TRISKEM
New Products and on-going Projects

1. TBP Resin characterisation
2. Update CL resin
3. Cesium resins
4. RaNucfilm discs
5. Carbon nanotubes
6. Other on-going work

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INTERNATIONAL

Characterization of a TBP Resin and development of methods for the separation of actinides and the purification of Sn

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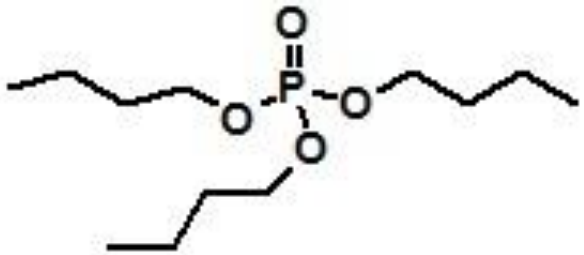
General

- TBP used in PUREX process (LLX)
- TRU Resin (contains TBP) used for Sn separation in geology/archeology
  - Elimination of matrix elements and isobaric interferences
- Determination of long-lived Sn isotopes in rad waste
  - Focus on matrix removal and elimination of isobaric interferences (Sn-121m, Sn-126)
- Sn-117m separation for use in nuclear medicine
  - Focus on Sn/Cd/Sb separation



TBP (Tributyl Phosphate)

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Resin characterisation

- Determination of D_w values for various elements
  - Multi-element solutions (HCl and HNO_3) for ICP-MS
    - 10 µg/mL of each element: Al, As, B, Ba, Ca, Cd, Co, Cr^{3+}, Cs, Cu, Fe, Ga, Li, Mg, Mn, Na, Ni, Pb, Rb, Sr, Th, U, V, Zr
    - 10 µg/mL of each element: B, Ge, Mo, Nb, P, Re, S, Si, Ta, Ti, W, Zr
  - Pu(IV), Np(IV), Th(IV) and U(VI) via LSC
  - 50mg resin contacted with 1.3 or 1.5mL solution for ≥ 1h
  - Centrifugation and filtration
  - Dilution with H_2O for ICP-MS measurements (multi-element solutions),
  - Evaporation and dilution in 0.1M HNO_3 for LSC measurements (Pu, Np, Th and U)

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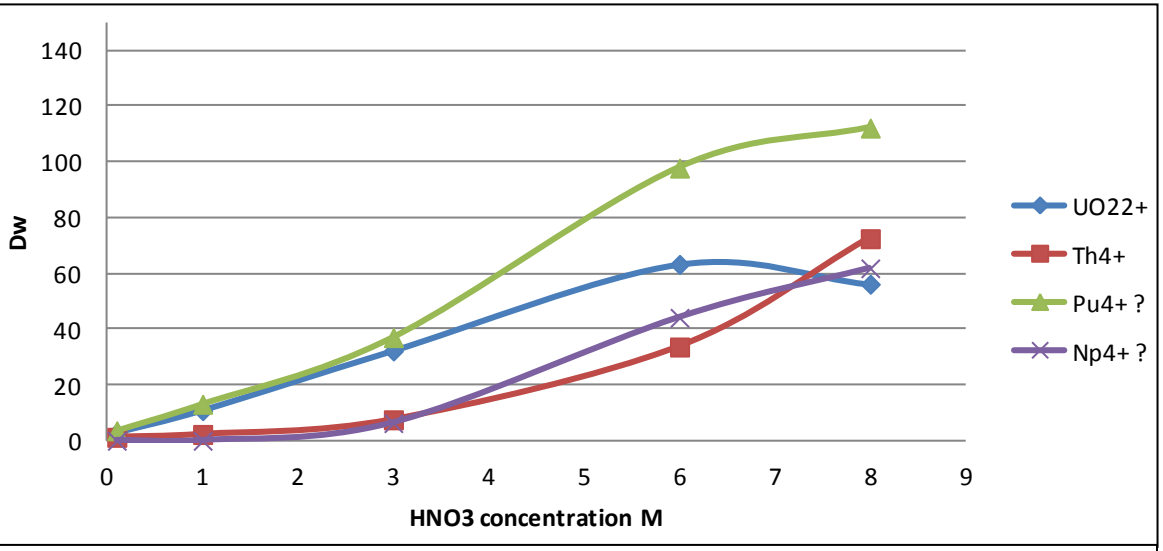
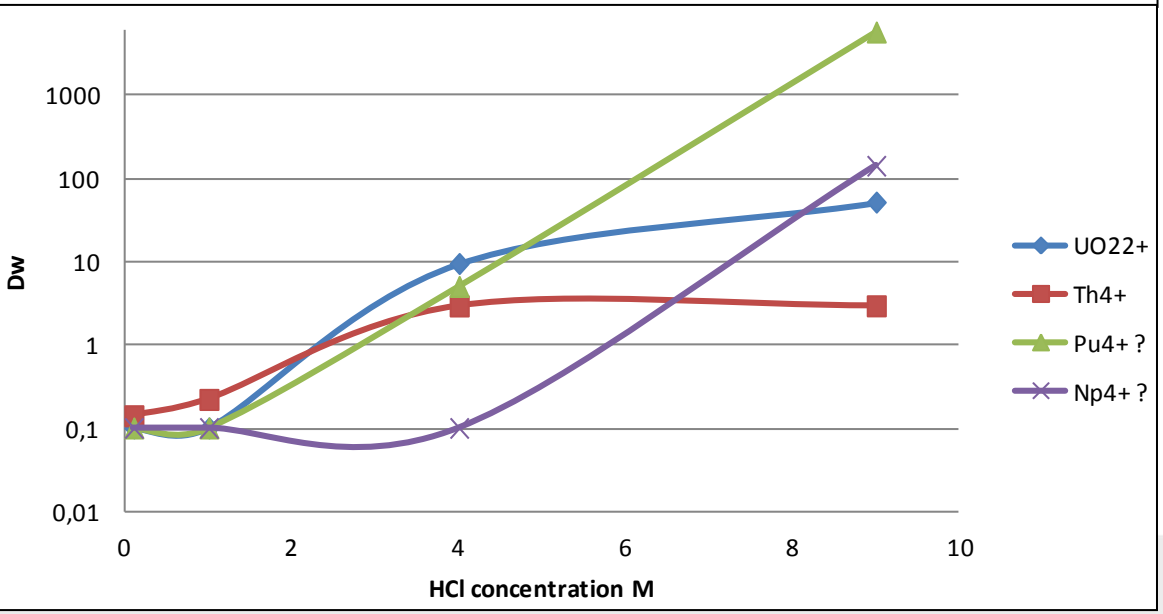
Resin characterisation

