassium dichromate then takes place in a sulfuric acid medium, adding vanadyl sulphate to sharpen the endpoint.

Technique for Uranium Analysis - Visible Spectroscopy

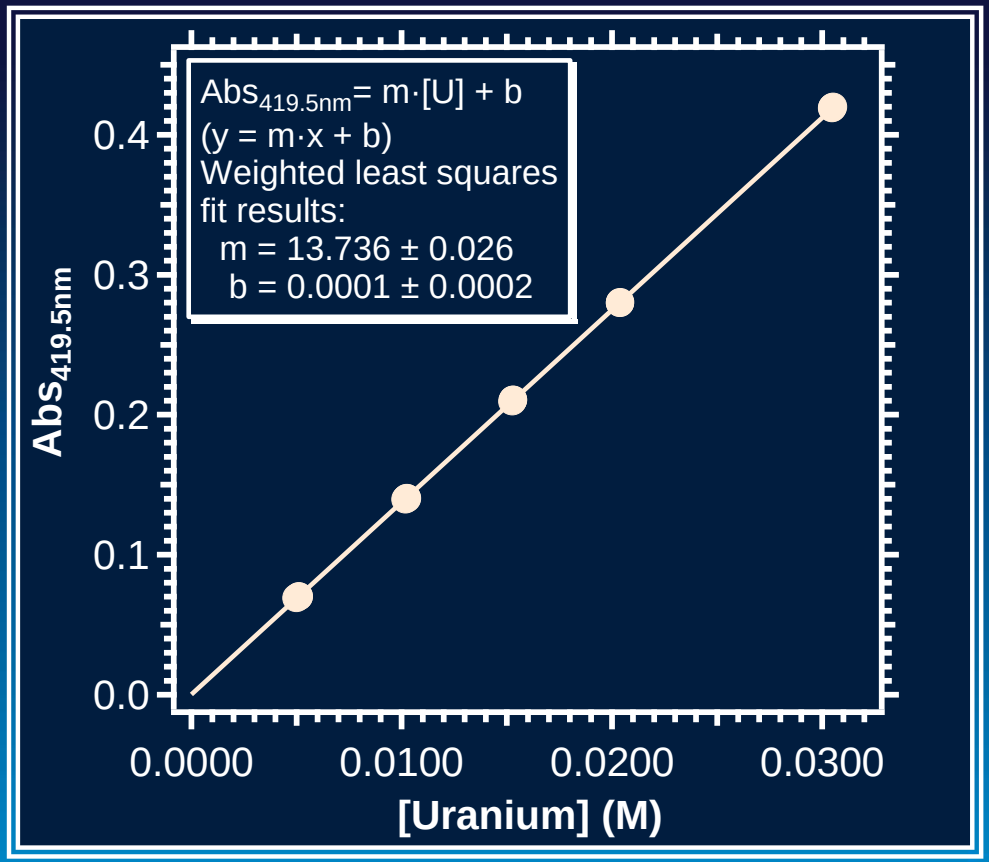
- Uranyl absorption spectra – can be applied to uranium concentration measurement in solution

- $A = \varepsilon c l$
  - A= absorbance
  - ε= molar absorptivity (M^{-1} cm^{-1})
  - c= concentration (M)
  - l= path length, cm
- λ_{max} (peak max, nm) and ε (molar absorptivity) vary with chemical composition
- A small aliquot of sample (*e.g.* 50 µL) and dilute in excess of either 1 M HNO_3 or H_2SO_4 (2000 µL)



