# News TrisKem

- Update CL resin
- Update CU resin
- Cs resins
- RaNucfilm discs
- Rapid method for the determination of Pb-210
- Other on-going work

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# Determination of Cl-36 / I-129 using CL resin

- CL resin originally planned for Pd separation
  - Method testing still on-going
  - Also showing high Ag uptake
- Halogen separation on $Ag^+$ loaded CL resin
- Sample loading
  - Acidic, neutral or slightly alkaline conditions
    - Might need to be done under reducing conditions
  - Original paper: water/effluents and leached solid samples
  - Iodine retention even in presence of very large excess of chloride (e.g. sea water)
  - Especially in case of iodine: load from elevated sample volumes at elevated flow rate
    - Example: 3g CL resin (plus 4g XAD-4 resin), > 10 L radioactive process effluent (1M $HNO_3$), flow rate up to 180 mL/min, iodine uptake: 85 – 95% (DOI: 10.1007/s10967-013-2503-1)

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. Radanal Nucl Chem, 286(2), 539-546

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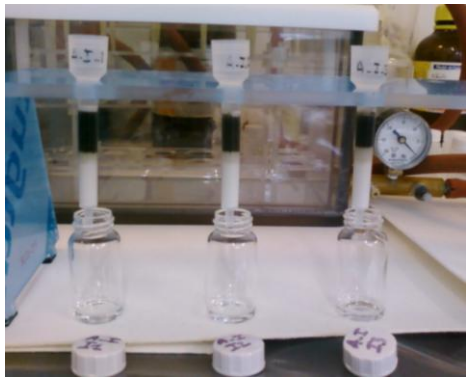
# Determination of Cl-36 / I-129 using CL resin

- Rinse with 10ml of deion. Water
  - Eliminates matrix elements
- Elute chloride with 5ml of 0.1M $SCN^-$,
  - Directly mixed with LSC cocktail and counted
- Rinse with 10ml of 1% NaOH
  - Increases iodide yield
- Elute iodide with 5ml of 0.35M $Na_2S$, mix with LSC cocktail
  - Fume hood…
  - Directly mixed with LSC cocktail and counted
- Yields in general > 90 - 95%
- Updated method uploaded in a few days
  - Modified Ag loading of the CL resin column
- Larger solid samples?



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# Pyrolyser method


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)

- 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 (1ml water)
- Decomposition products trapped in bubbler containing alkaline solution
  - 6 mM $Na_2CO_3$ used (yield > 80%)

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# Pyrolyser method


- Bubbler connected directly with furnace via glass connector
  - Avoid losses due to condensation in tubing
- $^{36}Cl$ separated via $Ag^+$ loaded Cl resin
  - Separation similar to standard method, but bubbler solution loaded directly onto column
  - When loading column directly from 6 mM $Na_2CO_3$ additional rinsing with 0.1M $H_2SO_4$ necessary for improved C-14 decontamination (« modified wash »)
- Similar method currently tested for iodide

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# Pyrolyser method

- Decontamination factors $D_f$:

| | $^{36}Cl$ 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 Cl-36 / I-129 separation
- Cl-36 separation yield > 95%

- Analysis of spent resin

| Sample type | Expected value | Measured value |
|---|---|---|
| Ion exchange resin | 4.1 kBq | $4.3 \pm 0.1$ kBq |

- Good agreement

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

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# Cu-64/7 separation on CU resin

- 350 mg columns allow for Cu elution in small volume
- Load rinse pH 2 (HCl)
- Vacuum assisted flow, rapid separation
- Quantitative recovery of Cu in 1 – 1,5 mL 8M HCl
  - Cu  yield > 90% in 1 mL 8M HCl
  - 97,6% ± 2,3% (k = 1, N=25) in 1.5 mL 8M HCl
- Pure Cu fraction
  - $D_f$ (ICP-MS)
  - $\gamma$-spectrometry
- Obtained Cu suitable for labelling (ARRONAX)
- Ni recovered in small volume of 8M HCl
  - 10 – 13 mL load and rinse
  - Further purification for reuse e.g. via diect load on AIX

