Determination of actinides and strontium in large soil samples

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Am and Pu in large soil samples

Maxwell, S.L.; Culligan, B.K.: Rapid Column Extraction Method for Actinides in Soil, Journal of Radioanalytical and Nuclear Chemistry, Vol. 270, No. 3, pp 699-704(2006)

Maxwell, S.L.: Rapid Method for Determination of Plutonium, Americium and Curium in Large Soil Samples, Journal of Radioanalytical and Nuclear Chemistry, Vol. 275, No. 2(2007)

Horwitz, E.P.; et al: Synergistic Enhancement of the Extraction of Trivalent Lanthanides and Actinides by Tetra-(n-Octyl) Diglycolamide from Chloride Media, Solvent Extraction & Ion Exchange, Vol. 26(1), in press(2008)

Tait, D., Kock B.: Further development of a fast methd for determining plutonium and americium in soild in Germany. Environmental Radiochemical Analysis IV. Ed.: Peter Warwick, RCS Publishing, 2011, 9 – 20

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Determination of Am and Pu in large soil samples

- Detection limits requested in environmental monitoring make analysis of large soil samples necessary
  - Depending on country 30g to >100g
- Existing methods:
  - TRU sensitive to Fe(III) interference, Fe needs to be removed or reduced quantitatively
  - e.g. Ca-Oxalate precipitation for matrix/Fe removal
- DGA shows very high Am uptake and robustness against Fe interference
- New methods based on DGA developed

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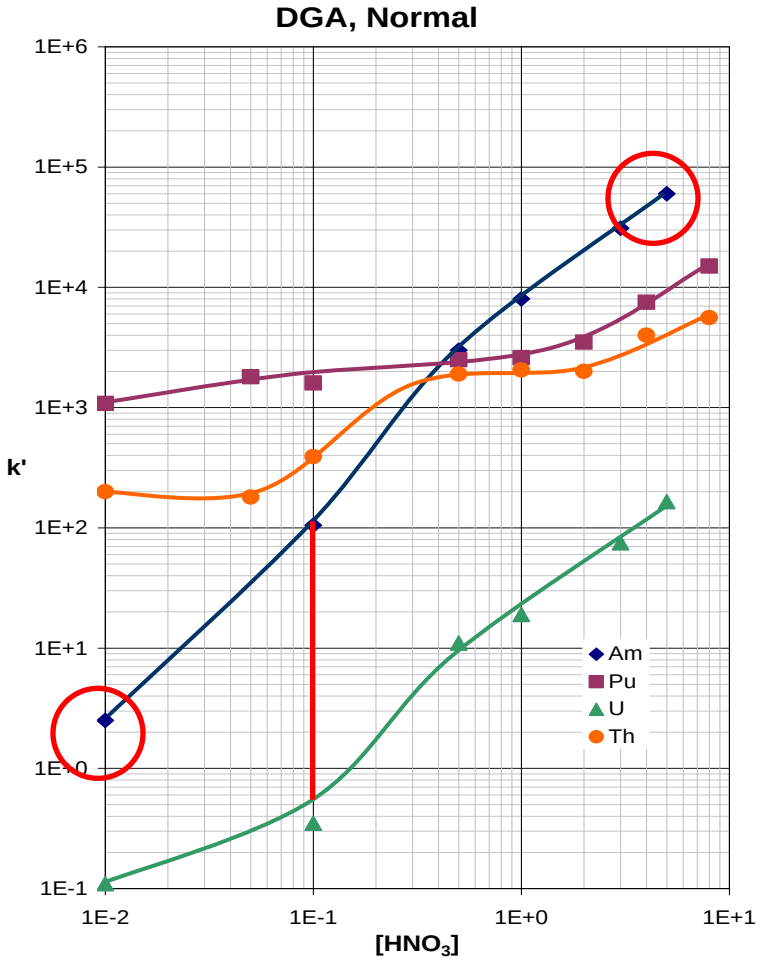
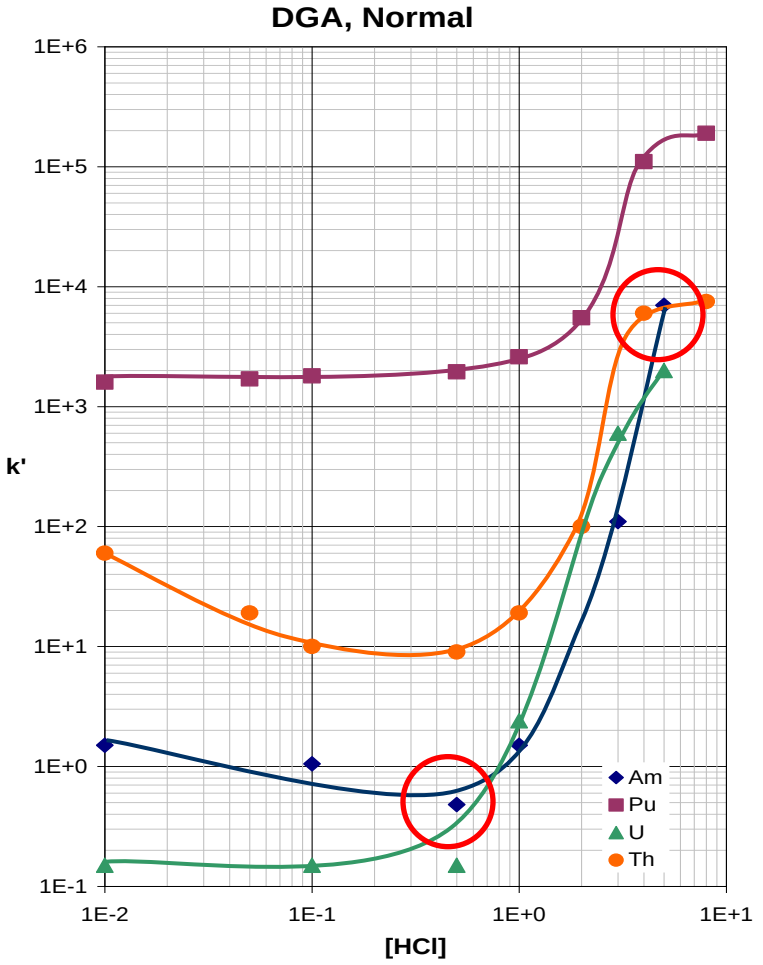
Acid dependency of k' for Am, Pu, U and Th in HNO_3 and HCl on DN