- D_W values of the actinides in HNO_3 and HCl





- D_w Pu >100 in ≥ 6MHNO_3/HCl
- D_w U < 100 all acids/acid concentrations

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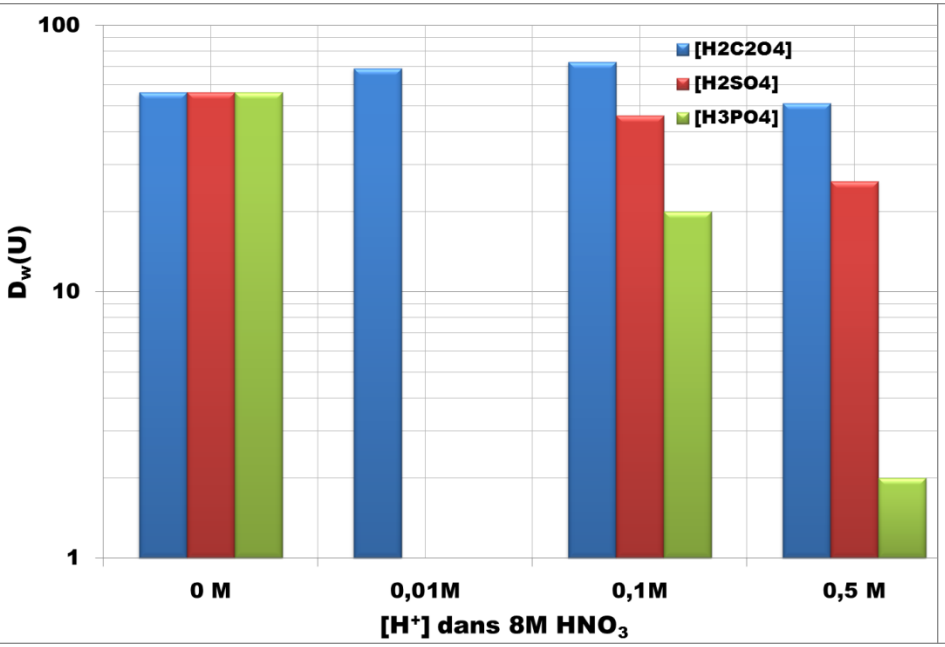
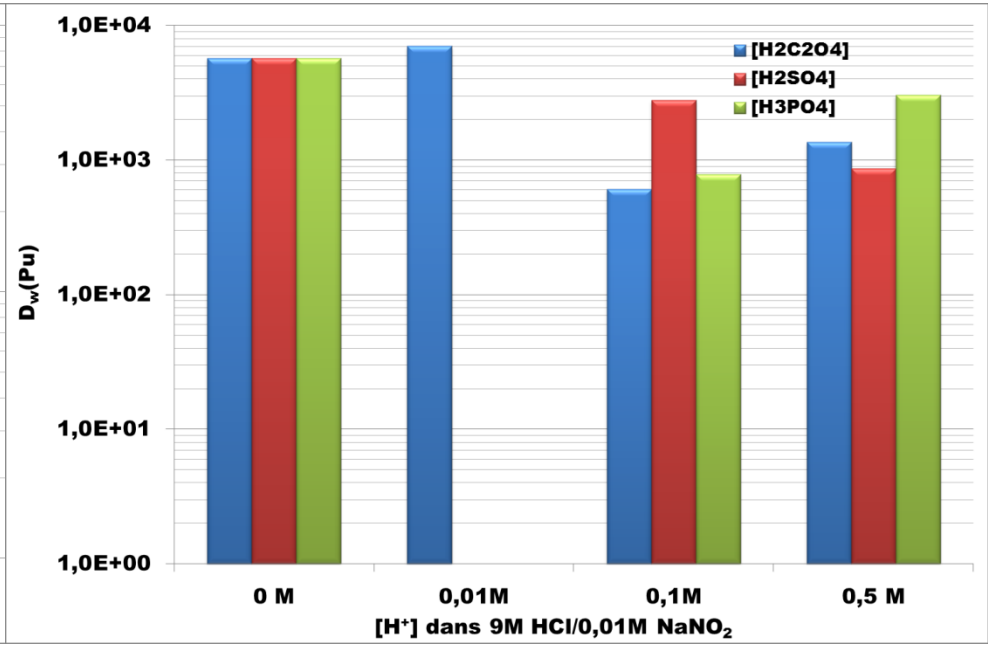
Resin characterisation

- Anionic interferences





- U in 8M HNO_3:
  - No/little interference from oxalate, interference form sulfates and especially phospates
- Pu in 9M HCl/0,01M $NaNO_2$:
  - Interferences, but D_w(Pu) >500 => little impact on Pu retention

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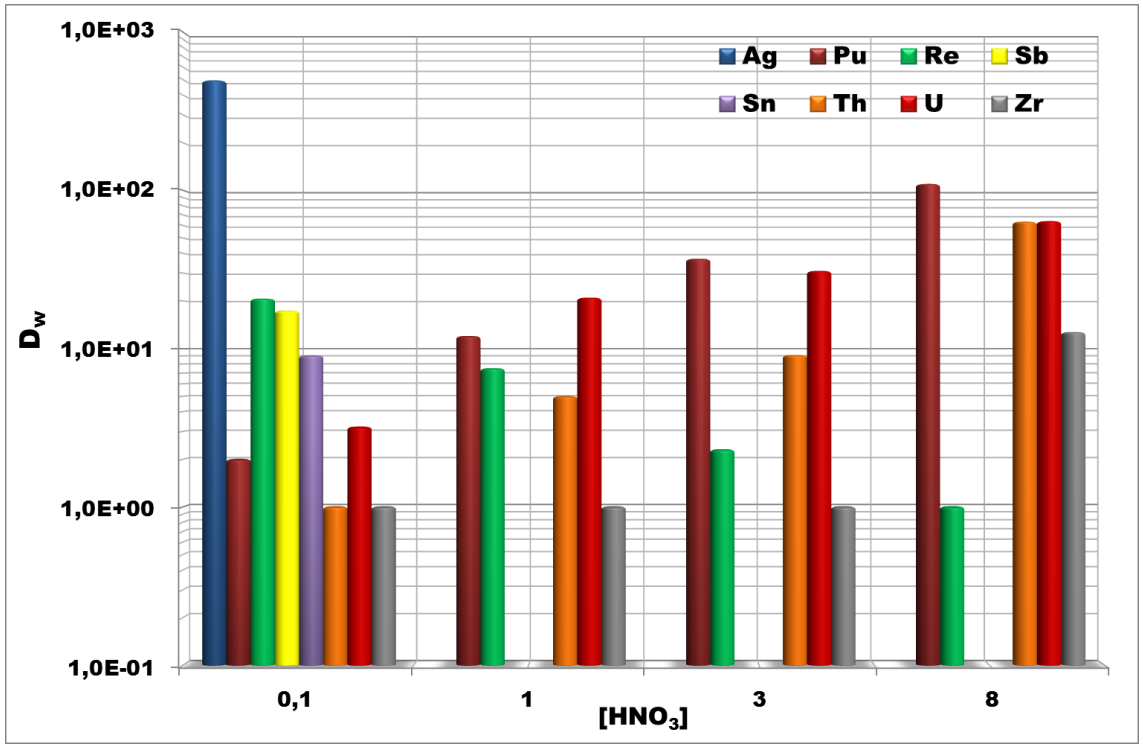
Resin characterisation

- HNO_3: only elements with D_w >10 shown
- D_W(Ag) ~ 500 in 0.1M HNO_3 and Dw(Pu) ~ 100 in 8M HNO_3
- Other elements show very little affinity in HNO_3



