TRISKEM
New Products and on-going Projects

1. New product lines
2. Update CL resin
3. Cesium resins
4. RaNucfilm discs
5. On-going works:
    51. Scandium separation,
    52. Zirconium separation,
    53. Carbon nanotubes (CNTs),
    54. Gallium separation
6. TK100 Resin
7. TBP Resin

TRISKEM INTERNATIONAL

1. New Product Lines

- **Glassware and laboratory consumables in small quantities** (beakers, spatulas, pH indicator, filter support,…) => Non – exhaustive list available

- **Certified ICP-MS mono- and multi-elements standard solutions** => list available

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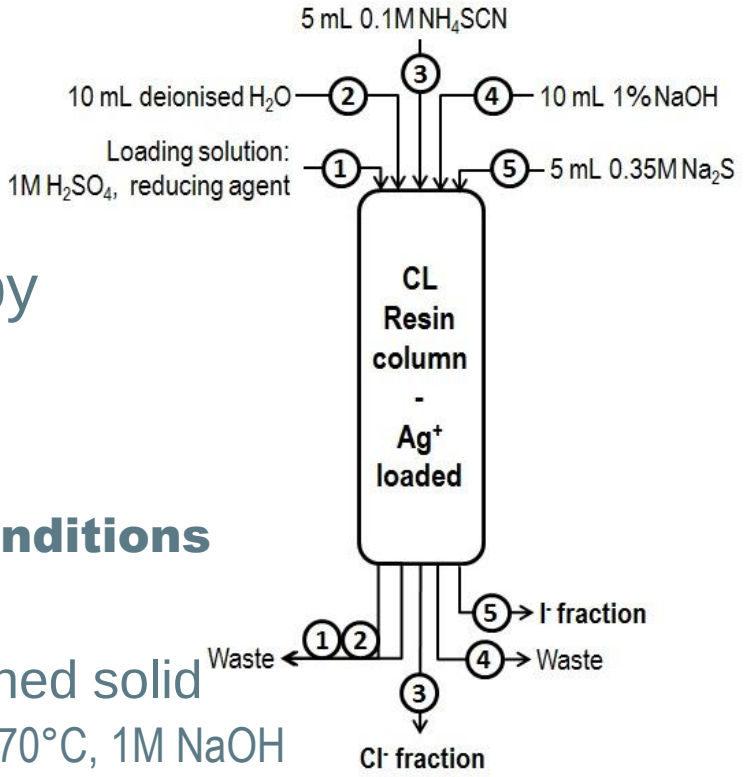
2. Updates on CL Resin

- **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*)
  - Original paper[§]: water/effluents and leached solid samples (concrete/soil/filter) : Leaching: 4h, 70°C, 1M NaOH
  - 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

TRISKEM INTERNATIONAL

2. Updates on 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 CL- Ag^+ 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 improved C-14 decontamination (« modified wash »)
- Similar method will be tested for I-129

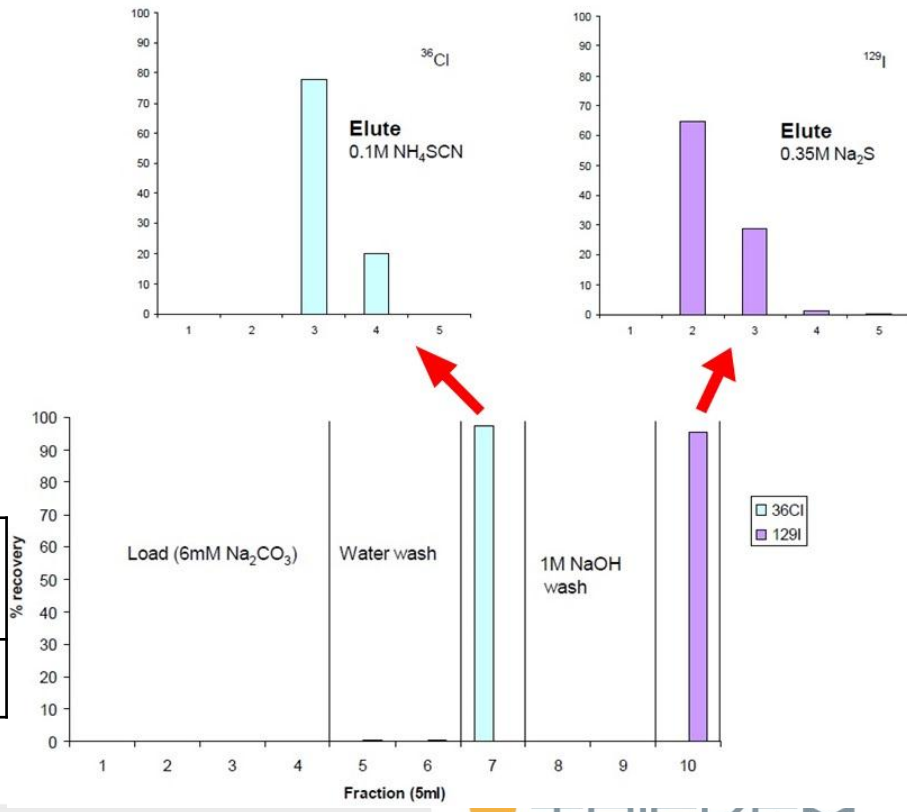
P E Warwick, A Zulauf, S Happel, I W Croudace: Determination of 36Cl in decommissioning samples using a Pyrolyser furnace and extraction chromatographic separations. Presentation at the 11th ERA Symposium, 16/09/2010, Chester (UK)

TRISKEM INTERNATIONAL

2. Updates on 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)

2. 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

TRISKEM INTERNATIONAL

3. Cesium Resins

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

- **AMP-PAN for Cs separation in liquid radioactive wastes[1][2][3][4][5]** – use in acidic media
  - **Resistance to radiation** makes AMP-PAN very well suited for measurement of Cs in **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

3. Cesium Resins

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

- **KNiFC-PAN** for Cs separation in environmental samples (Seawater/milk/urine/…) [6][7][8][9] **– use in slightly acidic to neutral media**
  - **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

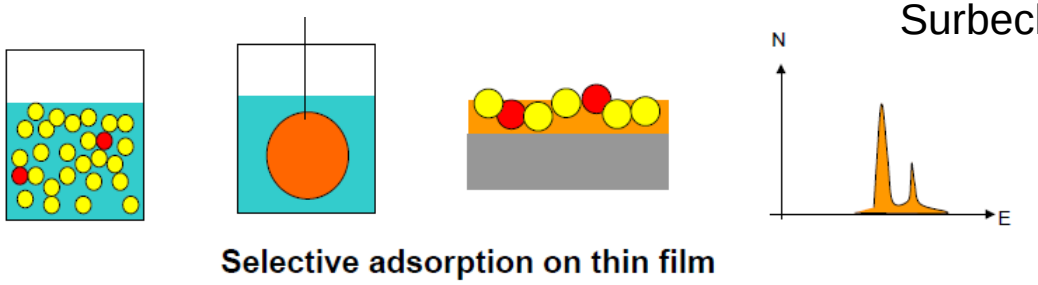
[7] Kamenik J. et al., Fast Concentration of Dissolved forms of Cesium Radioisotopes from Large Seawater Samples, J. Radioanal. Nucl. Chem, DOI 10.1007/s10967-012-207-4, 2012