- High uptake of Am at high HCl / HNO_3
- Am easily eluted with dilute HCl / very dilute HNO_3
- Am / U separation at 0.1M HNO_3

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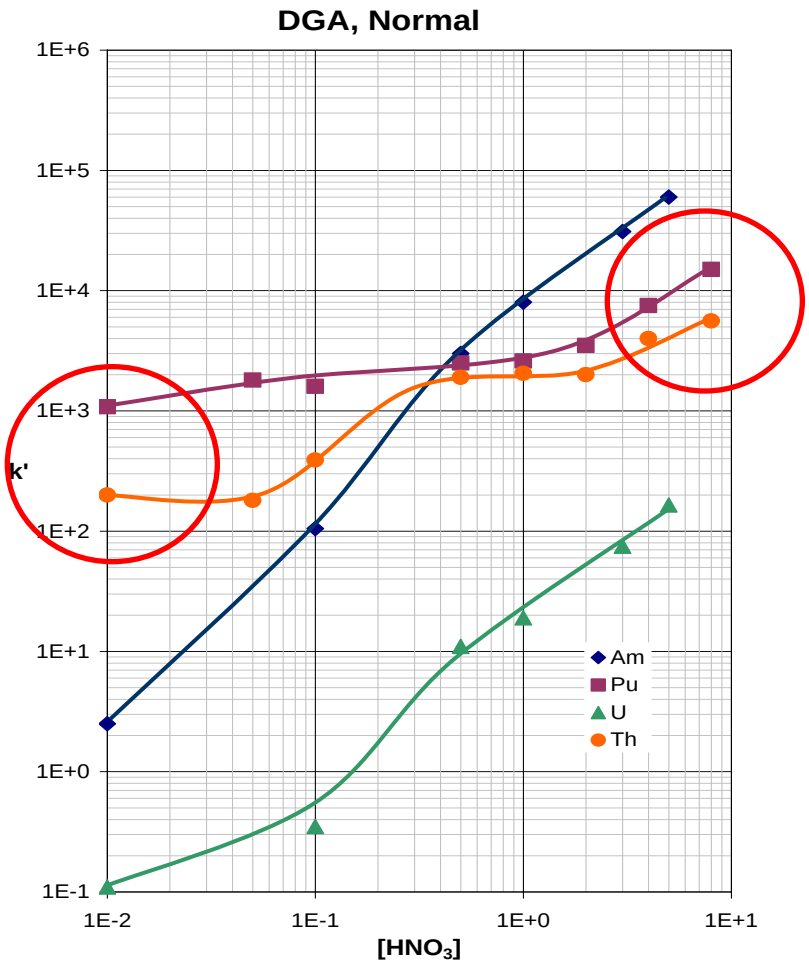
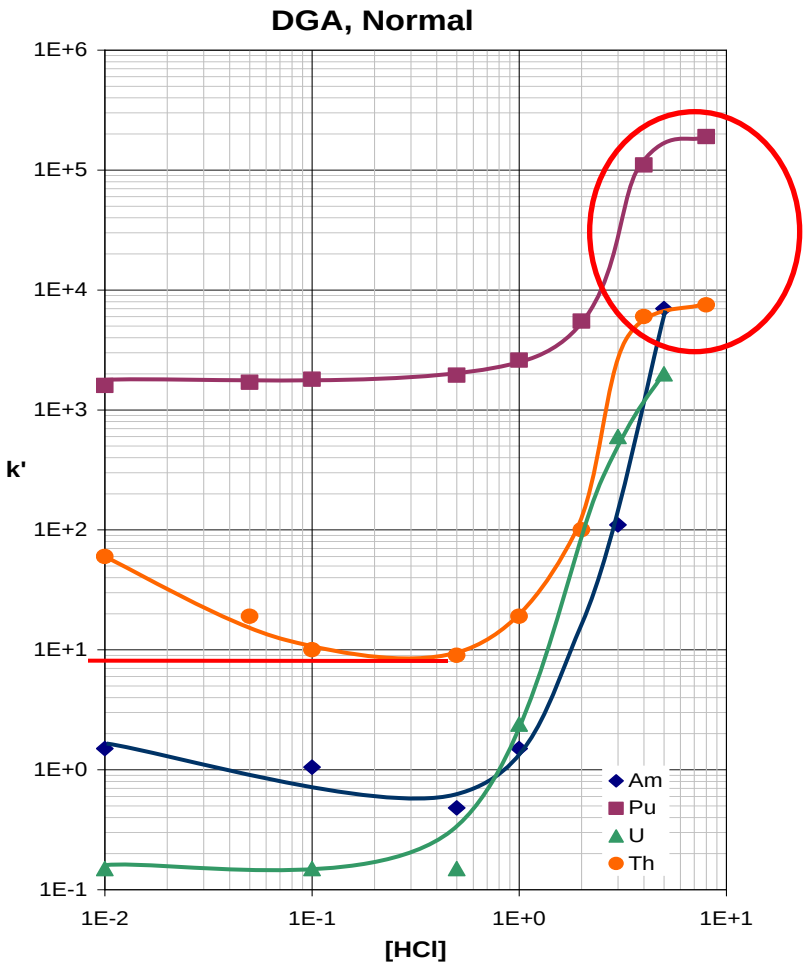
Acid dependency of k' for Am, Pu, U and Th in HNO_3 and HCl on DN