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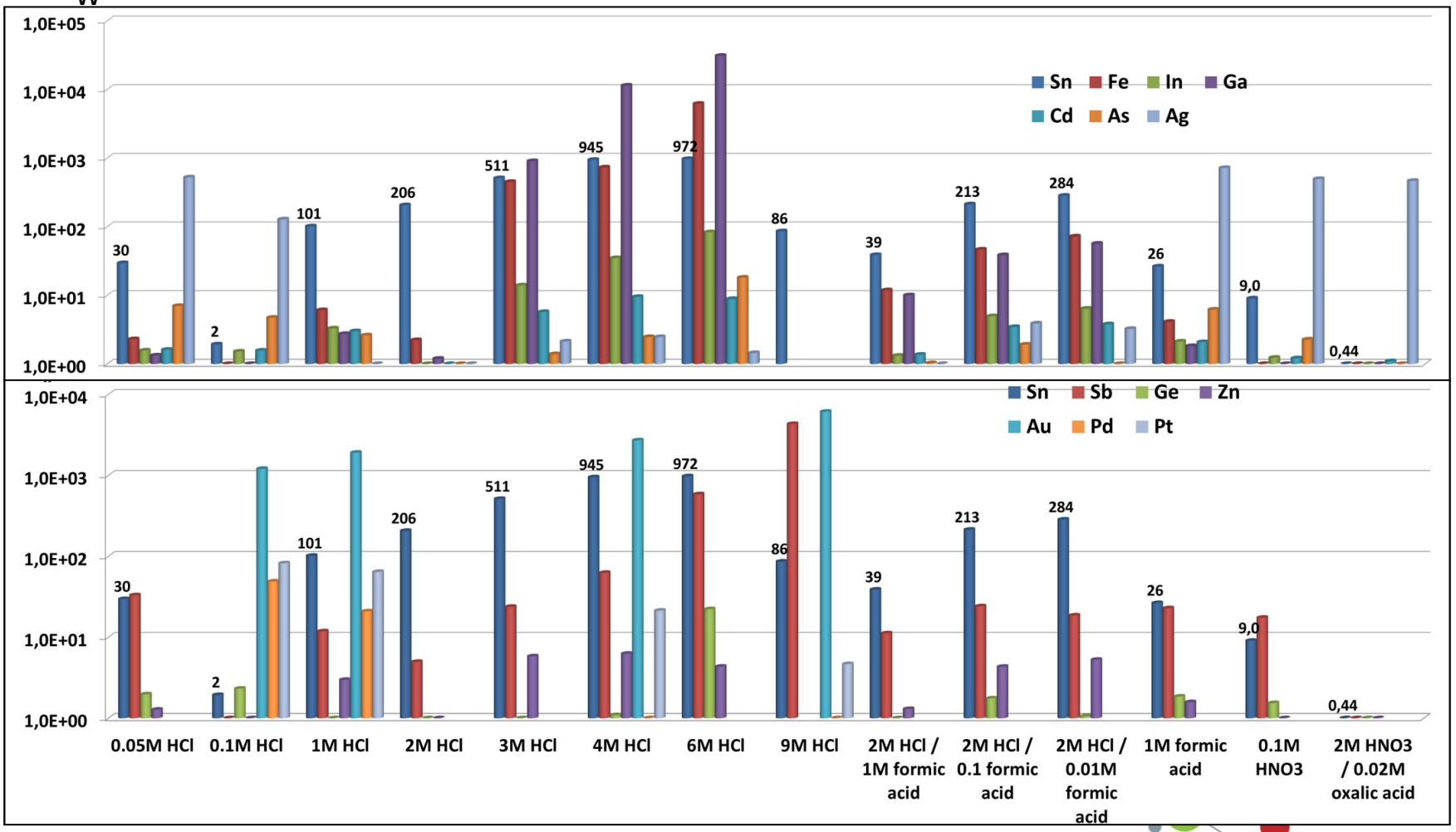
Resin characterisation

- D_W values in various other conditions



Resin characterisation

- **U capacity**
  - Batch experiments
  - U_{nat}, 50mg resin, 8M HNO_3
  - Filtration, evaporation, dissolution in 0.1M HNO_3
  - Mixed with LSC cocktail (ProSafe+)
  - LSC measurement
- **Results:**
  - capacity =71-76 mg U/g dry resin in 8M HNO_3
    - comparable (although significantly lower) to UTEVA resin

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- Determination of Pu in drinking water
  - 300-500mL acidified water
    - spiked with Pu-239, Am-241, Th-230 and U-233 (each 2Bq)
  - $Fe(OH)_2$ precipitation
  - Preconditioning: 10 mL 8M HNO_3/0.01M $NaNO_2$
  - Load from 10mL 8M HNO_3/0.1M $NaNO_2$
  - Rinse: 2 x 10 mL 8M HNO_3/0.01M $NaNO_2$
  - Th Elution: 10 mL 9M HCl/0.01M $NaNO_2$,
  - Th+U Elution: 30 mL 9M HCl/0.01M $NaNO_2$
  - Pu Elution: 20 mL 1M HCl (or reducing conditions)
- Results :
  - Chemical yield for Pu ~ 69%.
  - U contamination in Pu source is <1.4%, no Am or Th found
  - Procedure can be performed in 1 day.
  - More suitable methods available

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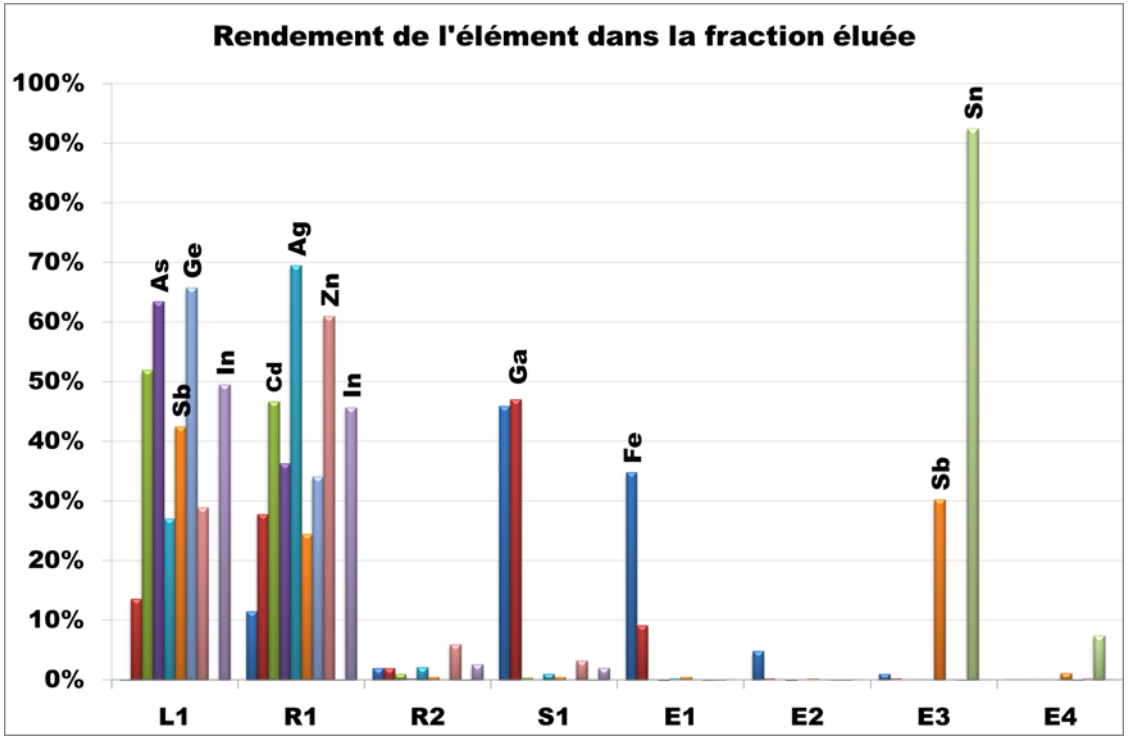
Sn separation