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# Conversion of Cu eluate

- Aim: recovery of Cu in small volume of dilute HCl, water or NaCl solution
- Anion exchange resins (AIX) shows necessary selectivity
- Cu eluate (1 – 1,5 mL 8M HCl) from Cu resin column directly loaded onto small AIX column
- Rinse with 8M HCl
- Elution with deion. Water
- Cu yield > 90%; add. decontamination (Ni, Zn, Au, organics)

- Overall separation time (full method): <10 minutes

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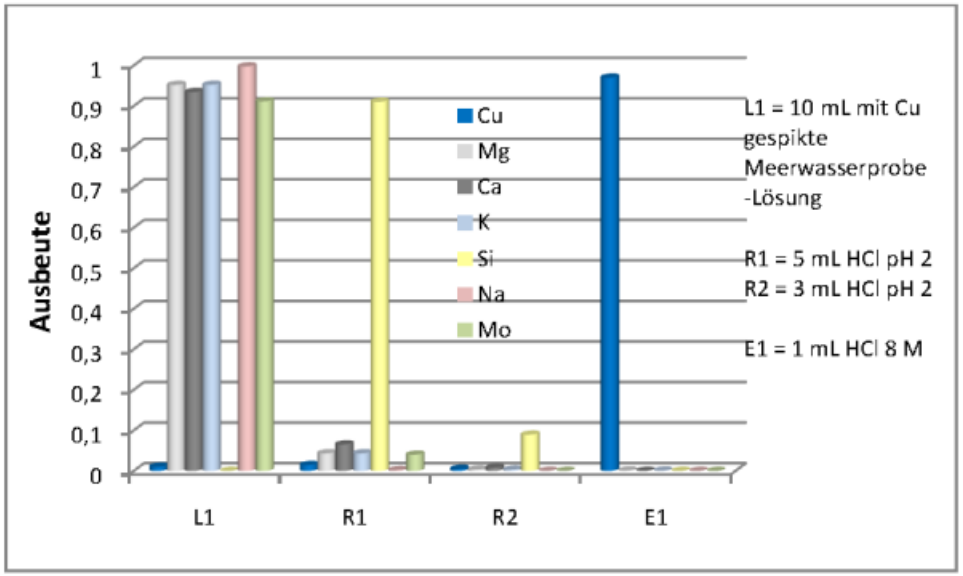
# Other applications

- Removal of trace Cu-64 before Ni-64 plating[+] / Zn-64 recycling[*]

[+] Thieme et al. Module-assisted preparation of 64Cu with high specific activity. , Applied Radiation and Isotopes, 70, 2012, Pages 602-8

[*] Thieme et al. High specific activity $^{61}$Cu via $^{64}$Zn(p,α)$^{61}$Cu reaction at low proton energies, Applied Radiation and Isotopes, 72, 2013, Pages 169–176

- Cu concentration and purification for analytical purpose (e.g. Cu in sea water)