- High uptake of Pu and Th in high HNO_3 / HCl
- Pu and Th elution more difficult, for separation preferably TEVA or AIX upfront

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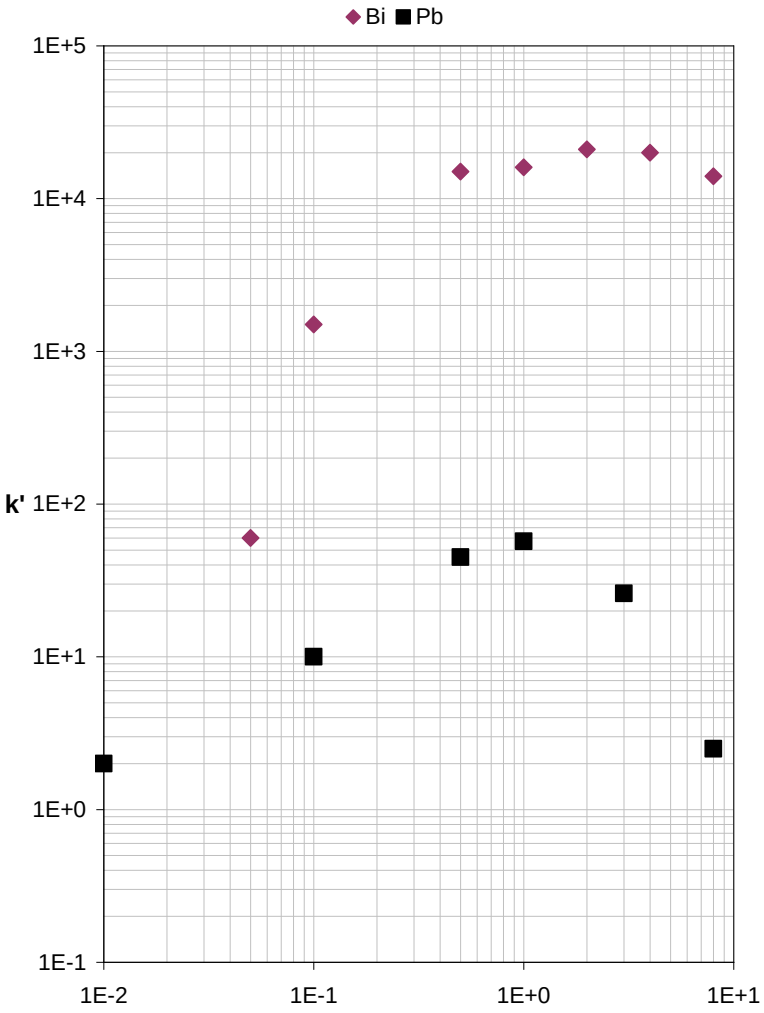
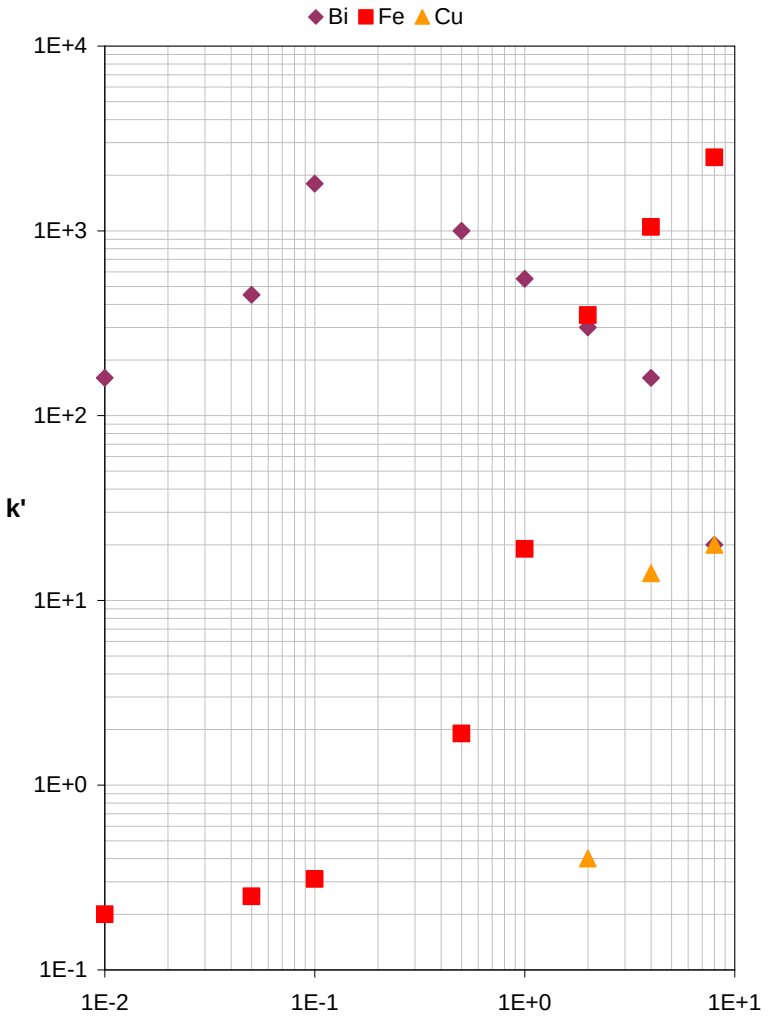
Interferences



