eichrom TECHNOLOGIES INC

GROSS ALPHA DETERMINATION IN DRINKING WATER USING A HIGHLY SPECIFIC RESIN AND LSC

S. HAPPEL*[a], P. LETESSIER[a], J.H. EIKENBERG[c], A.H. THAKKAR[b], E.P. HORWITZ[b]

[a]EICHROM EUROPE - Parc de Lormandière - Bât. C - Rue Maryse Bastié - Campus de Ker Lann - 35170 Bruz – France

[b]EICHROM TECHNOLOGIES - 8205 S. Cass Ave / Suite 106 - Darien, IL 60561 - USA

[c]PAUL SCHERRER INSTITUTE - Villigen PSI - 5232 - Switzerland

Introduction

- Drinking Water Directive 98/83/EC
- Planchet Evaporation
- Resin / LSC Approach
  - Extraction
  - Interferences
  - LS counting
- Gross alpha protocol
- Real samples
- Conclusions / Next steps

Drinking Water Directive 98/83/EC

- Covers water intended for human consumption
  - Water for drinking, food preparation and other domestic use
  - Implementation by latest 25 December 2003
- Radiological aspects implemented
  - Recommended by WHO guidelines
  - H-3 < 100 Bq L^{-1}
  - Total indicative dose < 0.1 mSv a^{-1}

    (H-3,K-40, Rn-222 & daughters excluded)
- Screening approach (guideline values, WHO):
  - 0.1 Bq L^{-1} gross alpha activity
  - 1 Bq L^{-1} gross beta activity
  - No further action if determined activities are below

Planchet Evaporation

- Commonly used method
  - Evaporation of 100 – 1000 ml water on 50 – 200 mm Ø planchets
  - Gas proportional counting
- Pro:
  - Number of samples counted simultaneously
  - $\beta-\alpha$-spill-over
- Drawbacks:
  - Evaporation time
  - Dissolved solids (self absorption correction)
  - Inhomogeneous distribution of solids => precision
  - Detection efficiency / counting time