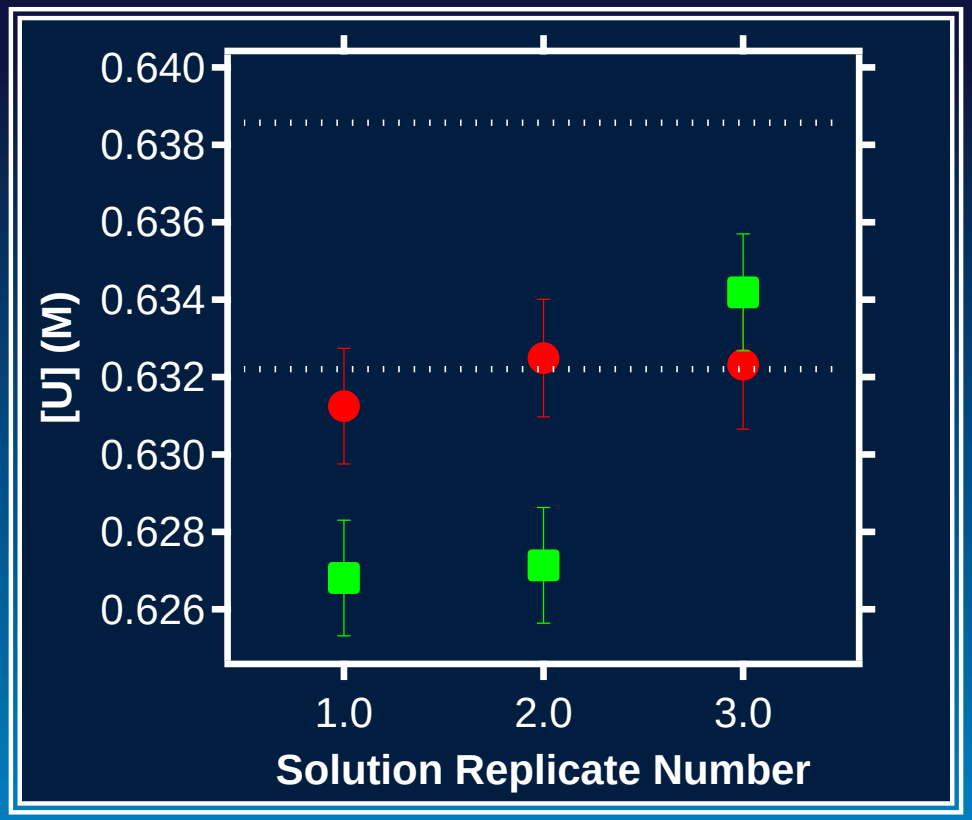
Molar Absorptivity of Uranium(VI) Determined from Matrix of Standard Uranium Solutions

- The molar absorptivity of uranium(VI) in 1.0 ± 0.1 M H_2SO_4 at 19.5 ± 1.7 °C is 13.736 ± 0.026 cm^{-1} M^{-1} at 419.5 nm.
- Accurate molar absorptivity values could be obtained for a wide range of chemical matrices