k' for V(V), **Ti(IV), Al(III), Fe(III)**, Co(II), Cu(II), Ni(II), Zn(II) **< 2 for all [HNO_3]**



k' for **Ti(IV), Al(III)**, Co(II), Ni(II), Pb(II), Zn(II) **< 2 for all [HCl]**

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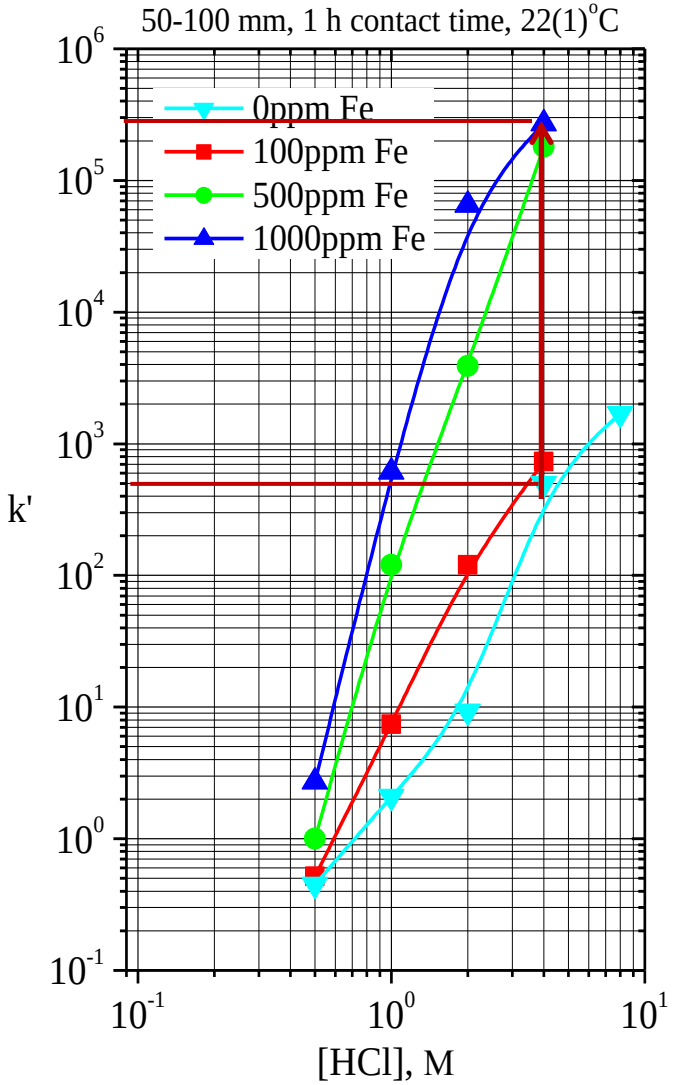
Particular case Am(III) in presence of Fe(III) in HCl on DN