[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

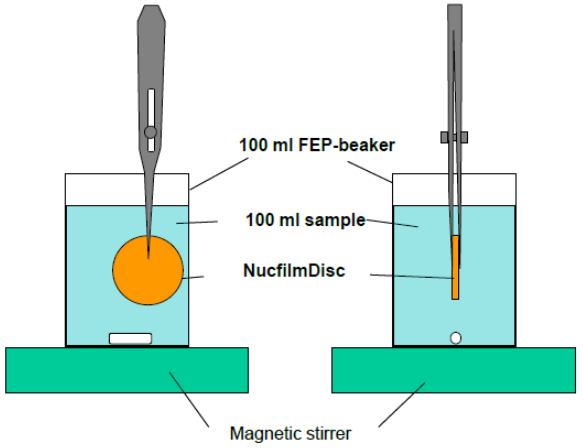
4. Ra-226 via Ra NucFilm Discs

- 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



4. 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

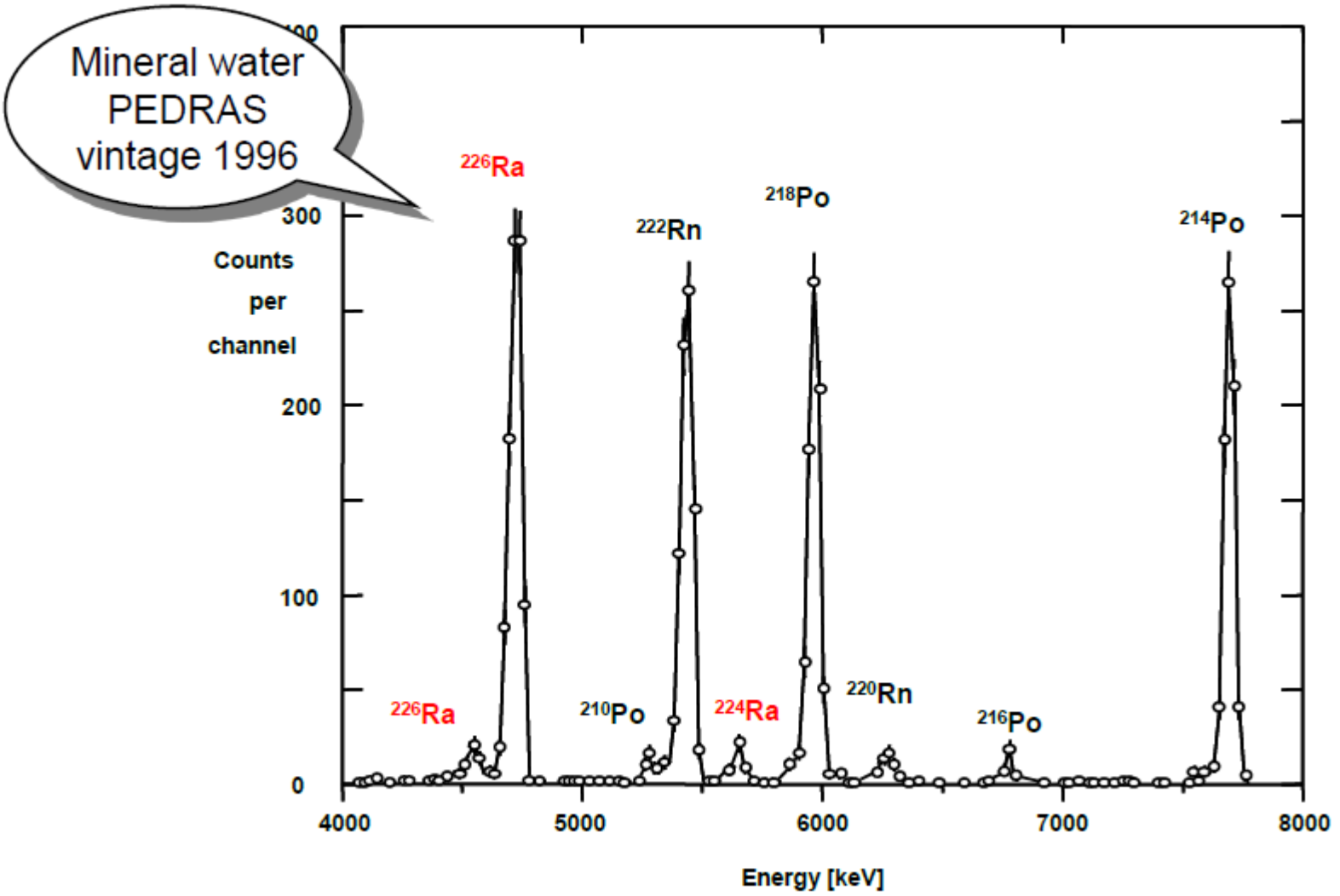
↓

- 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

TRISKEM INTERNATIONAL

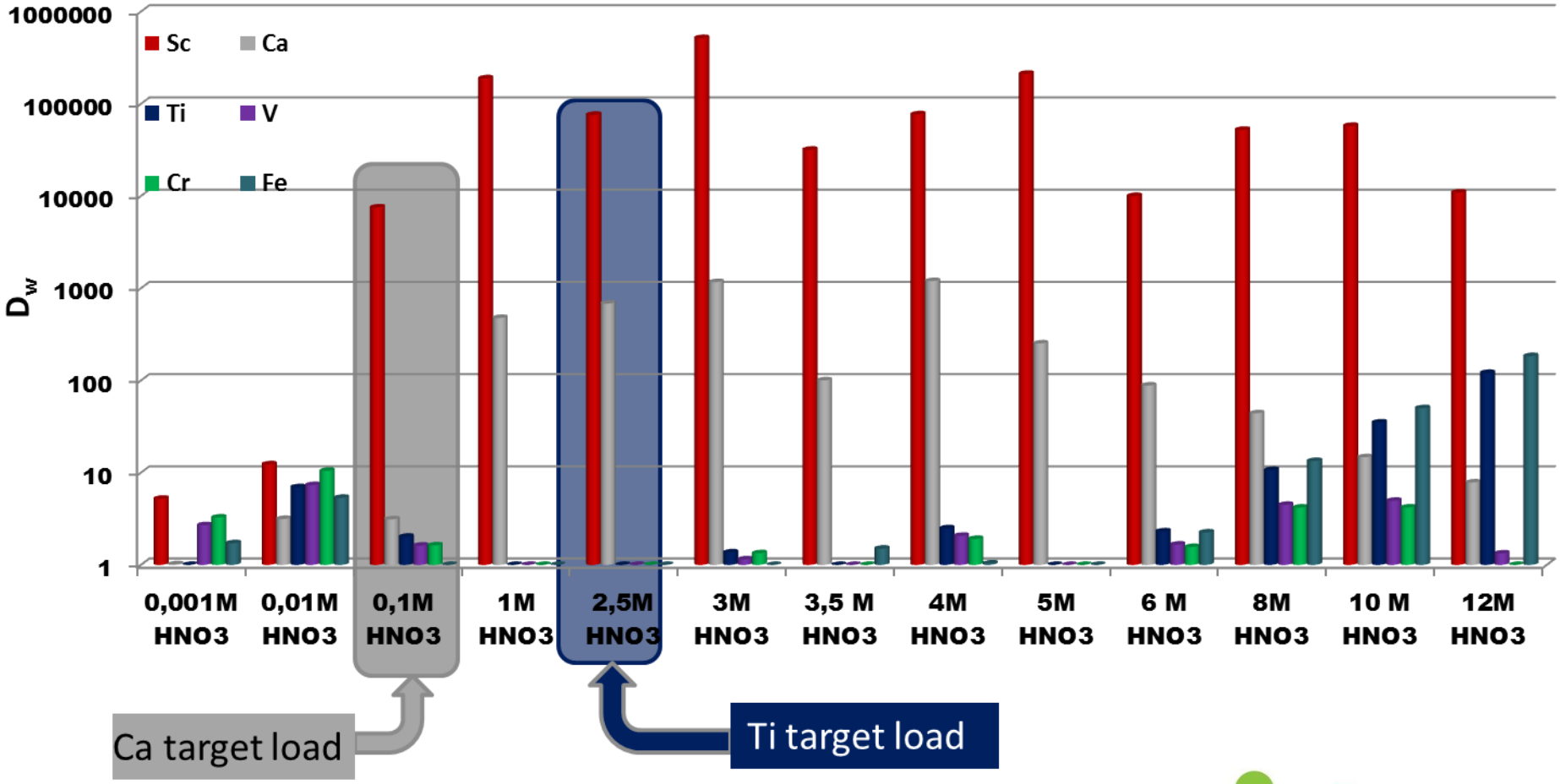
5.1 Selective separation of Scandium

- Radiopharmaceutical applications:
  - PET imaging (i.e. ^{44}Sc , β^+)
  - Therapy (i.e. ^{47}Sc, β^-)
- Production via irradiation of ^{43}Ca, ^{44}Ca, ^{48}Ca, ^{44}Ti, ^{46}Ti, ^{47}Ti, ^{48}Ti or ^{49}Ti
  - Excellent Sc/Ca-Ti separation needed
- Tests on TRU and DGA Resins

TRISKEM INTERNATIONAL

5.1 Selective separation of Scandium

- D_W values on DGA Resin – HNO_3



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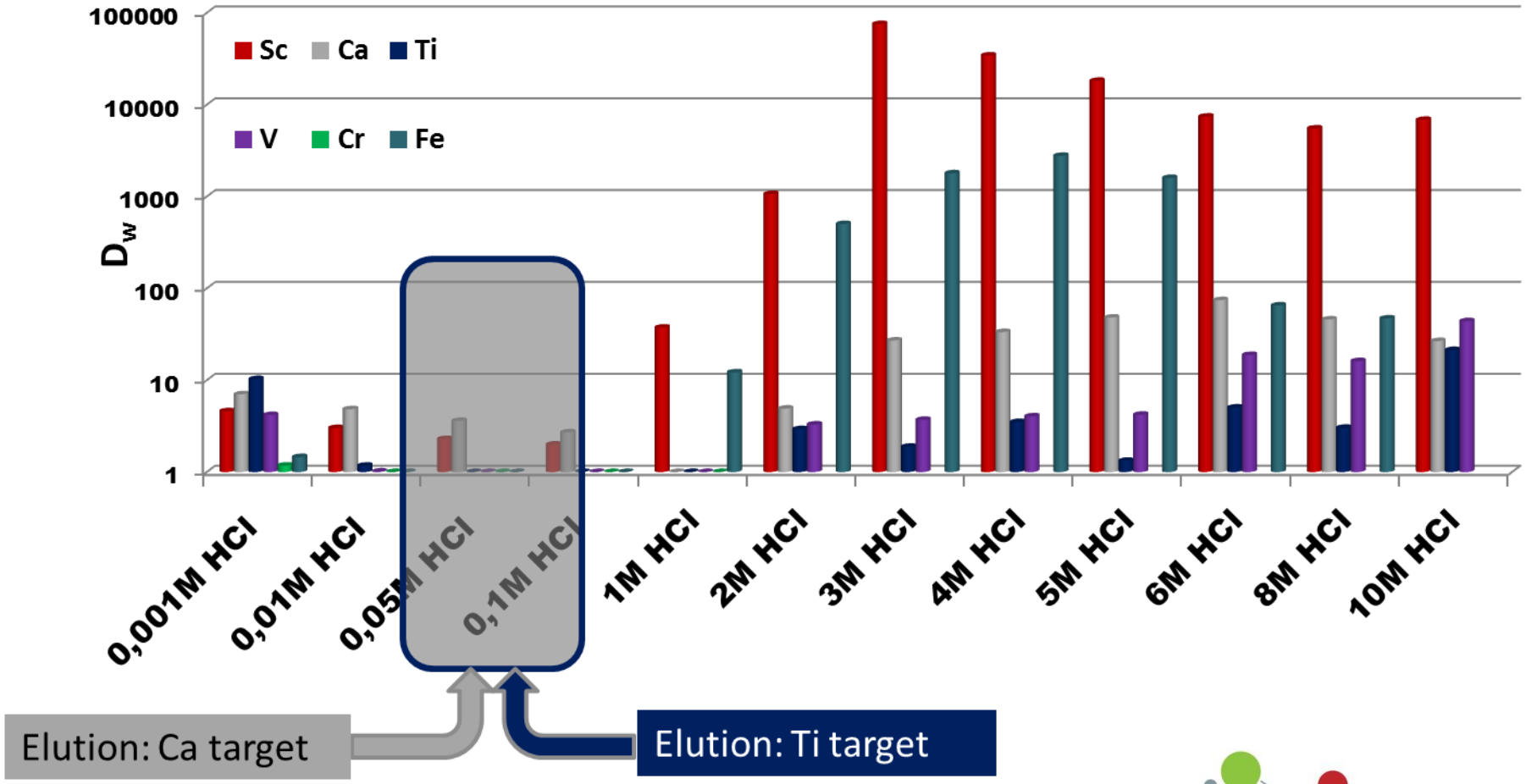
5.1 Selective separation of Scandium

