TrisKem International

Jahrestagung 2016
Fachverband für Strahlenschutz

26.09.16

TRISKEM
SHARING INNOVATION

TrisKem International

- Sitz in Rennes (Frankreich)
- Seit 02/07 eigenständig
  - Zuvor Teil von Eichrom Europe
  - Heute: 15 Personen
- Produktion und Verkauf extraktionschromatographischer Harze
  - 'Historische' Harze (UTEVA, TEVA, SR,…): Europa, ehemalige GUS, Afrika, Mittlerer Osten und China
  - Neue Harze (z.B. CL, CS, TK100/1, TBP, CU, ZR, TK400) weltweit
- Vertrieb:
  - LSC Verbrauchsmaterialien
  - Raddec Pyrolyser
  - PEEK Säulen

MERIDIAN BIOTECHNOLOGIES Ltd
Vials & Cocktails for Liquid Scintillation

RADDEC International Ltd

Neuigkeiten

- 11/2015 Umzug in neuen Sitz => Neue Adresse/Fax Nummer
- Alle Abteilungen (F&E, Produktion, Qualitätskontrolle, Administration, Vertrieb…) in einem Gebäude
  - Organische Synthese
  - Integration Produktion Ra NucFilm Discs & PAN Resins

- Neue Säulentrichter (Einzelstück)

AC-120-TK : funnels

Neue Resins

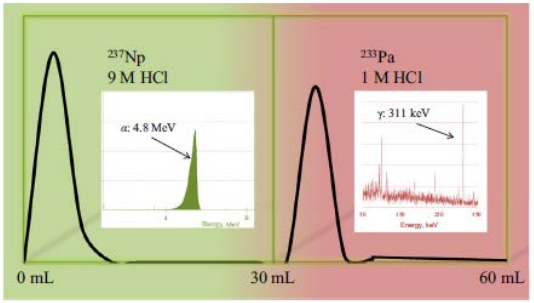
- CU Resin
  - Produktion von Cu Isotopen für die Nuklearmedizin
  - Bestimmung von Cu Isotopenverhältnisen über MS (biomedizinische Proben)
- CL Resin
  - Ursprünglich für die Trennung von Platin Gruppen Elementen (PGE), Au, Ag,… entwickelt
  - Nach Beladen mit Ag: I / Cl Trennung und Bestimmung
    - Cl-36 und I-129 e.g. in Rückbau- und Überwachungsproben
    - Hauptsächlich zur Messung via LSC
  - ➢ Neue Methode für 2L Wasserproben in Arbeit (US Norm)
  - Mehrere laufende Arbeiten zur Ag Bestimmung

Neue Resins

- CS Resins
  - AMP-PAN & KNiFC-PAN
  - Dr. Sebesta CVUT Prag
  - Typische Anwendungen:
    - Aufkonzentrierung von Cs
      - 100 L Meerwasserproben
      - 25 mL Resin
      - 300 – 450 mL/min
      - Gamma Messung des Resins nach Trocknung
    - Dekontamination von wässrigen Proben
      - Abwässer
      - Becken

Neue Resins

- TK100/1
  - Direktes Laden von Sr (TK100) oder Pb (TK101) aus Wasserproben (pH 2 - 7) & DGT
  - Aufkonzentrierung und Trennung auf demselben Harz
  - Bei hohen HNO_3 Konzentrationen Selektivität ähnlich dem SR Resin
    - TK100:
      - Sr: 500 mL, U, Pb mehrere L für 2 mL Säule
      - Sr-90 via ICP-MS (3Q): bessere Zr-90 Entfernung als Sr Resin
      - Ra-226 Bestimmung via ICP-MS (3Q), Ra/Ba Trennung möglich
    - TK101:
      - Pb-210 Schnellmethode / Disks
- TK400
  - Pa Abtrennung (keine Selektivtät für U, Th, Np,…)
  - Auch selektiv für Nb