- Method for analysis of Am, Pu (and Np) in large soil samples (Horwitz, SRS)
  - Applied to 100 – 200 g samples leached with HNO_3 and HCl
  - Rapid separation method using cartridges and vacuum box
- Preconcentration and Am separation on DGA
- Also applicable to other complex matrices
- Method updated by Tait et al. in 2010
  - Takes longer but obtains higher yields

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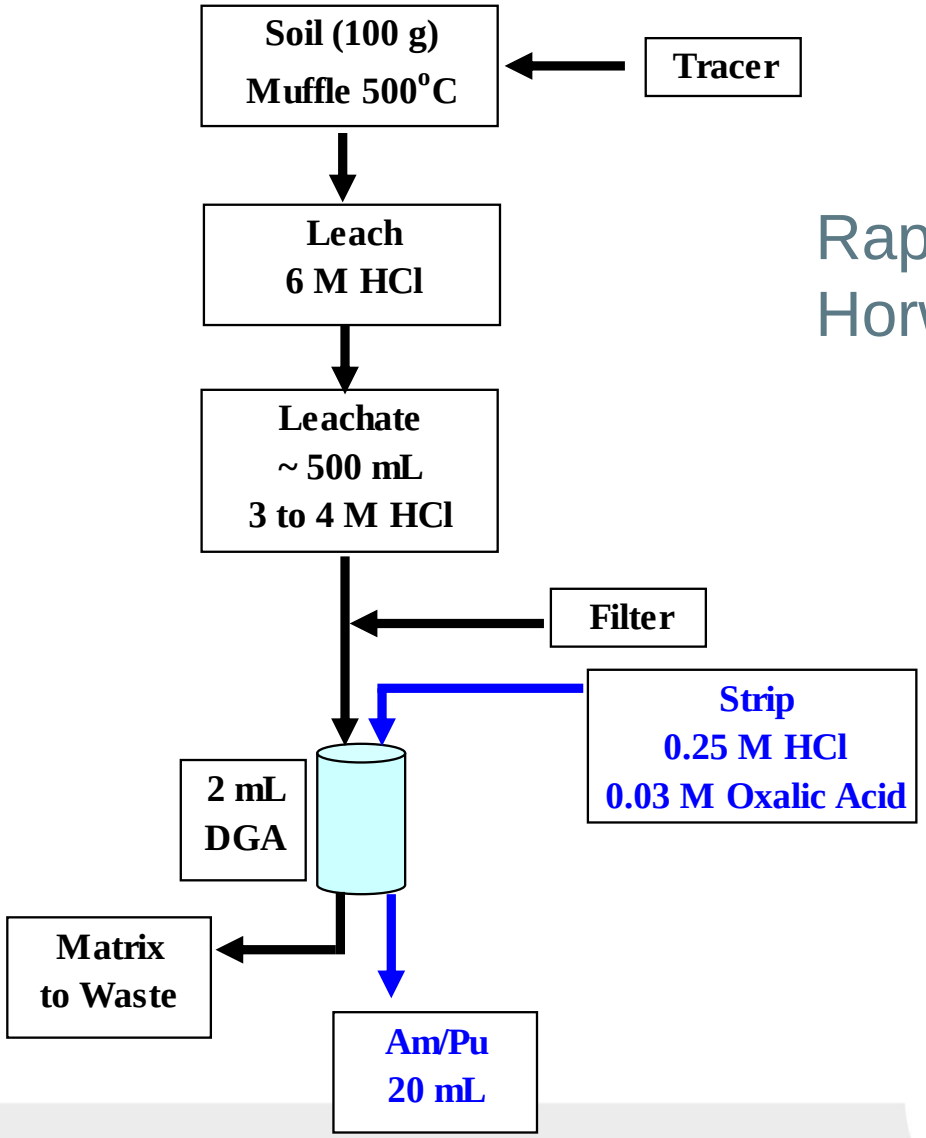
Flowchart for the Preconcentration of Am and Pu from 100 g of Soil



Rapid method
Horwitz et al.