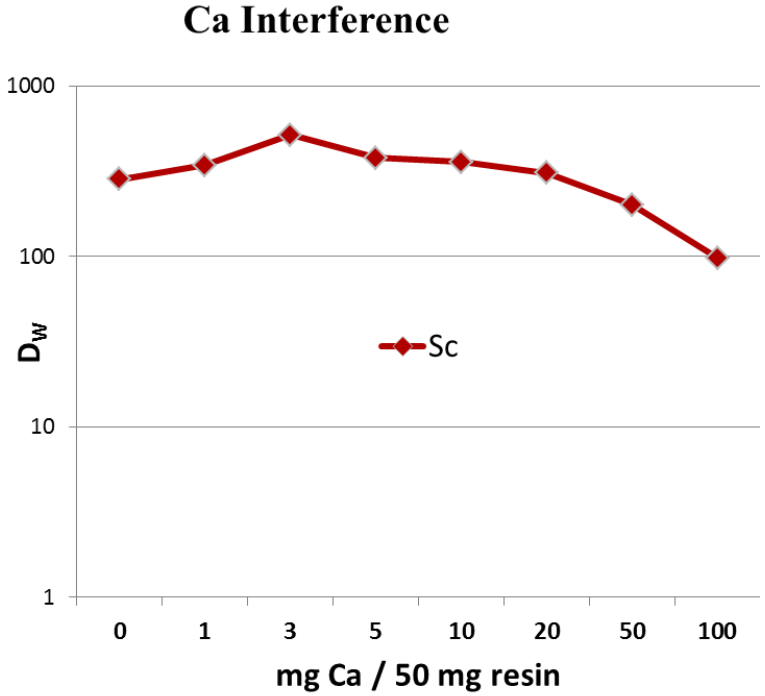
- D_W values on DGA Resin – HCl

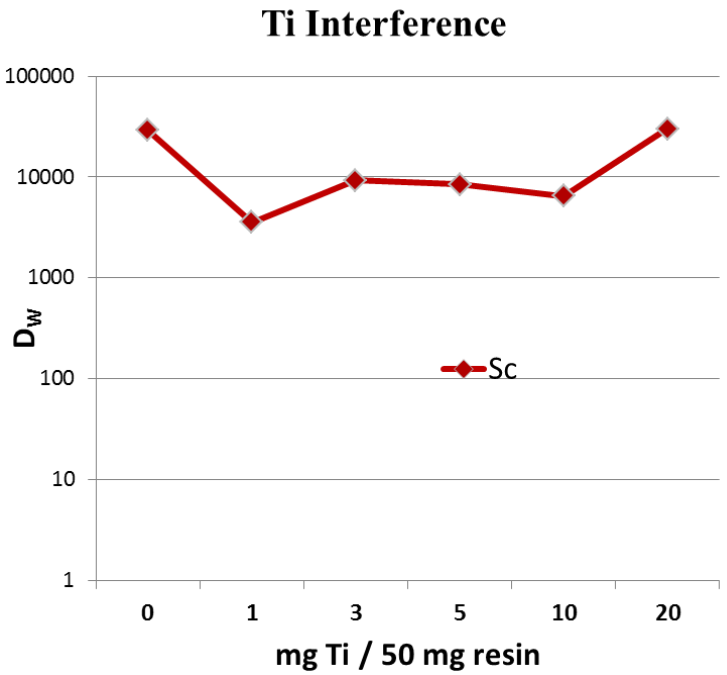


TRISKEM INTERNATIONAL

5.1 Selective separation of Scandium

- Interference from target materials - DGA Resin - 0.1M HNO_3



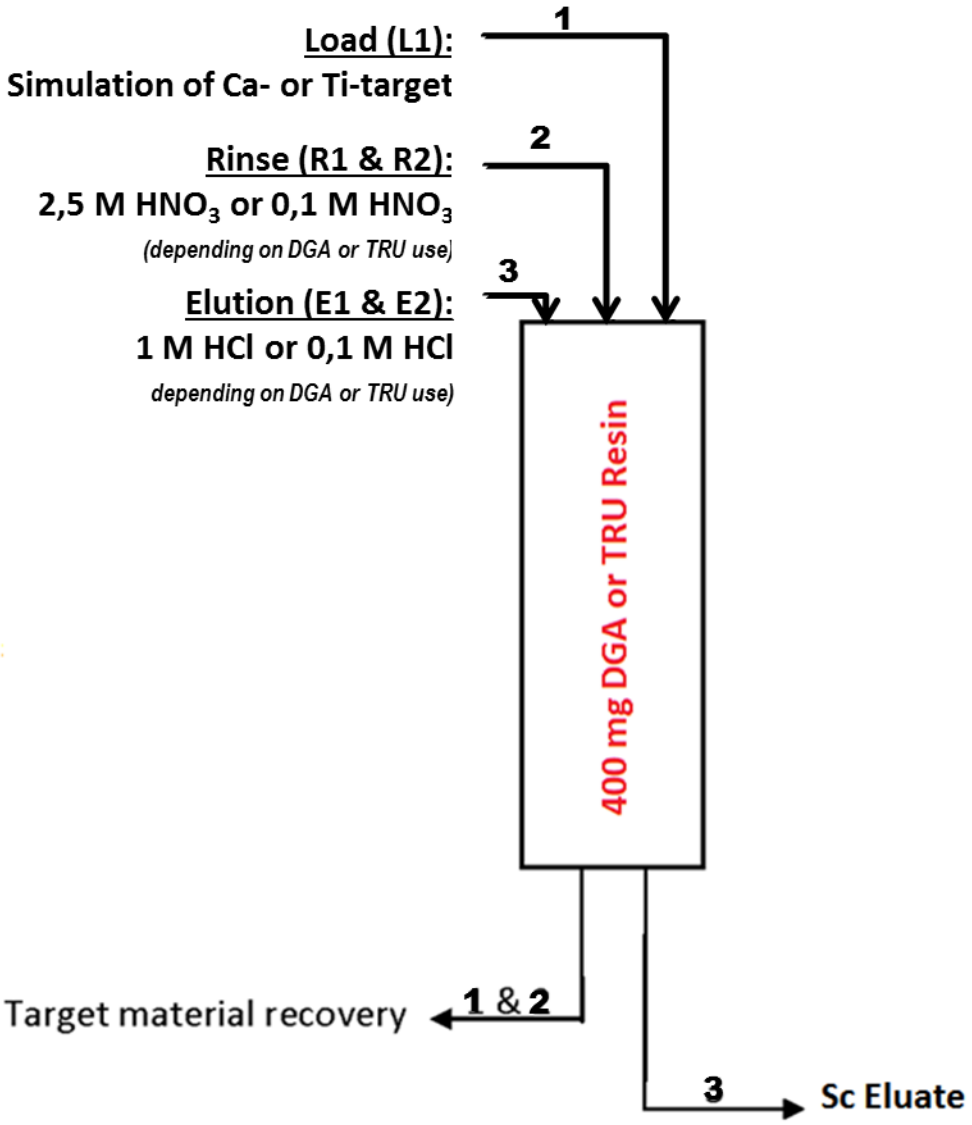


- Stable, high D_w Sc in HNO_3
- No impact on Sc uptake from Ca or Ti even when present in high amounts
- **Interferences are negligeable**