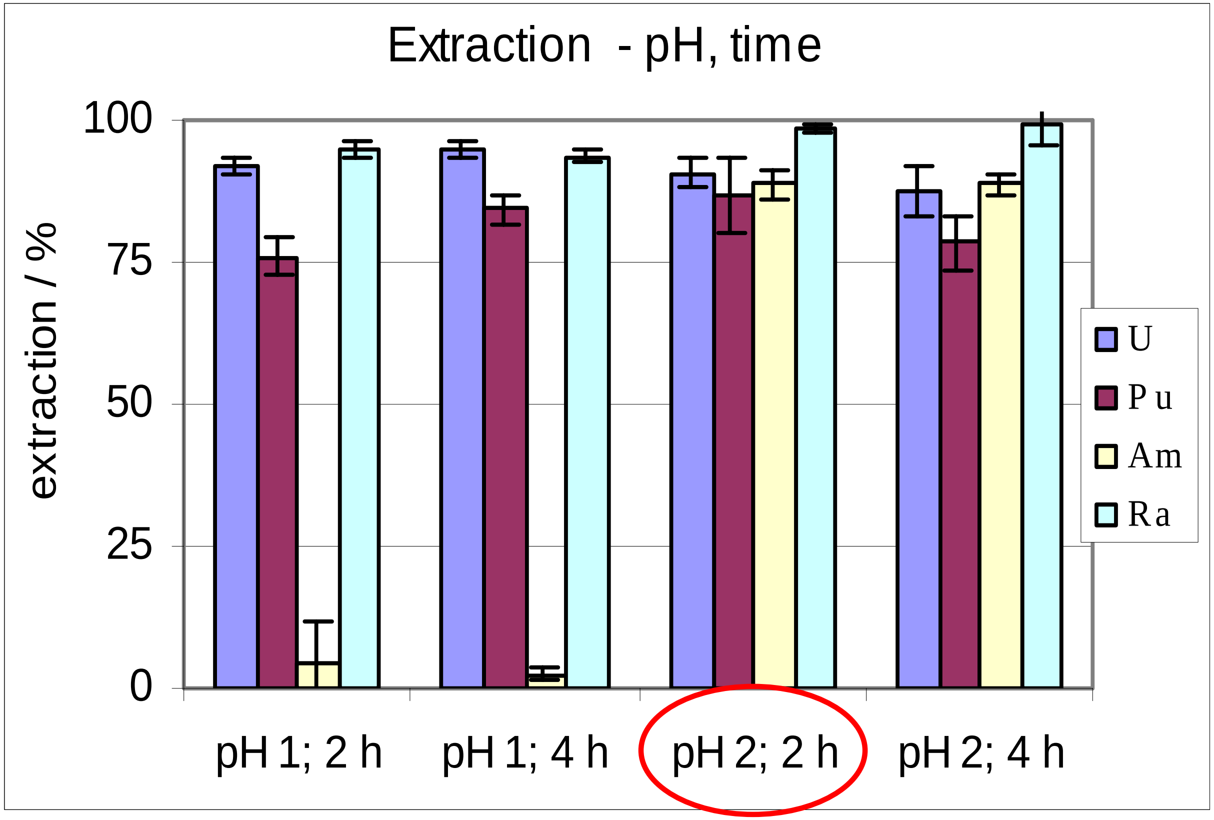
Resin / LSC Approach

- Resin approach
  - Large number of samples prepared simultaneously
  - Batch extraction
  - Matrix removal
  - Resin and filter are dried and mixed with scintillation cocktail
    - Samples with very similar composition / SQP(E) value
    - No extensive quench correction

Resin / LSC Approach

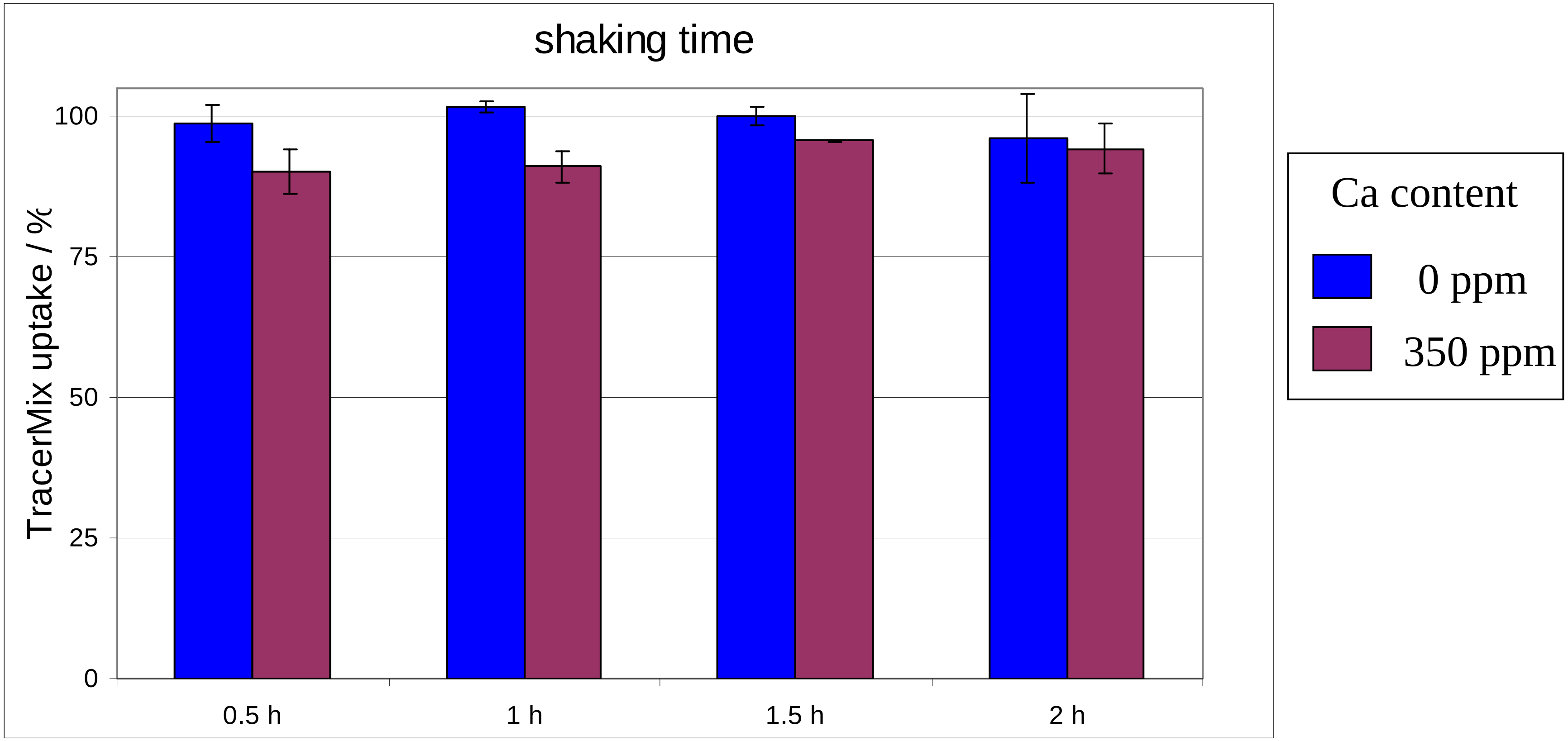
- α-/β-discrimination LS-counting
  - High detection efficiency
  - Low background count rates
  - Shorter counting times
- Used in routine in The Netherlands (Actinide Resin®)
  - Drinking and waste water
  - Drawback: Ra uptake interfered by Ca (>100 ppm)

