



Laboratoire de
Radioécologie

Quantification of main radionuclides of uranium decay series in mining residues through sequential extraction

Claire Dalencourt
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RRMC - May 2018



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Département de chimie

Repurposing of mining residues



Phosphates

Repurposing

7000 to 8000 tons
a day

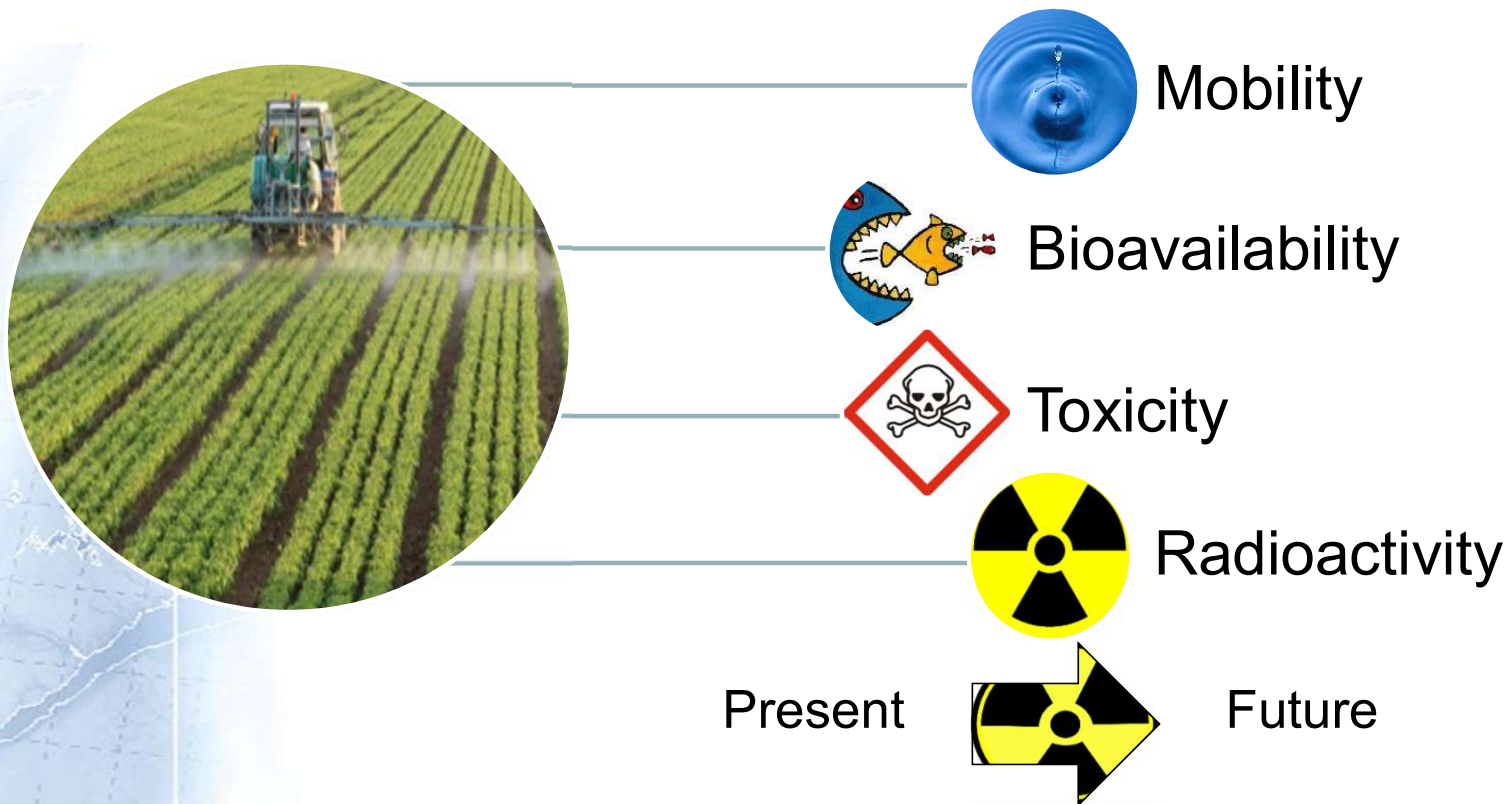


Savard, J. Y. (1981). *Étude de mise en valeur des rejets de carbonate-apatite de la mine Niobec dans le but d'une utilisation comme engrais en agriculture*. Université du Québec à Chicoutimi.

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Risk assessment



Université 
de Montréal

INRS
Université d'avant-garde

Centre d'expertise
en analyse
environnementale
Québec 

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Governmental regulations

- S Factor

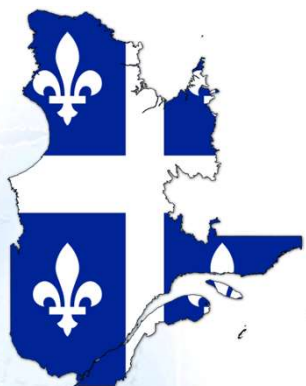
$$S = \sum_{i=1}^{i=n} \frac{A_i}{A_{i,max}} \leq 1$$

- Example

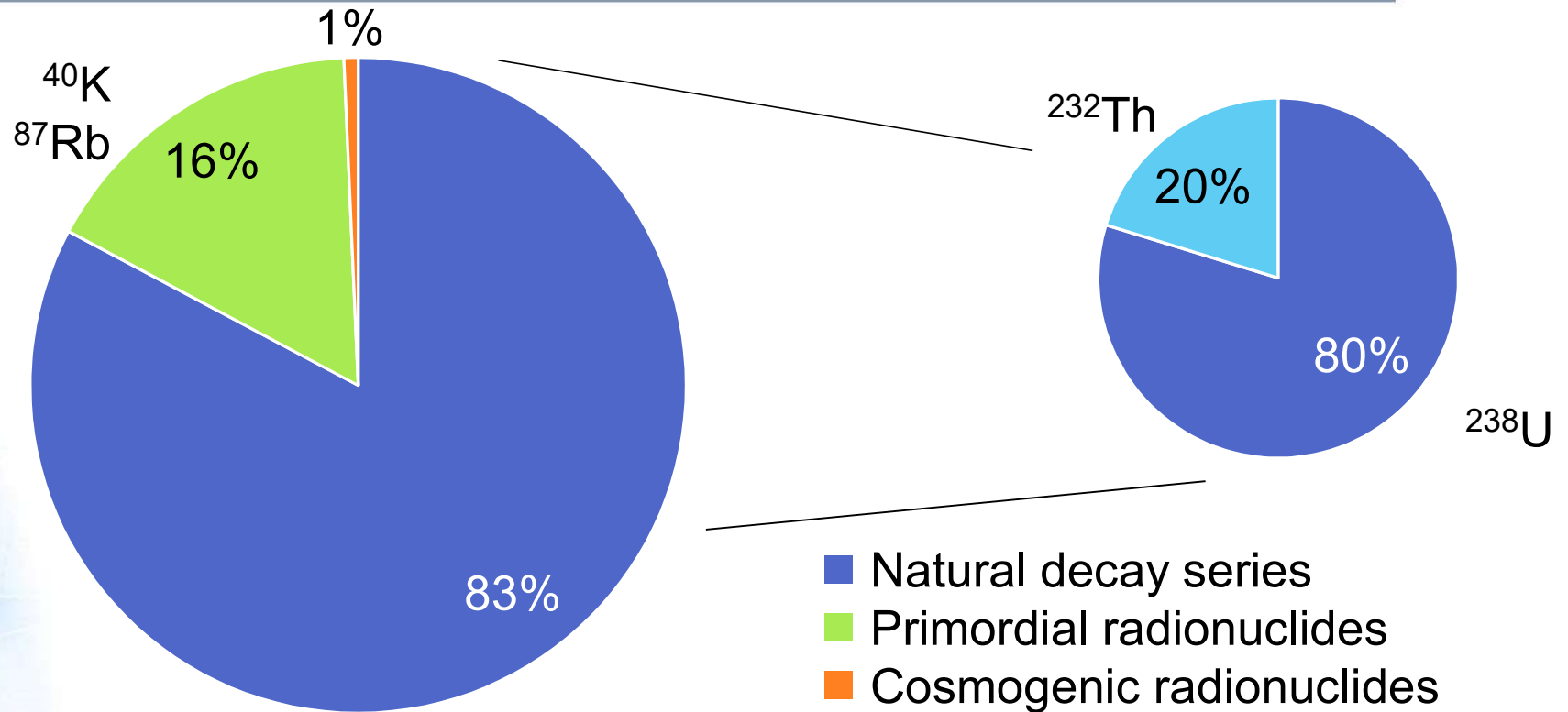
$$S = \frac{A(^{40}K)}{400 \text{ Bq/g}} + \frac{A(^{87}Rb)}{400 \text{ Bq/g}} + \frac{A(^{14}C)}{4000 \text{ Bq/g}}$$