TRISKEM INTERNATIONAL

5.1 Selective separation of Scandium

Suggested separation scheme



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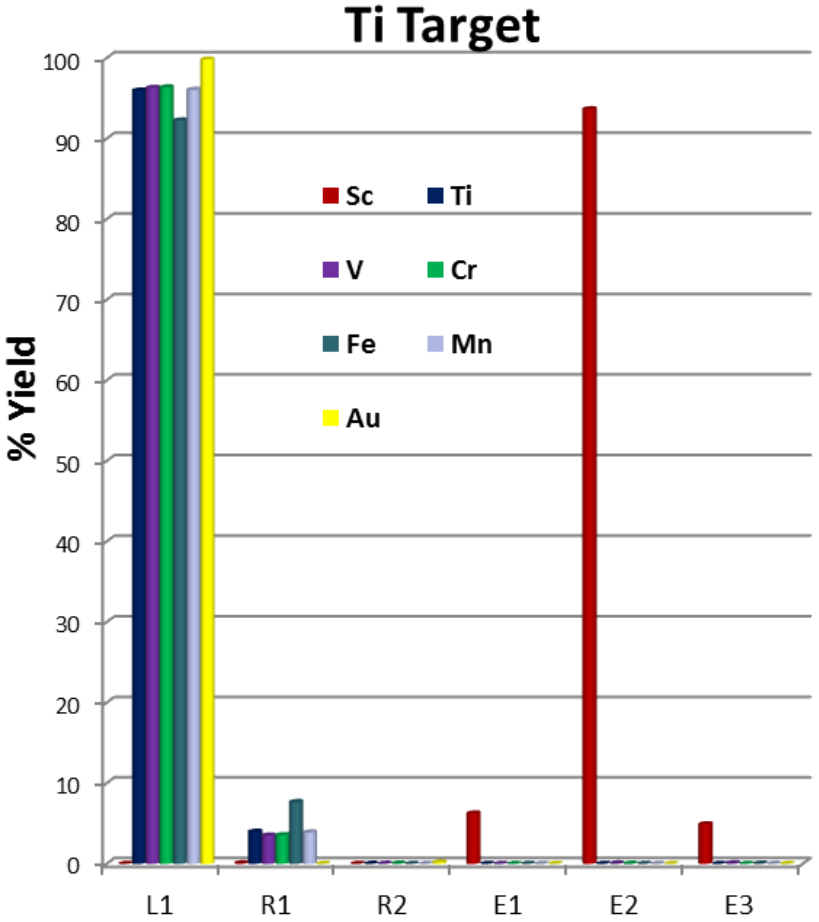
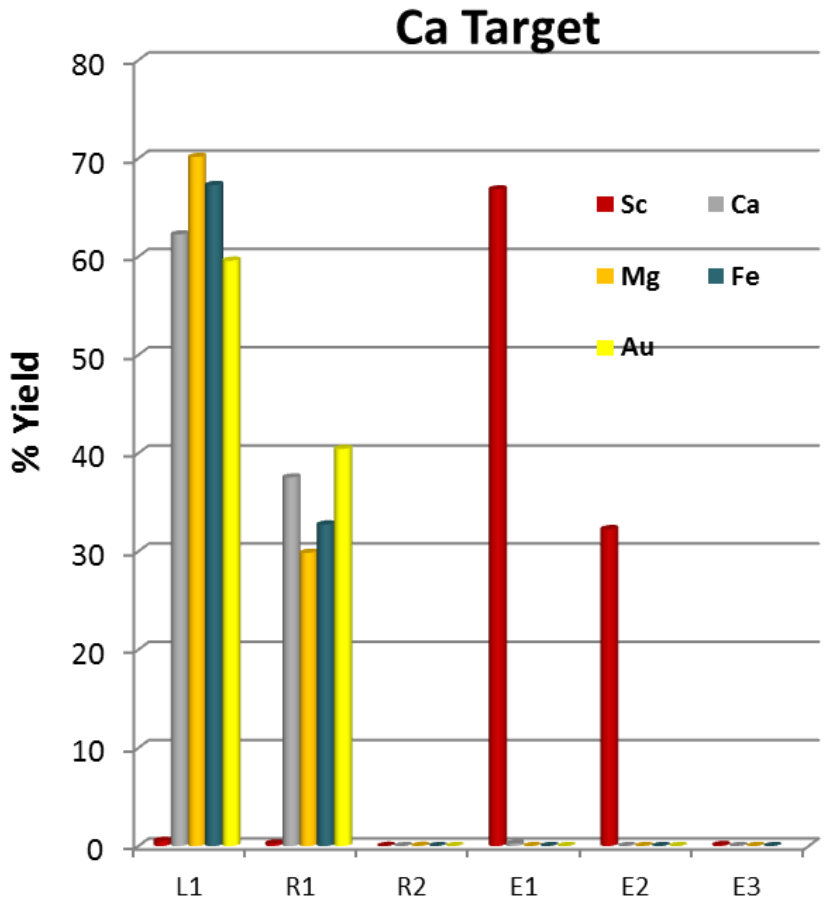
5.1 Selective separation of Scandium

Separation scheme on DGA Resin





L1: 5 mL 2.5 M or 0.1 M HNO_3

R1 / R2 : 2 x 5 mL 2,5 M or 0.1 M HNO_3

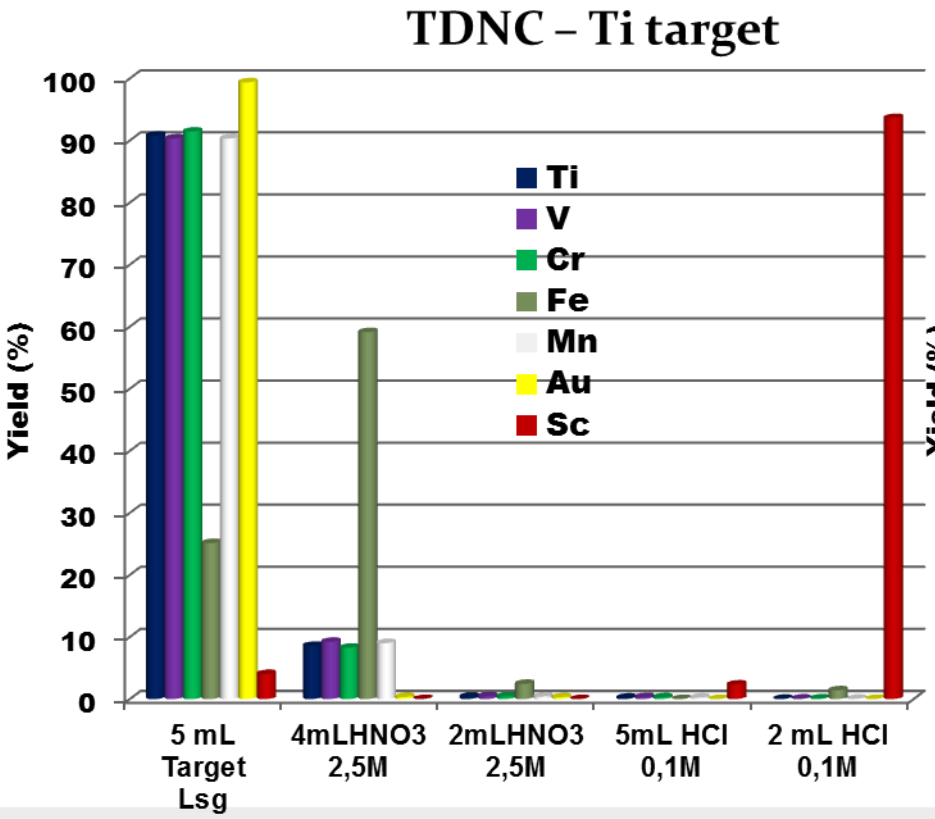
E1 / E2 / E3 : 3 x 5 mL 0.1 M HCl

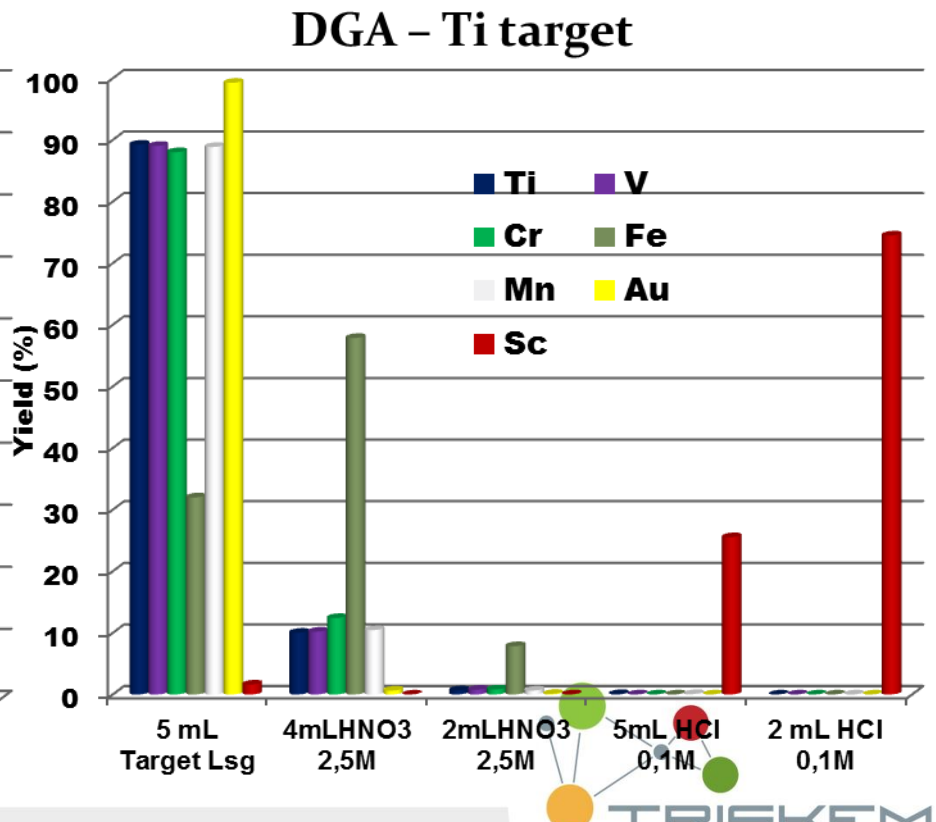
TRISKEM INTERNATIONAL

5.1 Selective separation of Scandium

tests on nanotubes

- Same experiments done on DGA-nanotube Resin (TDNC) to compare impact of the support
- TDNC vs. DGA on Ti Target:





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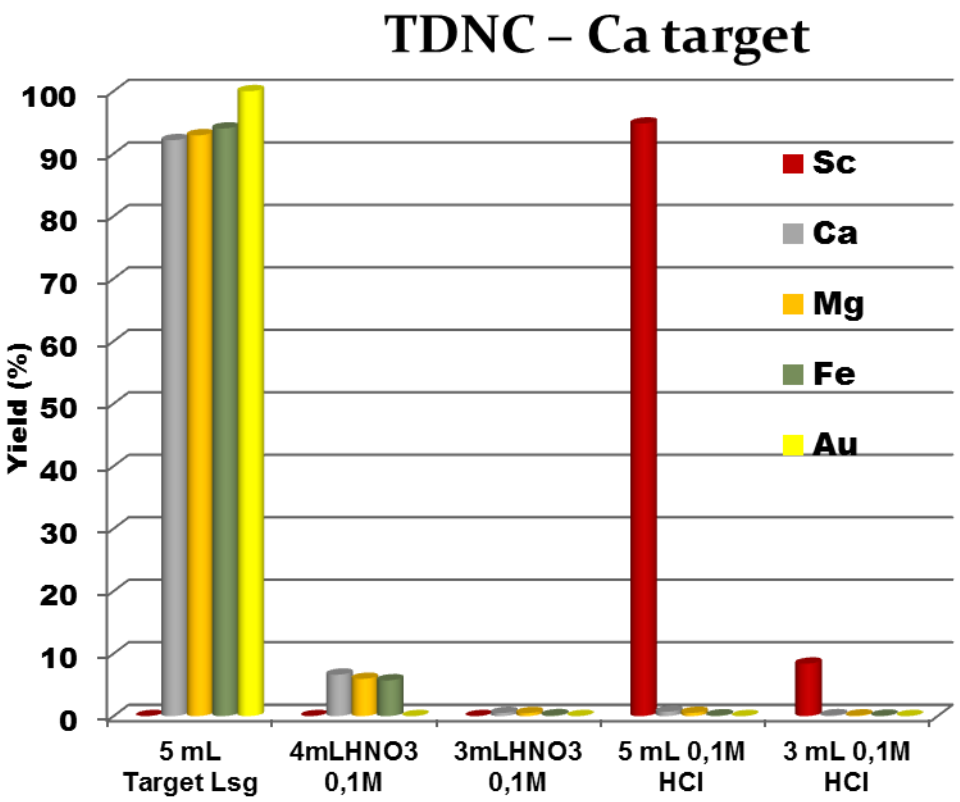
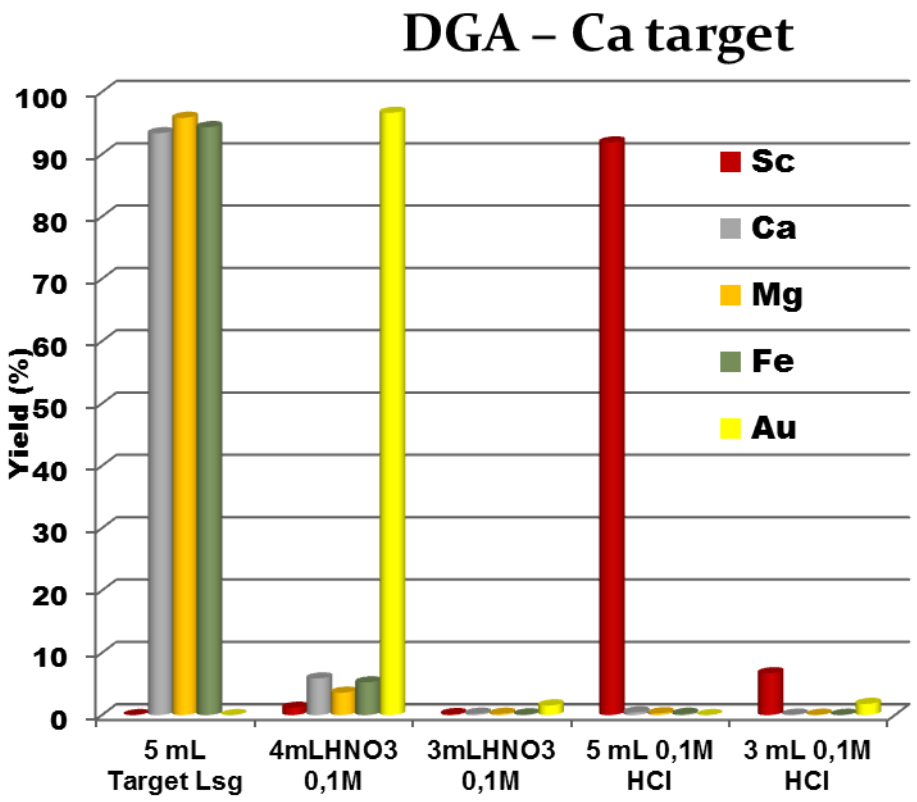
5.1 Selective separation of Scandium

tests on nanotubes

- TDNC vs. DGA on Ca Target:





TRISKEM INTERNATIONAL

5.1 Selective separation of Scandium

Conclusions

- High selectivity for Sc on both DGA and TRU Resins
- Interferences are negligeable for Ca and Ti
  - TRU Resin: **strong Ti interferences for 2mg Ti /50mg**
- High Decontamination factors
- Fast kinetics
- Quantitative elution of Sc: **chemical yield Sc >98%**
- High purity of Sc fraction
- Ca and Ti can be quantitatively recovered small volumes (5-10mL)
- Use of nanotubes gives comparable results to standard resins

TRISKEM INTERNATIONAL

5.1 Selective separation of Scandium

Future works

- COT analysis of Sc fraction
- Recovery of Ti for preparation of new targets
- Flow rate optimisation
- Irradiation of Ca- and/or Ti-targets
- Radiolysis stability of DGA

TRISKEM INTERNATIONAL

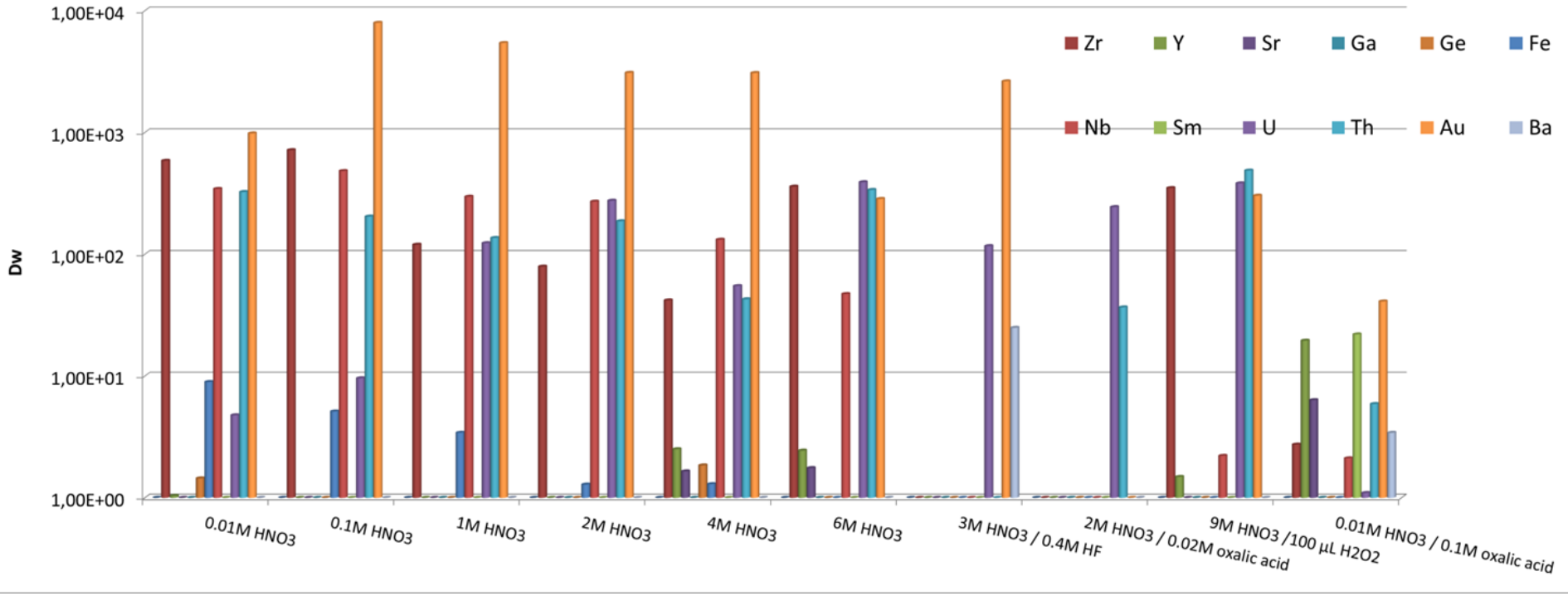
5.2 Selective separation of Zirconium-89

- Half-life: 78,4h
- β^+(22.7%), ε(73.3%) et γ(~100%)
- Production *via* ^{89}Y (p, n) ^{89}Zr or ^{89}Y (d, 2n) ^{89}Zr
- Application i.e. immuno-PET
  - monoclonal antibodies, mAbs
- Tests done on UTEVA Resin

TRISKEM INTERNATIONAL

5.2 Selective separation of Zirconium-89

- D_w values on UTEVA Resin - HNO_3



- Zr uptake generally high in HNO_3
- Oxalate and fluoride interfere with Zr uptake