Neue Resins

- TBP Resin
  - Interessante Selektivitäten für Sn, Ga, Sb, Hauptaugenmerk: Sn
  - Sn-121m/Sn-126 via ICP-MS
  - AIX zur Matrixentfernung, TBP Feinreinigung (R_{Sn} > 90%, Te decon > 10^5)
- ZR Resin
  - Hydroxamat Resin
  - Radionuklidproduktion (Targets bis zu 25g)
    - Zr/Y, Ti/Sc, Ge/Ga, Ga/Zn
    - Zr/Nb Trennung
- DGA Sheets
  - Dünnschichtchromatographie
  - Qualitätskontrolle von Radionukliden für die Radiopharmazie
  - 2D DC zur schnellen Charakterisierung von RN Gemischen

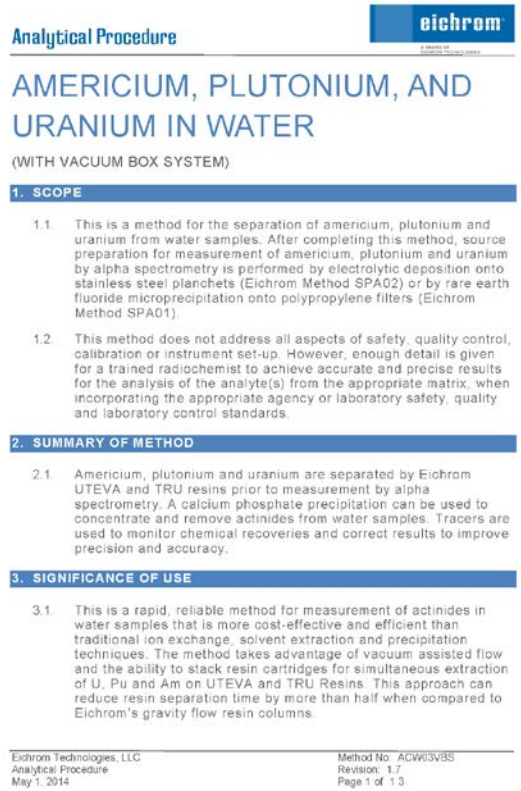
Raddec – Mini Pyrolyser

- Demnächst erhältlich
- 2 Positionen/Proben (mehrere g)
- Geringe Stellfläche

➢ In Erprobung: ASRS

Neue Methoden

- Aktualisierte Version der Eichrom Methoden
- Zusätzliche Vakuumbox Methoden



Analytical Procedure

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AMERICIUM, PLUTONIUM, AND URANIUM IN WATER

(WITH VACUUM BOX SYSTEM)

1. SCOPE

1.1. This is a method for the separation of americium, plutonium and uranium from water samples. After completing this method, source preparation for measurement of americium, plutonium and uranium by alpha spectrometry is performed by electrolytic deposition onto stainless steel planchets (Eichrom Method SPA02) or by rare earth fluoride microprecipitation onto polypropylene filters (Eichrom Method SPA01).

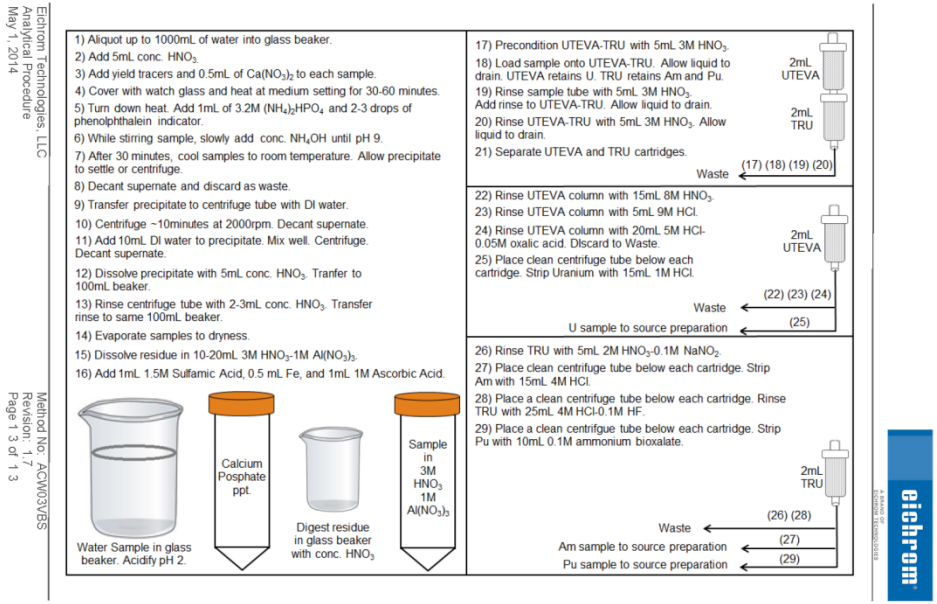
1.2. This method does not address all aspects of safety, quality control, calibration or instrument set-up. However, enough detail is given for a trained radiochemist to achieve accurate and precise results for the analysis of the analyte(s) from the appropriate matrix, when incorporating the appropriate agency or laboratory safety, quality and laboratory control standards.