- 10 mL sea water (pH 2.3)
- Cu yield > 95% in 1 mL 8M HCl
- Pure Cu fraction

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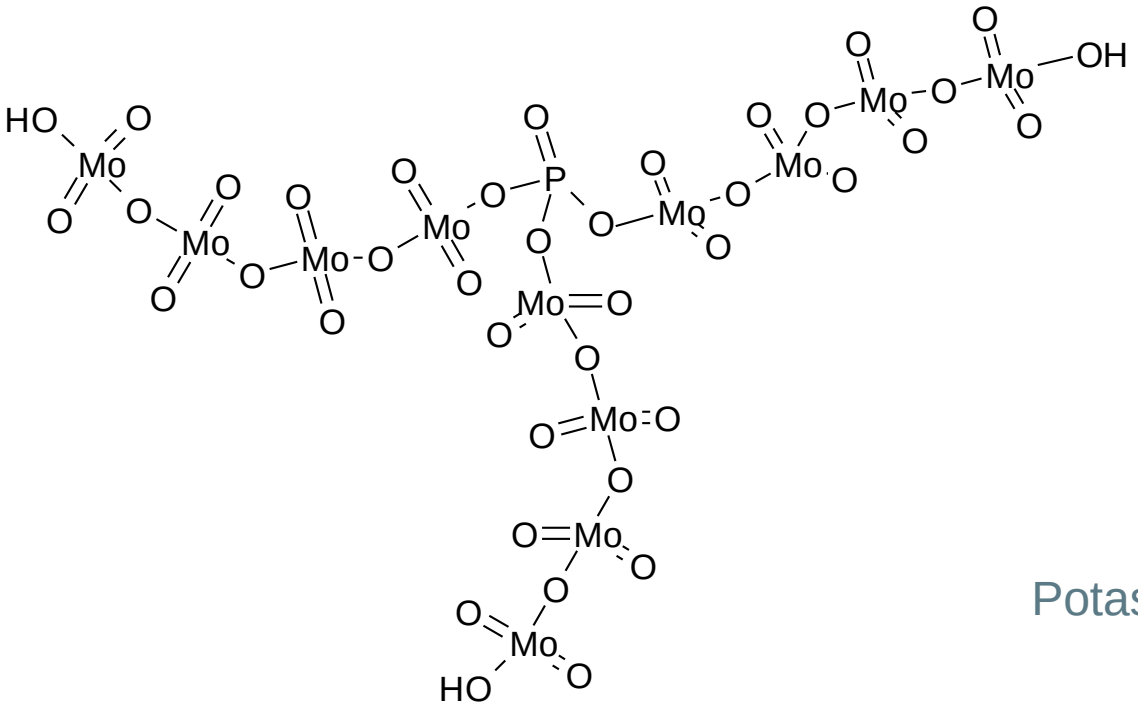
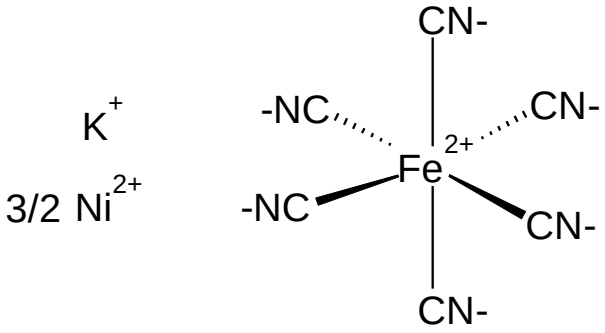
# Cesium Resins

AMP-PAN and KNiFC-PAN developped by Dr Sebesta from CVUT

- AMP and KNiFC known to strongly bind Cs



**A**mmonium **M**olybdo**P**hosphate




Potassium(**K**) **Ni**ckel **F**erro**C**yanate

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# Cs Resins

AMP-PAN and KNiFC-PAN developped by Dr Sebesta from CVUT

- AMP and KNiFC known to strongly bind Cs

| | AMP-PAN | KNiFC-PAN |
|---|---|---|
| **Dynamic Capacity*** | 64 mg Cs/g dry resin[3] | 256 mg Cs/g dry resin[4] |
| **Density** | 0.27 g.mL$^{-1}$ | 0.20 g.mL$^{-1}$ |
| **Radiation resistance** | $10^6$ Gy | NA |
| **Use** | Acidic to neutral media (nuclear effluent waste, environmental) | Slightly acidic, neutral (environmental samples) |

*Dynamic Capacity, $DC = \frac{([Cs^+]_0 - [Cs^+])V}{M}$ with

V=volume at a specified breakthrough of Cs (liters),

$[Cs^+]_0$= initial Cs concentration (g.l$^{-1}$)

M=mass of sorbent (dry weight, grams)

$[Cs^+]$=Cs concentration in column effluent (g.l$^{-1}$)

[3] 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

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

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# Cs Resins Properties

- AMP-PAN:
  - Sample load in acidic media
  - Elution of Cs from AMP-PAN
    - with concentrated ammonium salt solutions (e.g. 5M $NH_4Cl$, 5M $NH_4NO_3$)
    - By dissolution and washing out of the AMP with alkaline solutions (e.g. 1 - 5M NaOH)
  - Direct $\gamma$-counting of the Cs fixed on AMP-PAN
- KNiFC-PAN:
  - Sample load in slightly acidic to neutral media
  - Direct $\gamma$-counting of the Cs fixed on KNiFC-PAN

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# AMP-PAN for Cs separation in liquid radioactive wastes[2][5][6][7]

- 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


[5] 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

[6] 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

[7] 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


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# Cs measurements in Seawater [8][9]