Extraction conditions



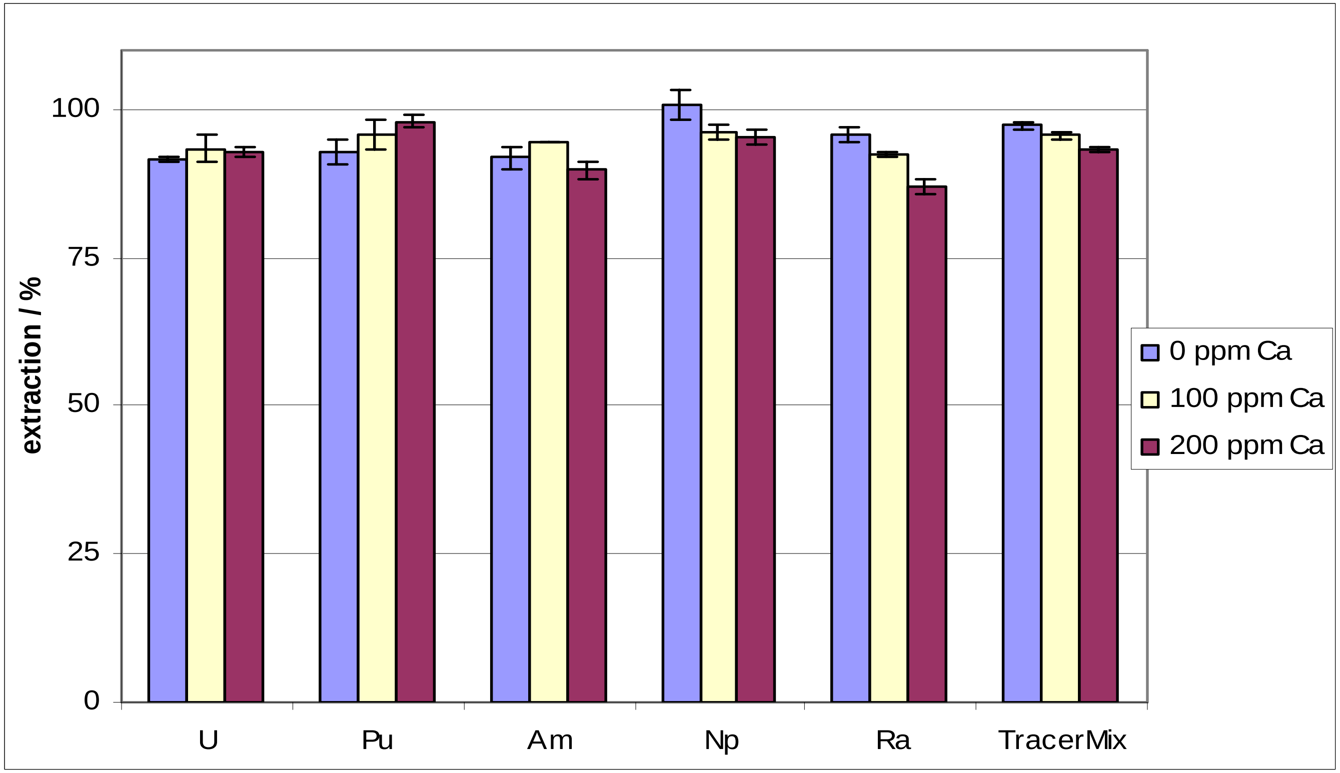
- pH 1: no Am uptake
- pH 2: overall good extraction
- No further improvement by shaking for 4 h