2. SUMMARY OF METHOD

2.1. Americium, plutonium and uranium are separated by Eichrom UTEVA and TRU resins prior to measurement by alpha spectrometry. A calcium phosphate precipitation can be used to concentrate and remove actinides from water samples. Tracers are used to monitor chemical recoveries and correct results to improve precision and accuracy.

3. SIGNIFICANCE OF USE

3.1. This is a rapid, reliable method for measurement of actinides in water samples that is more cost-effective and efficient than traditional ion exchange, solvent extraction and precipitation techniques. The method takes advantage of vacuum assisted flow and the ability to stack resin cartridges for simultaneous extraction of U, Pu and Am on UTEVA and TRU Resins. This approach can reduce resin separation time by more than half when compared to Eichrom's gravity flow resin columns.



1) Aliquot up to 1000mL of water into glass beaker.
2) Add 5mL conc. HNO_3.
3) Add yield tracers and 0.5mL of $Ca(NO_3)_2$ to each sample.
4) Cover with watch glass and heat at medium setting for 30-60 minutes.
5) Turn down heat. Add 1mL of 3.2M $(NH_4)_2HPO_4$ and 2-3 drops of phenolphthalein indicator.
6) While stirring sample, slowly add conc. NH_4OH until pH 9.
7) After 30 minutes, cool samples to room temperature. Allow precipitate to settle or centrifuge.
8) Decant supernate and discard as waste.
9) Transfer precipitate to centrifuge tube with DI water.
10) Centrifuge ~10minutes at 2000rpm. Decant supernate.
11) Add 10mL DI water to precipitate. Mix well. Centrifuge. Decant supernate.
12) Dissolve precipitate with 5mL conc. HNO_3. Tranfer to 100mL beaker.
13) Rinse centrifuge tube with 2-3mL conc. HNO_3. Transfer rinse to same 100mL beaker.
14) Evaporate samples to dryness.
15) Dissolve residue in 10-20mL 3M HNO_3-1M $Al(NO_3)_3$.
16) Add 1mL 1.5M Sulfamic Acid, 0.5 mL Fe, and 1mL 1M Ascorbic Acid.

Water Sample in glass beaker. Acidify pH 2.

Calcium Posphate ppt.

Digest residue in glass beaker with conc. HNO_3

Sample in 3M HNO_3 1M $Al(NO_3)_3$

17) Precondition UTEVA-TRU with 5mL 3M HNO_3.
18) Load sample onto UTEVA-TRU. Allow liquid to drain. UTEVA retains U. TRU retains Am and Pu.
19) Rinse sample tube with 5mL 3M HNO_3. Add rinse to UTEVA-TRU. Allow liquid to drain.
20) Rinse UTEVA-TRU with 5mL 3M HNO_3. Allow liquid to drain.
21) Separate UTEVA and TRU cartridges.

2mL UTEVA
2mL TRU
Waste ← (17) (18) (19) (20)

22) Rinse UTEVA column with 15mL 8M HNO_3.
23) Rinse UTEVA column with 5mL 9M HCl.
24) Rinse UTEVA column with 20mL 5M HCl-0.05M oxalic acid. DIscard to Waste.
25) Place clean centrifuge tube below each cartridge. Strip Uranium with 15mL 1M HCl.