- Procedure:
  - Seawater Sample volumes: 100L,
  - Acidified (pH 1-2) and raw samples,
  - Column bed 25ml of AMP-PAN or KNiFC-PAN,
  - Flowrate: maximum at 300ml.min$^{-1}$,
  - Gamma spectrometry measurement

[8] 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

[9] 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

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# Cs measurements in Seawater [8][9]

- Results:

| Resins | Matrix | Chemical Yield in Cs/% |
|---|---|---|
| AMP-PAN | Acidified seawater (pH 1) | 88,1 +/- 3,3 |
| KNiFC-PAN | | 92,9 +/- 1,1 |
| KNiFC-PAN | Raw seawater | 90,2 +/- 2,7 |

  - Both resins can be used with either acidified or non-acidified seawater sample at flow-rate as high as 300ml.min$^{-1}$.
  - At flow-rate of 470ml.min$^{-1}$ on KNiFC-PAN, more than 85% Cs is recovered from a 100l raw seawater sample
  - 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$^{-3}$ for $^{134}$Cs,
    - 0,15 Bq.m$^{-3}$ for $^{137}$Cs.

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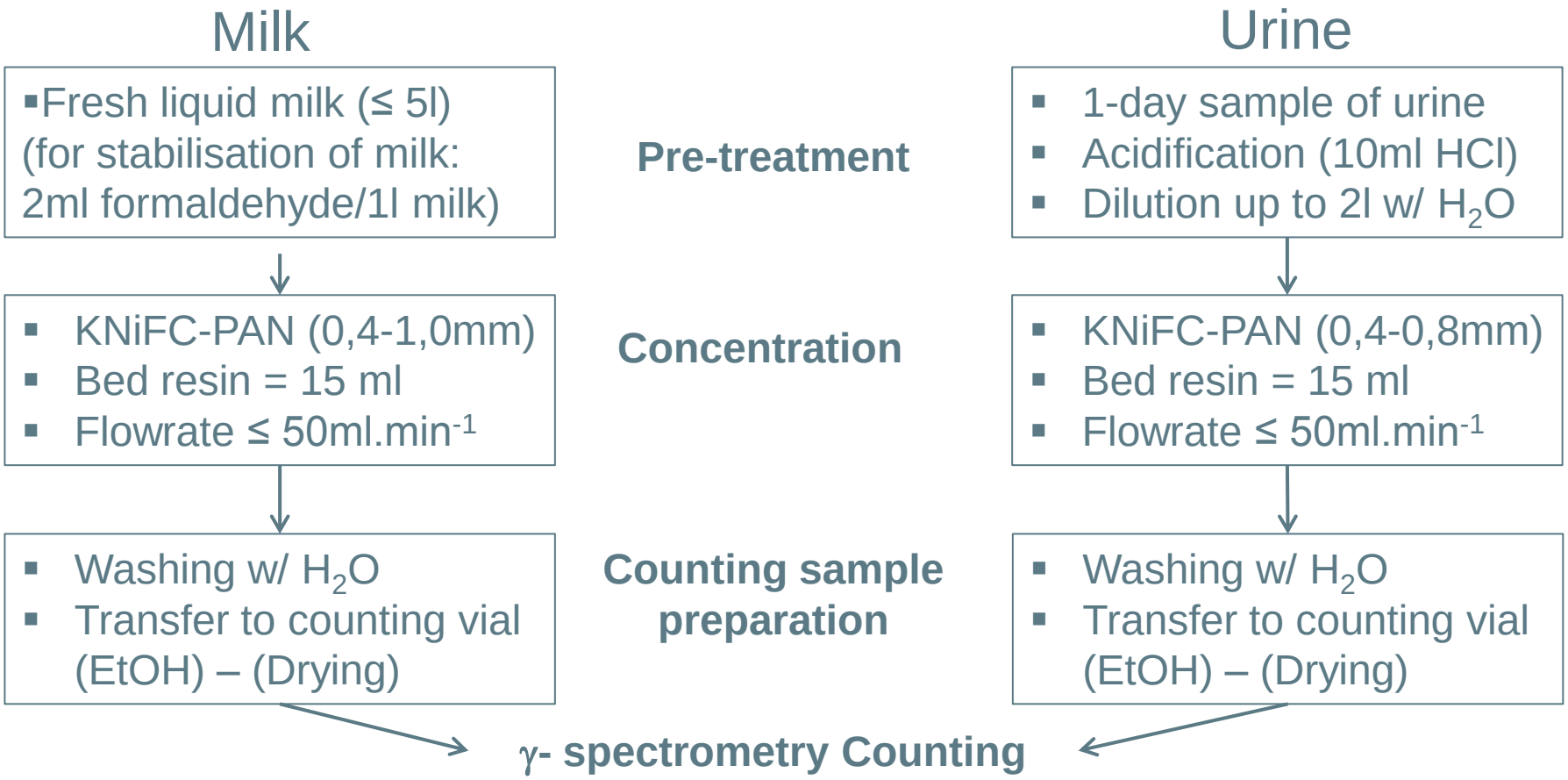
# Cs Measurements in Milk, Urine [10][11]