$$S = \frac{250 \text{ Bq/g}}{400 \text{ Bq/g}} + \frac{100 \text{ Bq/g}}{400 \text{ Bq/g}} + \frac{1000 \text{ Bq/g}}{4000 \text{ Bq/g}}$$

$$S = 1,125 > 1$$



Environmental radioactivity



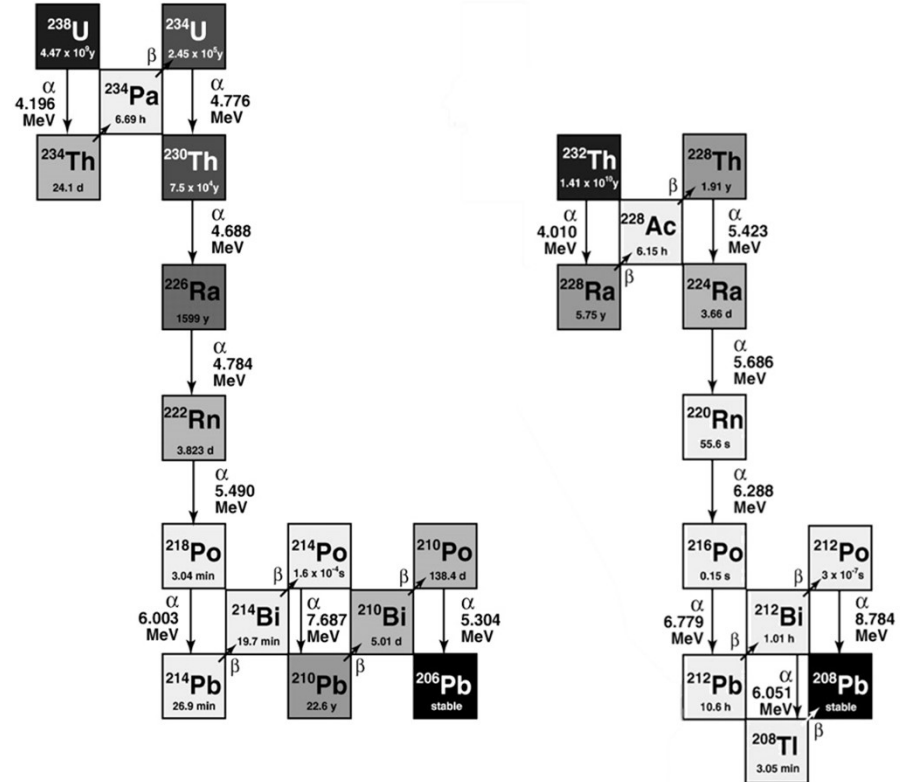
Percentage contribution to the annual dose from natural radionuclides

Th and U decay series

A_{son} linked to A_{father}
 Transient equilibrium
 Secular equilibrium



Approximation

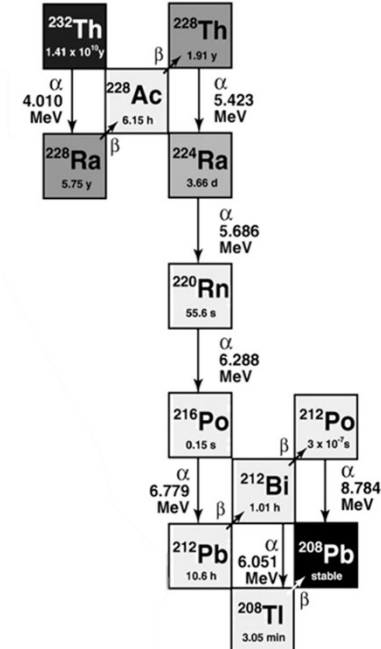
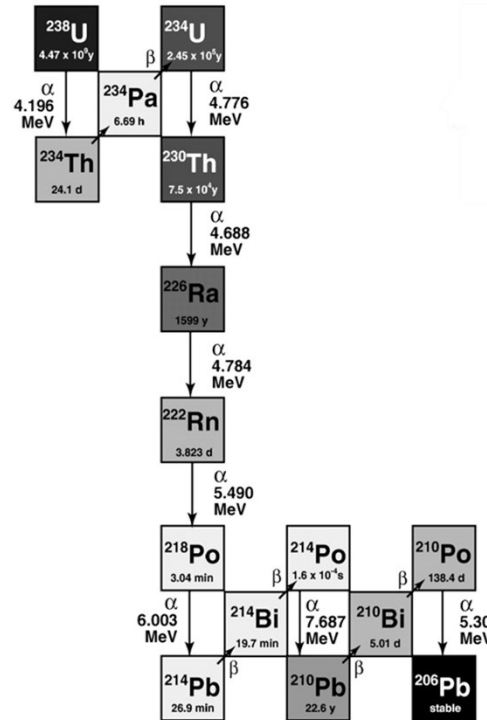
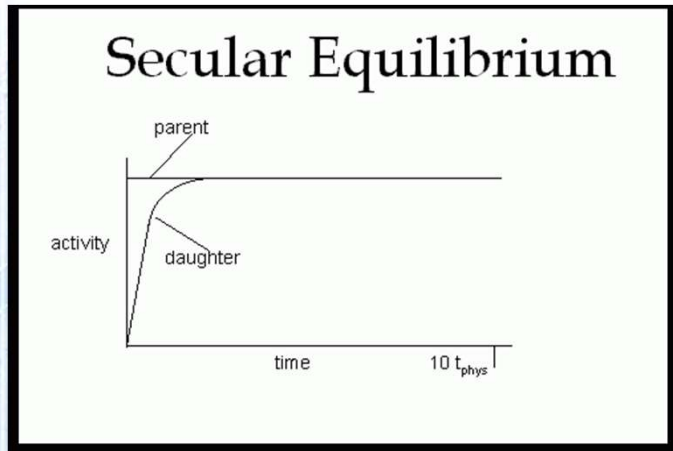


