Extraction Chromatographic Resins, News Triskem International

Irtech Technical Workshop, 21-22nd May 2024 - Krakow





Overview

- Extraction chromatograpic resins: principles
- Sample preparation
- Sr separations
- New Resins
 - TK-ELScint: TK-SrScint and TK-TcScint
 - TK102
 - TK221
 - TK225
- Methods under development
 - Ra separation
- Conclusions



TrisKem International

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- Based in Rennes (France)
- Independent company since 02/07
 - Formerly part of Eichrom Europe
 - ISO 9001 since 2007
- Main products: extraction chromatographic resins
- Staff : 22
- ➢ R&D, QC and TechSupport group:
 - 5 RadChem PhD, 3 Technicians
- R&D: Development of new resins, techniques and applications
- Products used in several domains









Extraction chromatography Principles

Organic phase impregnated onto an inert support referred as:

« Supported Solvent Extraction » / « Solvent Impregnated Resins »

Combination of liquid/liquid extraction and chromatographic techniques:

- Distribution between two non-miscible phases
- Stationary phase impregnated onto inert support (Choice of inert support depending on application (Radiolysis stability, plastic scintillators,...
- High density of functional groups
- Fast kinetics/small volumes => rapid separations
- High variety of selectivities:
 - Depending on extractant pure or in mixture used
 - Aim: selectivity for analyte(s), no selectivity for matrix/ impurities
- Combining several cartridges can improve/facilitate separation



Stationary

Mobile





Types of extractants



Complex + Organic === Extracted

Horwitz et al.

Choice of resin depends on

- Radionuclide/Metal to separate
- Matrix
- Type of measurement

=> Sample preparation = very important step for a good separation⁶



Classic Resins: SR Resin



Classic Resins: DGA,N Resin

- Extractant: DGA, Normal (N,N,N',N'tetra-noctyldiglycolamide)
- Separation of Actinides, especially Am
- Robust against Fe
 interference, often used for soil samples







Sample preparation

Eliminate the matrix / preconcentrate the elements of interest

Non exhaustive list:

- Alkaline Fusion
- Mineralisation
- Lixiviation
- Coprecipitation



Mineralisation + Coprecipitation

Rapid Determination of Sr in 50g Soil Samples (AN-1403-10):

- Drying @ 110°C, blend/size to easily mineralise (1-2 hours)
- Add carrier* + aqua regia to mineralize the sample
- Heat to dryness + mineralise with 70% HNO₃
- Centrifuge + collect supernate (X2)
- Evaporate supernate + dissolve in 1M HCI
- Coprecipitate Sr with Ca₃(PO₄)₂
- Centrifuge + dissolve precipitate

Figure 1. Sample Preparation Dry soil at 110°C. Blend and Size.

Remove 50g aliquot into 600mL glass beaker .

Muffle at 550°C for 1-2 hours.

Add 6mg Sr Carrier*, 50mL 70% HNO₃, and 25mL 37% HCl.

*may need to adjust Sr carrier amount to account for native Sr content in soil.

Heat to dryness on hot plate, medium setting.

Add 50mL 70% HNO₃. Warm sample. Transfer solids and liquid to 250mL centrifuge tube.

Centrifuge 3500 rpm, 10 min. Transfer supernate to 600mL beaker.

Add 25mL 70% HNO₃ to Solids. Mix and Centrifuge. Transfer supernate to same 600mL beaker. Repeat once. Discard solids to waste.

Evaporate supernate in 600mL beaker to dryness. Dissolve residue in 15-20mL 1M HCl. Transfer to 250mL centrifuge tube.

Dilute to 160mL. Add 1mL 1.25M Ca(NO₃)₃, 2mL 3.2M (NH₄)₂HPO₄, and 25mL 57% NH₄OH. Mix. Centrifuge. Decant supernate to waste.

Continue to load solution preparation.



Mineralisation + Coprecipitation

Rapid Determination of Sr in 50g Soil Samples (AN-1403-10):

- Drying @ 110°C, blend/size to easily mineralise (1-2 hours)
- Add carrier* + aqua regia to wet mineralize the sample
- Heat to dryness + mineralise with 70% HNO₃
- Centrifuge + collect supernate (x 2)
- Evaporate supernate + dissolve in 1M HCI
- Coprecipitate Sr with Ca₃(PO₄)₂
- Centrifuge + dissolve precipitate
- Coprecipitate Sr with CaF₂
- Centrifuge + dissolve precipitate
- Load solution

Dry soil at 110°C. Blend and Size. Remove 50g aliquot into 600mL glass beaker. Muffle at 550°C for 1-2 hours. Add 6mg Sr Carrier*, 50mL 70% HNO3. and 25mL 37% HCl. *may need to adjust Sr carrier amount to account for native Sr content in soil. Heat to dryness on hot plate, medium setting. Add 50mL 70% HNO3. Warm sample. Transfer solids and liquid to 250mL centrifuge tube. Centrifuge 3500 rpm, 10 min. Dissolve residue in 40ml 1 5M HCL Dilute to 170mL with H₂O. Add 25ml 49% HF Mix well. Centrifuge 10 min. Discard Supernate. Υ Dissolve residue in 7mL 70% HNO₃, 7mL 3M HNO3-0.25M Boric Acid, 7mL 2M Al(NO3)3.