Extraction at pH 2



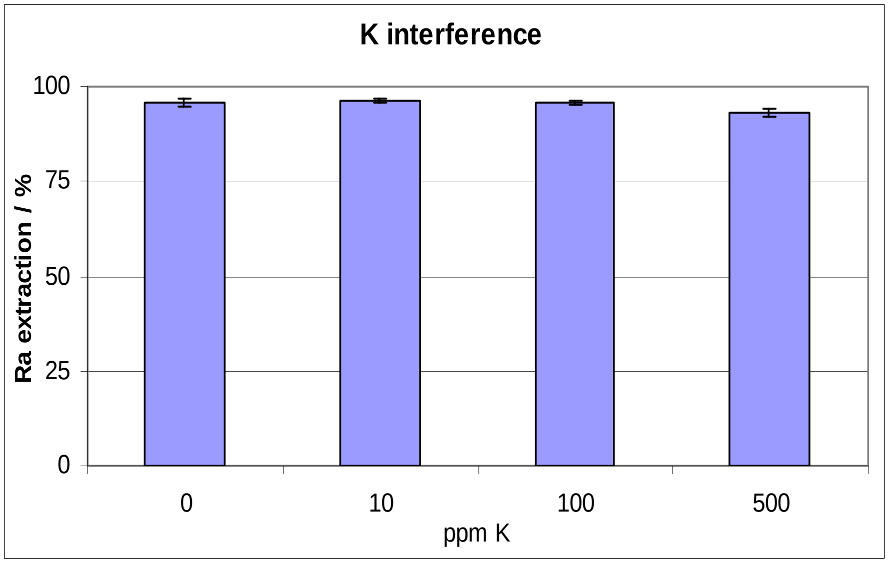
- TracerMix: equal activities of Ra, U, Pu, Am
- pH 2: overall good extraction
- 30 min shaking time sufficient

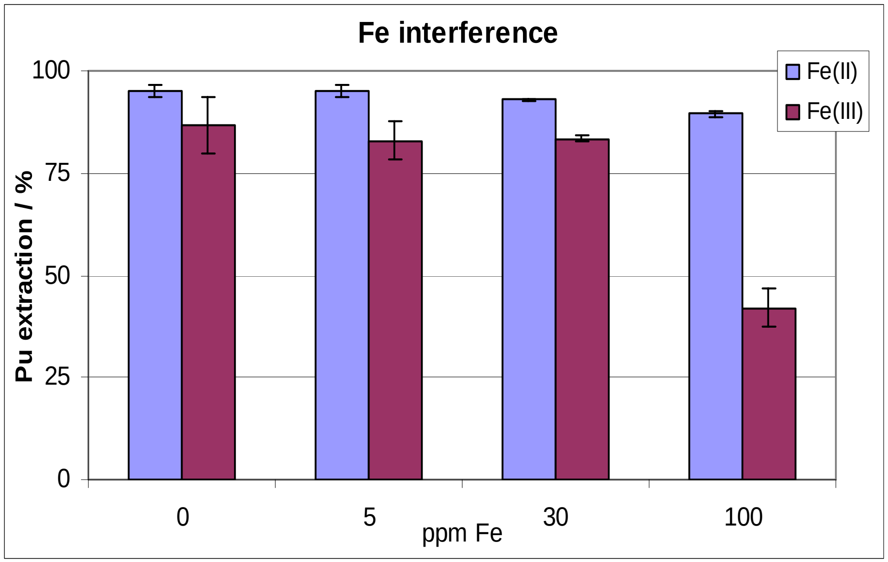
Ca-Interference



- U, Pu, Am, Np and Ra uptake high for varying Ca contents (> 90 – 100 %)
- Ra-uptake is good (> 90 %) even at high Ca contents (200 ppm)
  - Ca content of European Drinking water 30 – 150 ppm