Secular equilibrium

Closed system

$$A_{son} = A_{father,0} \left(1 - e^{-\frac{t}{T_{1/2son}}} \right)$$

$$\Rightarrow A_{son} \approx A_{father}$$



- U
- Pa
- Th
- Ac
- Ra
- Fr
- Rn
- At
- Po
- Bi
- Pb
- Tl

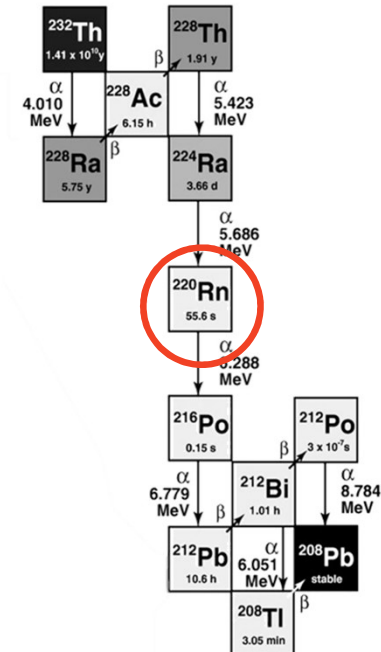
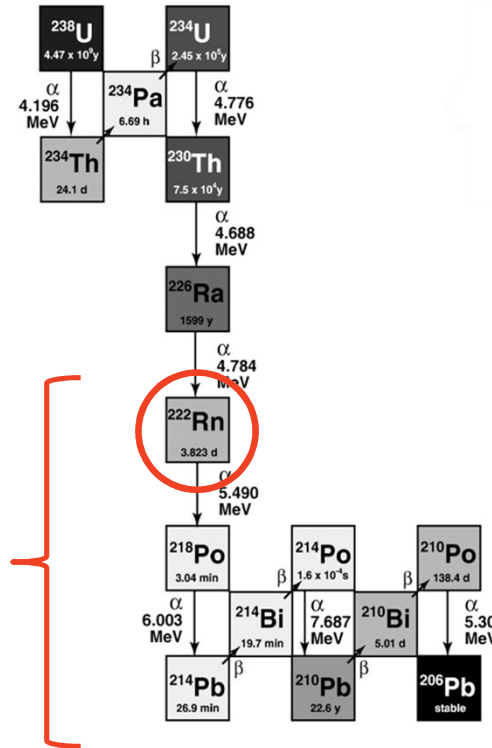
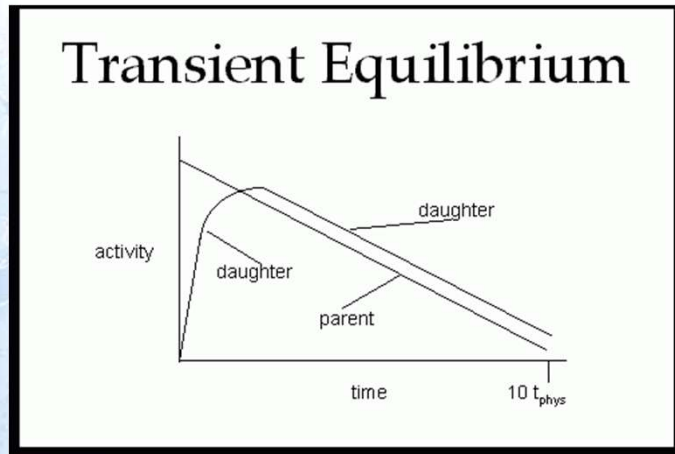
Bourdon, B., Turner, S., Henderson, G. M., & Lundstrom, C. C. (2003). *Reviews in Mineralogy and Geochemistry*, 52(1), 1–21.
 L'Annunziata, M. F. (2007). *Radioactivity - Introduction and History*. Elsevier B.V.
 nucmedtutorials.com



Transient equilibrium

Opened system

$$\frac{A_{father}}{A_{son}} = 1 - \frac{T_{1/2son}}{T_{1/2father}}$$



- U
- Pa
- Th
- Ac
- Ra
- Fr
- Rn
- At
- Po
- Bi
- Pb
- Tl

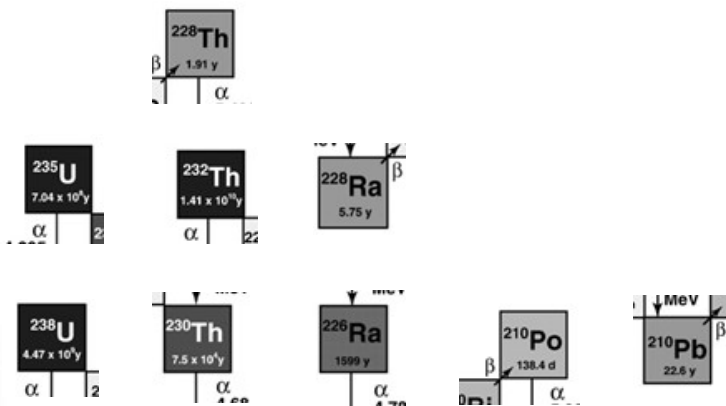
Bourdon, B., Turner, S., Henderson, G. M., & Lundstrom, C. C. (2003). *Reviews in Mineralogy and Geochemistry*, 52(1), 1–21.
 L'Annunziata, M. F. (2007). *Radioactivity - Introduction and History*. Elsevier B.V.
 nucmedtutorials.com



Targeted radionuclides

- High $T_{1/2}$
- Approximation S Factor
- Information: System evolution

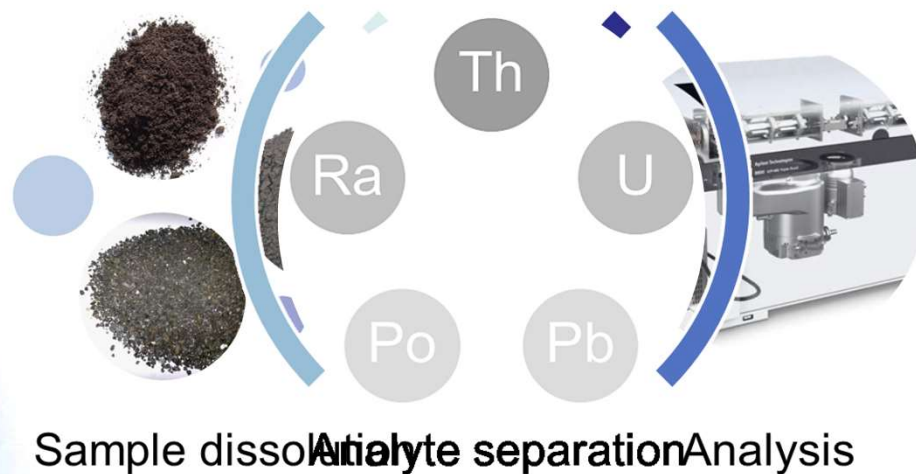
$$S = \sum_{i=1}^{i=n} \frac{A_i}{A_{i,max}} \leq 1$$



Radionuclide	Max Activity (Bq/g)
228Ra	40
Autres	4



Method development



Specifications

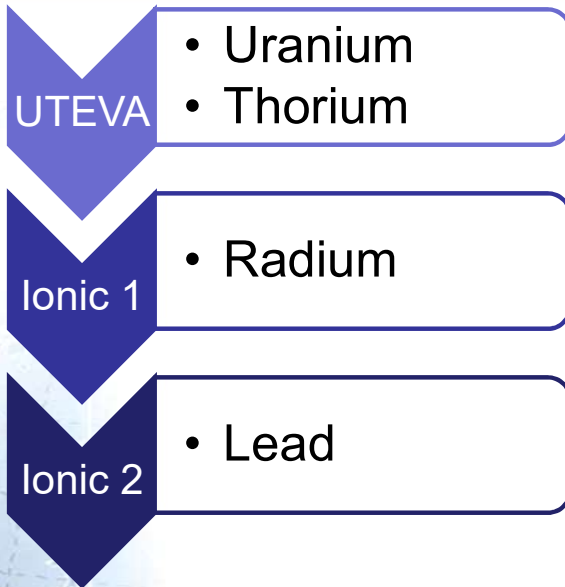
- Fast
- Robust
- Ease of implementation
- Cost

Interferences

Sequential extraction



Oliveira et al.



- Sequenced extraction of the **5** radionuclides
 - Resins (ionic and UTEVA) + spontaneous deposition
 - α spectroscopy
 - Many intermediary steps
 - 2 months to analyse Pb

Table 1. Recovery yields (mean $\pm 1\sigma$) of the radiochemical separation procedures applied in the analyses of n independent environmental samples, determined with the internal isotopic tracers added to the sample

Sample matrix	Separation technique	n	U	Th	Ra	Po	Pb
Water	2	16	0.71 ± 0.10	0.37 ± 0.10	0.16 ± 0.09	0.86 ± 0.09	0.47 ± 0.20
	1	23	0.58 ± 0.17	0.51 ± 0.18	0.27 ± 0.20	0.86 ± 0.09	0.47 ± 0.16

Lozano et al.