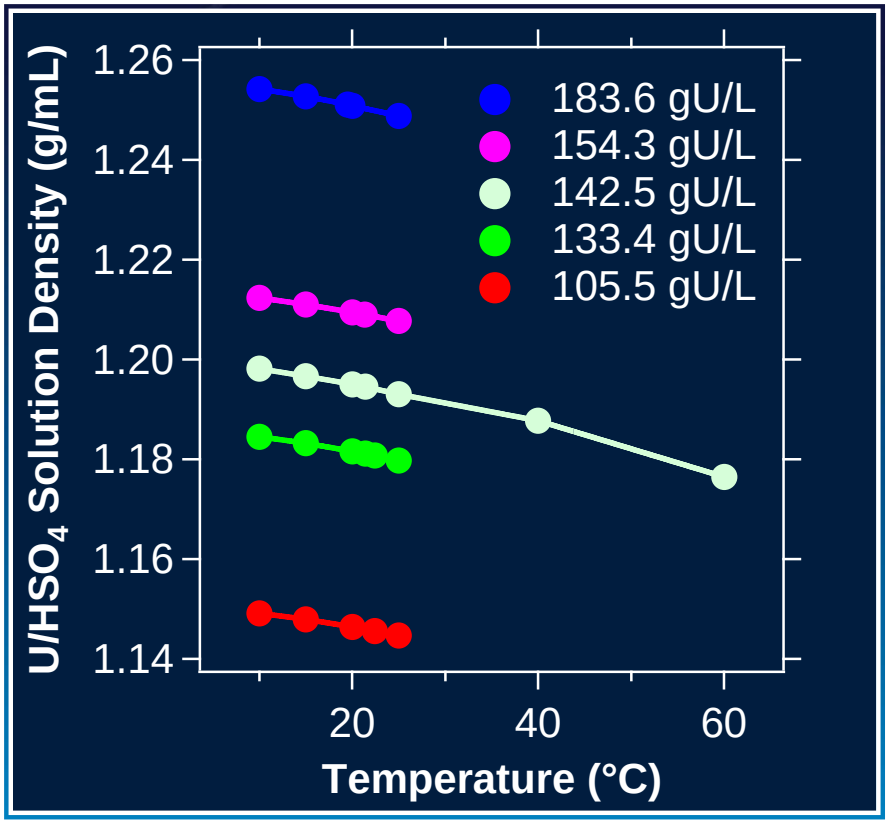


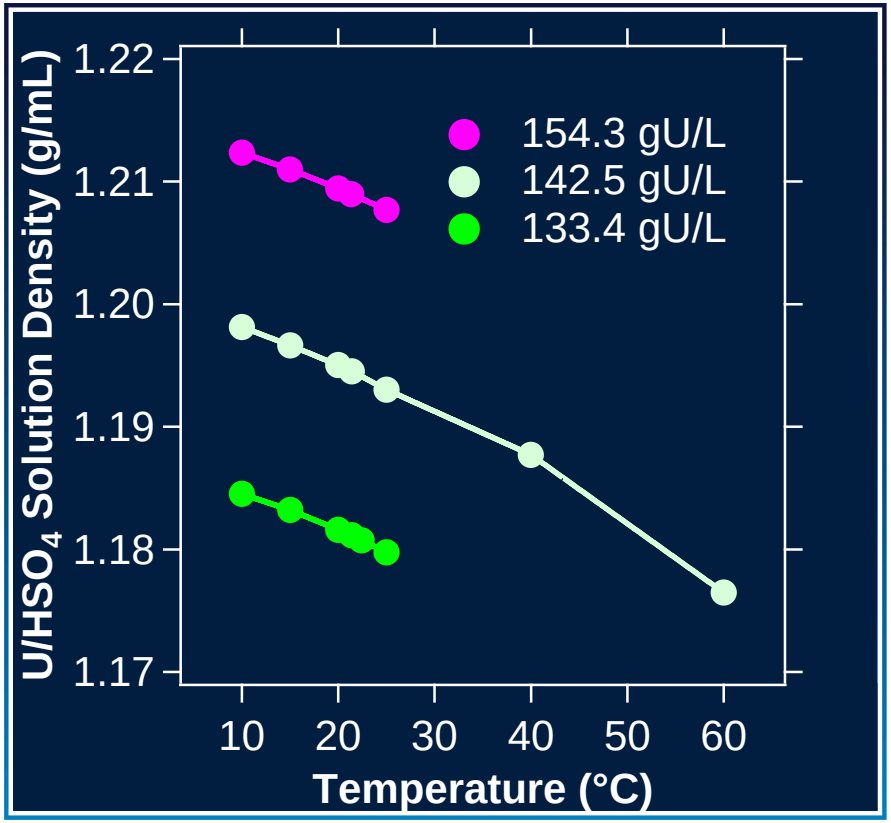
Assay Method Accuracy Testing (151.2 gU/L, 0.6353 mol/L)

- The white lines represent 1 standard deviation of the known molar uranium concentration based on gravimetric data from solution preparation.
- The square and circle points are the uranium concentrations measured by the spectroscopy assay method using 90 or 50 µL uranium aliquots, respectively.