2mL UTEVA
Waste ← (22) (23) (24)
U sample to source preparation ← (25)

26) Rinse TRU with 5mL 2M HNO_3-0.1M $NaNO_2$.
27) Place clean centrifuge tube below each cartridge. Strip Am with 15mL 4M HCl.
28) Place a clean centrifuge tube below each cartridge. Rinse TRU with 25mL 4M HCl-0.1M HF.
29) Place a clean centrifgue tube below each cartridge. Strip Pu with 10mL 0.1M ammonium bioxalate.

2mL TRU
Waste ← (26) (28)
Am sample to source preparation ← (27)
Pu sample to source preparation ← (29)

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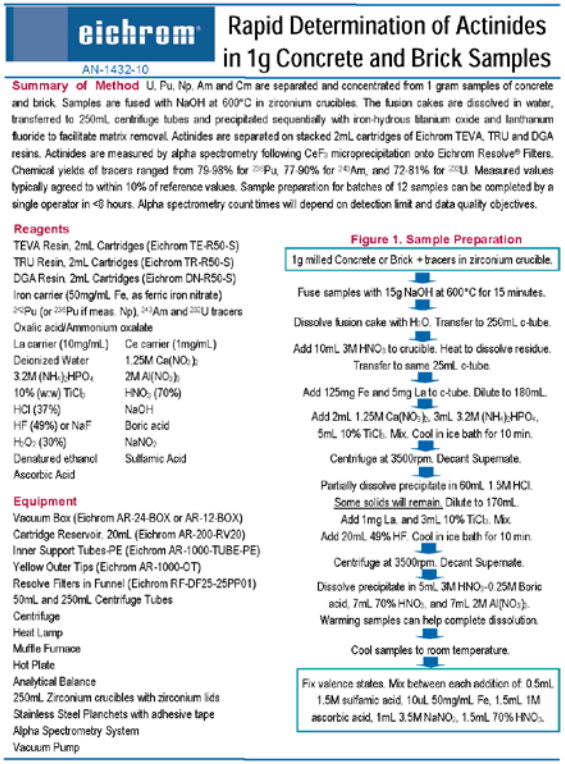
Applikationsnoten

- Sr-89/90 in 50g Bodenproben (4 mL SR Resin),…
- Sr-90 in 40 – 80L Meerwasser (DGA Resin)
- Ra-226 in Vegetationasproben,…
- Aktiniden in 100g Boden, Nahrung, 80L Meerwasser,…



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AN-1432-10

Rapid Determination of Actinides in 1g Concrete and Brick Samples

Summary of Method U, Pu, Np, Am and Cm are separated and concentrated from 1 gram samples of concrete and brick. Samples are fused with NaOH at 600°C in zirconium crucibles. The fusion cakes are dissolved in water, transferred to 250mL centrifuge tubes and precipitated sequentially with iron-hydrous titanium oxide and lanthanum fluoride to facilitate matrix removal. Actinides are separated on stacked 2mL cartridges of Eichrom TEVA, TRU and DGA resins. Actinides are measured by alpha spectrometry following CeF_3 microprecipitation onto Eichrom Resolve® Filters. Chemical yields of tracers ranged from 79-98% for ^{236}Pu, 77-90% for ^{243}Am, and 72-81% for ^{232}U. Measured values typically agreed to within 10% of reference values. Sample preparation for batches of 12 samples can be completed by a single operator in <8 hours. Alpha spectrometry count times will depend on detection limit and data quality objectives.

Reagents

TEVA Resin, 2mL Cartridges (Eichrom TE-R50-S)
TRU Resin, 2mL Cartridges (Eichrom TR-R50-S)
DGA Resin, 2mL Cartridges (Eichrom DN-R50-S)
Iron carrier (50mg/mL Fe, as ferric iron nitrate)
^{242}Pu (or ^{236}Pu if meas. Np), ^{243}Am and ^{232}U tracers
Oxalic acid/Ammonium oxalate