- Sn separation:
  - Method development based on D_W values obtained via batch experiments
  - Addition of formic acid depending on matrix
- Results:



L1: 4mL loading solution: 2M HCl/0,01M formic acid

R1: 5mL 2M HCl/0,01M formic acid

R2: 2mL 2M HCl/0,01M formic acid

S1: 3mL 1M HCl

E1: 3mL 1M HCl

E2: 3mL 1M HCl

E3: 4mL 0,1M HCl

E4: 2mL 0,1M HCl

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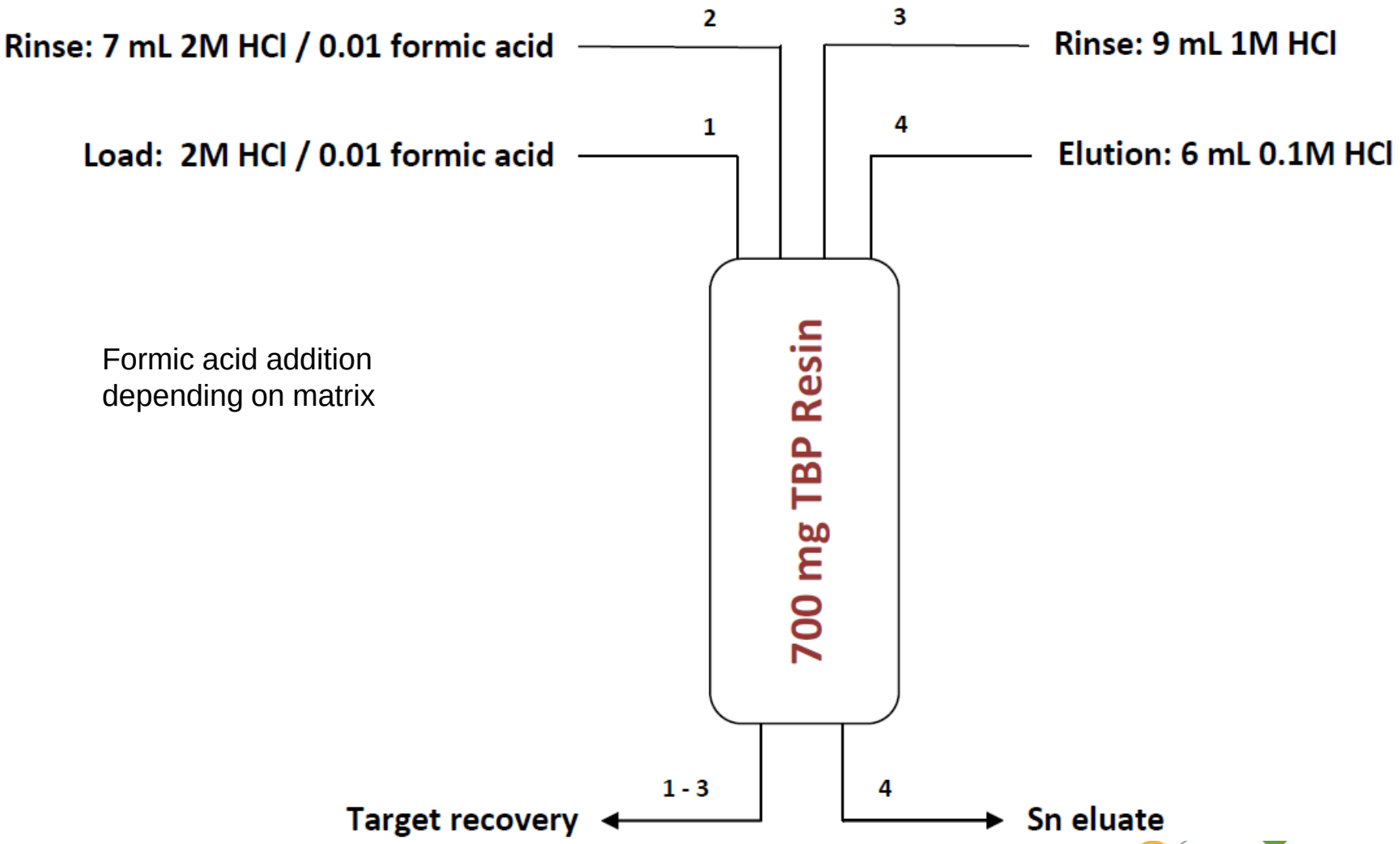
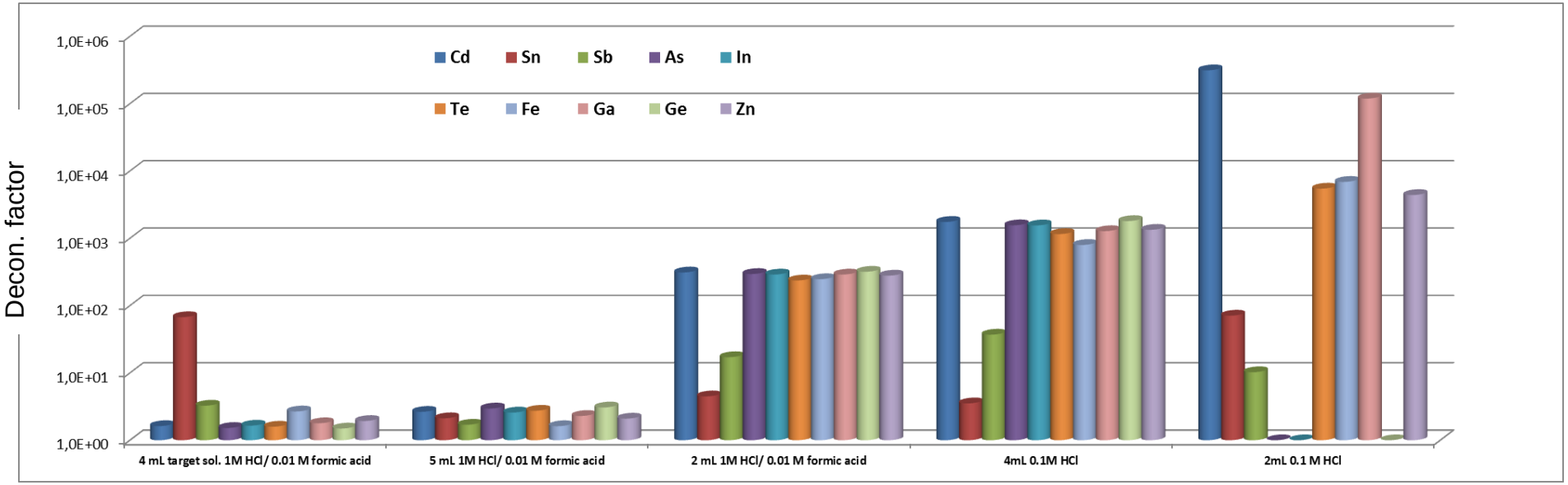
Proposed Sn separation procedure



Sn separation

- Main isobaric interference for Sn-126 (ICP-MS determination): Te-126
- Decon factor study to verify Sn/Te separation



➢ Te decon.factor in Sn fraction > 1000

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Sn separation

- Results
  - TBP Resin can be used for the purification of Sn
  - Most elements are eluted during load and first rinse (Cd, As, Ag, Ge, Zn, In, ~70% Sb) => 11mL
  - Fe/Ga are removed with 9mL 1M HCl
  - For Fe rich sample loading under reducing conditions might be necessary
  - >90% Sn eluted in 6mL 0.1M HCl
  - ~ 30% Sb co-eluted with Sn => control of Sb oxidation state
  - Clean Se/Te separation
  - On-going project on Sn-126 determination in rad waste via ICP-MS
    - First step AIX, followed by TBP