Figure 1. Sample Preparation

Continue to load solution preparation.



Alkaline fusion + Coprecipitation

Rapid determination of SR in vegetation samples (AN-1405-10):

- Sample drying (2-4 hours)
- Wet mineralization with 70% $HNO_{3+}H_2O_2$
- Fusion (15g NaOH for 5-10g sample) (10 minutes)
- Dissolution + add carrier + Fe
- Coprecipitation with Ca₃(PO₄)₂ and Fe(OH)₃
- Centrifuge + dissolve precipitate
- Load solution

Figure 1. Sample Preparation



Muffle at 600°C. 2 hours for 5g sample. 4 hours for 10g sample.

Wet ash on hotplate with 5mL 70% HNO₃ and 5mL 30% H₂O₂.

Fuse samples with 15g NaOH at 600°C for 10 minutes.

Dissolve fusion cake with H₂O. Transfer to 250mL centrifuge tube. Add 125mg Fe and 4mg Sr. Dilute to 180mL.

Add 4mL 1.25M Ca(NO₃)₂, 5mL 3.2M (NH₄)₂HPO₄. Mix. Cool in ice bath for 10min.

Centrifuge at 3500rpm. Decant Supernate.

Dissolve precipitate in 5mL warm 3M HNO₃, 7mL 70% HNO₃, and 7mL 2M Al(NO₃)₃.

Coprecipitations

Rapid Determination of 90Sr in up to 40 Liter Seawater Samples (AN-1414-10):

- Acidification to pH2 + Y+La+Fe carriers
- Fe(OH)₃ coprecipitation
- Centrifuge
- Dissolve precipitate in 1.5M HCI + Ca carrier
 + HF
- CaF₂ coprecipitation
- Centrifuge + Dissolve precipitate
- Load solution

Figure 1. Sample Preparation

Up to 40L Sample of Seawater. Acidify to pH 2 with 37% HCl. Add 1mg Yttrium carrier.

Add 10mg La carrier. Add 50mg Fe carrier per liter of sample. Mix Well.

Adjust to pH 9 with 56% NH₄OH. Mix. Allow precipitate to settle. Decant supernate until ~2L remains.

Transfer remaining supernate and precipitate to 500mL centrifuge tubes. Centrifuge 3000rpm for 10 minutes. Decant supernate. Repeat until entire sample centrifuged.

> Wash precipitate with 100mL water. Centrifuge. Decant supernate.

Dissolve precipitate in 100mL 1.5M HCl. Add 75mg Ca and 50mL 49% HF. Mix. Wait 15 minutes. Centrifuge. Decant supernate.

Dissolve precipitate in 10mL 3M HNO₃-0.25M Boric acid, 10mL 70% HNO₃, and 10mL 2M Al(NO₃)₃.



SR separations

SR separation in vegetation and soils (SR Resin)

AN-1403-10/AN-1407-10

- Precondition SR Resin with 10ml 8M HNO₃
- 2. Load sample solution
- 3. Rinse beaker with 5ml 8M HNO_3 , add rinse to SR resin
- 4. Rinse SR Resin with:
 - 15ml 8M HNO₃
 - 10ml 3M HNO₃-0.05M H₂C₂O₄
 - 10ml 8M HNO₃
- 5. Elute Sr with 20ml 0,05M HNO₃





SR separations

SR separation in vegetation and soils (SR Resin)

AN-1403-10/AN-1407-10

- Precondition SR Resin with 10ml 8M HNO₃
- 2. Load sample solution
- 3. Rinse beaker with 5ml 8M HNO_3 , add rinse to SR resin
- 4. Rinse SR Resin with:
 - 15ml 8M HNO₃
 - 10ml 3M HNO₃-0.05M H₂C₂O₄
 - 10ml 8M HNO₃
- 5. Elute Sr with 20ml 0,05M HNO₃

SR separation in 40L seawater (DGA Resin)