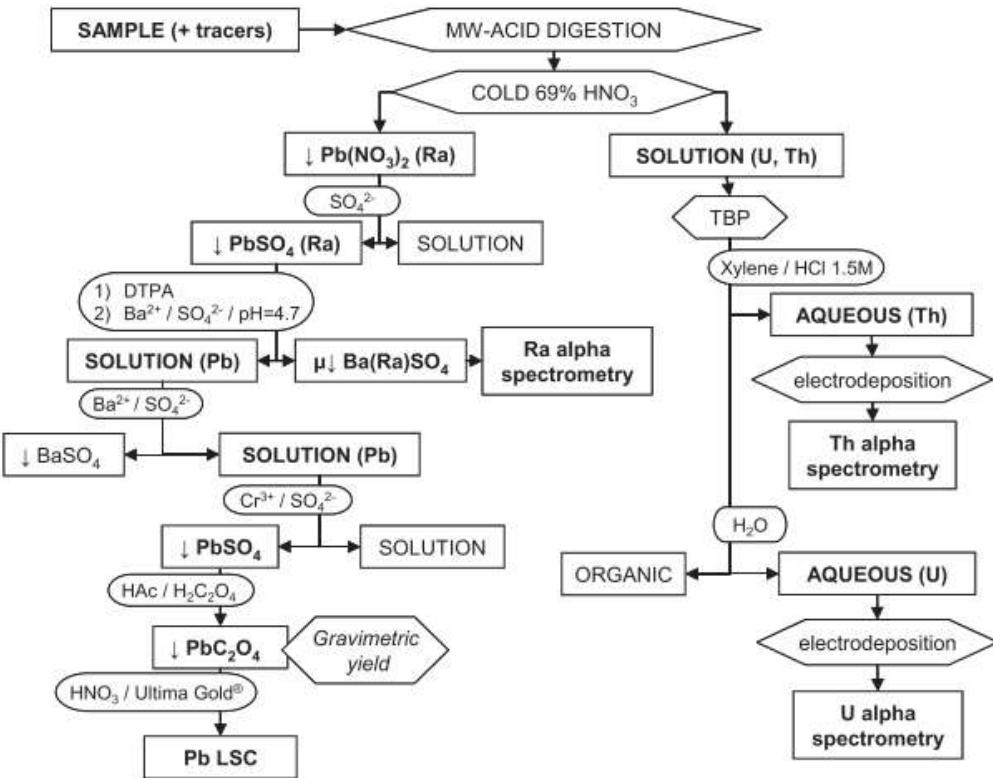


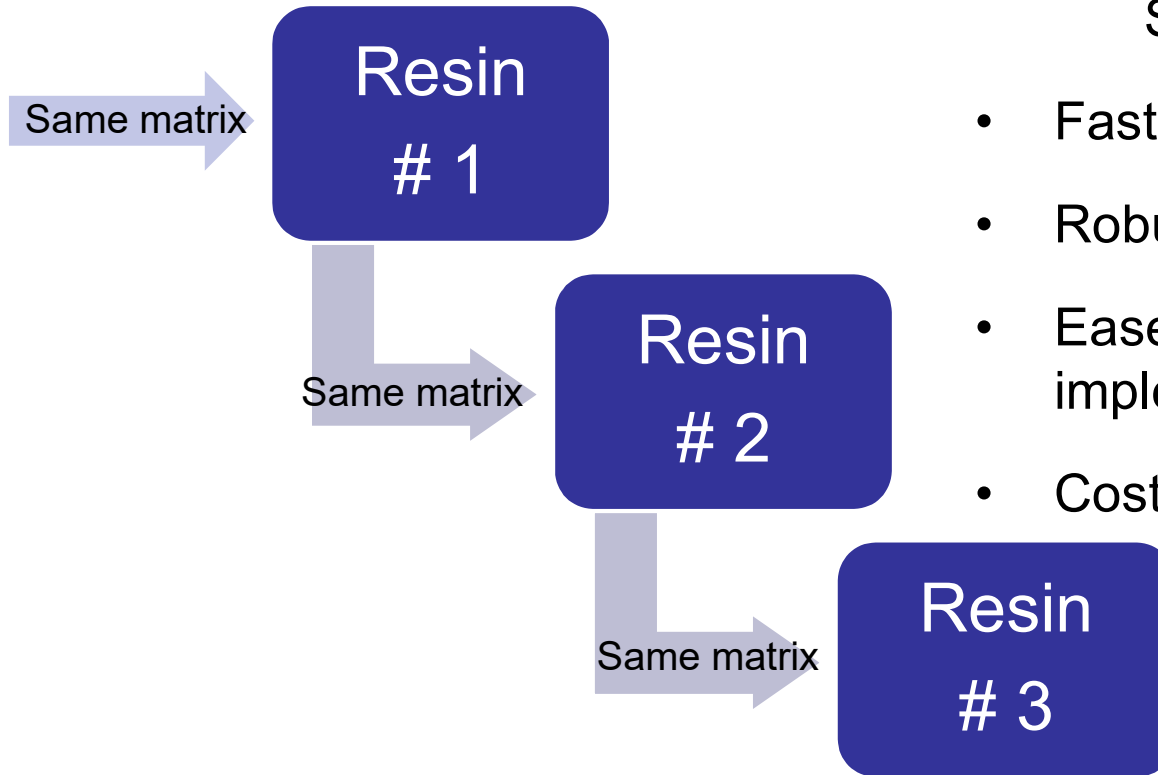
Fig. 1. Scheme of the radiochemical procedure.

- Sequenced extraction of **4** radionuclides
 - Precipitation / LLE
 - α spectrometry / LSC
 - Many steps
 - No Po

Table 1
Radiochemical yields and activity concentrations

Radionuclide	Yield (%)
^{238}U	44 ± 2
^{230}Th	52 ± 4
^{226}Ra	43 ± 6
^{210}Pb	63 ± 8