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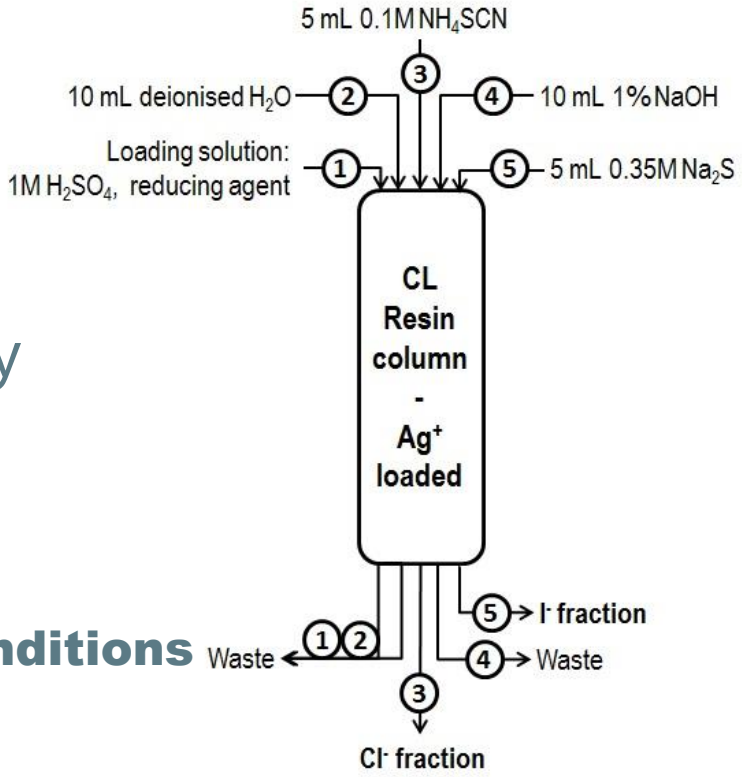
CL Resin - Reminder

- **CL Resin** originally developed for **Pd separation**
  - **Method testing on-going**
  - Currently tested for **Ag separation**
- **Selective for PGE, Ag, Au,…**
- **Halogen selectivity** introduced by loading with **Ag^+**
- Sample loading on CL- Ag^+ Resin
  - **Acidic, neutral or slightly alkaline conditions** (*Might need to be done under reducing conditions*)
  - Rinse with 1% NaOH④ : increases I^- elution yield
  - Yields in general > 90 - 100%
  - Updated method available: modified Ag^+ loading of the CL Resin



§A. Zulauf, S. Happel, M. B. Mokili, A. Bombard, H.Jungclas: Characterization of an extraction chromatographic resin for the separation and determination of 36Cl and 129I. J. RadanalNuclChem, 286(2), 539-546

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CL Resin
Pyrolyser method

- Allows for analysis of **large solid samples** (several g)
- Thermal decomposition of the samples and desorption of Cl species in Pyrolyser furnace at 900°C (ca. 2h)
- System flushed with humidified air (samples also humidified w/ 1mL H_2O)
- Decomposition products trapped in bubbler containing alkaline solution - Bubbler connected directly with furnace *via* glass connector (Avoid losses due to condensation in tubing)
- ^{36}Cl separated via Ag^+ loaded CL Resin
  - Similar separation to standard method, but bubbler solution (6 mM Na_2CO_3) directly loaded onto CL column
  - When loading column with 6 mM Na_2CO_3 => additional rinsing step w/ 0.1M H_2SO_4 to improve C-14 decontamination (« modified wash »)
- Similar method will be tested for I-129

P E Warwick, A Zulauf, S Happel, I W Croudace: Determination of 36Cl in decommissioning samples using a Pyrolyser furnace and extraction chromatographic separations. Presentation at the 11th ERA Symposium, 16/09/2010, Chester (UK)

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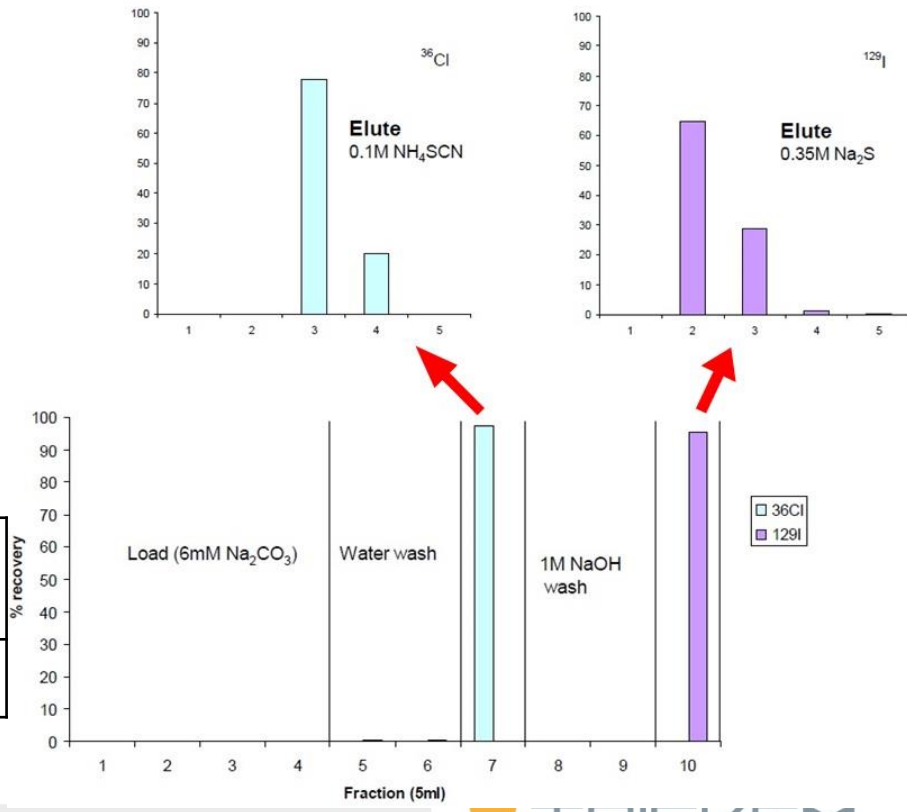
CL Resin Pyrolyser method

Decontamination factor (D_f)	^{36}Cl fraction	^{129}I fraction
^{3}HTO	> 500	> 2000
$^{14}CO_3$	7	5000
^{14}C modified wash	700	
^{35}S modified wash	1500	1000
^{36}Cl		> 2000
^{129}I	1300	

- ➢ **High D_f**
- ➢ **Clean ^{36}Cl / ^{129}I separation**
- ➢ ^{36}Cl separation yield **> 95%**



- Analysis of spent resin

Sample type	Expected value	Measured value
Ion exchange resin	4,1 kBq	4,3 +/- 0,1 kBq

- ➢ **Good agreement**

All Data from P. Warwick, GAU Radioanalytical, Southampton (UK)