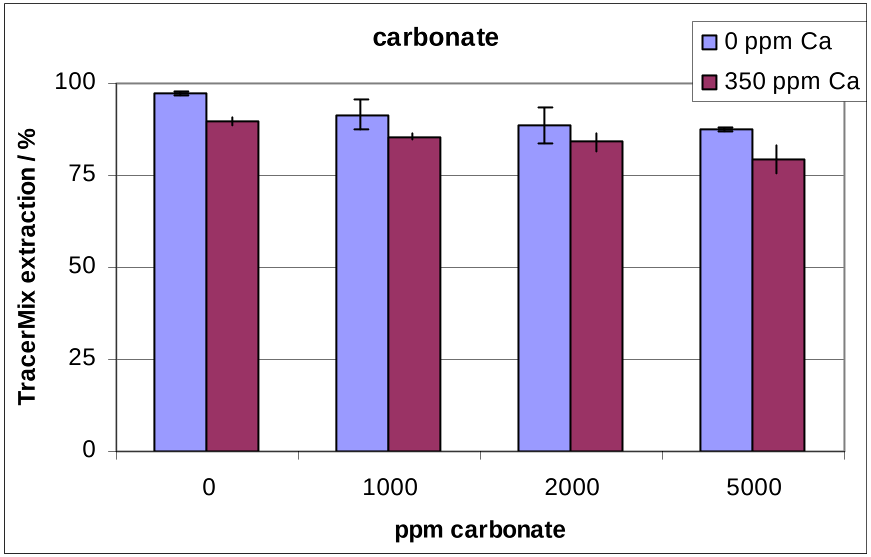
K and Fe interferences

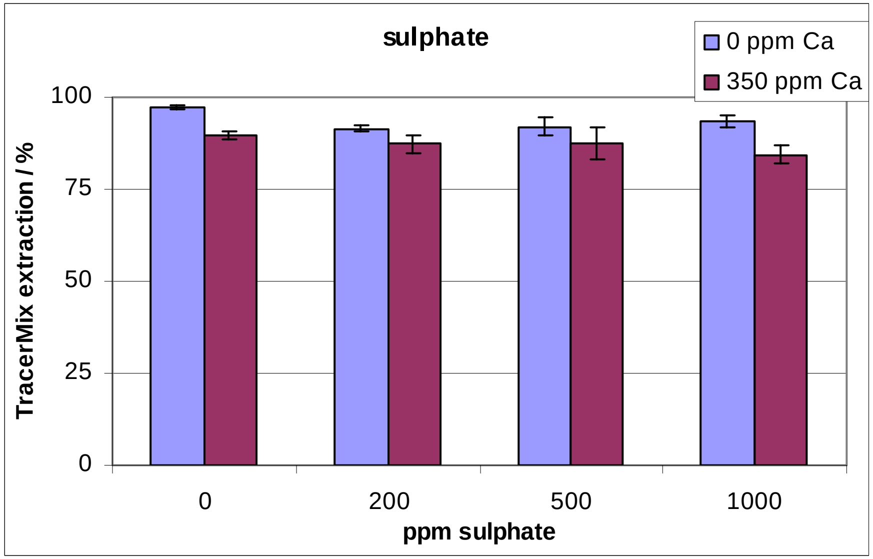




- Only slight interference even for 500 ppm K
  - Drinking water content usually < 30 ppm K
- High Fe(III) amounts (100 ppm) interfere with Pu uptake
- Fe(II) shows no interference
  - 0.2 ppm Fe allowed (Drinking Water Directive 98/83/EC)

Carbonate and Sulphate interferences





- ➢ Carbonate and Sulphate interfere when present in high concentrations (e.g. carbonate > 2000 ppm)
- ➢ interference is increased by large amounts of Ca (350 ppm)
- Carbonate content of drinking water usually < 1000 ppm
- Sulphate content restricted to 240 ppm (Drinking Water Directive 98/83/EC)