[10] 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.

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

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# Cs Measurements in Milk, Urine [8][9]

- Results:
  - Chemical yield: ~95% Cs on KNiFC-PAN for both milk and urine,
  - **Milk**: MDA = 2mBq.l$^{-1}$ for $^{137}$Cs in 5l milk sample (HPGe detector, relative efficiency 140%, counting time 600000 s, $\rho$ = 1g.cm$^{-3}$).

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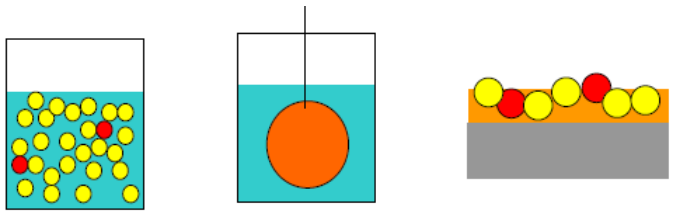
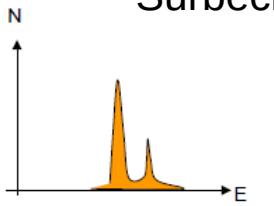
# Ra-226 via Ra NucFilm Discs

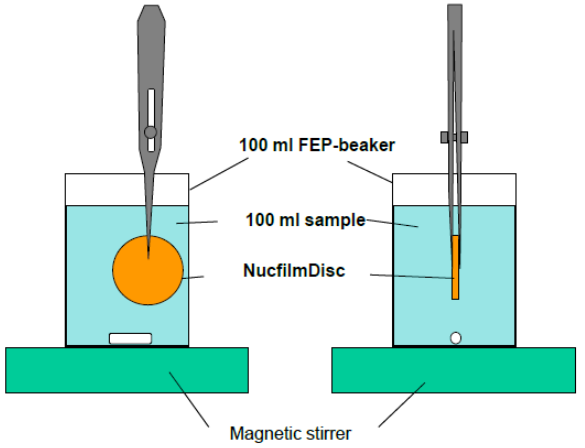
- Thin $MnO_2$ layer on nylon disc
  - Very smooth surface
- Direct Ra extraction from water samples
  - 100 mL
  - Min. 4 – 6h, pH 4 – 8
- Yield via Ba-133
- After rinsing sample ready for $\alpha$-spectrometry
- Yield typically 75 – 90% (depending on matrix)
  - Ca, Ba



Selective adsorption on thin film




Surbeck 2010



# Ra-226 determination 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)
- Measurement of original Ba-133 activity in the solution ($\gamma$-spectrometry)

