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Validation of a method for the determination of Ra-226

UGM05 -09/12/05 - Manchester

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Validationfolder

- Choice of the method
- Description of the method
- Critical points
- Equipment
- SOP
- Principle of the validation including acceptance criterias
- Results and Performance data
- Conclusions

Choice of the method

- Normative methods:
  - Short description
  - Pros and contras of the methods
  - Statement that, due to the contras, another method has been chosen
- Summary of the criteria the method should satisfy
- Literature

Description of the method (RAW03)

- Summary of the SOP
- Information on calibration
- Statement, that the method satisfies the acceptence criteria

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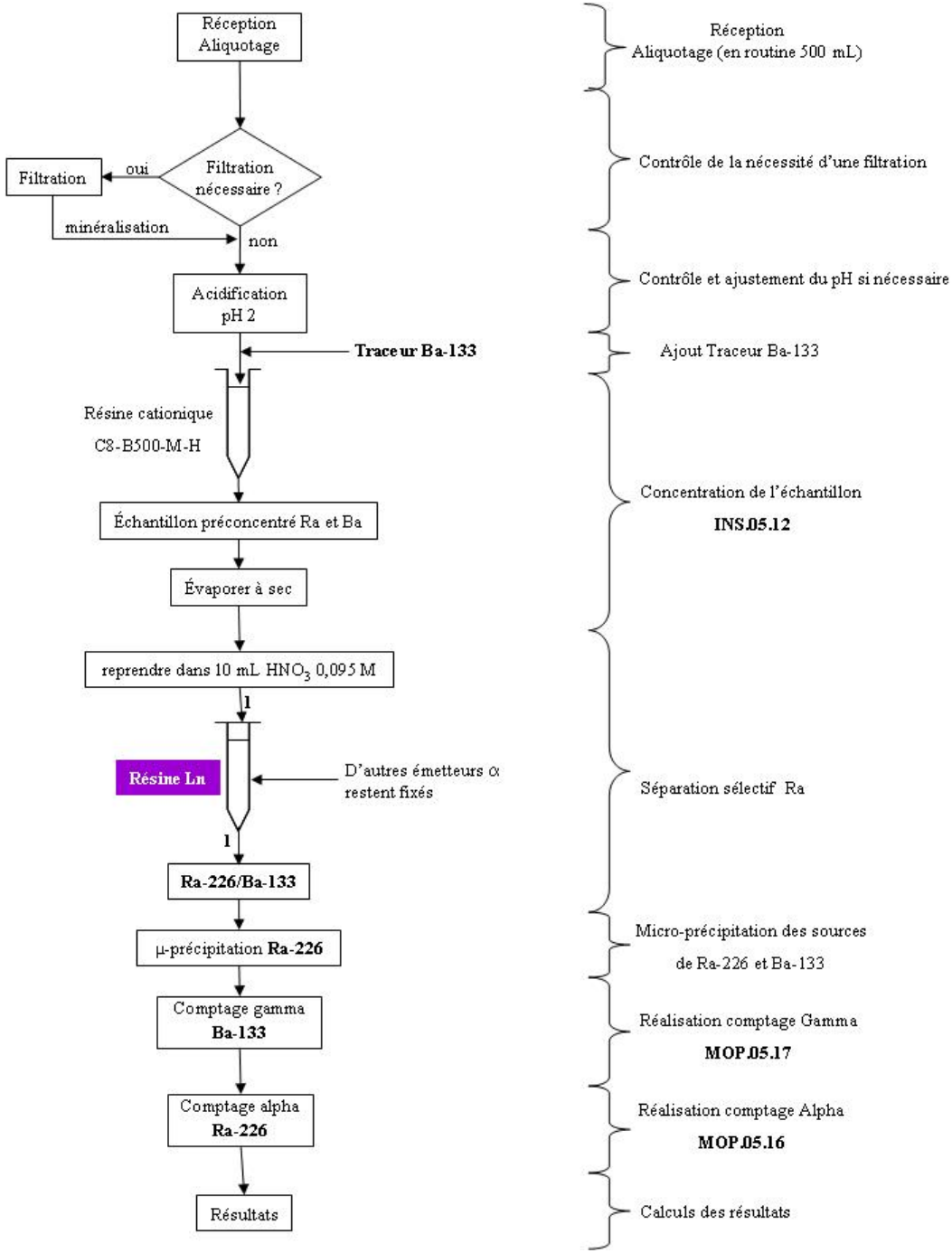
Description of the Method (RAW03 – without Ra-228)