- The error bars are the standard deviations in these measurements.
- Difference between known and measured values all < 0.7 %. For the 90 µL assays.



Density Measurements on pH1 Uranium Sulfate Solutions





Analysis of Contaminants and Impurities

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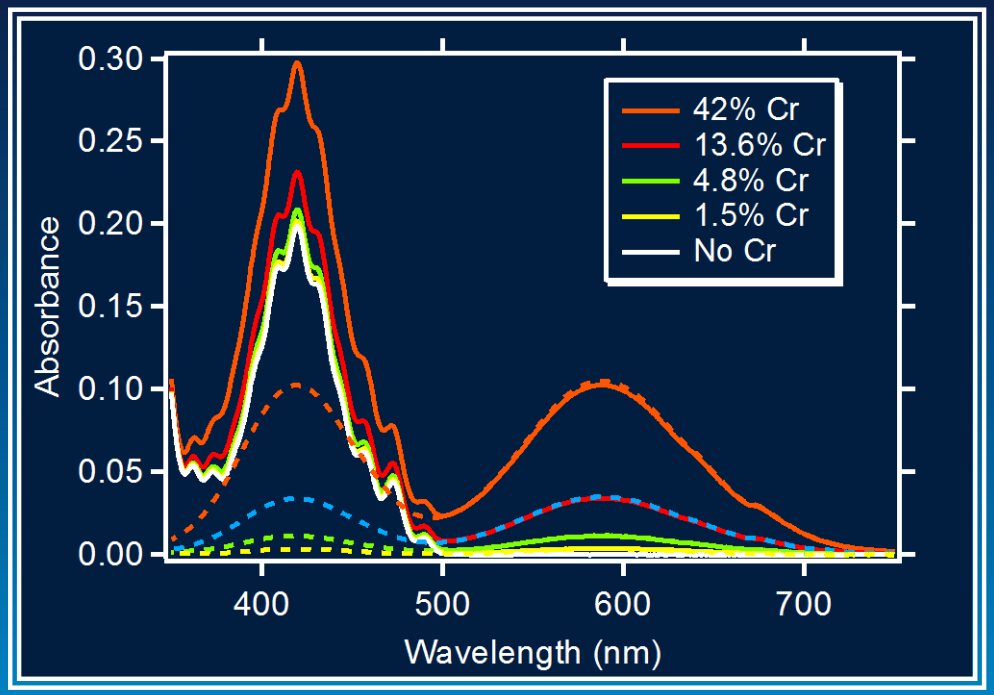
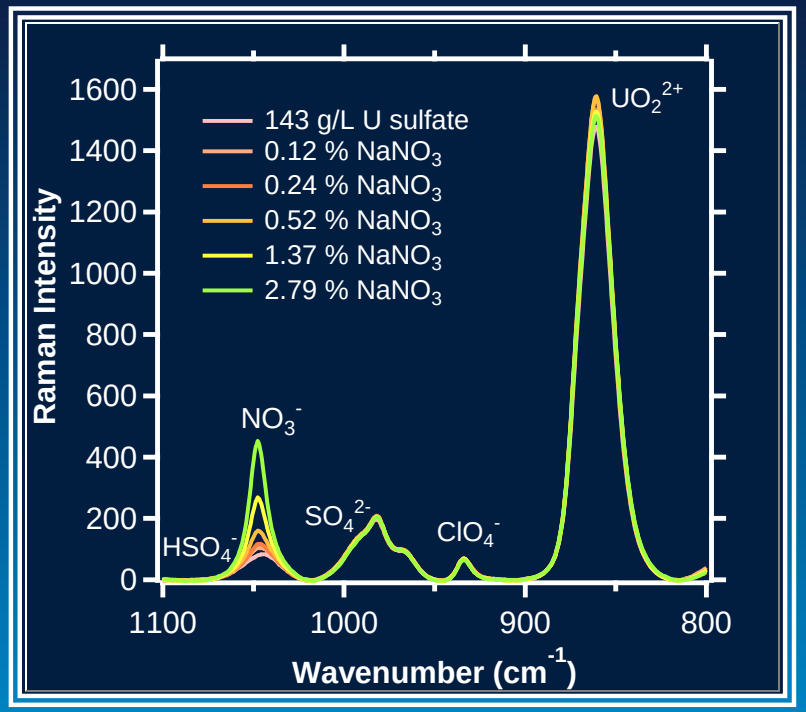
Impact of Cr(III) on the uranium spectroscopy technique