Strategy: Sequential extraction

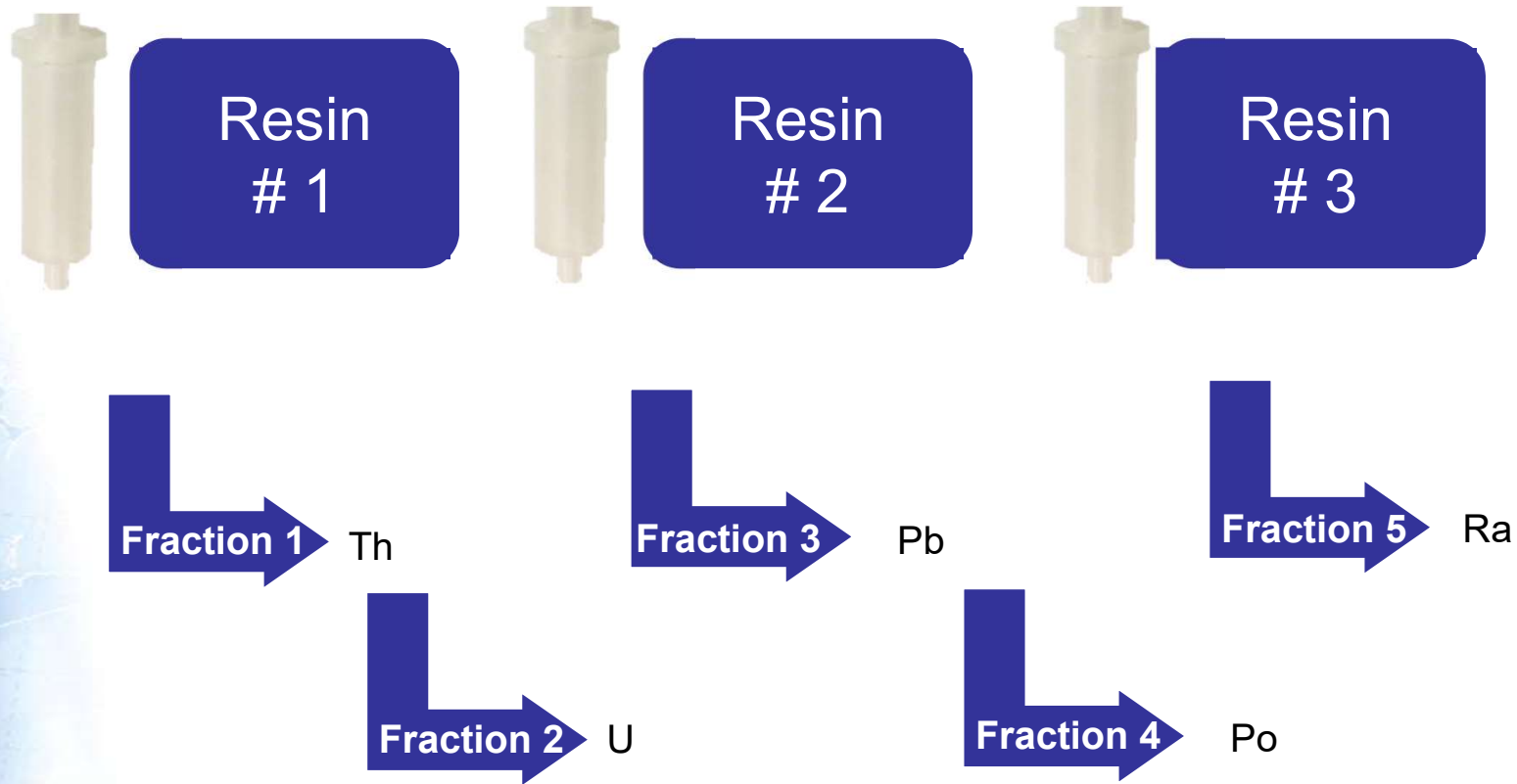


Specifications

- Fast
- Robust
- Ease of implementation
- Cost



Strategy: Sequential extraction





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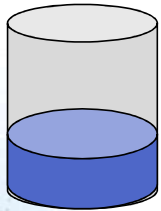
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Adsorption diagram: Sr resin

HNO₃ 3M
NH₄Cl 19g/L

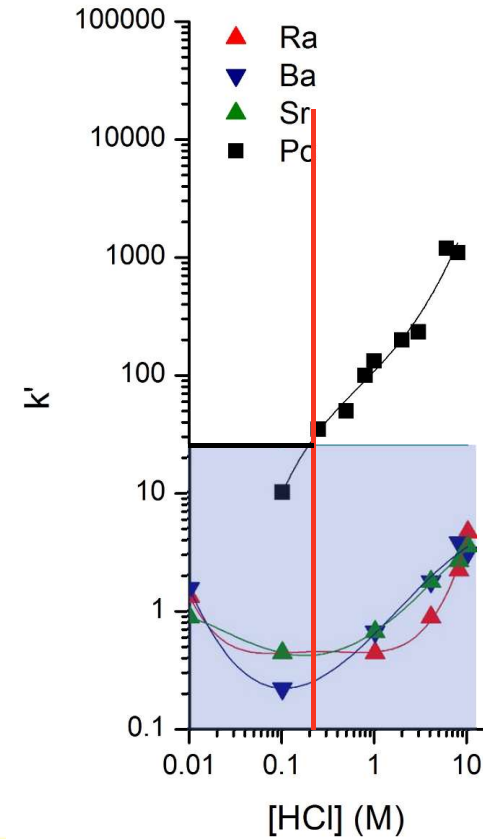
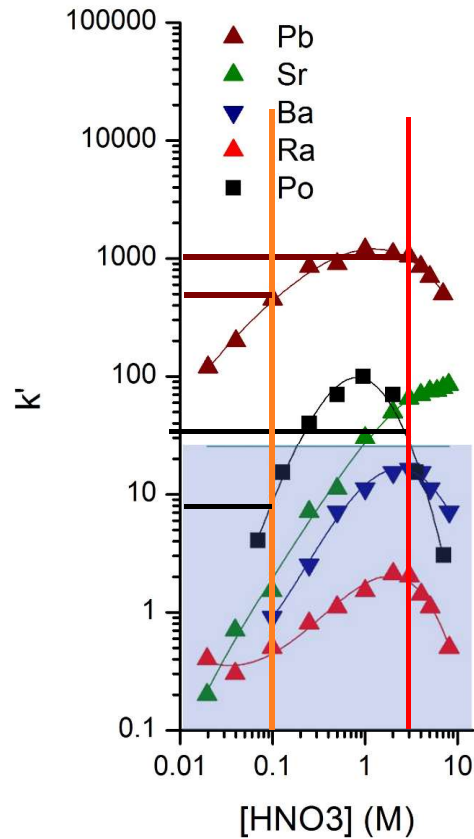


100 mL
HNO₃ 3M

HNO₃ 0.1 M

Po

Non retention



Pb elution from Sr resin

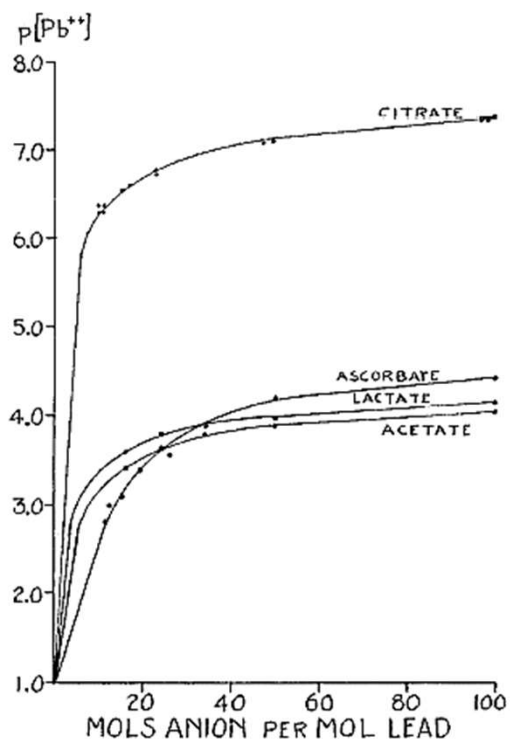
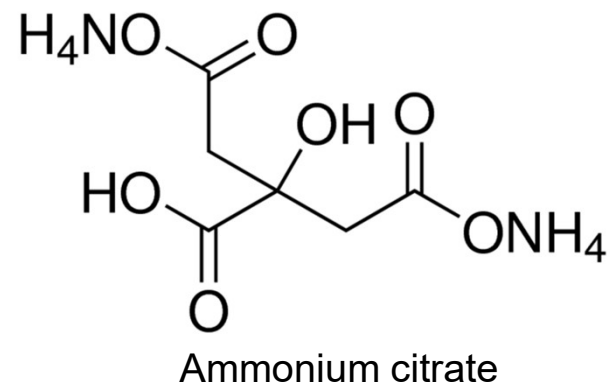


FIG. 2. Changes in lead ion concentration in 0.1 M lead nitrate upon the addition of sodium citrate, sodium ascorbate, sodium lactate, and sodium acetate.



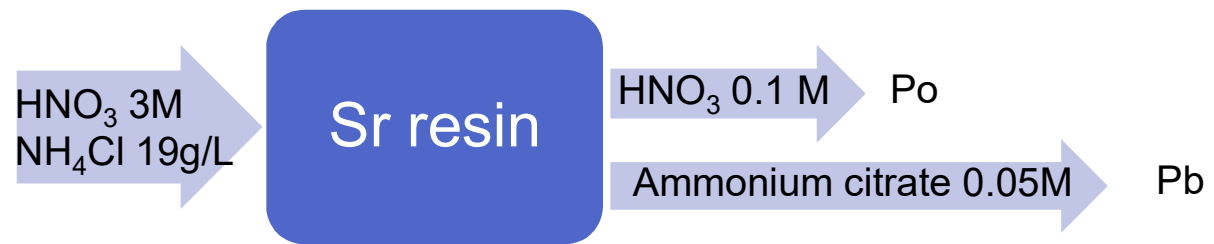
Complexation constant (pK)	Pb ²⁺
Citrate	5.74
Crown ether	3.35

Ammonium Citrate 0.05M → Pb

Kety, S. (1942). *The Journal of Biological Chemistry*, 142, 181–192.