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Critical points

- Some points which need to be considered in addition to performance data
  - IEX
    - Precision
    - Ca Interference
  - Ln Resin
    - Precision
    - Interferences
    - Selectivity
  - Microprecipitation
    - Precision
    - Ca Interference
    - Linearity
    - Behaviour of U
  - Method
    - Equivalence of Ba and Ra

- Equipment
  - Types and numbers of the counting equipment used
  - Softwares used
  - No information on the calibration requested
- Reference of the SOP in the QS

Principle of the Validation

- No binding regulation
- Acceptance criteria:
  - Chemical similarity of Ba and Ra
  - Accuracy/Bias
  - Precision
  - Linearity and Working range
  - Limit of detection
  - Uncertainty budget
  - Selectivity
  - Ruggedness
  - Interferences

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Chemical similarity of Ba and Ra

- 10 samples of known Ba-133 and Ra-26 activity
  - Recovery determination via calibrated gamma-/alphaspectrometer
- Acceptance criteria:
  - Bias between determined recoveries ≤ 10 %
  - t-value of determined recoveries ≤ 1

Sample	Ba-133		Ra-226			
	Recovery	u R	Recovery	u R	bias in %	t-value
Test 01	0,79	0,05	0,81	0,19	-2,6	0,1
Test 02	0,73	0,05	0,71	0,18	2,9	0,1
Test 03	0,62	0,04	0,60	0,18	2,7	0,1
Test 04	0,68	0,04	0,66	0,17	3,2	0,1
Test 05	0,74	0,04	0,70	0,20	4,6	0,2
Test 06	0,65	0,04	0,62	0,18	3,8	0,1
Test 07	0,69	0,04	0,65	0,17	4,7	0,2
Test 08	0,68	0,04	0,70	0,14	-3,9	0,2
Test 09	0,61	0,04	0,63	0,14	-2,9	0,1
Test 10	0,64	0,04	0,67	0,14	-3,7	0,2

- Ba-133 can be used as internal standard

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Accuracy/Bias

$$t = \frac{\left| c_{A,\text{determiné}} - c_{A,\text{reference}} \right|}{\sqrt{Uc^2_{A,\text{reference}} + Uc^2_{A,\text{determine}}}}$$

t-value [corresponding to E_n - ISO/IEC Guide 43-1]

$t \leq 1$: no significant bias, result accepted as accurate

t > 1 : significant bias, result inaccurate

	Referenzwert ($Bq.L^{-1}$)	Uc Referenzwert ($Bq.L^{-1}$)	Ermittelte Aktivitätskonzentration ($Bq.L^{-1}$)	Uc Ermittelte Aktivitätskonzentration ($Bq.L^{-1}$)	t Wert
Ra 1a	2.18E-01	2.84E-03	2.23E-01	2.16E-02	0,1
Ra 1b	2.17E-01	2.83E-03	2.11E-01	2.06E-02	0,1
Ra 2a	1.07E+00	9.36E-03	1.21E+00	1.11E-01	0,6
Ra 2b	1.05E+00	9.26E-03	1.10E+00	1.02E-01	0,2
Ra 3a	2.13E+00	1.84E-02	2.33E+00	2.25E-01	0,4
Ra 3b	2.13E+00	1.83E-02	2.27E+00	2.10E-01	0,3
Ra 4a	1.58E-01	1.65E-03	1.84E-01	1.82E-02	0,7
Ra 4b	1.56E-01	1.64E-03	1.65E-01	1.62E-02	0,3
Ra 5a	7.60E-01	3.50E-03	8.51E-01	7.64E-02	0,6
Ra 5b	7.34E-01	3.40E-03	7.81E-01	7.05E-02	0,3
Ra 6b	1.50E+00	6.43E-03	1.61E+00	1.42E-01	0,4
IRSN 73 SH 300	4,37E-01	1,85E-02	4,87E-01	5,33E-02	0,4
IRSN 73 SH 300	4,37E-01	1,85E-02	4,43E-01	9,02E-02	0,0