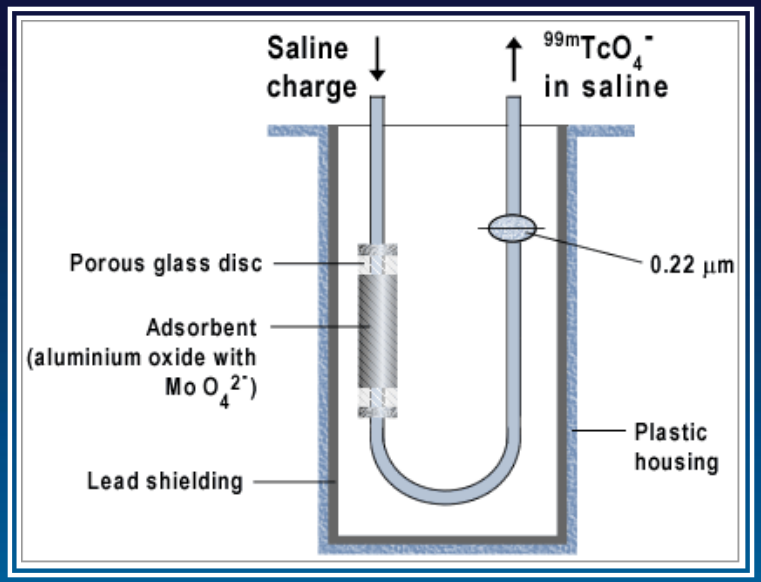


Raman Spectroscopy Detection of Nitrate in 143 gU/L (pH 1) Uranium Sulfate Solution



Chemical Process for the Recovery of Fission Molybdenum-99

- ^{99}Mo recovery and purification processes
  - Initial solid target dissolution step undertaken using acid or base (MDS Nordion use a HNO_3 dissolution process)
- HEU to LEU conversion: - increase in no. of solid targets, processing runs & waste volume
- Most currently operating flow sheets are not well suited to the recycle of uranium
- LEU solution target concepts linked to the application of titania based sorbents for ^{99}Mo recovery (uranyl nitrate in dilute HNO_3 is a potential fuel solution)
- Alumina is the 'Industry Standard' sorbent



http://nucleus.iaea.org/HHW/Radiopharmacy/VirRad/Eluting_the_Generator/Generator_Module/Design_principles/index.html

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^{99}Mo Retention on Alumina – Impact of Uranium Concentration