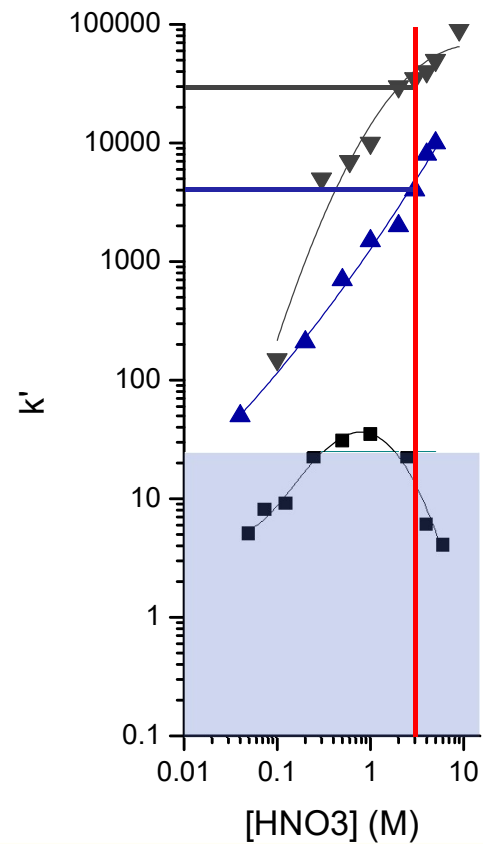
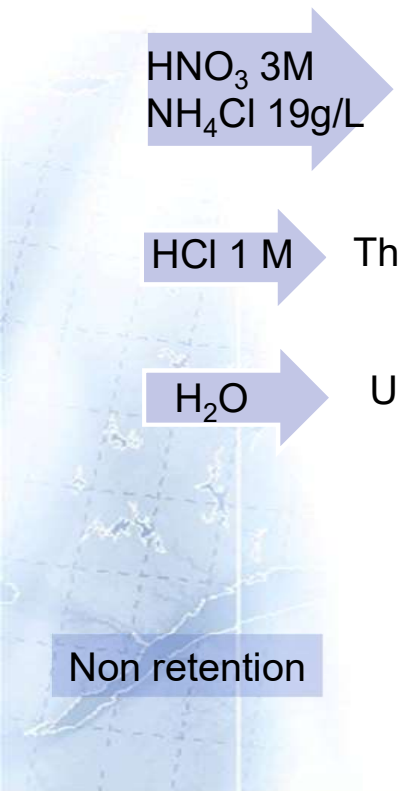


Extraction: Sr resin

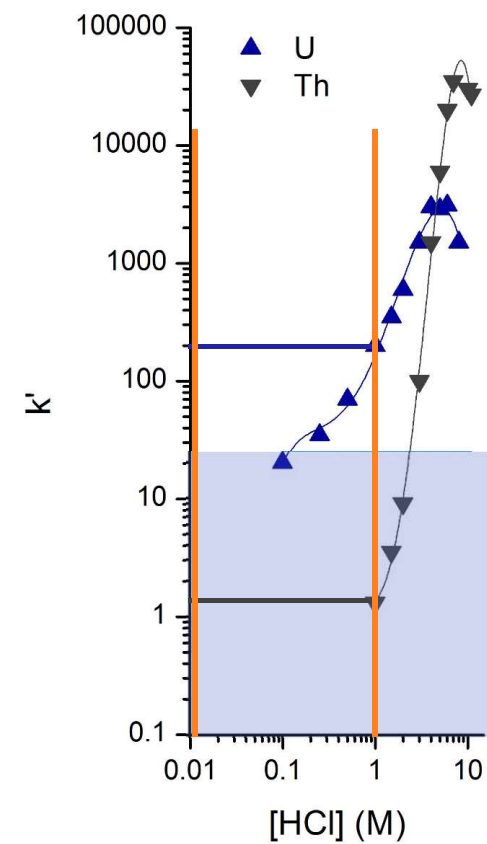


	Recovery (%)				
	U	Th	Ra	Pb	Po
Loading					
Po Elution					
Pb Elution					

Adsorption diagram: TRU



▲ U
 ▼ Th
 ■ Po

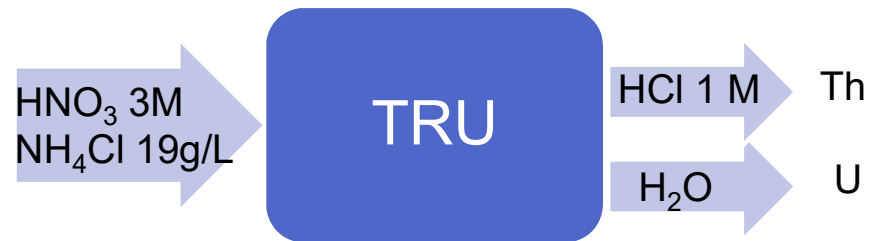


▲ U
 ▼ Th

Horwitz, E. P., Chiarizia, R., Dietz, M. L., & Diamond, H. (1993). *Analytica Chimica Acta*, 281, 361–372.



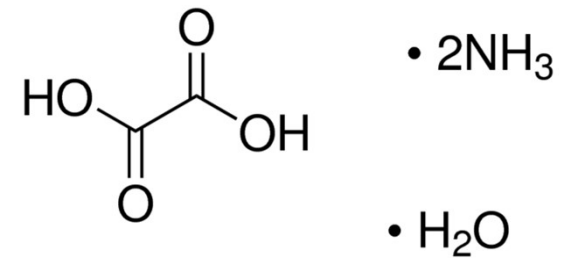
Extraction: TRU



	Recovery (%)				
	U	Th	Ra	Pb	Po
Loading					
Th Elution					
U Elution					

U elution from TRU

Complexation constants (pK)	Ammonium oxalate	CMPO
UO ₂ ²⁺	6.00	1.65
Th ⁴⁺	7.06	2.65



Ammonium Oxalate

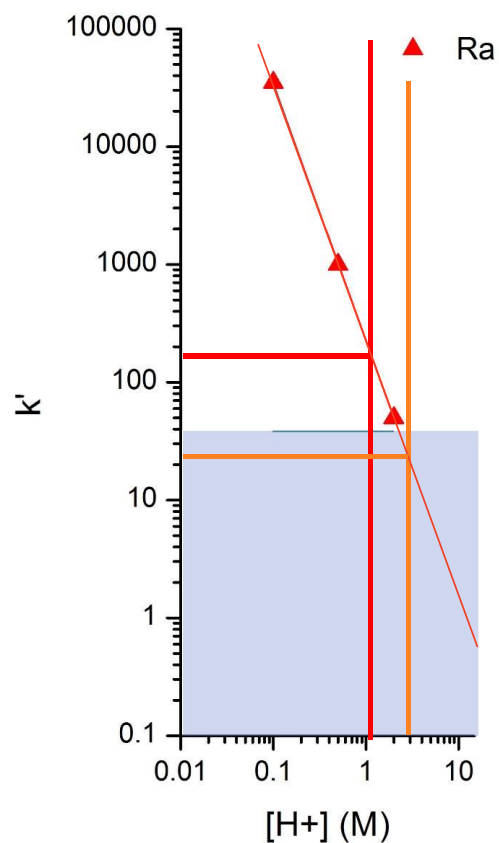
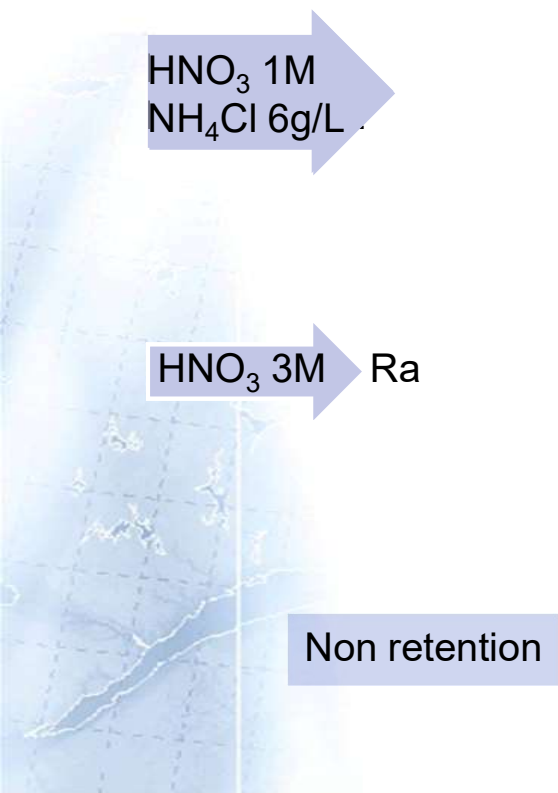
Am. bioxal. 0.1 M
HCl 0.025 M

U

TRU	Recovery (%)			
	U	Th	Ra	Pb
U Elution				



Adsorption diagram: AGW50x8



Dietz, M. L., Chiarizia, R., Horwitz, E. P., Bartsch, R. A., & Talanov, V. (1997). *Analytical Chemistry*, 69(15), 3028–3037.