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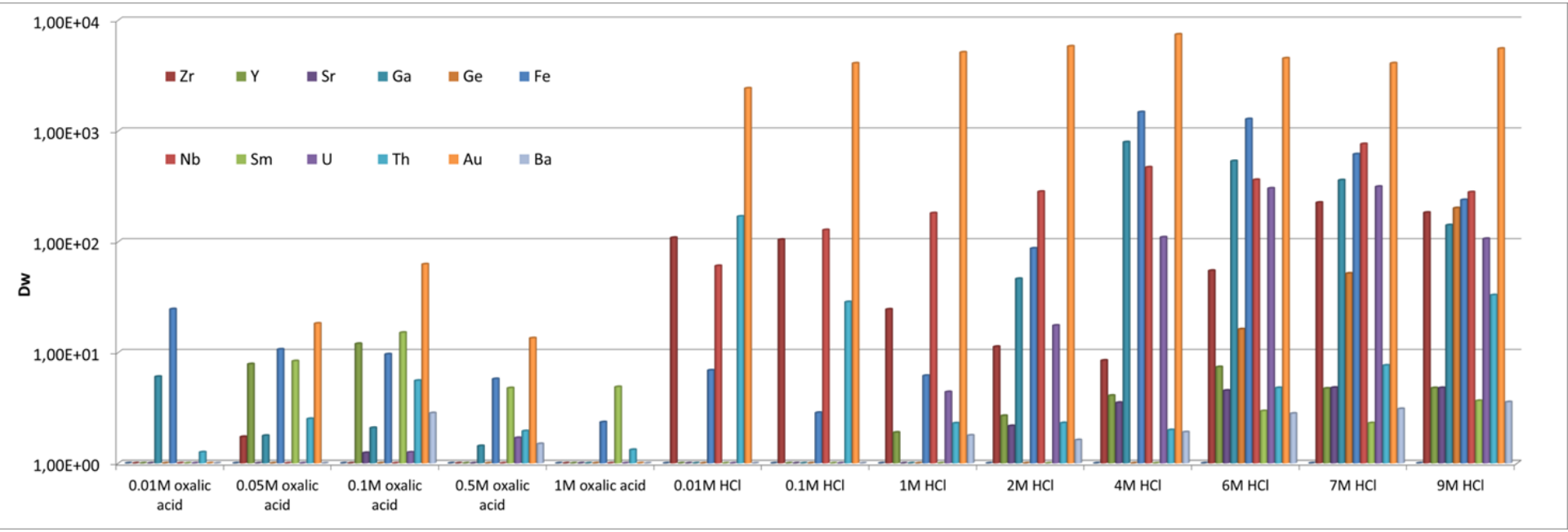
5.2 Selective separation of Zirconium-89

- D_w values on UTEVA Resin – HCl and oxalic acid



- Zr uptake high for high HCl
- Oxalate well suited for elution

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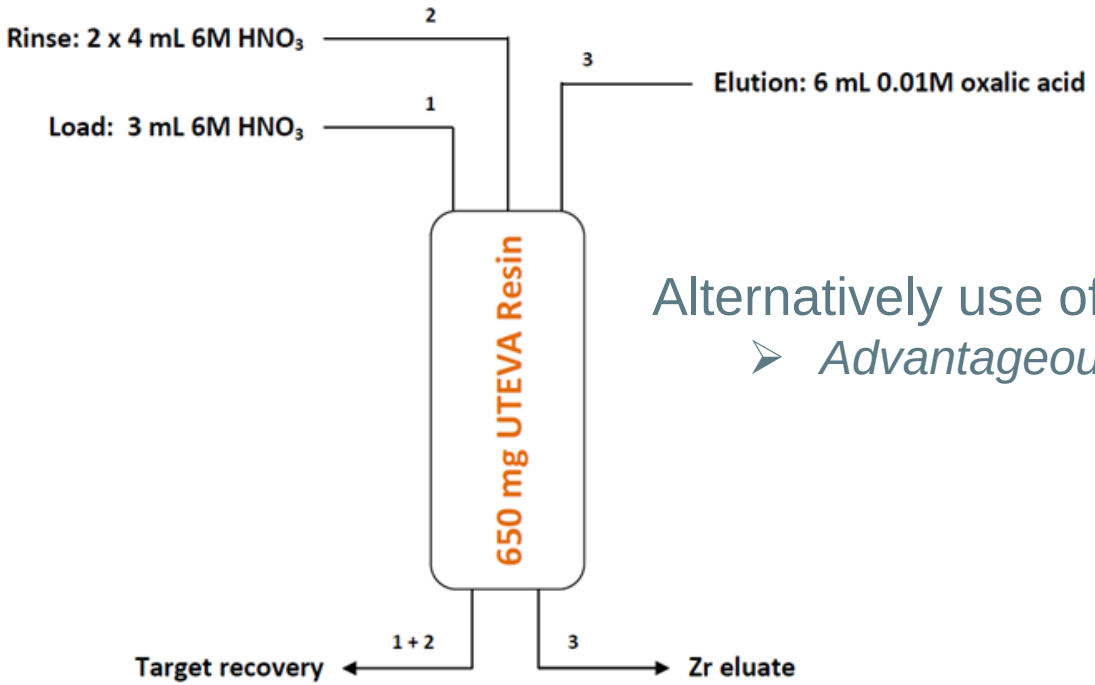
5.2 Selective separation of Zirconium-89

- Results:



Alternatively use of high HCl concentrations

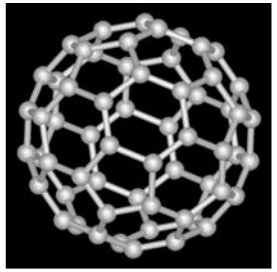
- ➢ *Advantageous for some matrices*

- Method optimisation *via* elution study
- Zr chemical yield (6 mL 0.01M oxalic acid): ≥ 93%
- High decontamination factors: > 100 000 for Y, Sr, Fe, Ba
- UTEVA also used for ^{90}Nb (Radchenko et al.)

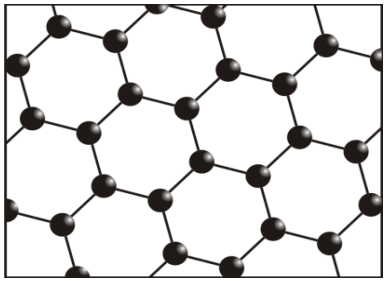
TRISKEM INTERNATIONAL

5.3 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**



Fullerene C_{60}
http://fr.wikipedia.org/wiki/Fuller%C3%A8ne



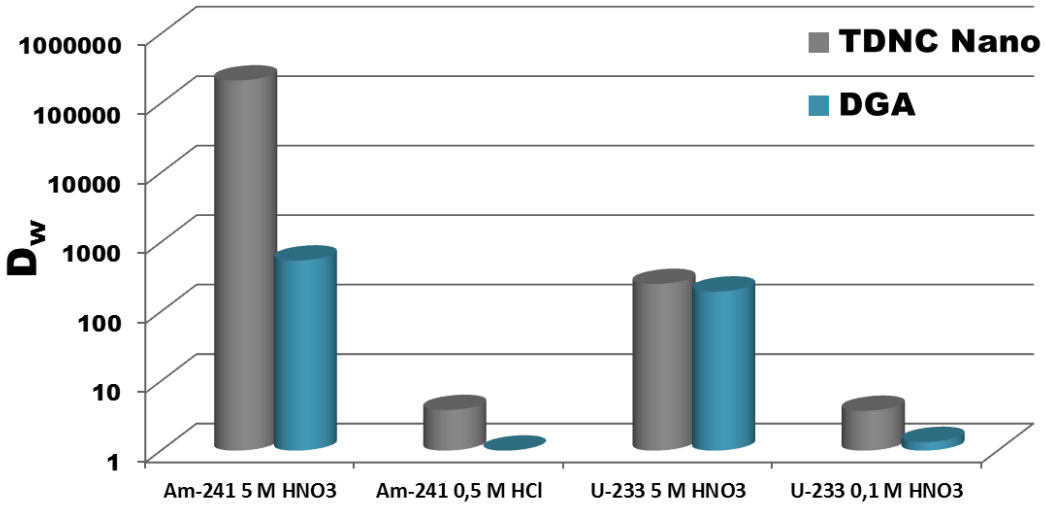
Graphene
(http://fr.wikipedia.org/wiki/Graph%C3%A8ne)

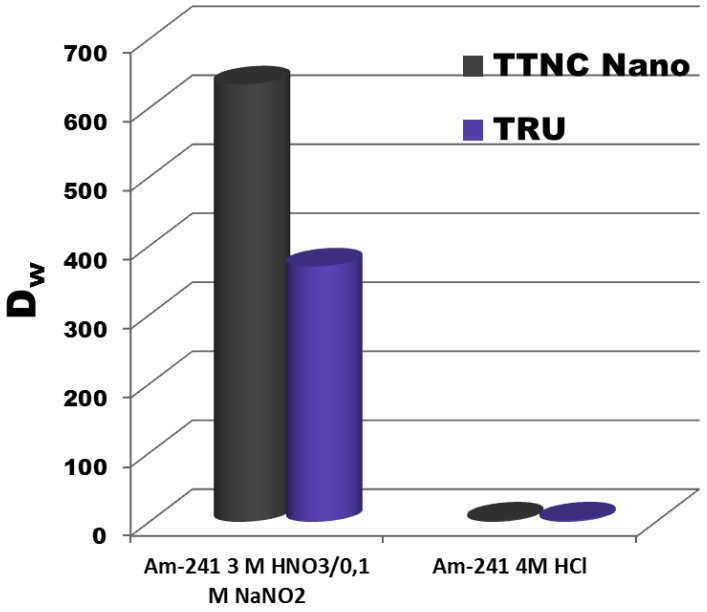
[a] H.W. Zhu, C.L. Xu, D.H. Wu, B.Q. Wei, R. Vajtai und P.M. Ajayan,Science 2002, 296, 884.