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Precision

- Repeatability (s_r) and Reproducibility (s_R)

s_r and $s_R \leq 15$ % : Precision is acceptable

s_r and/or $s_R > 15$ % : Precision is inacceptable

Criteria taken from the "recommendations of the D.19 committee of the ASTM" (e.g. "Standard Test Method for Lead-210 in water")

- Repeatability (N=5) s_r: 12%
- Reproducibility (N=5) s_R: 11 %

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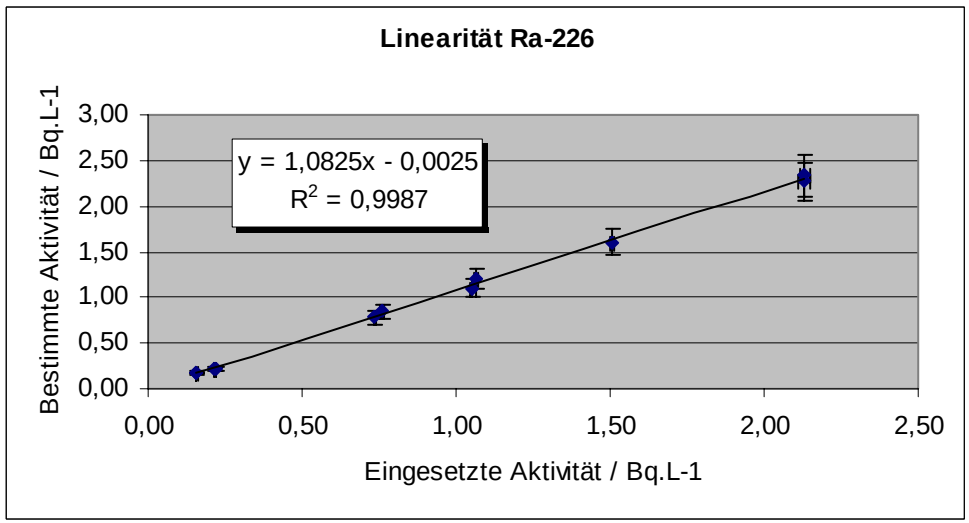
Linearity and working range

- R^2 (Correlation coefficient)

$R^2 \geq 0{,}995$: Linearity accepted

$R^2 < 0{,}995$: Method not linear



Working range: LoD to 2,5 $Bq.L^{-1}$

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Limit of detection

- Regulation: 40 mBq.L^{-1}
- Calculated in analogy to NF M60-804-2

$$LD_{c_A} = \frac{2 \times 2 \times \left(1 + \sqrt{\left[1 + 2N_0\right]}\right)}{R_C \times \eta \times t_N \times V}$$

Detection Limit LD_{CA} in Bq.L^{-1}

Probe	NWG in (Bq.L^{-1})
Ra 1a	9.39E-04
Ra 1b	9.55E-04
Ra 2a	1.16E-03
Ra 2b	1.04E-03
Ra 3a	1.26E-03
Ra 3b	1.10E-03
Ra 4a	1.11E-03
Ra 4b	1.03E-03
Ra 5a	1.04E-03
Ra 5b	1.16E-03
Ra 6b	1.10E-03

In the order of 1 mBq.L^{-1}

(60.000 s counting time, 500 mL)