↓

- Place $MnO_2$ disc in sample holder
- Sir for 10 h

↓

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

↓

- $\alpha$-spectrometry

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

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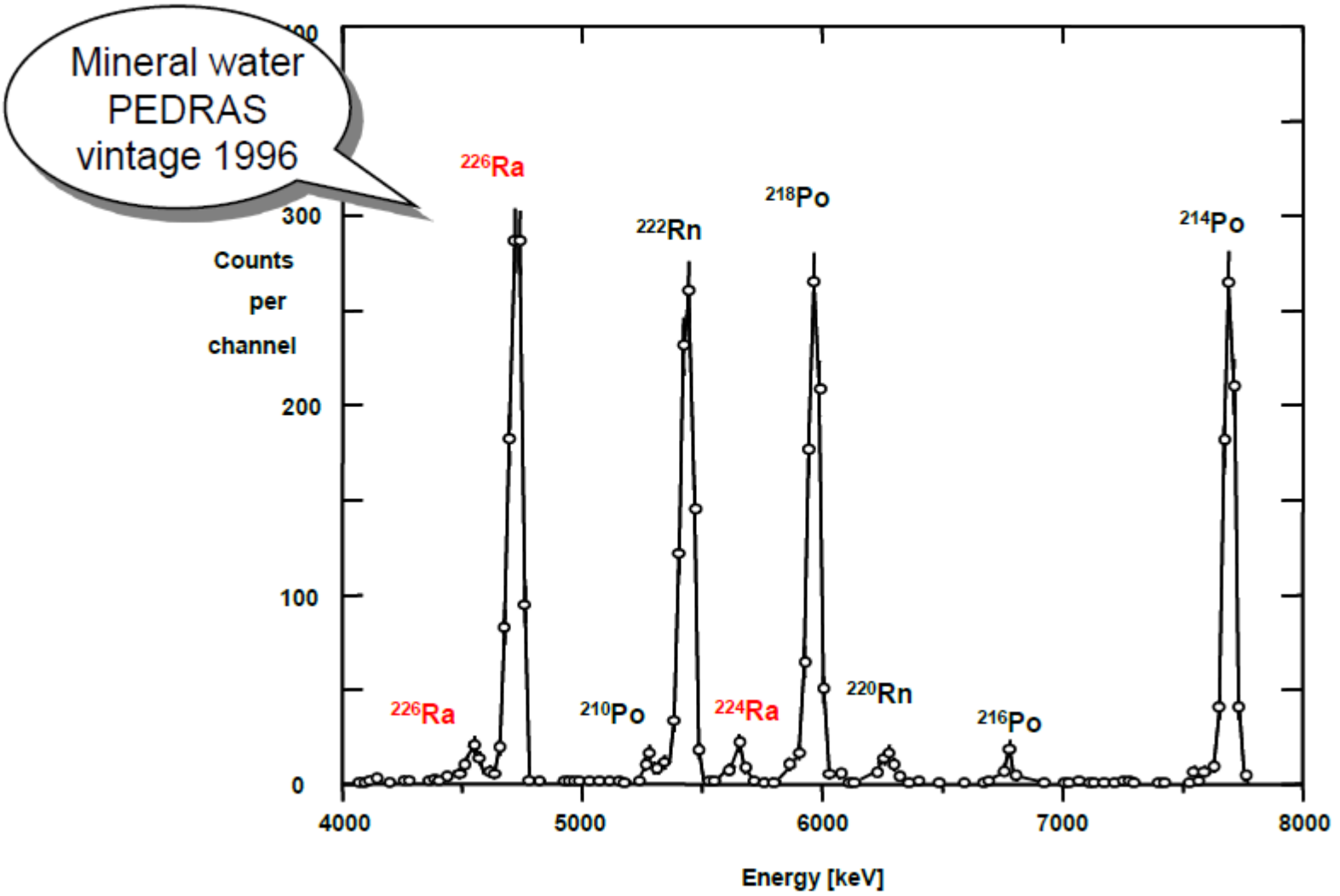


Surbeck 2010

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# Rapid method for the determination of Pb-210 in water samples

- On-going work
- Original project: Rapid extraction and separation of Sr from water samples (pH5–8)
  - « Passive sampling »
    - Use in DGT (Diffusive gradients in thin-films) units
    - Weakly bound/complexed species (« bioavailability »)
    - Technique also used in NORM monitoring
      - Ra-226 via $MnO_2$ (resin and Ra Nucfilm discs), U
  - Rapid method
    - Concentration and separation on same resin/column
    - Load in batch, disc or column mode

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# First application tests

- Elution study 1L sample (column experiment)
  - pH7, 1 mg Sr, 100 mg Ca, 5 mg K, 0.1 mg Pb, Y, U per sample
  - 1L samples, 100 mL aliquots
  - 2 mL columns (650 mg resin)
  - Vacuum supported separation, 5 mL/min
  - Incl. Pb elution step (6M HCl)
  - ICP-MS measurement of effluents
- Extractive discs
  - Elevated flow rates (30mL/min in gravity flow)
  - Pb retention ≥ 95% even up to 5L loading volume
  - Direct LSC measurement of retained, purified Pb-210