TRISKEM INTERNATIONAL

5.3 Use of Carbon nanotubes

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





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

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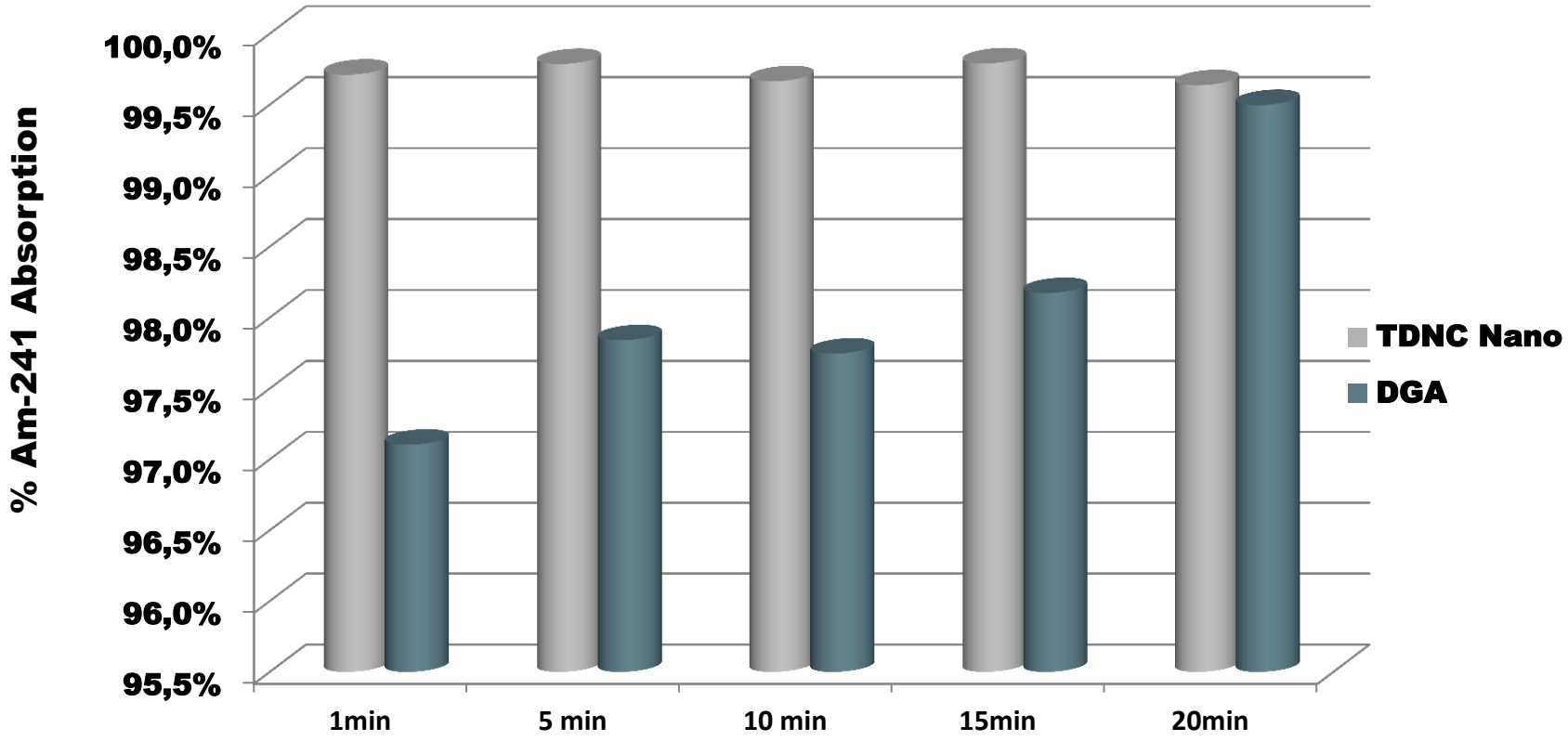
5.3 Use of Carbon nanotubes

Kinetics: TDNC vs. DGA



Nanotubes: near quantitative absorption after ~ 1min

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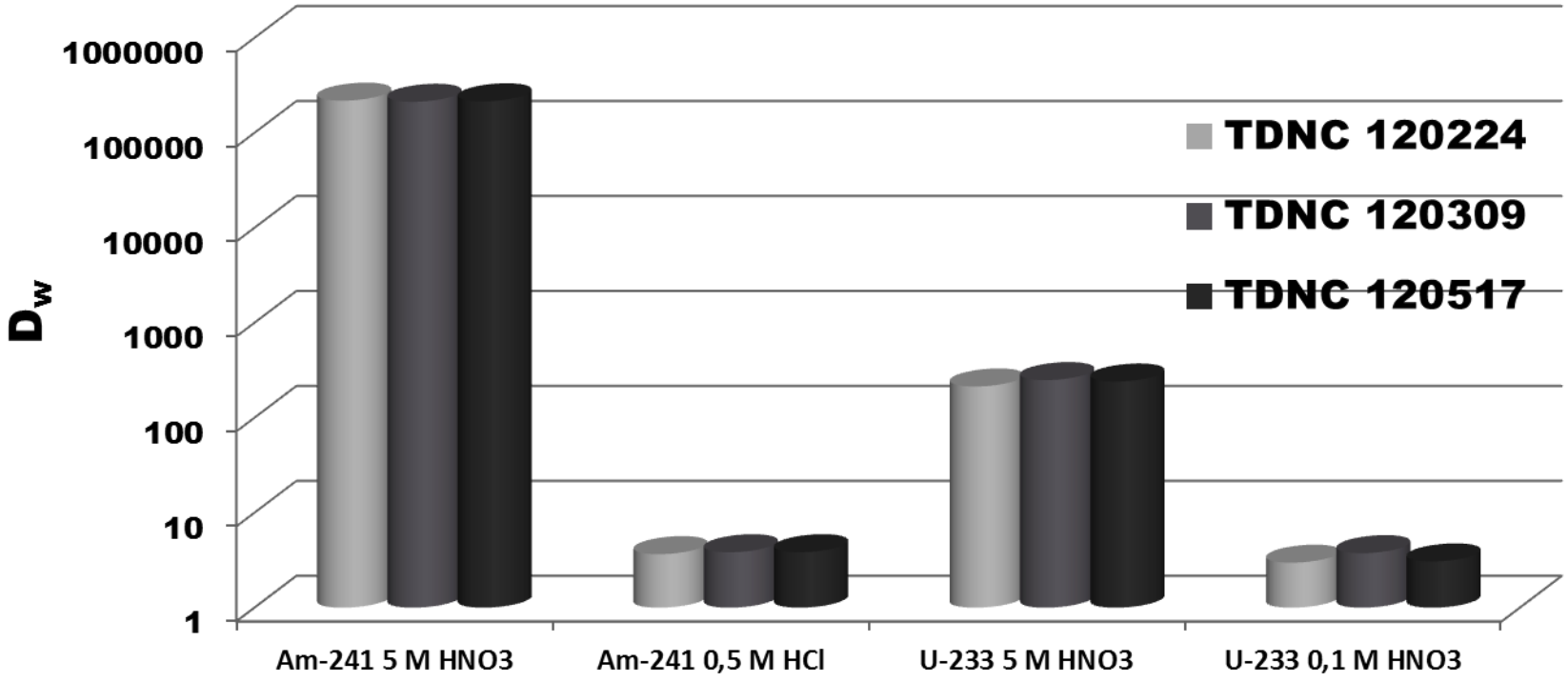
5.3 Use of Carbon nanotubes

- Coating reproducibility of DTNC



- **Coating is reproducible**

TRISKEM INTERNATIONAL

5.3 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

TRISKEM INTERNATIONAL

5.4 Gallium separation

- **Ga-68** and **Ga-67** frequently used in **radiopharmacy**
  - Ga-68: b^+: 88.88(41)%, e:11.11(41), $T_{1/2}$: 67.83(20) min; PET
  - Ga-67: e: 100%, g, $T_{1/2}$: 3.2613(5) d; SPECT
- **Ga-68** obtained from **Ge-68/Ga-68 generator**
  - Elution typically with 0.1M HCl, rarely 5M HCl
  - Removal of Ge, Zn and Fe from generator eluates necessary
- **Ga-67** obtained from **irradiated Zn targets**
  - Rapid method for Ga/Zn separation
  - Robust against Zn interference
- Several resins tested
  - Determination of D_W values
  - Elution studies
- **Best results obtained with LN resin**