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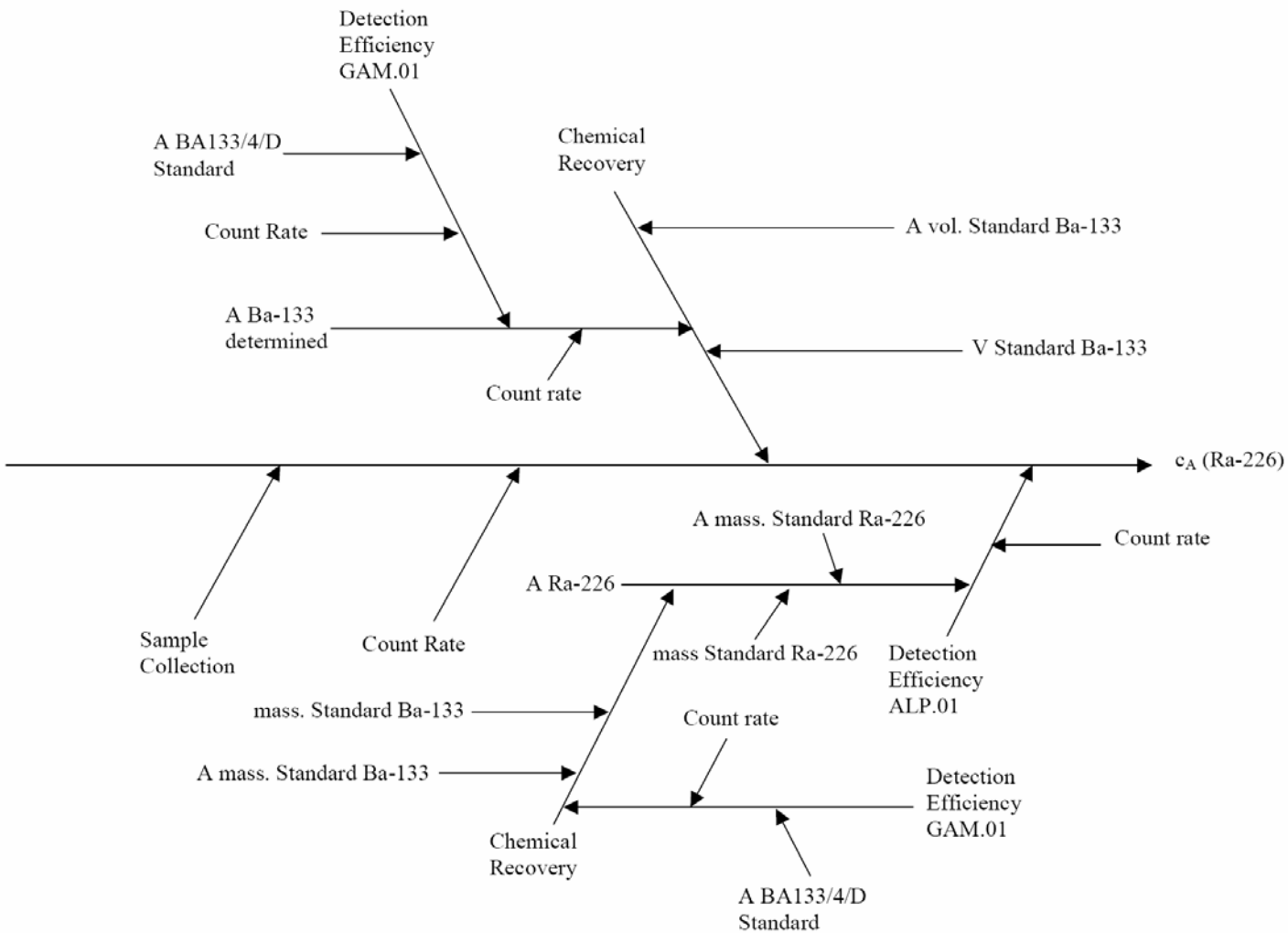
Uncertainty budget