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Updates on CL Resin

- **Nottoli et al.: I-129 in spent resin via AMS[#]**
  - Microwave digestion or oxygen bomb combustion
  - Separation on CL Resin (load and rinses in 0.2 – 4M NaOH, elution with Na_2S)
  - S^{2-} removal *via* oxidation / $BaSO_4$ precipitation
  - Sample prep. of iodine fraction for AMS by AgI precipitation
- **Decamp et al.: Iodine removal from elevated sample volumes at high flow rates[§]**
  - > 10 L radioactive process effluent (1M HNO_3),
  - Flow rate up to **180 mL/min**,
  - 3g CL resin (plus 4g XAD-4 resin), iodine uptake: 85 – 95%
- **On-going**: Iodine retention in presence of very large excess of chloride (sea water)

[#] E. Nottoli et al: Accurate determination of (129)I concentrations and (129)I/(137)Cs ratios in spent nuclear resins by Accelerator Mass Spectrometry. Applied Radiation and Isotopes, Volume 86, April 2014, Pages 90–96

[§] C. Decamp (IRE), S. Happel: Utilization of a mixed-bed column for the removal of iodine from radioactive process waste solutions, Journal of Radioanalytical and Nuclear Chemistry, online April 2013, DOI: 10.1007/s10967-013-2503-1

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Cesium Resins - AMP-PAN

AMP-PAN and KNiFC-PAN developped by Dr Sebesta from CVUT (Czech Republic)

- **AMP-PAN for acidic media – e.g Cs separation from liquid radioactive wastes[1][2][3][4][5]**

➢ **Resistance to radiation** makes AMP-PAN very well suited for measurement in and/or removal of Cs from **liquid radioactive wastes**

  – AMP-PAN = first step in general process to separate RN in nuclear tank wastes

  – Also used for the **determination of Cs** in **acidified sea water samples**

[1] Herbst R.S. et al., Integrated AMP-PAN, TRUEX, and SREX Flowsheet Test to Remove Cesium, Surrogate Actinide Elements, and Strontium from INEEL Tank Waste Using Sorbent Columns and Centrifugal Contactors, INEEL/EXT-2000-00001, Janurary 2000

[2] Kamenik J., Comparison of Some Commercial and Laboratory Prepared Caesium Ion-Exchangers, Czechoslovak Journal of Physics, Vol.53 (2003), Suppl.A, A571-A576

[3] Brewer K.N. et al., AMP-PAN column Tests for the Removal of 137Cs from Actual and Simulated INEEL High-Activity Wastes, Czechoslovak Journal of Physics, Vol. 49 (1999), Suppl. S1, 959-964

[4] John J. et al., Application of a New Inorganic-Organic Composite Absorbers with Polyacrylonitrile Binding Matrix for the separation od Radionuclides from Liquide Radioactive Wastes, Chemical Separation Technologies and Related Methods of Nuclear Waste Management, Kluwer Academic Publishers, Netherlands 1999, 155-158

[5] Todd T.A. et al. Cesium sorption from Concentrated acidic Tank Wastes using Ammonium molybdophosphate-polyacrylonitrile composite sorbents, J. Radioanal. Nuc. Chem., Vol.254, No.1 (2002) 47-52

Cesium Resins – KNiFC-PAN

AMP-PAN and KNiFC-PAN developped by Dr Sebesta from CVUT (Czech Republic)

- **KNiFC-PAN** for **slightly acidic to neutral media -** Cs separation in environmental samples (seawater/milk/urine/…) [6][7][8][9]
  - **Seawater samples**
    - 100L at about 300mL.min^{-1}. At 470mL.min^{-1}=> 85% Cs retained
    - No interferences of large amounts of Na or K on Cs measurement as long as capacity of sorbent is not exceeded
    - MDA for 100L samples, 50-70h counting => 0,18 Bq.m^{-3} ^{134}Cs, 0,15 Bq.m^{-3} ^{137}Cs
    - **Alternatively use of AMP-PAN**
  - **Milk**: MDA = 2mBq.L^{-1} for ^{137}Cs in 5L milk sample (HPGe detector, relative efficiency 140%, counting time 600000 s, ρ = 1g.cm^{-3})

[[6] Pike et al., Extraction of Cesium from Seawater off Japan using AMP-PAN Resin and Quantification via Gamma Spectrometry and Inductively Coulped Mass Spectrometry, J. Radioanal. Nucl. Chem, DOI 10.1007/s10967-012-2014-5, 2012

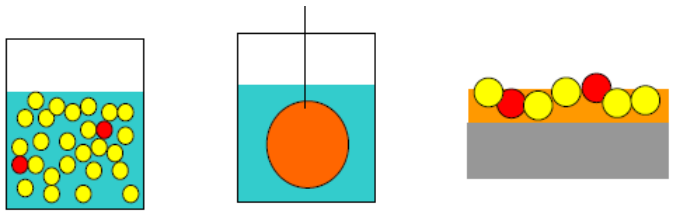
[7] Kamenik J. et al., Fast Concentration of Dissolved forms of Cesium Radioisotopes from Large Seawater Samples, J. Radioanal. Nucl. Chem, DOI 10.1007/s10967-012-207-4, 2012

[8] Sebesta et al., Separation and Concentration of Contaminants using Inorganic-Organic Composite Absorbers, 2nd International Symposium and Exhibition on Environmental Contamination in Central and Eastern Europe, September 20-23, 1994 – Budapest,Hungary.

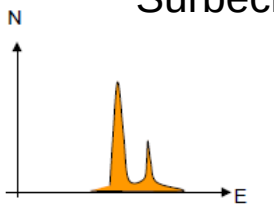
[9] Kamenik J. et al., Long Term Monitoring of 137Cs in Foodstuffs in the Czech Republic, Applied Rad. Isotopes., 67 (2009) 974-977

Ra-226 via Ra NucFilm Discs

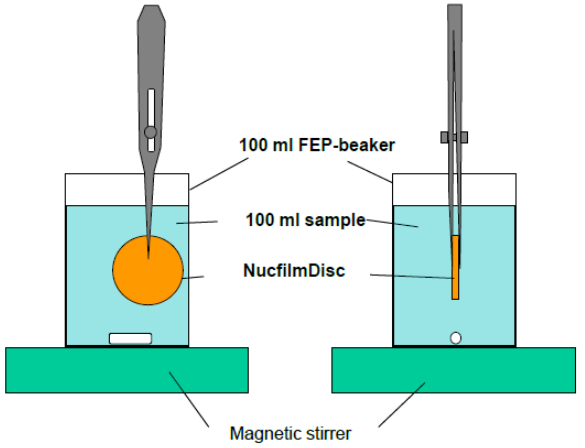
- Thin MnO_2 layer on nylon disc
  - Very smooth surface
- Direct Ra extraction from water samples (only)
  - 100 mL
  - Min. 4 – 6h, pH 4 – 8
- Yield via Ba-133
- After rinsing sample ready for α-spectrometry
- Yield typically 75 – 95% (depending on matrix)
  - Ca, Ba



Selective adsorption on thin film



Surbeck 2010



Ra-226 *via* MnO_2 Discs

accredited method (Subatech, France)

- Sample volume 50 - 100 mL (filtered water, acidified to pH = 0,5 – 2)
- Addition of Ba-133 (10 - 100 Bq) as internal standard
  - **Ba content of the sample < 10µg**
- Addition of EDTA to complex interferents

↓

- pH adjustment to 7 - 8,5 with NaOH and addition of $NaHCO_3$ (buffer, U complexation)
- Measurement of original Ba-133 activity in the solution (γ-spectrometry)