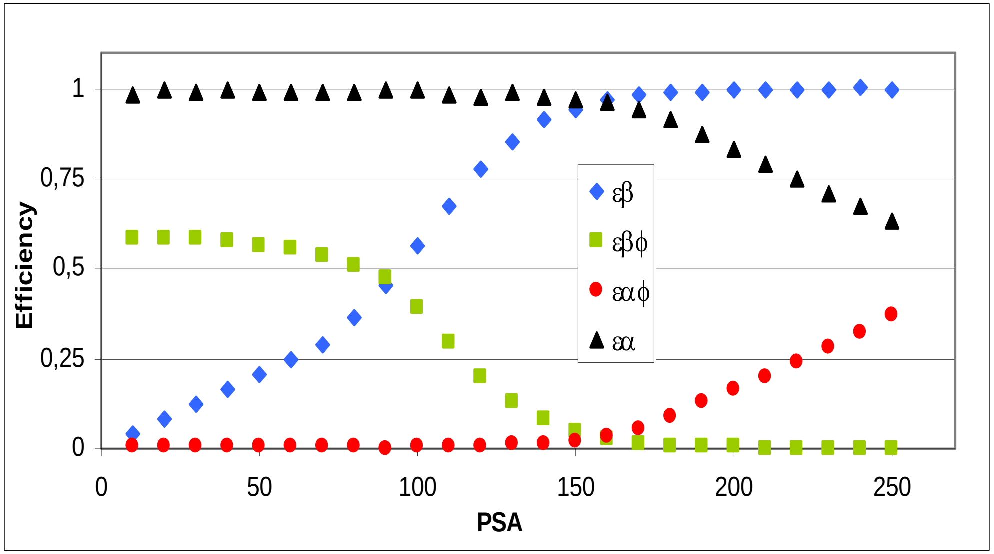
Resin approach

- Extraction near quantitative
  - Actinides and Ra
  - pH 2 (commonly used)
  - 30 min shaking time
- 60 samples of different chemical composition
  - Chemical Yield (mean): 0,9
  - Reproducibility s_R = 5 % (k=1)
  - Repeatability s_r = 5 % (k=1)
- Interferences
  - Ca, Fe(III), carbonate and sulphate do not interfere
  (except when present in contents usually not found or not allowed in water)
  - No K interference

- Resin approach suited

LS-counting

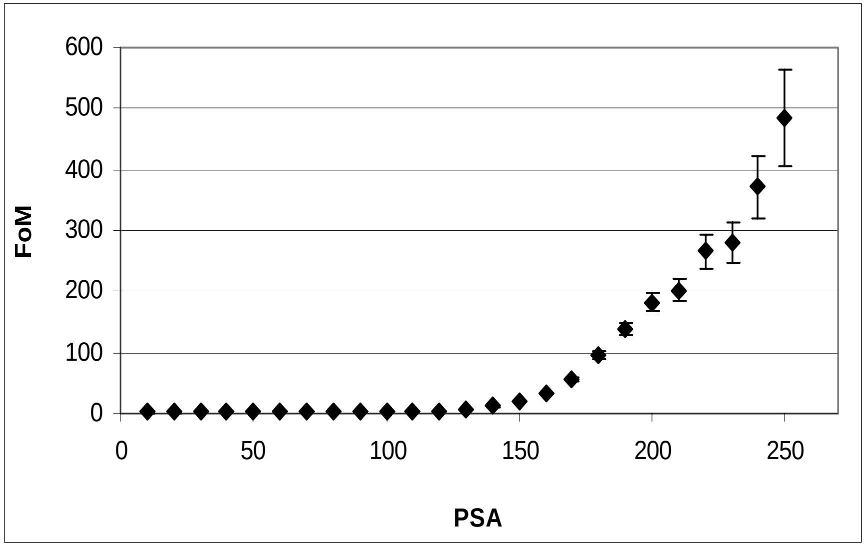
- α-/β-discrimination LS-counting (1220 Quantulus)
- 18 mL UltimaGold AB, dried Resin and filter (Am-241, Sr-90)
- Good reproducibility of samples SQP(E) value (800 +/- 10)