La carrier (10mg/mL)	Ce carrier (1mg/mL)
Deionized Water	1.25M $Ca(NO_3)_2$
3.2M $(NH_4)_2HPO_4$	2M $Al(NO_3)_3$
10% (w:w) $TiCl_3$	HNO_3 (70%)
HCl (37%)	NaOH
HF (49%) or NaF	Boric acid
H_2O_2 (30%)	$NaNO_2$
Denatured ethanol	Sulfamic Acid
Ascorbic Acid	

Equipment

Vacuum Box (Eichrom AR-24-BOX or AR-12-BOX)
Cartridge Reservoir, 20mL (Eichrom AR-200-RV20)
Inner Support Tubes-PE (Eichrom AR-1000-TUBE-PE)
Yellow Outer Tips (Eichrom AR-1000-OT)
Resolve Filters in Funnel (Eichrom RF-DF25-25PP01)
50mL and 250mL Centrifuge Tubes
Centrifuge
Heat Lamp
Muffle Furnace
Hot Plate
Analytical Balance
250mL Zirconium crucibles with zirconium lids
Stainless Steel Planchets with adhesive tape
Alpha Spectrometry System
Vacuum Pump

Figure 1. Sample Preparation

1g milled Concrete or Brick + tracers in zirconium crucible.
↓
Fuse samples with 15g NaOH at 600°C for 15 minutes.
↓
Dissolve fusion cake with H_2O. Transfer to 250mL c-tube.
↓
Add 10mL 3M HNO_3 to crucible. Heat to dissolve residue. Transfer to same 25mL c-tube.
↓
Add 125mg Fe and 5mg La to c-tube. Dilute to 180mL.
↓
Add 2mL 1.25M $Ca(NO_3)_2$, 3mL 3.2M $(NH_4)_2HPO_4$, 5mL 10% $TiCl_3$. Mix. Cool in ice bath for 10 min.
↓
Centrifuge at 3500rpm. Decant Supernate.
↓
Partially dissolve precipitate in 60mL 1.5M HCl. Some solids will remain. Dilute to 170mL.
↓
Add 1mg La and 3mL 10% $TiCl_3$. Mix. Add 20mL 49% HF. Cool in ice bath for 10 min.
↓
Centrifuge at 3500rpm. Decant Supernate.
↓
Dissolve precipitate in 5mL 3M HNO_3-0.25M Boric acid, 7mL 70% HNO_3, and 7mL 2M $Al(NO_3)_3$. Warming samples can help complete dissolution.
↓
Cool samples to room temperature.
↓
Fix valence states. Mix between each addition of: 0.5mL 1.5M sulfamic acid, 10uL 50mg/mL Fe, 1.5mL 1M ascorbic acid, 1mL 3.5M $NaNO_2$, 1.5mL 70% HNO_3.

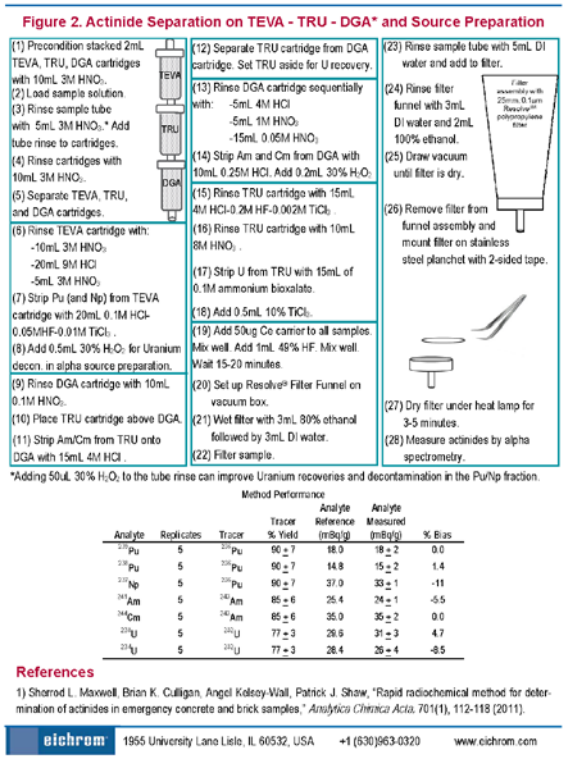

Figure 2. Actinide Separation on TEVA - TRU - DGA* and Source Preparation

(1) Precondition stacked 2mL TEVA, TRU, DGA cartridges with 10mL 3M HNO_3.
(2) Load sample solution.
(3) Rinse sample tube with 5mL 3M HNO_3.* Add tube rinse to cartridges.
(4) Rinse cartridges with 10mL 3M HNO_3.
(5) Separate TEVA, TRU, and DGA cartridges.