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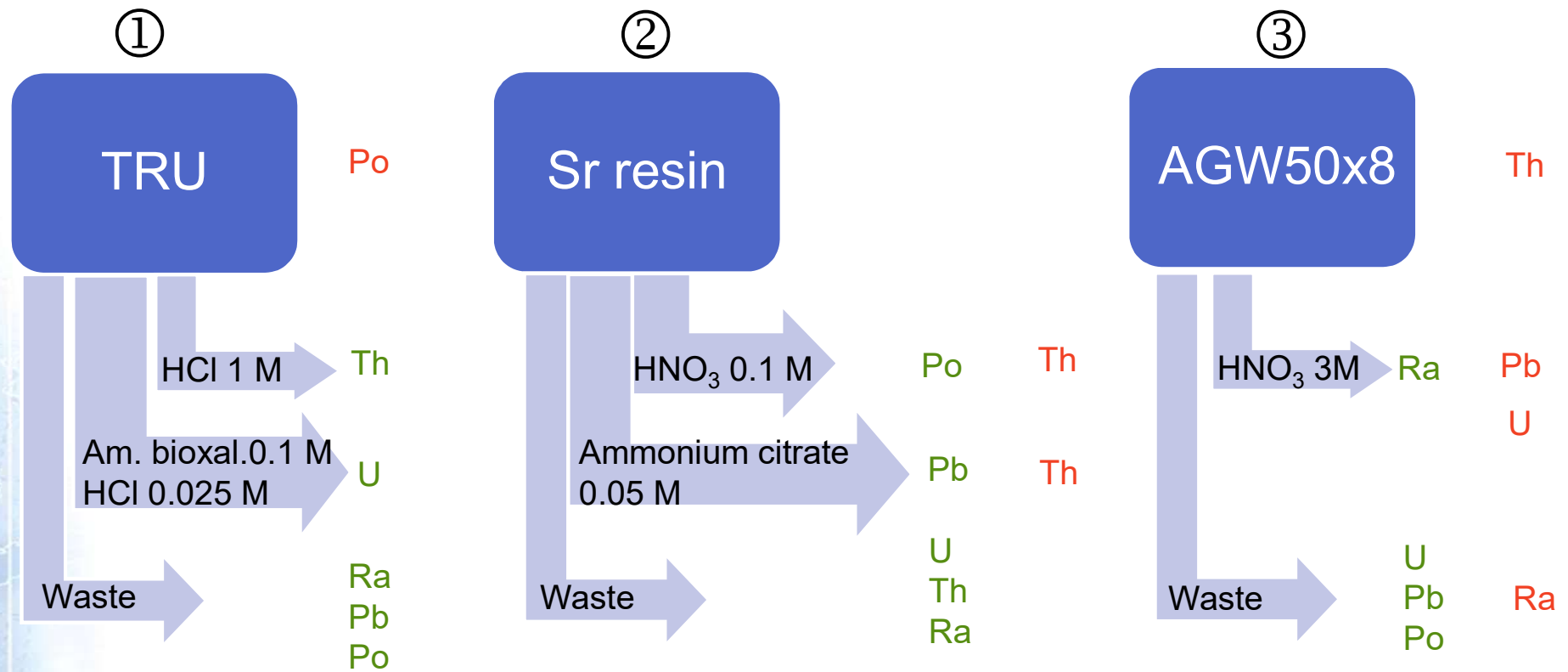


Extraction: AGW50x8



AGW50x8	Recovery (%)				
	U	Th	Ra	Pb	Po
Loading					
Ra Elution					

Sequential extraction



TRU x Sr x AG50Wx8



	Actual method	Lozano <i>et al.</i>	Oliveira <i>et al.</i>
Element	Recovery (%)	Recovery (%)	Recovery (%)
U		44 ± 2	71 ± 10
Th		52 ± 4	37 ± 10
Ra		43 ± 6	16 ± 9
Pb		63 ± 8	47 ± 20
Po			86 ± 9

Waste : 40 % Ra

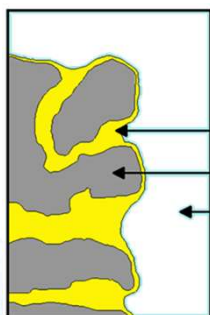
Lozano, J. C., Tomé, F. V., Rodriguez, P. B., & Prieto, C. (2010). *Applied Radiation and Isotopes*, 68(4–5), 828–831.

Oliveira, J. M., & Carvalho, F. P. (2006). *Czechoslovak Journal of Physics*, 56(4), 545–555

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TRU Po extraction

SOLVENT EXTRACTION AND ION EXCHANGE
2017, VOL. 35, NO. 2, 77–90
<http://dx.doi.org/10.1080/07366299.2017.1279917>



Stationary phase
Inert phase
Mobile phase

Solvent: TBP

Solvent Extraction of Polonium(IV) with Tributylphosphate (TBP)

A. Younes^a, C. Alliot^{b,c}, B. Mokili^{a,b}, D. Deniaud^d, G. Montavon^a, and J. Champion^a

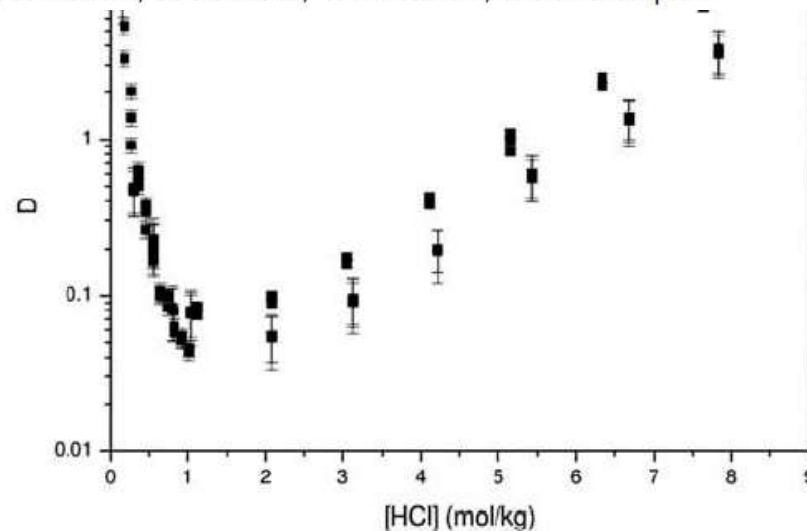
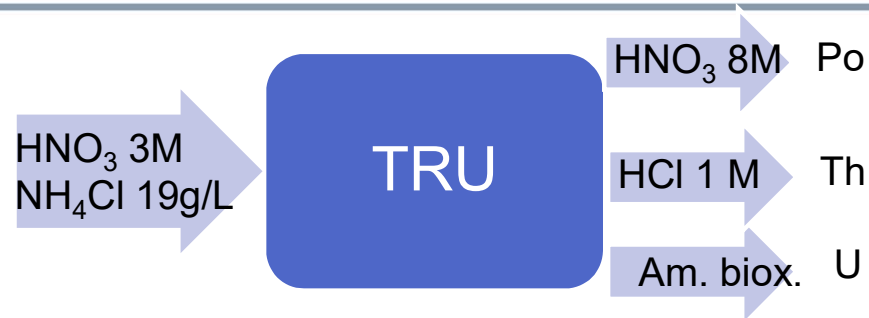


Figure 6. Distribution ratio of polonium as a function of HCl molality in TBP 10% diluted in *p*-xylene.