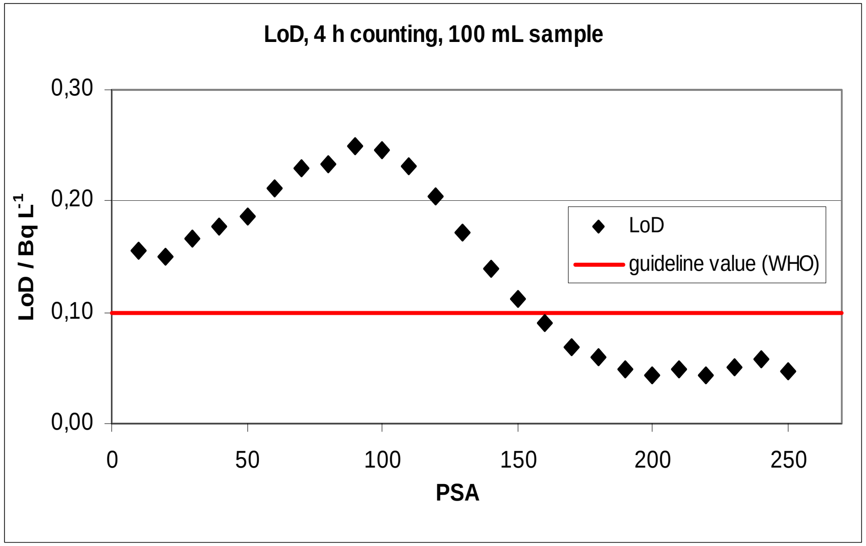


- High PSA values (>200) best suited
    - Low β-spill-over
    - α detection efficiency still high (60 - 80 %)

LS-counting

➢ High PSA values (>200) best suited





- FoM ($\varepsilon_{\alpha}^{2}/\varepsilon_{\beta f}$) values > 100
- Good detection limits
  - 40 mBq L^{-1} (< 4 h, 100 mL sample)
  - 90 mBq L^{-1} (< 90 min, 100 mL sample)

Calculations

$$c_{A_\alpha} = \frac{R_\alpha - \left(\frac{\varepsilon_{\beta f} R_\beta}{\varepsilon_\beta}\right)}{\left(\varepsilon_\alpha - \left(\frac{\varepsilon_{\beta f}\varepsilon_{\alpha f}}{\varepsilon_\beta}\right)\right)\cdot V \cdot 60 \cdot R}$$

Gleichung 1: Gesamt-Alpha-Aktivitätskonzentration, α–/β-LSC in $Bq.L^{-1}$

$$\frac{U_{c_{A_\alpha}}}{c_{A_\alpha}} = k \cdot \sqrt{\left[\frac{\sqrt{sR_\alpha^2 + \left(\left(\frac{s\varepsilon_{\beta f}}{\varepsilon_{\beta f}} + \frac{s\varepsilon_\beta}{\varepsilon_\beta} + \frac{sR_\beta}{R_\beta}\right)\cdot\frac{\varepsilon_{\beta f} R_\beta}{\varepsilon_\beta}\right)^2}}{\left(R_\alpha - \left(\frac{\varepsilon_{\beta f} R_\beta}{\varepsilon_\beta}\right)\right)}\right]^2 + \left[\frac{\sqrt{s\varepsilon_\alpha^2 + \left(\left(\frac{s\varepsilon_{\beta f}}{\varepsilon_{\beta f}} + \frac{s\varepsilon_\beta}{\varepsilon_\beta} + \frac{s\varepsilon_{\alpha f}}{\varepsilon_{\alpha f}}\right)\cdot\frac{\varepsilon_{\beta f}\varepsilon_{\alpha f}}{\varepsilon_\beta}\right)^2}}{\left(\varepsilon_\alpha - \left(\frac{\varepsilon_{\beta f}\varepsilon_{\alpha f}}{\varepsilon_\beta}\right)\right)}\right]^2 + \left(\frac{u_V}{V}\right)^2 + \left(\frac{s_R}{R}\right)^2}$$