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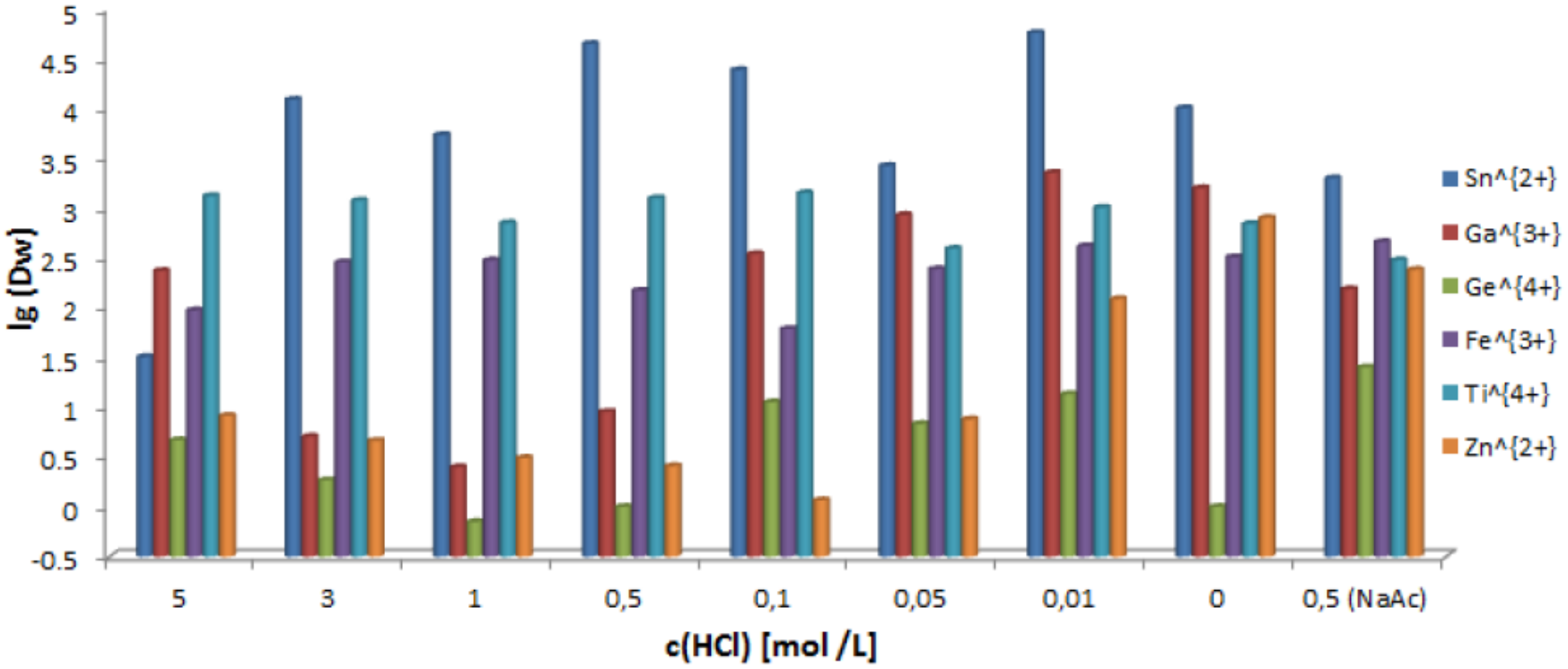
5.4 Gallium separation

D_W values of selected elements on LN resin

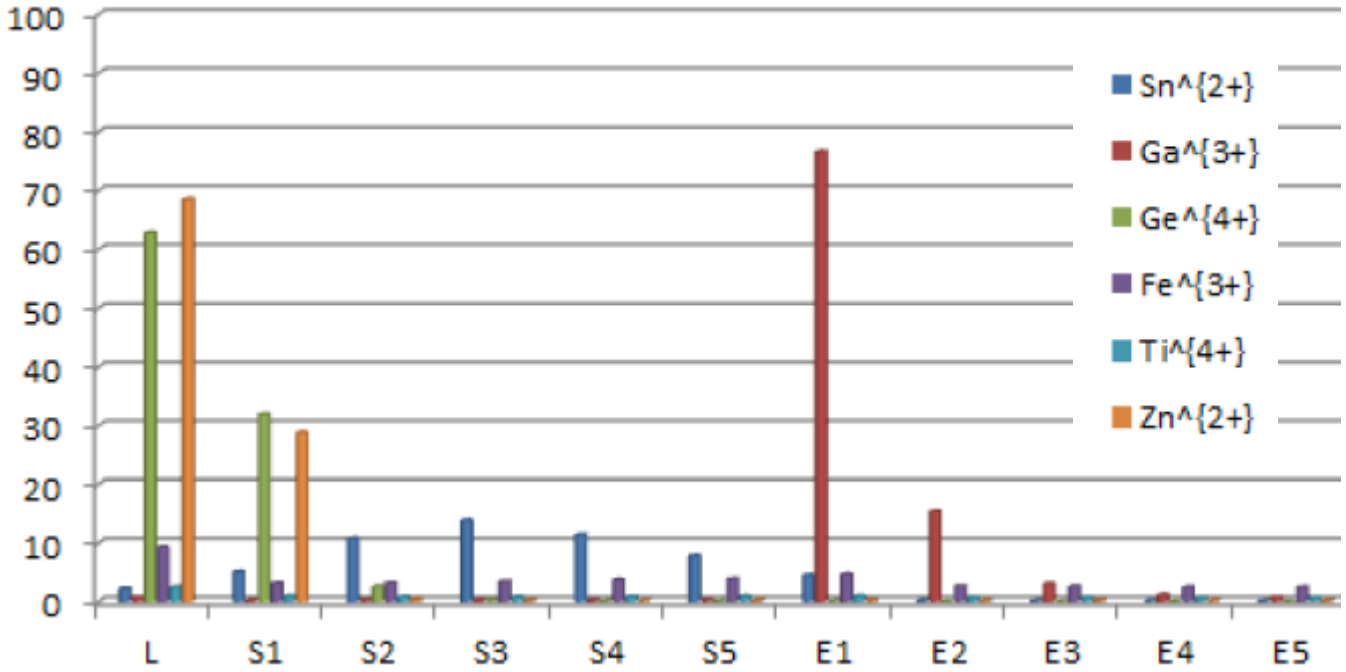


- High D_W values for Ga at high (5M) and low (≤ 0.1M) HCl concentrations
- Low selectivity for Ge and Zn, selectivity generally high for Fe
- **Ga elution possible with 0.5M or 1M HCl**
- **Low selectivity for Zn in high HCl – interesting for Ga-67 production**

TRISKEM INTERNATIONAL

5.4 Gallium separation

Elution study – LN resin – Load from 5M HCl



- **Load:** 5 mL 5M HCl; **S_N:** 2 mL 5M HCl; **E_N:** 2 mL 1M HCl
- All fractions collected and analysed by ICP-MS
- Suitable selectivity, **Ga elution in 4 mL 1M HCl**

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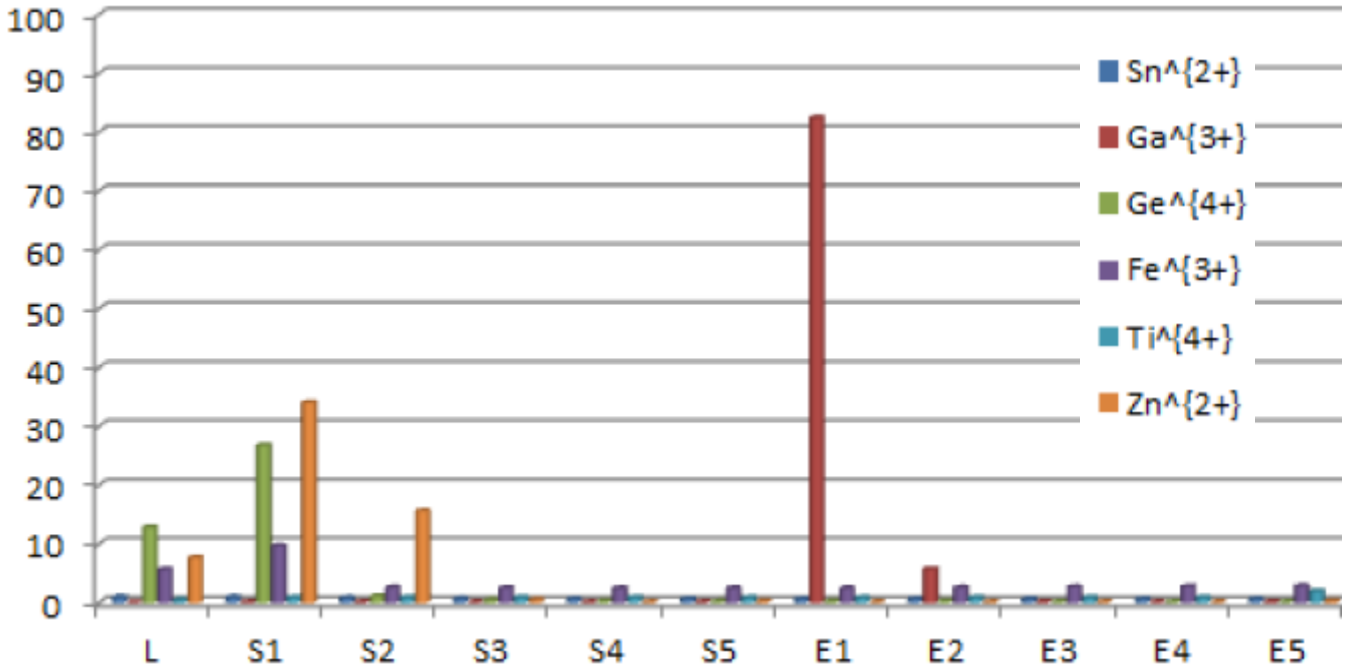
5.4 Gallium separation

Elution study – LN resin – **Load from 0.1M HCl**



- **Load**: 5 mL 0.1M HCl; **S_N**: 2 mL 0.1M HCl; **E_N**: 2 mL 1M HCl
- All fractions collected and analysed by ICP-MS
- Suitable selectivity, near **quantitative Ga elution in 2 mL 1M HCl**

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6. Upcoming new resin : TK100/1

7. Upcoming new resin : TBP Resin

=> Specific presentations during this meeting

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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
- Radiolysis stability
- …

- Very interested in R&D collaboration with you

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Thank you for your attention!

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