A. Younes, C. Alliot, B. Mokili, D. Deniaud, G. Montavon, J. Champion, Solvent Extr. Ion Exch. 35 (2017) 77–90.



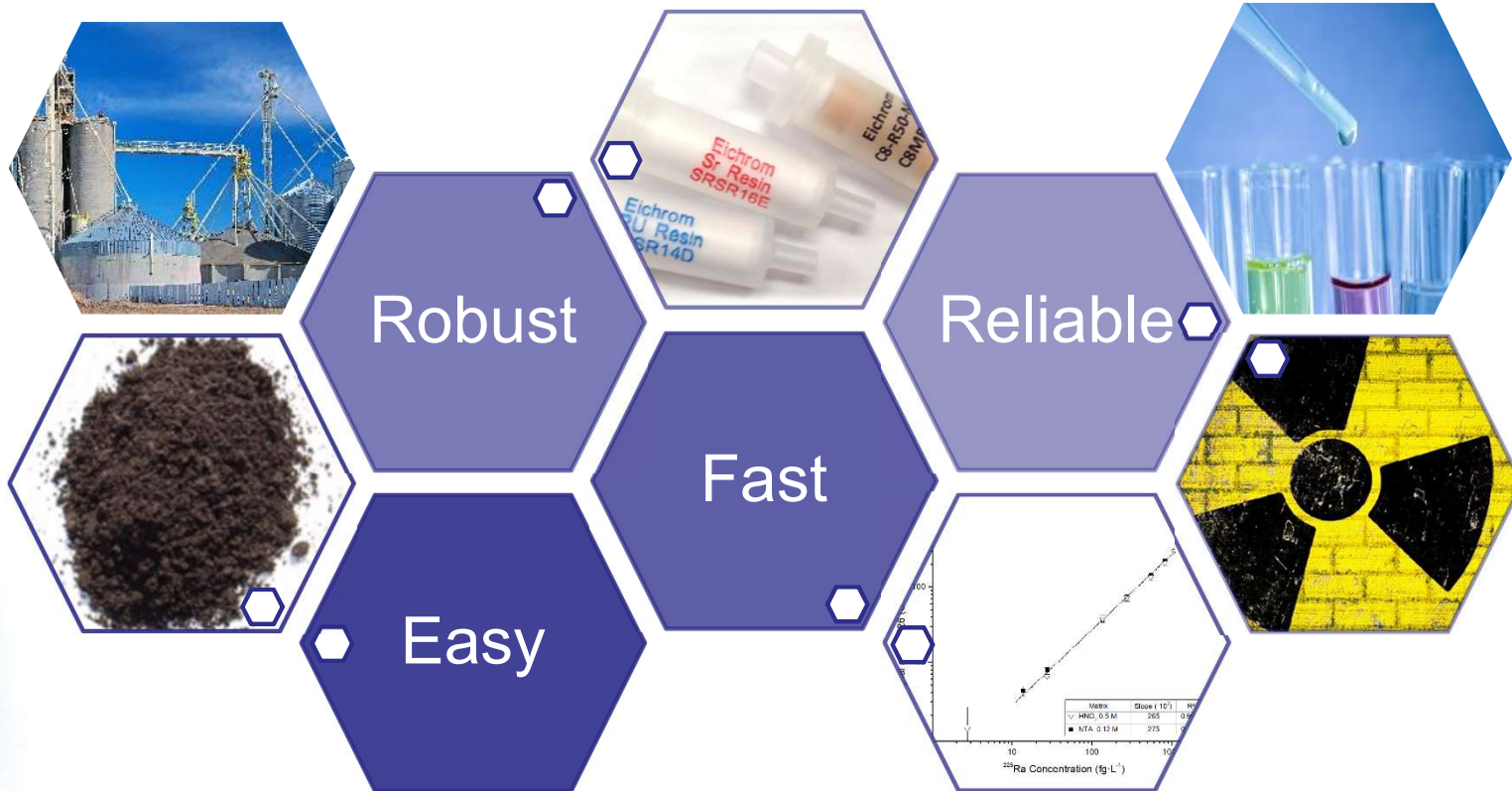
Extraction: TRU



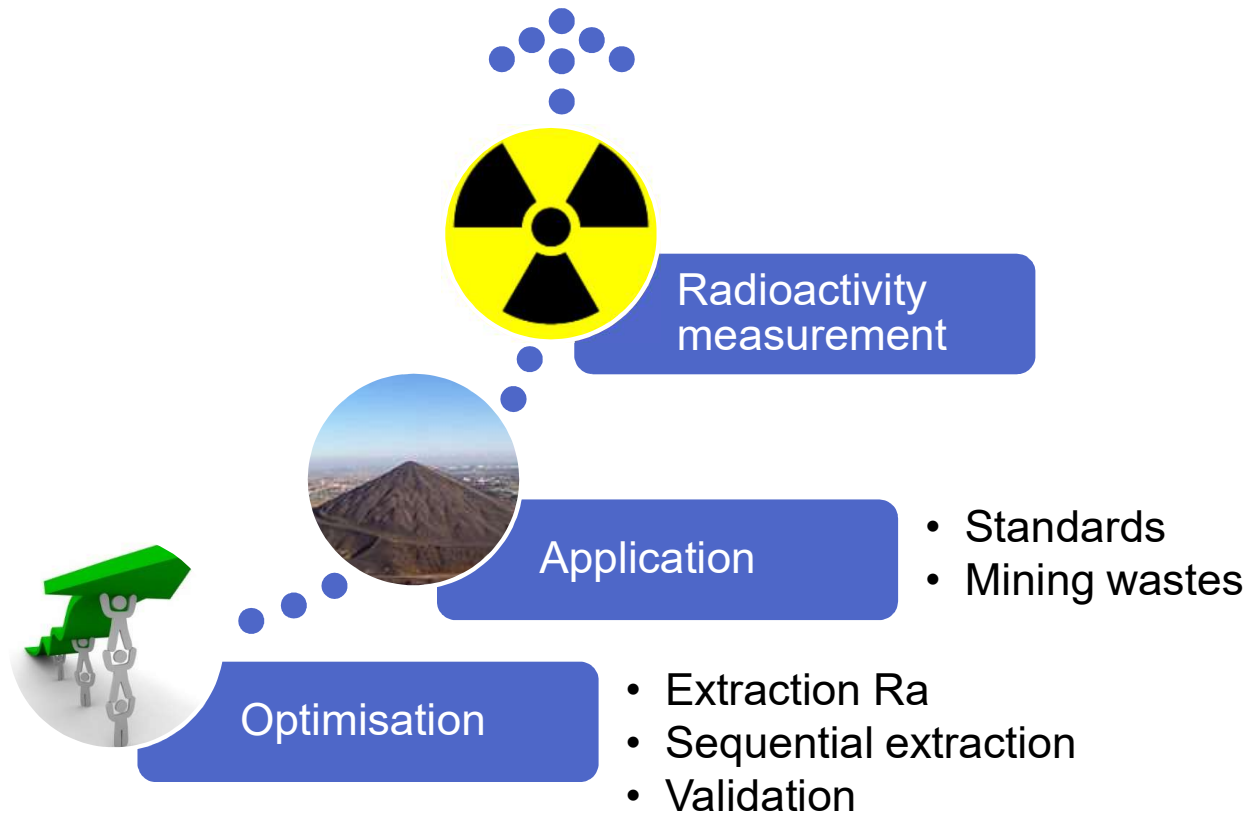
	Recovery (%)		
	Po		
Loading	74	±	9
Po Elution	19	±	5
Th Elution	0	±	0
U Elution	0	±	5



Conclusion



Perspectives



Aknowledgments


Fonds de recherche
Nature et
technologies

Québec 



Santé
Canada Health
Canada

Centre d'expertise
en analyse
environnementale

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- Serge Groleau
- Steeve Roberge (CEAEQ)
- Jean-François Mercier (Health Canada)
- Michael Cooke (Health Canada)





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