AN-1414-10

- Precondition DGA,N Resin with 5ml 8M HNO₃
- 2. Load sample solution
- 3. Rinse beaker with 5ml 8M HNO₃, add rinse to DGA,N Resin
- 4. Rinse DGA, N Resin with:
 - $15ml 8M HNO_3$ (Ca, Sr, Pb)
 - 20ml 0,05M HNO₃ (La, Ce, Sr, U)
 - 10ml 3M HNO₃-0.25M HF (U,Th)
 - 10ml 3M HCl (Ca, La, Pb)
- 5. Elute Y with 20ml 0,25M HCl



New Resins

TK-EIScint Resins – scintillating resins



=> presentation by Ines Llopart right after this presentation



TK102 Resin

- Modified version of SR Resin
 - Same crown-ether
 - Solvent, inert support and ratios => different
 - Solvent is a fluorinated alcohol
- Distribution coefficient Kd ~50% higher (Pb, Sr, Ba)
- Higher capacity (Pb and Sr)
- SR resin separation procedures can be transposed on TK102
- Specific separating methods under development



TK102 Resin – Kd values



Fig. 1: Distribution coefficients of selected elements on TK102 Resin in HNO₃
▶ Sr, Ba, Pb and TI show
high D_W in HNO₃ Fig. 2: Distribution coefficients of selected elements on TK102 Resin in HCl

Pb, Tl, Sn, Sb, Ga show hight D_W in HCl Fig. 3: Distribution coefficients of Sr on TK102 Resin in 3 M HNO_3 in the presence of different salts

- ► D_w Sr decreases with KNO₃ starting at 0,05 M,
- ▶ no effect of NaNO₃ and 19 $Ca(NO_3)_2$ up to 1 M.



TK102 Resin – Sr separation



Sr elution study in 8M HNO₃ load medium

Resins TK102 and SR similar for the separation of elements Th/U/Pb/Sr/Ca/Bi/Y/Ca/Ba







Pb elution study with 2M HCI loading medium

Resins TK102 and SR **similar** for the separation of elements Th/U/Pb/Sr/Ca/Bi/Y/Ca/Ba



TK221 Resin

(Papp, I., Vajda, N. & Happel, S.. *J Radioanal Nucl Chem* **331**, 3835–3846 (2022). https://doi.org/10.1007/s10967-022-08389-9)

Resin based on a mixture of diglycolamide and phosphine oxide + traces long chained alcohol on inert support

Main applications in radpharm

Applications for the separation of actinides





TK221 Resin

(Papp, I., Vajda, N. & Happel, S.. *J Radioanal Nucl Chem* **331**, 3835–3846 (2022). https://doi.org/10.1007/s10967-022-08389-9)





Table 3 Recovery of actinide tracers from spiked water samples

	Actinides determiantion	
	Without Np separation Yield %	With Np separation Yield %
TAP water		
²³⁰ Th	90±8	86±7
²³⁹ Pu	108 ± 7	95 ± 7
²³⁷ Np	_	91 ± 9
²⁴¹ Am	103 ± 7	97±6
²³³ U	103 ± 7	70 ± 7
SEA water		
²³⁰ Th	71±7	61 ± 6
²³⁹ Pu	91±7	87±6
²³⁷ Np	_	93±8
²⁴¹ Am	89±7	92 ± 6
²³³ U	88±7	59 ± 6



TK225 Resin

- TO-DGA plus ionic liquid
- Very high retention of lanthanides at medium to high acid
- Especially heavy lanthanides also very well retained at low acid concentrations
- Main application: Removal of radiolanthanides from effluents







Under development Ra purification/recycling

- In case Ra needs to be purified on-column (e.g. dissolved Ra needles) => Use of TK101 for Ra retention / purification
- TK101 => crown-ether + but ionic liquid
 Use of ionic liquid (=> TK101 Resin) allows for retention of Pb, Sr, Ba, Ra,... from pH ~2 – 7 without extensive extraction of other elements
- Ra separation from TK101 + further purification of Ra from Ba on TK102



Under development Ra purification/recycling



- Good Ra separation when loading from dilute HNO₃/HCI
- When eluting Ra in 3M HNO₃, Ba, Pb, Sr remain retained
- No retention of U, Th, Pt, Ir,...
- Ra eluted in 3M HNO₃
- TI and Ba eluted in 8M HNO₃



Under development Ra purification/recycling



Further Ra fraction purification from Ba on TK102

Elution study - Ra separation from Ba on TK102 Resin in 3M HNO₃ - Ra data courtesy of N. Vajda (RadAnal)



Elution study - Ra separation from Ba on SR Resin in 3M HNO₃ - Ra data courtesy of N. Vajda (RadAnal)



Conclusions

To perform the measurement of a RN/Metal from a given matrix

- Choice of resins
- Pretreatment of the sample to
 - Eliminate matrix
 - Concentrate RN/metal of interest
- Perform separation to collect RN/Metal of interest in pure fraction
- Perform measurements

Thank you for your attention !

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