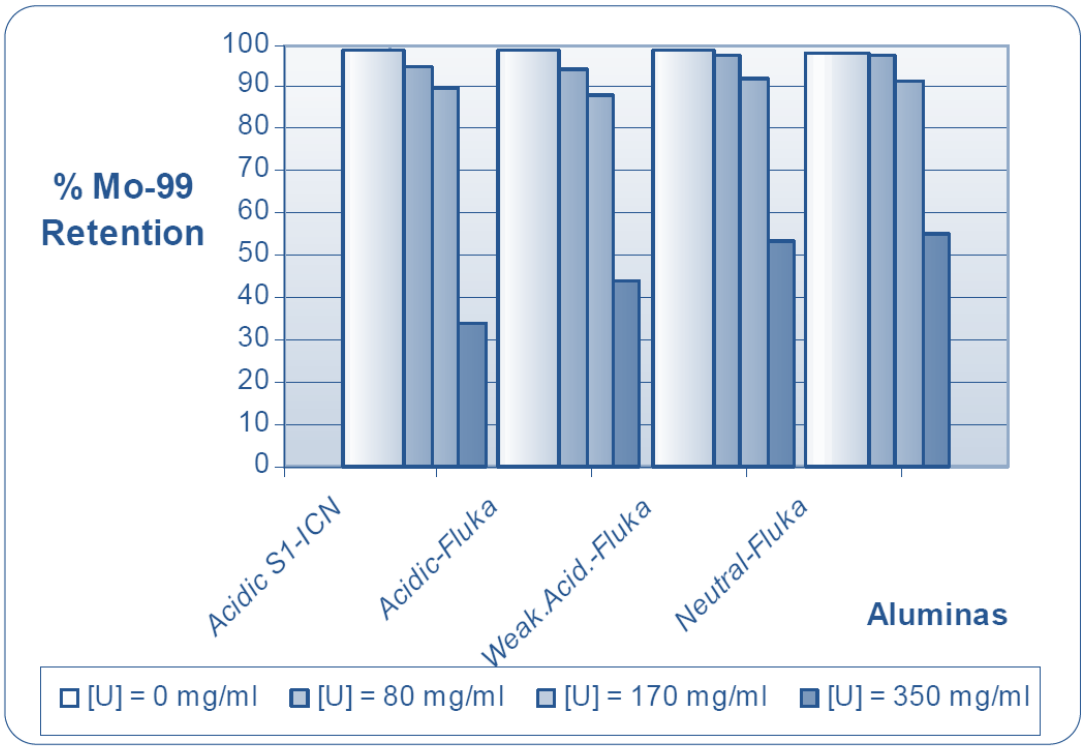
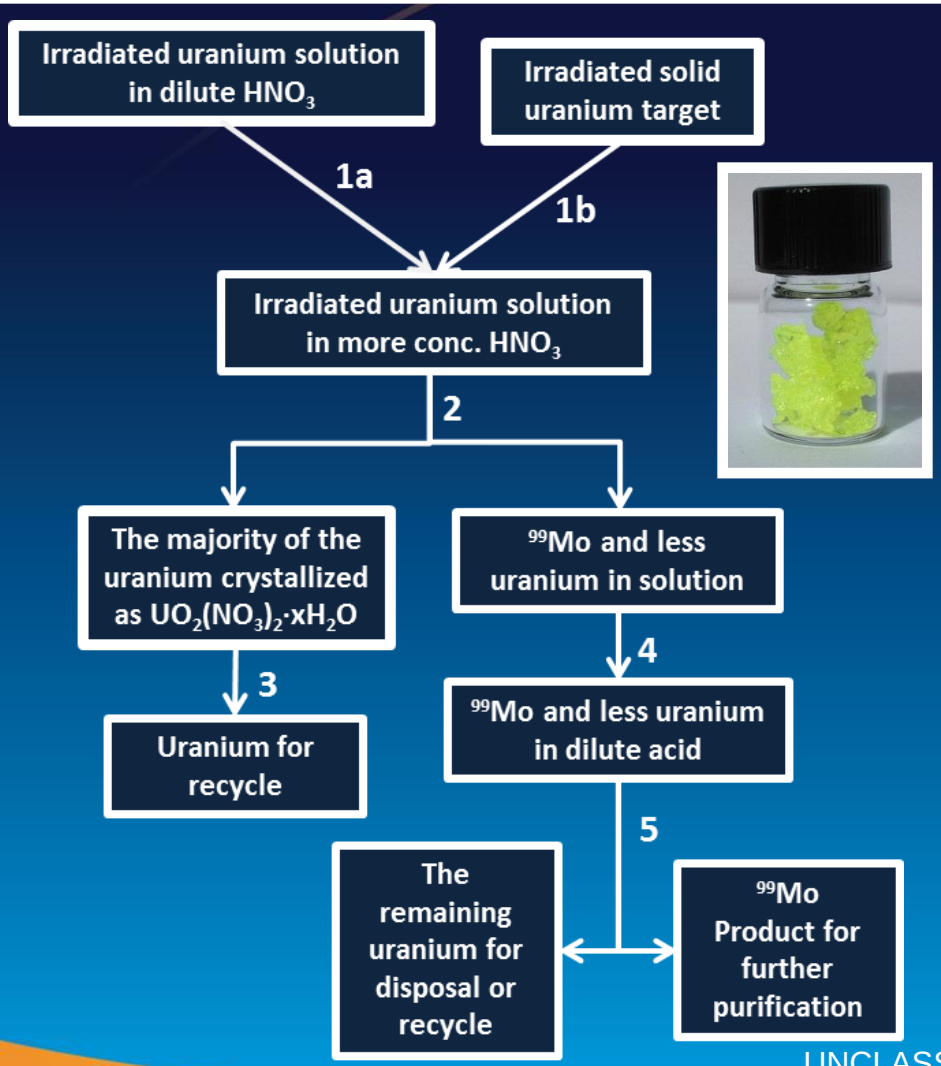