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Uncertainty budget

Ecantillon **Test**

cA(Ra-226) en Bq.L-1

	Contributor	Type	Value	unit	uncertainty	unit	Conversion facto	Standard uncerta	rel. Stand Uncerta	Sensitivity factor	ci2*ui2	Contrbution to Sc	Remark
V	Sample collection	u	0,5	L	0,005	L	1	0,005	1,00E-02	-9,00E-02	2,02E-07	0,9	min. requir. of sample taking precision - overest.
NN	Count rate (Netto	s	264	counts	16,24807681	counts	1	16,24807681	6,15E-02	1,70E-04	7,67E-06	33,4	Calculated by Genie2000
R	Chemical Recove	uc	7,680E-01		4,417E-02		1	0,044168976	5,75E-02	-5,86E-02	6,69E-06	29,2	Determined via Gammapectrometry
n	Detection Efficien	uc	0,2547		0,0164		1	0,0164	6,44E-02	-1,77E-01	8,39E-06	36,6	Calculated by Genie2000
										Somme ci2*ui2 :	2,30E-05		

cA	Determined activity	4,499E-02	Bq.L-1
Uc(cA)	enl. combined uncertainty (k=2)	9,581E-03	Bq.L-1
rUc(cA)	rel. Enl. comb. Uncertainty (k=2)	21,30	%

cA = NN/(V*RC*n*60000)

Uc(cA)=2*cA*[(u(V)/V)2+[(N0+NE)/(NE-N0)2]+(uc(RC)/RC)2+(uc(n)/n)2]1/2

rUc(cA)=(Uc(cA)/cA)*100

Chemical Recovery RC

	Contributor	Type	Value	unit	uncertainty	unit	Conversion facto	Standard uncerta	rel. Stand Uncerta	Sensitivity factor	ci2*ui2	Contrbution to Sc	Remark
cA(Ba-133)	activity concentra	uc	3,906E+00	Bq.mL-1	3,030E-02	Bq.mL-1	1	0,030302903	7,76E-03	-1,97E-01	3,55E-05	1,8	Dilution of certified standard solution
V(Ba-133)	Volume Ba-133 s	u	1	mL	0,006	mL	1	0,006	6,00E-03	-7,68E-01	2,12E-05	1,1	Conformity criteria of ISO 8655 - overestimation
A(Ba-133)	Ba-133 activity or	uc	3,00	Bq	0,17	Bq.mL-1	1	0,17	5,67E-02	2,56E-01	1,89E-03	97,1	Calculated by Genie2000
										Somme ci2*ui2 :	1,95E-03		

RC	Chemical Recovery	7,680E-01	
Uc(RC)	enl. combined uncertainty (k=2)	8,834E-02	
rUc(RC)	rel. Enl. comb. Uncertainty (k=2)	11,50	%

RC = A(Ba-133)/(V(Ba-133)*cA(Ba-133))

Uc(RC)=2*RC*[(u(V(Ba-133))/V(Ba-133))2+(uc(A(Ba-133))/A(Ba-133))2+(uc(cA(Ba-133))/cA(Ba-133))2]1/2

rUc(RC)=(Uc(RC)/RC)*100

Uncertainty budget

$$U_c\left(c_A(Ra-226)\right) = 2 \times c_A \times \sqrt{\left[\frac{(N_0+N_E)}{(N_E-N_0)^2}\right] + \left(\frac{u(V)}{V}\right)^2 + \left(\frac{u_c(R_C)}{R_C}\right)^2 + \left(\frac{u_c(\eta)}{\eta}\right)^2}$$

Unsicherheit $U_C(c_A(Ra\text{-}226))$, k=2

$$u_c\left(R_C\right) = R_C \times \sqrt{\left(\frac{u_c\left(c_A\left(Ba-133\right)\right)}{c_A\left(Ba-133\right)}\right)^2 + \left(\frac{u\left(V\left(Ba-133\right)\right)}{V_{Ba-133}}\right)^2 + \left(\frac{u_c\left(A(Ba-133)\right)}{A_{Ba-133}}\right)^2}$$