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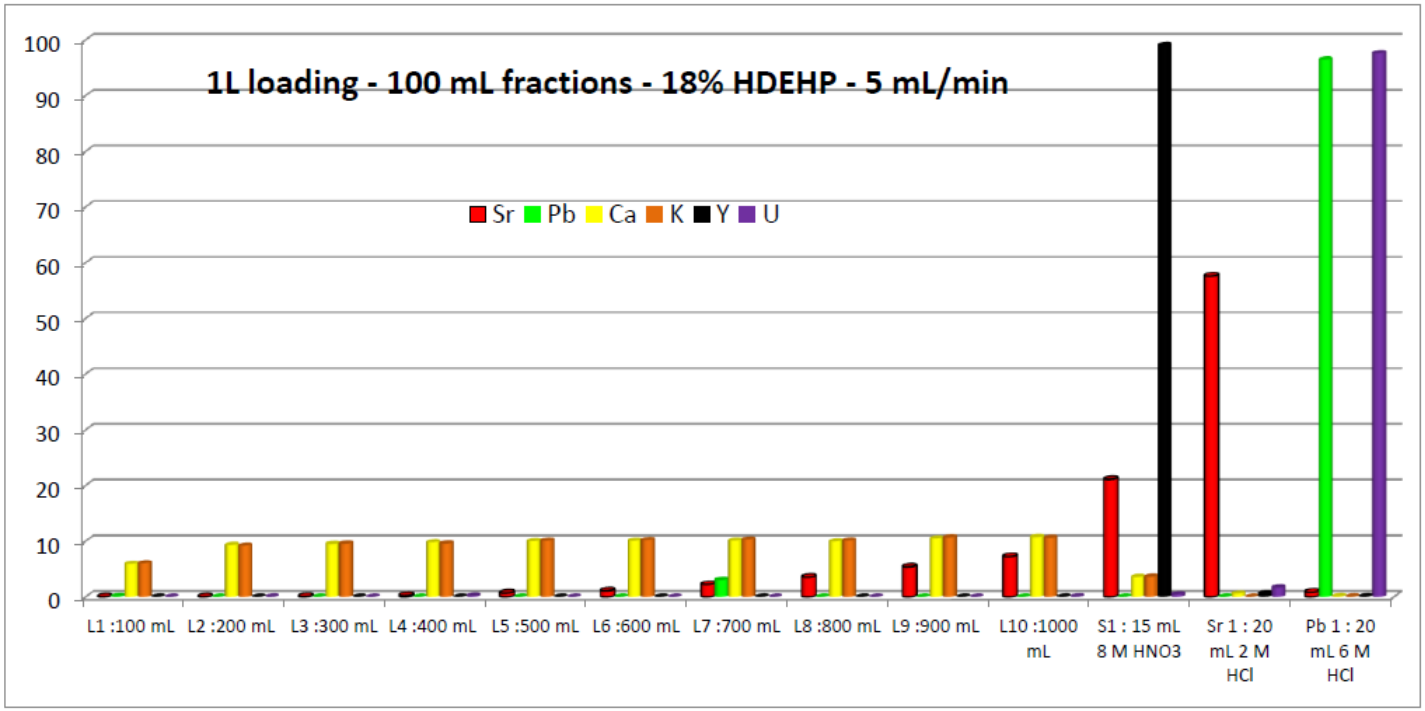
# Elution study mod. SR resin




- K and Ca break through during load
- Sr breakthrough starts at approx 600 mL
- Y eliminated with 8L $HNO_3$, Sr eliminated with 2M HCl
- Pb quantitatively recovered in 20 mL 6M HCl, co-eluted with U….