↓

- Place MnO_2 disc in sample holder
- Stir for 10 h

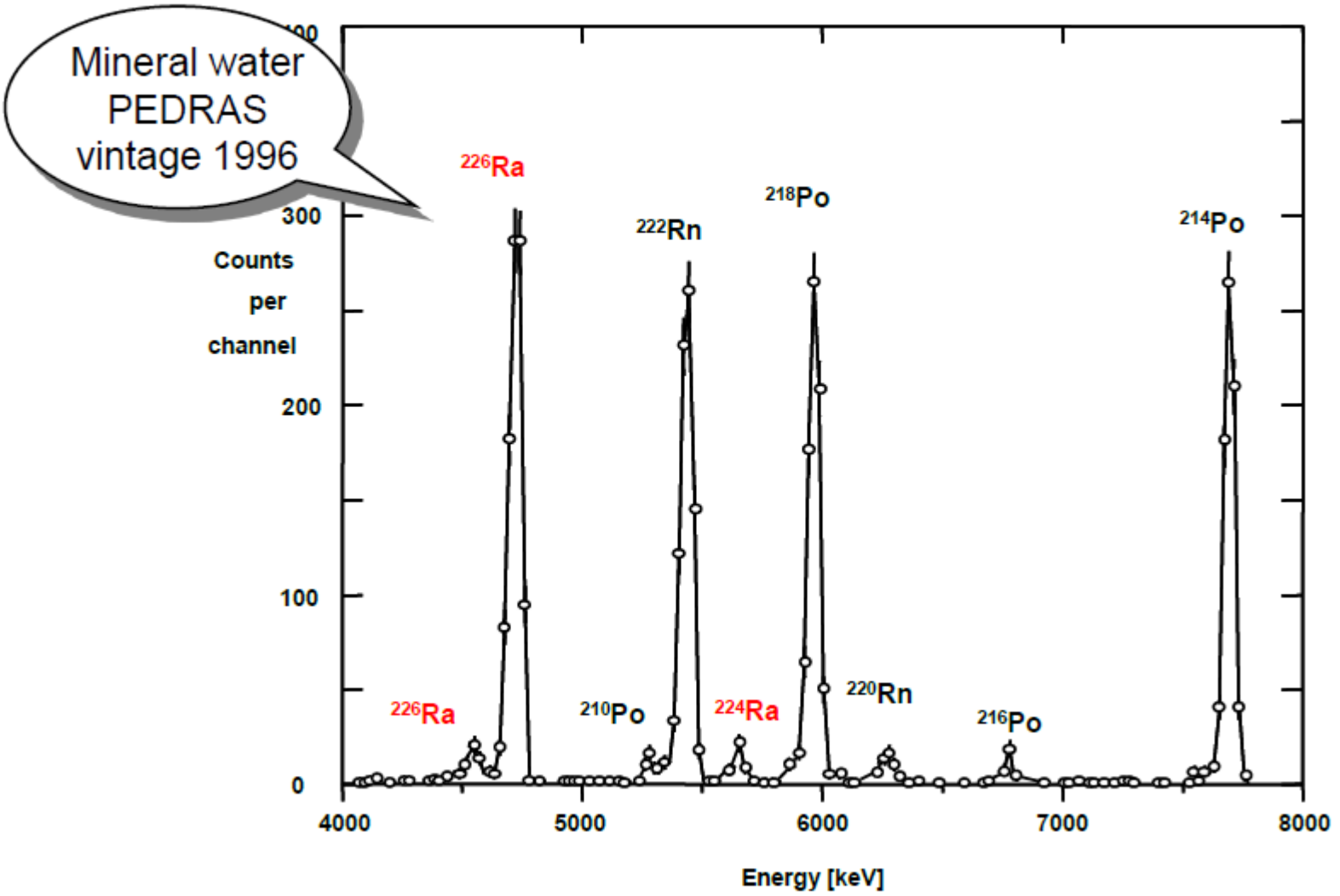
↓

- Withdraw MnO_2 disc, rinse and dry
- Measurement of Ba-133 activity in the solution after extraction (γ-spectrometry)

↓

- α-spectrometry

➢ LD: 5 - 10 mBq.L^{-1} for 50 – 100 mL samples and 24 – 48h counting



Surbeck 2010

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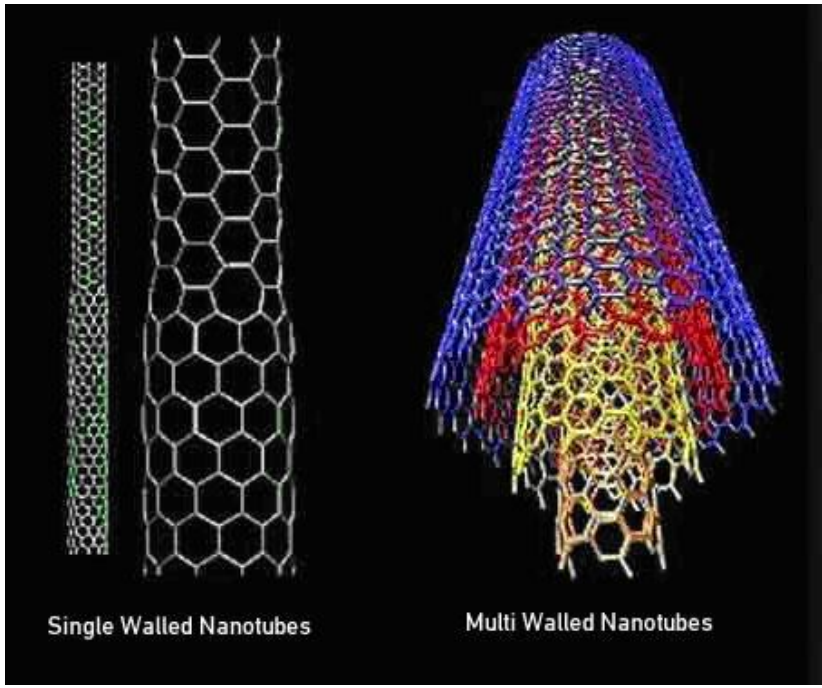
Use of Carbon nanotubes

- 0.4 to 100 nm diameter
- Length up to 1 mm (record: 20 cm [a])
- Different interesting properties:
  - **High specific area: high reactivity**
  - High resistance : stronger to traction and lighter than steel
  - Similar conductivity to Cu
  - Thermal conductivity similar to diamond
  - Conductor or semi-conductor
  - **High chemical resistance**

  - **MWT chosen (less expensive)**



http://www.tedpella.com/gold_html/Nanotubes.htm

[a] H.W. Zhu, C.L. Xu, D.H. Wu, B.Q. Wei, R. Vajtai und P.M. Ajayan,Science 2002, 296, 884.