Gleichung 2: Unsicherheit Gesamt-Alpha-Aktivitätskonzentration,α–/β-LSC in $Bq.L^{-1}$

$$c^*_{\min} = \left(k_{1-\alpha}\cdot\sqrt{\left(\varepsilon_{\beta f}R_\beta + R_{\alpha,0}\right)\cdot\left(\frac{1}{t_0}+\frac{1}{t_m}\right)} + \frac{1}{4}\left(k_{1-\alpha}+k_{1-\beta}\right)^2\left(\frac{1}{t_0}+\frac{1}{t_m}\right)\right)$$

Gleichung 3: Erkennungsgrenze c^*_{min} Gesamt-Alpha-Aktivitätskonzentration, α–/β-LSC in $Bq.L^{-1}$

$$c_{\min} = \frac{1}{\varepsilon_\alpha \cdot V \cdot 60 \cdot R}\left(\left(k_{1-\alpha}+k_{1-\beta}\right)\sqrt{\left(\varepsilon_{\beta f}R_\beta + R_{\alpha,0}\right)\cdot\left(\frac{1}{t_0}+\frac{1}{t_m}\right)} + \frac{1}{4}\left(k_{1-\alpha}+k_{1-\beta}\right)^2\left(\frac{1}{t_0}+\frac{1}{t_m}\right)\right)$$

Gleichung 4: Nachweisgrenze c_{mn} Gesamt-Alpha-Aktivitätskonzentration, α–/β-LSC in $Bq.L^{-1}$

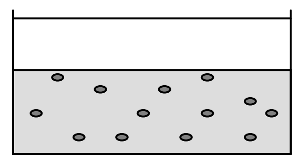
ε_α: Korrekt klassifizierte α-particles; $\varepsilon_{\alpha f}$: Inkorrekt klassifizierte α-particles; ε_β: Korrekt klassifizierte β-particles; $\varepsilon_{\beta f}$: Inkorrekt klassifizierte; Z_α / Z_β: Alpha-/Beta-Fenster netto Zählrate; $k_{1-\alpha}$ and $k_{1-\beta}$: Quantile der Normalverteilung (3,0 and 1,645), Z_0: Untergrundzählrate, t_0 and t_m: Messzeit Untergrund/Probe.

eichrom TECHNOLOGIES INC

Gross alpha protocol

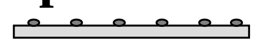
100 ml water sample acidified pH 2 (HCl)

Resin



30 min shaking

Sample filtration



Dry Resin and filter, transfer to LSC vial (UGAB)

1.5 - 4 hours counting by α/β-LSC

Real samples

table 1: determined and reference values, gross-alpha determination, real samples

Probe	reference value / Bq L^{-1}	determined value / Bq L^{-1}	d/r / %
Marburg	404 +/- 11 +	408 +/- 18	100,9 +/- 4,5 %
Dueseldorf	414 +/- 11 +	408 +/- 19	98,6 +/- 4,5 %
Kaiserquelle Aachen	401 +/- 11 +	391 +/- 18	97,5 +/- 4,4 %
BfS 3/03 MW	4,32 +/-0,11 *	3,94 +/- 0,14	91,2 +/- 4,0 %
BfS 3/03 RW	7,72 +/-0,27 *	7,16 +/- 0,39	92,7 +/- 4,4 %

+ TracerMix-activity added

* obtained using established evaporation protocol

- Good recoveries for spiked drinking water samples
- Good agreement between LSC and evaporation results

Conclusions

- Uptake of Actinides is good; high Ca contents do not interfere
- Resin shows high Ra-uptake (> 95%) for low Ca-content; for high Ca-contents (200 ppm) uptake is > 90 %
- Fe(III), carbonate and sulphate do not interfere

  (except when present in contents not found or not allowed in water)
- Direct α-/β-discrimination LS-counting of dried resin
  - good reproducibility of SQP(E)
  - LoD of 40 mBq L^{-1} in less than 4 h counting time
  - LoD of 90 mBq L^{-1} in less than 90 min counting time
- Good precision
- Quick results
- First test with real samples showed good results

Next steps

- Improvement of LS-counting conditions
- Further evaluation with intercomparison/reference samples
- CETAMA Intercomparison
  - Comparison between Resin vs. Planchet Evaporation
  - Mineralwater
- Seawater