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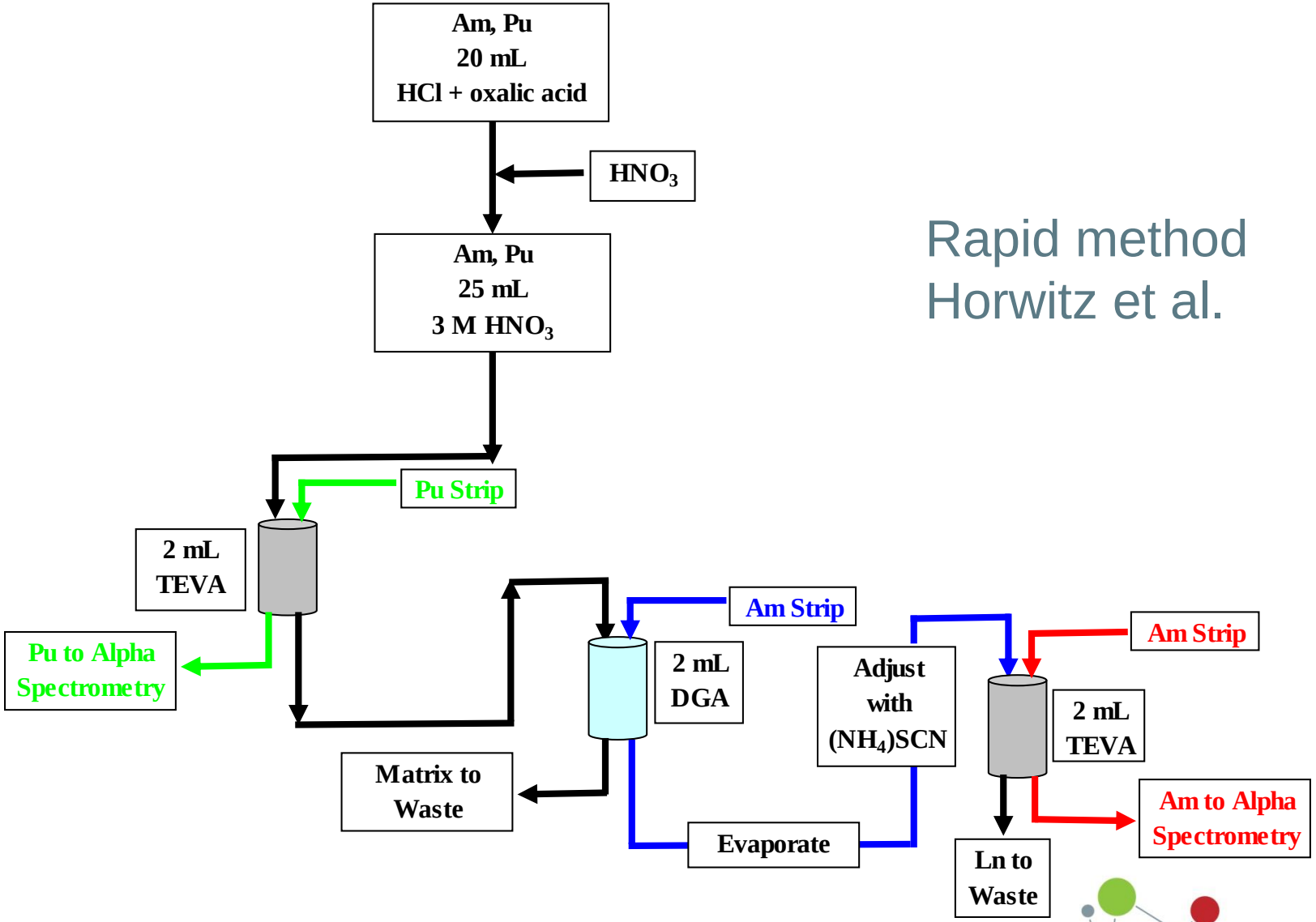
Flowchart for the Separation of Pu and Am from Preconcentrate



Rapid method
Horwitz et al.

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Modified Horwitz method Tait et al. (2010)

- 100g soil ash (can also be applied to ash samples of hay, maize, sediments and sludge)
- Ashing of sample at 700°C for 18h
- Micro-wave supported acid extraction (10 bar)
- Filtration through 3 glassfiber filters and one membrane filter to remove fine particles
- Preconcentration / matrix removal via DGA
- 2 TEVA columns before 2nd DGA column
  - removal of Th from Am spectra
- Tested method against in-house reference method
  - Very good agreement of results
- Obtained chemical yields:
  - Pu: 87% ± 11%; Am: 72% ± 14%