Figure II. Molybdenum retention in different kinds of aluminas varying uranium concentration in loading solution.

http://www.rertr.anl.gov/Web2002/2003Web/Wilkinson.html. See also D.C. Stepinski et al. in IAEA-TECDOC-1601, 2008 (P73)

"Inventive Application" of Individual Separation Processes



1. *a. Evaporation and addition of HNO_3*
   b. Target dissolution in HNO_3.
2. *i) Lower soln. temp. and/or evaporate under reduced pressure to crystallize out uranium. ii) Separation of crystalline phase from solution.*
3. *Preparation of final uranium product, option for recycle/reuse.*
4. *Remove excess nitric acid and add water to obtain the desired uranium and nitric acid concentration.*
5. *Recovery of a Mo-99 product using an alumina column.*

http://en.wikipedia.org/wiki/File:Uranyl_nitrate.jpg

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Experimental Validation

atlas
automated
synthesis system

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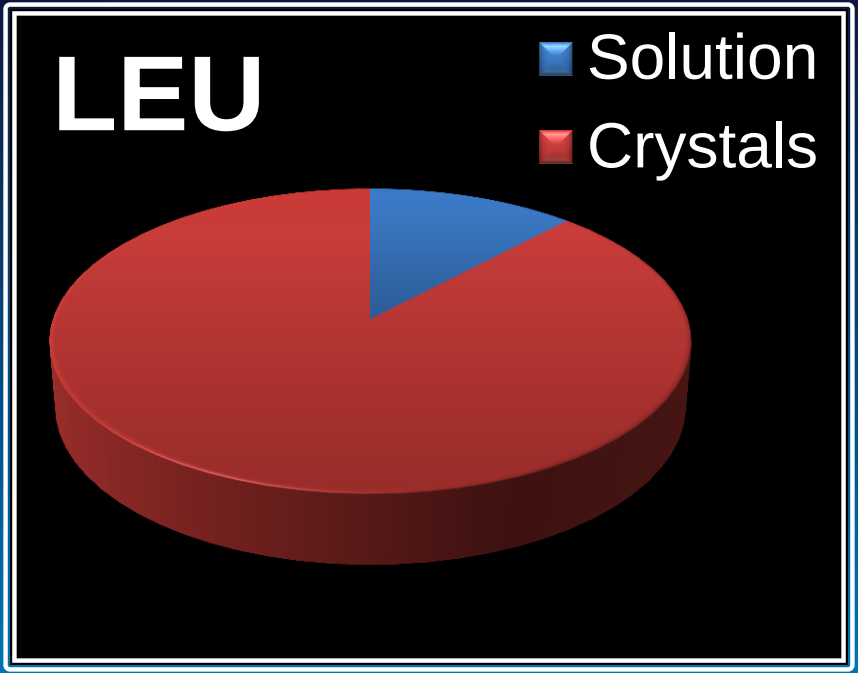
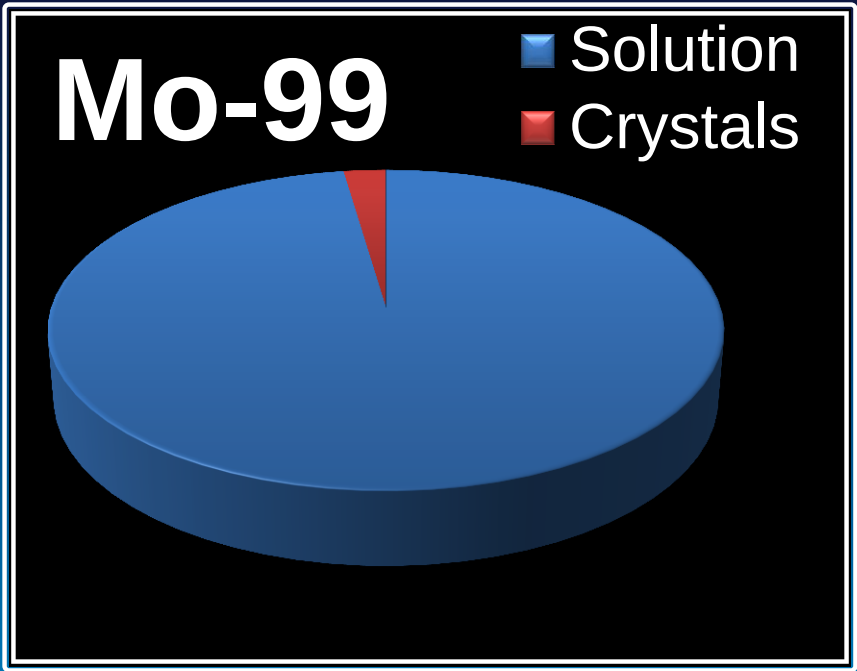
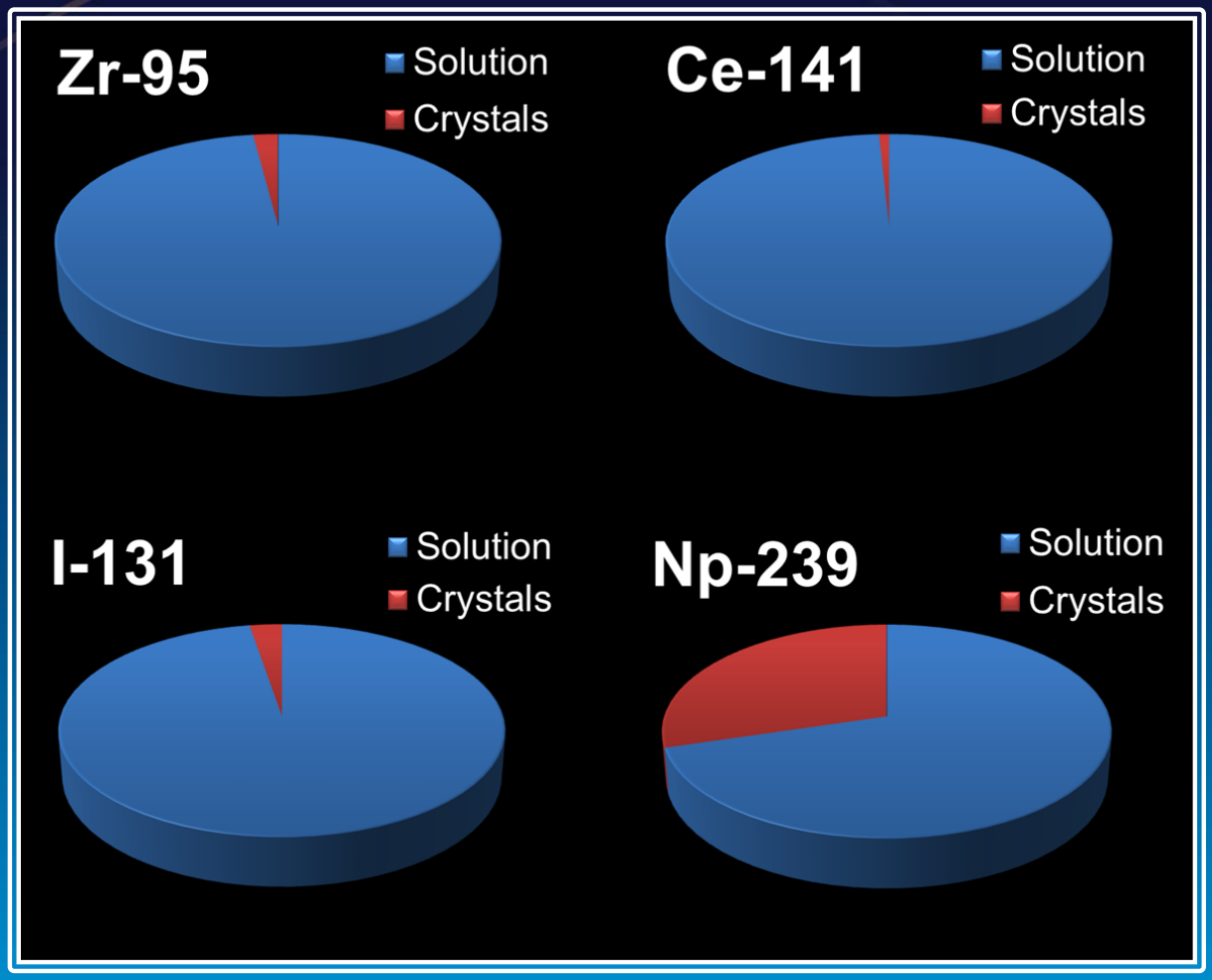
Crystallization Process Removes Most of the Uranium