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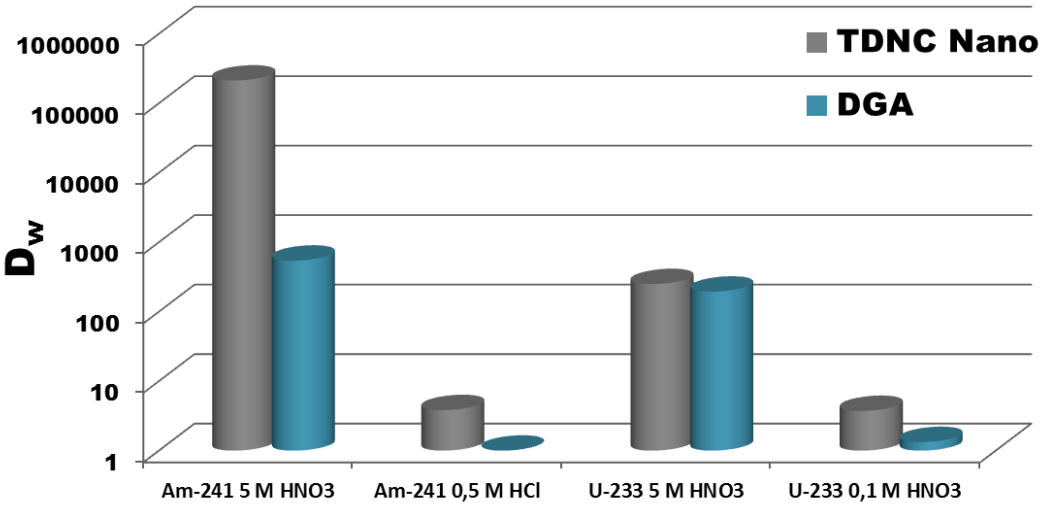
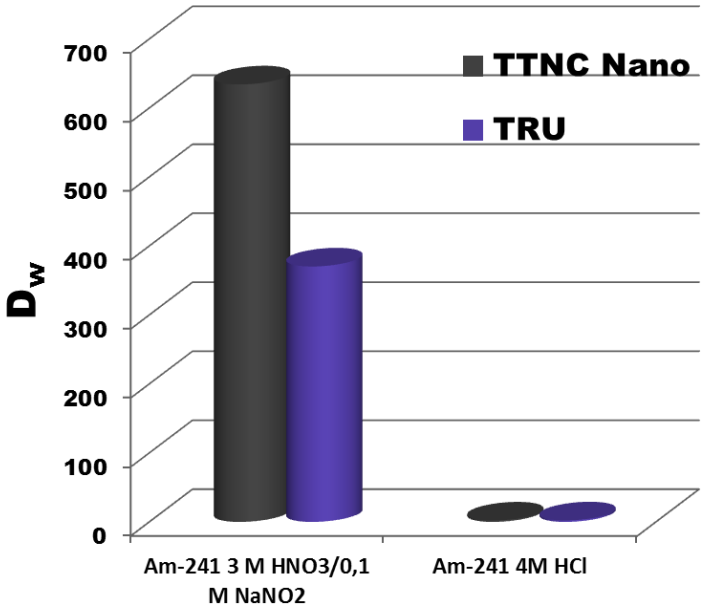
Use of Carbon nanotubes

- D_w comparison DGA vs DTNC and TRU vs TTNC for Am





- **Batch experiments**
- **D_w significantly higher with carbon nanotubes compared to classical support**

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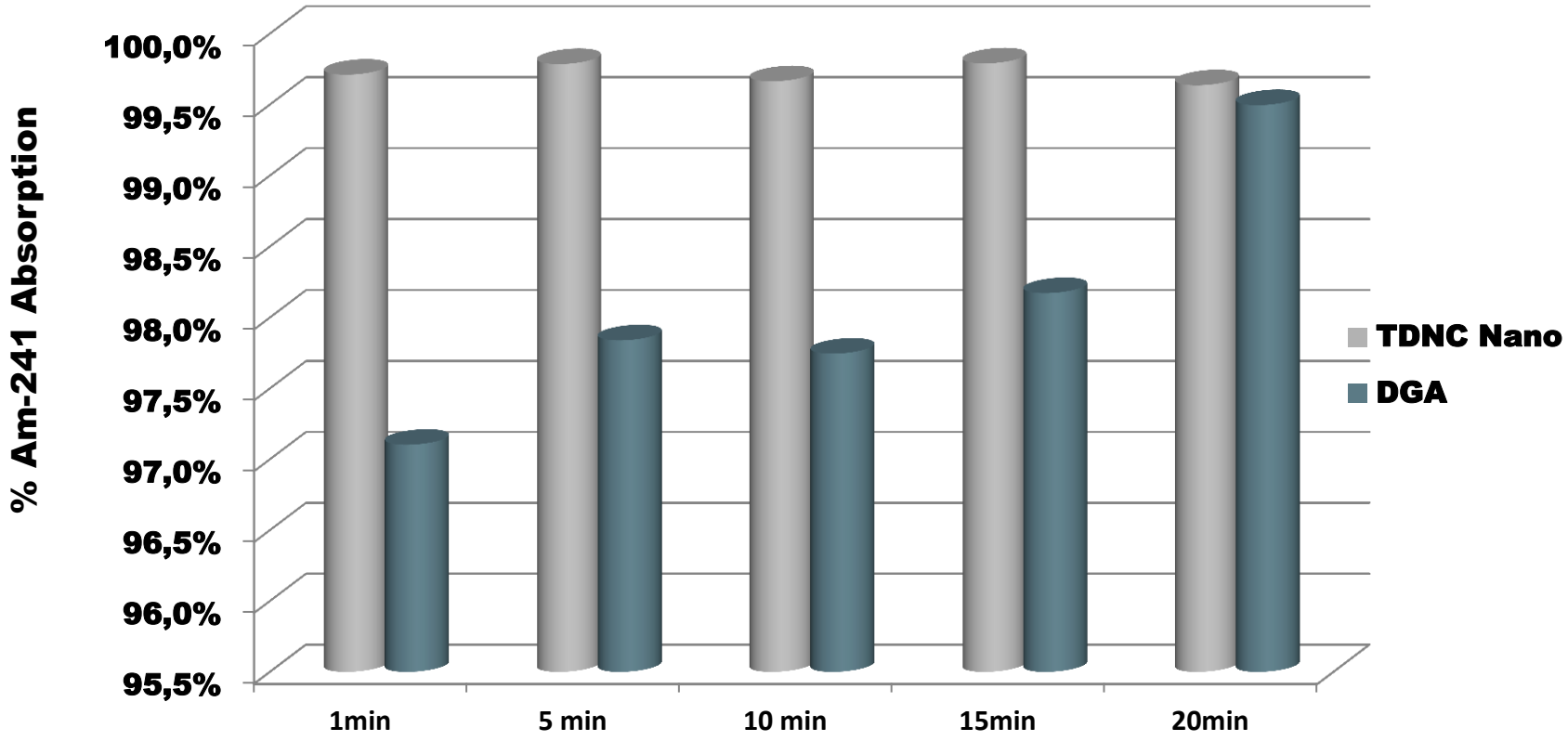
Use of Carbon nanotubes

Kinetics: TDNC vs. DGA



Nanotubes: near quantitative absorption after ~ 1min

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Use of Carbon nanotubes

Conclusions

- Upgrade from batch tests to column tests **difficult**
- Low flow-rates
- Use of filters/membrane with specific pore size
- **Solutions** :
  - Specific packing technique
  - Identification of the correct pore size
  - Use of 1-5 mL/min flow-rate possible (under vacuum)

✓ D_W obtained with TDNC and TTNC in batch tests are promising

✓ Very fast kinetic of extraction

✓ Possibility to use columns

✓ Adapted flow-rate

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Other on-going works

- Pd separation on CL Resin
- Long-lived radionuclides for decommissioning (Ag, Se-79,…)
- Discs (e.g. gross-alpha disc)
- Scintillating support
- Resin characterisation & method development (e.g. Dubna)
- Radiolysis stability
- …

- Very interested in R&D collaboration

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