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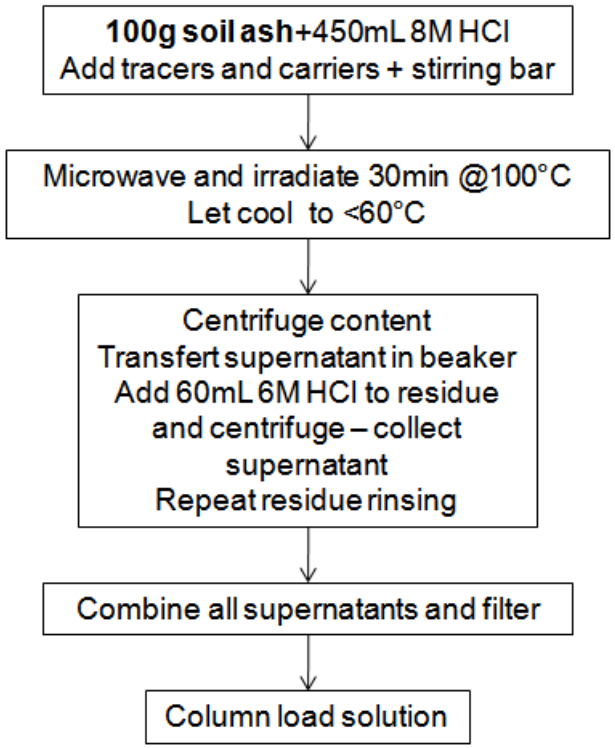
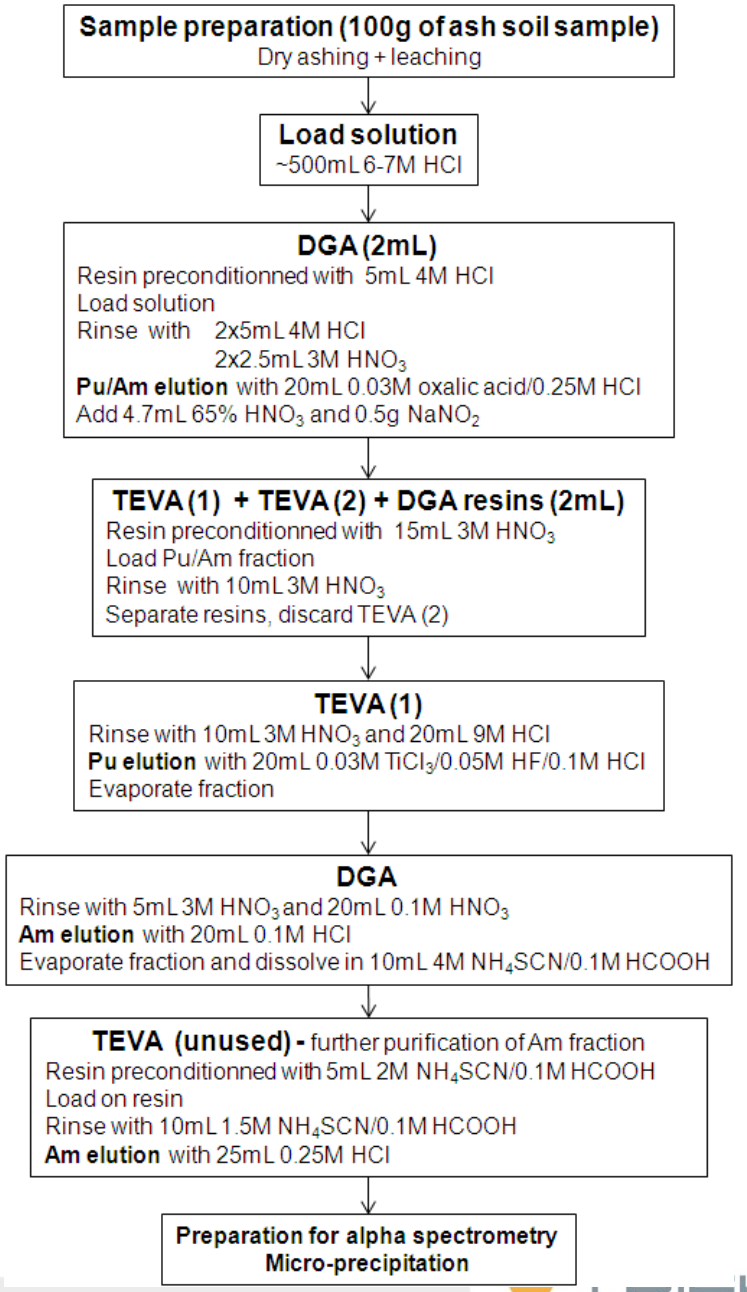


Total analysis in 2-3 days

RN	PTB ref value (Bq/kg dm)	Mean of lab means (Bq/kg dm)
^{238}Pu	19.6 (s=1.3)	20 (s=1.4)
$^{239/240}$Pu	1.1 (s=0.1)	1.2 (s=0.3)
^{241}Am	154 (s=5)	133 (s=12)