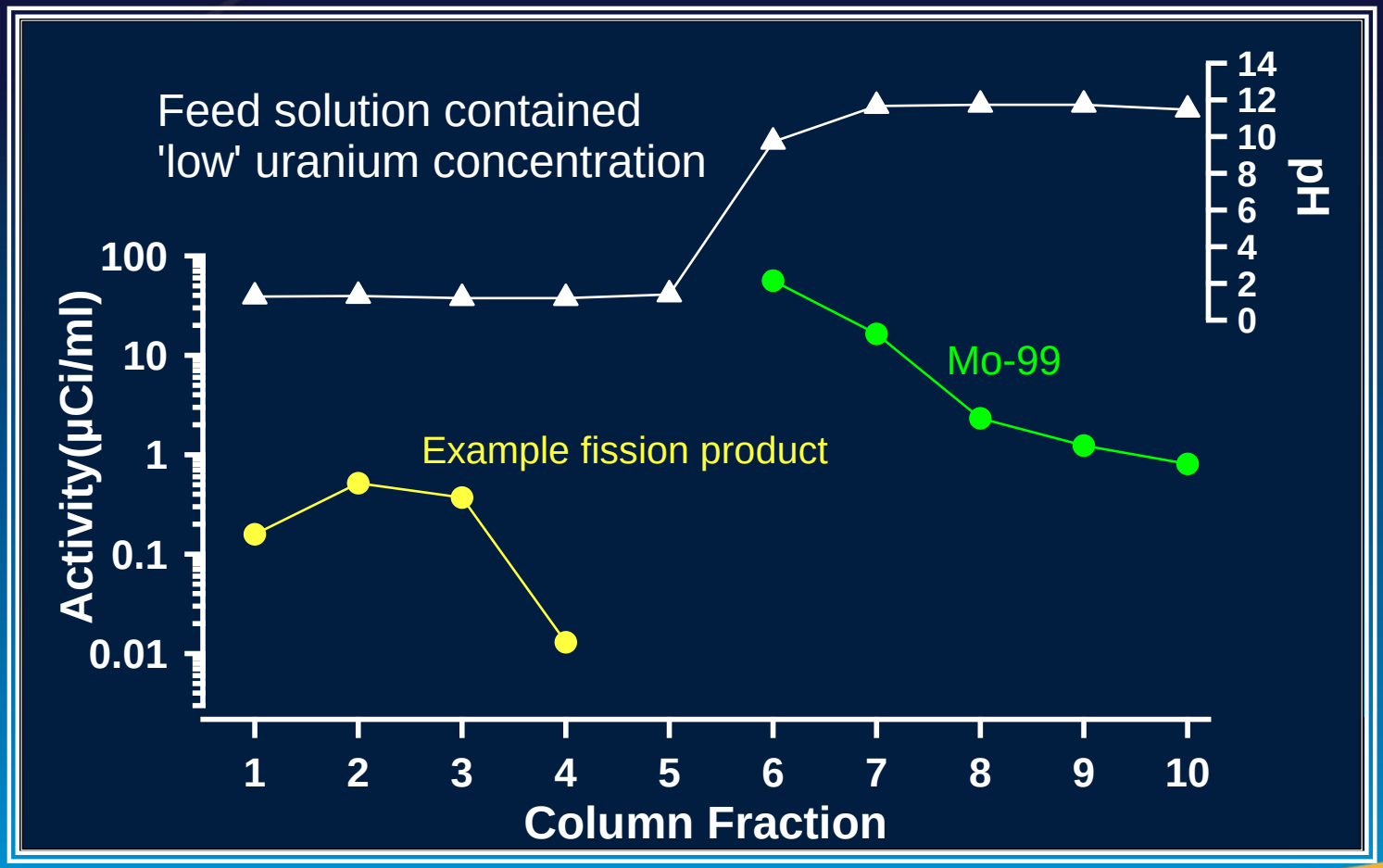




Crystallization Provides a Purified Uranium Nitrate 'Product'



Alumina Column Separation Recovers the ^{99}Mo



Acknowledgements

Analysis of Uranium

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- J. Driscoll (SHINE Medical Technologies)
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Uranium Crystallization Process

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- LANL Laboratory Directed Research & Development – Exploratory Research project