(6) Rinse TEVA cartridge with:
-10mL 3M HNO_3
-20mL 9M HCl
-5mL 3M HNO_3
(7) Strip Pu (and Np) from TEVA cartridge with 20mL 0.1M HCl-0.05MHF-0.01M $TiCl_3$.
(8) Add 0.5mL 30% H_2O_2 for Uranium decon. in alpha source preparation.
(9) Rinse DGA cartridge with 10mL 0.1M HNO_3.
(10) Place TRU cartridge above DGA.
(11) Strip Am/Cm from TRU onto DGA with 15mL 4M HCl.

(12) Separate TRU cartridge from DGA cartridge. Set TRU aside for U recovery.
(13) Rinse DGA cartridge sequentially with:
-5mL 4M HCl
-5mL 1M HNO_3
-15mL 0.05M HNO_3
(14) Strip Am and Cm from DGA with 10mL 0.25M HCl. Add 0.2mL 30% H_2O_2.
(15) Rinse TRU cartridge with 15mL 4M HCl-0.2M HF-0.002M $TiCl_3$.
(16) Rinse TRU cartridge with 10mL 8M HNO_3.
(17) Strip U from TRU with 15mL of 0.1M ammonium bioxalate.
(18) Add 0.5mL 10% $TiCl_3$.
(19) Add 50ug Ce carrier to all samples. Mix well. Add 1mL 48% HF. Mix well. Wait 15-20 minutes.
(20) Set up Resolve® Filter Funnel on vacuum box.
(21) Wet filter with 3mL 80% ethanol followed by 3mL DI water.
(22) Filter sample.

(23) Rinse sample tube with 5mL DI water and add to filter.
(24) Rinse filter funnel with 3mL DI water and 2mL 100% ethanol.
(25) Draw vacuum until filter is dry.
(26) Remove filter from funnel assembly and mount filter on stainless steel planchet with 2-sided tape.
(27) Dry filter under heat lamp for 3-5 minutes.
(28) Measure actinides by alpha spectrometry.

*Adding 50uL 30% H_2O_2 to the tube rinse can improve Uranium recoveries and decontamination in the Pu/Np fraction.

Method Performance

Analyte	Replicates	Tracer	Tracer % Yield	Analyte Reference (mBq/g)	Analyte Measured (mBq/g)	% Bias
^{239}Pu	5	^{236}Pu	90 ± 7	18.0	18 ± 2	0.0
^{238}Pu	5	^{236}Pu	90 ± 7	14.8	15 ± 2	1.4
^{237}Np	5	^{236}Pu	90 ± 7	37.0	33 ± 1	-11
^{243}Am	5	^{242}Am	85 ± 6	25.4	24 ± 1	-5.5
^{244}Cm	5	^{242}Am	85 ± 6	35.0	35 ± 2	0.0
^{233}U	5	^{232}U	77 ± 3	29.9	31 ± 3	4.7
^{234}U	5	^{232}U	77 ± 3	28.4	26 ± 4	-8.5

References

1) Sherrod L. Maxwell, Brian K. Culligan, Angel Kalsoy-Wall, Patrick J. Shaw, "Rapid radiochemical method for determination of actinides in emergency concrete and brick samples," *Analytica Chimica Acta*, 701(1), 112-118 (2011).

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Laufende Arbeiten

- Ra Resin
- Se Resin
  - Se-79
  - DGT (Speziation, Se(IV)/Se(VI))
- Mo Abtrennung / Mo Resin
- DGT/ “passive sampling”
- “Szintillierende TEVA beads” zur Tc-99 Bestimmung
  - Uni Barcelona
- Funktionalisierte Silicate und Polymere

Vielen Dank für Ihre Aufmerksamkeit!

Fragen?

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