Other matrix elimination steps

- Sherrod Maxwell (SRS laboratories)
  - CeF_3 or LnF_3 co-precipitation
    - Precipitation under oxidative conditions removes U
  - Stacked TEVA/TRU/DGA cartridges
  - complete dissolution (Pu/Am/Np)
    - (Na_2O_2 / NaOH fusion) up to 10 g soil
    - Rapid method (results in 24h possible)
    - High recoveries (> 80%)
  - leached soil samples up to 200 g (Pu/Am)
    - leaching HNO_3/HCl
    - Recoveries 80 – 90%
    - Detection limit: 1 mBq/kg (16h counting)

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Sr in large soil samples

Maxwell S L, Culligan B K, Shaw S J: Rapid determination of radiostrontium in large soil samples, Journal of Radioanalytical and Nuclear Chemistry (2012) DOI10.1007/s10967-012-1863-2

Maxwell S L, Culligan B K: Rapid determination of Radiostrontium in large soil samples, 31/10/12, 58th Annual RRMC, Fort Collins, CO October 29 to November 2, 2012

ISO 18589-5:2009: Measurement of radioactivity in the environment. Soil. Measurement of strontium 90

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SAVANNAH RIVER NATIONAL LABORATORY
Operated by Savannah River Nuclear Solutions, LLC

We Put Science To Work

Rapid Determination of Radiostrontium in Large Soil Samples

S. L. Maxwell and B. K. Culligan
Savannah River National Laboratory
October 31, 2012

Rapid Sr-89, Sr-90 Acid Leach Method for Larger Soil Aliquots

50 g samples

For smaller samples (25 g) also use of HF

Add Sr carrier to large soil sample

Acid leach with 15.8M HNO_3; centrifuge, decant and evaporate leachate

Redissolve with 15-20mL 1M HCl

Transfer to 225mL tube and dilute to 180mL with water

Fe hydroxide matrix removal (25mL con. NH_4OH, 50mg Ca, PO_4) Mix and centrifuge

Discard Supernatant

Add 40mL 1.5M HCl. Dilute to 170mL with 0.01M HCl

Ca Fluoride matrix removal Add 25mL 28M HF. Mix and centrifuge

Discard supernatant

Redissolve in 7mL 15.8M HNO3+7mL 3MHNO$_3$-0.25M H_3BO_3, 7mL $Al(NO_3)_3$

Column Load Solution

Maxwell et al. 2012

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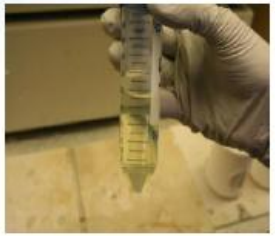
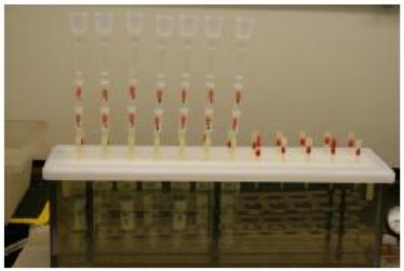
Rapid Sr-89, Sr-90 Column Separation Method for Soil





Column Load Solution

↓

Sr Resin* (3mL) cartridge

↓

Rinse column; 15mL 8M HNO_3; *5mL 3M HNO_3-0.05M Oxalic Acid; 15mL 8M HNO_3

← Sample matrix and ^{90}Y removal; start time for ^{90}Y ingrowth after final 8M HNO_3 rinse

↓

Elute Sr *15mL 0.05M HNO_3

↓

Evaporate on planchet; weigh for gravimetric yield

↓

Count $^{89,90}Sr$ by Gas Flow Proportional Counter

↓

Recount after ^{90}Y ingrowth 10 days later to determine ^{89}Sr and ^{90}Sr

For large soil aliquots:

*4 ml Sr Resin

*10mL 3M HNO_3-0.05M Oxalic Acid

*18 mL 0.05M HNO_3

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Results spiked soils samples

- Leached 50g soil samples:
  - 5.92 mBq.g^{-1} level
    - Yield: 94.0% (+/- 2.6%, N=7), Bias: 0.43%,
    - MDC: 0.41 mBq.g^{-1} for 90 min count
  - 11.84 mBq.g^{-1} level
    - Yield: 89.6% (+/- 2.7%, N=7), Bias: -2.51%,
    - MDC: 0,17 mBq.g^{-1} for 8h count
  - 59.2 mBq.g^{-1} level
    - Yield: 89.3% (+/- 5,3%, N=7), bias: -2,36%
- 25g HF digest
  - 11.84 mBq.g^{-1} level
    - Yield: 73,0% (+/- 5,1%, N=7), Bias: 6,14%,
    - MDC: 0,17 mBq.g^{-1} for 8h count

➢ All results corrected for 1.35 mBq.g^{-1} Sr-90 found in unspiked soil

➢ High Pb samples: hold before measurement or pass through 1 mL DGA cartridge for Bi removal

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Спасибо за внимание!

Вопросы?

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