- First tests with 'Disc': 5L water sample, loaded in 1L aliquots, flow rate 30 mL/min:
  - Pb breakthrough < 5 % during load
  - Direct count of disc by LSC possible – no interference from disc

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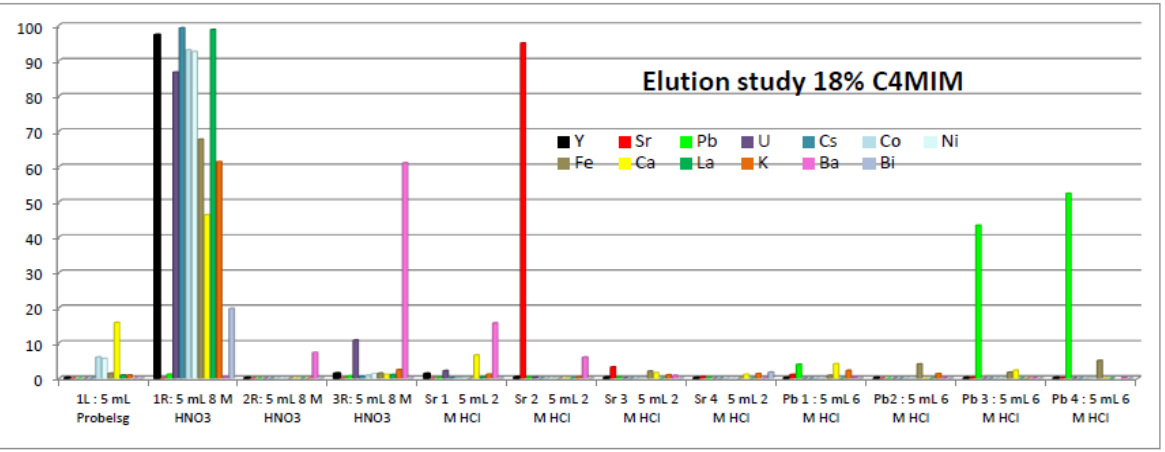
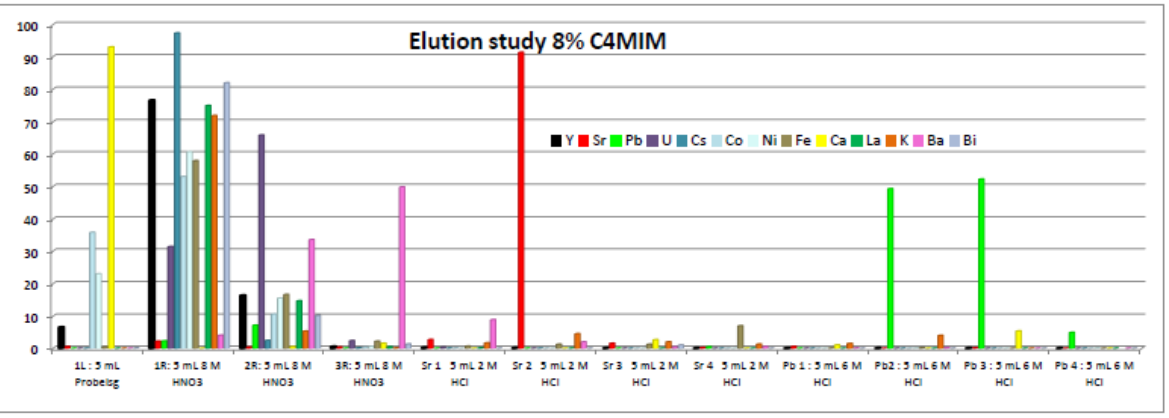
# Ionic liquids

- U selectivity introduced by HDEHP… improved selectivity by use of short chained ionic liquids?
- Preliminary testing (elution study)




- Sample load from pH 7
- Rinse with 3x5 mL 8M $HNO_3$,
- Sr elution with 4x5 mL 2M HCl
- Pb elution with 4x5 mL 6M HCl

- Y and U removed with 8M $HNO_3$
- Sharp Sr elution
- Good purity of Pb fraction

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# Some other on-going projetcs

- Sr-90 via DGT/modified Sr resin
- Sn separation via TBP resin
- Sc separation methods
  - Incl. work on nanotubes
- Pd separation
- Long-lived radionuclides for decommissioning
- …

- Very interested in R&D collaboration!

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# Спасибо за внимание!

# Вопросы?

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http://www.linkedin.com/company/triskem-international?trk=hb_tab_compy_id_2897456

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