Unsicherheit $u_C(R_G)$, k=1

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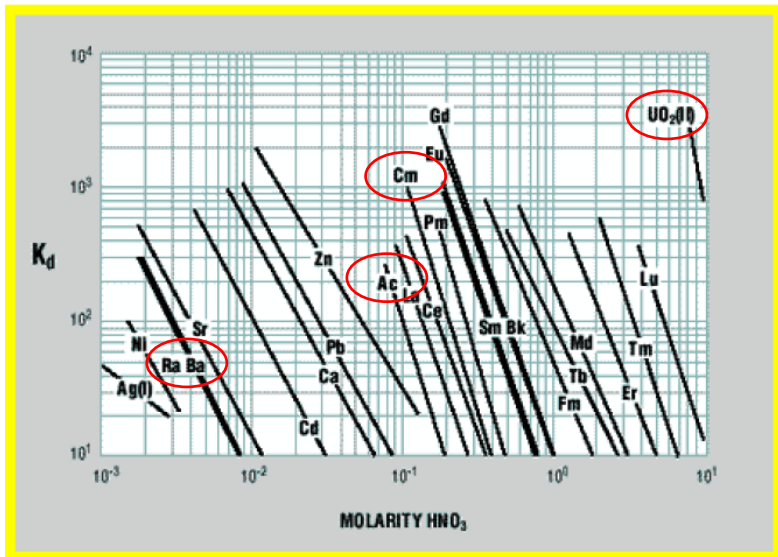
Selectivity

- Gamma spectrometry: Energy of the Ba-133 Lines
- Alphas pectrometry:
- Energy of the Ra-226 Line
  - For Control
- Ln Resin:
  - Extraction
- Micro-precipitation
  - Behaviour of U

Figure 1

Uptake of Various Elements by Ln Resin



Horwitz, et. al (1975)

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Selectivity

- **Decontamination factors (Df):**
  - Most important: U-234

(E$_\alpha$ = 4722,6 und 4774.9 keV)

  - high U/Pu Dfs

even at 300 ppm Ca

  - Possible Am breakthrough

at high Ca Concentrations

  - Control of the Spectrum
  - Df (Th) > 100
  - To be determined: DKF (Np)

0 ppm Ca (500 mL Probe)	Elément	Dekontaminationsfaktor
	Am	391
	Pu	> 60
	U-App	>200
150 ppm Ca (500 mL Probe)	Elément	Dekontaminationsfaktor
	Am	23
	Pu	> 60
	U-App	>200
300 ppm Ca (500 mL Probe)	Elément	Dekontaminationsfaktor
	Am	3
	Pu	> 60
	U-App	>200

Selectivity

- Ra-226 determination in presence of 0.5 Bq U (5 samples)
  - t-values < 1
- Ra-226 determination in presence of 2.48 +/- 0.29 $Bq.L^{-1}$ U-234

	Referenzwert ($Bq.L^{-1}$)	Uc Referenzwert ($Bq.L^{-1}$)	Ermittelte Aktivitätskonzentration ($Bq.L^{-1}$)	Uc Ermittelte Aktivitätskonzentration ($Bq.L^{-1}$)	t Wert
IRSN 73 SH 300	4,37E-01	1,85E-02	4,87E-01	5,33E-02	0,4
IRSN 73 SH 300	4,37E-01	1,85E-02	4,43E-01	9,02E-02	0,0

Ruggedness / Interferences

- Ruggedness: $s_R < s_r$
- Interference of Ca - IEX

	Widerfindung	Standardabweichung	Standardabweichung / %
100 ppm Ca	0,858	0,017	1,9
200 ppm Ca	0,803	0,050	6,2
300 ppm Ca	0,854	0,007	0,8

Calcium Interferenz - Ionenaustauschchromatographie

- Interference of Ca and U – Ln Resin
  - Lower Am Df in presence of high Ca amounts
  - Ra-226 determined accurately even in presence of 2.5 $Bq.L^{-1}$ U-234

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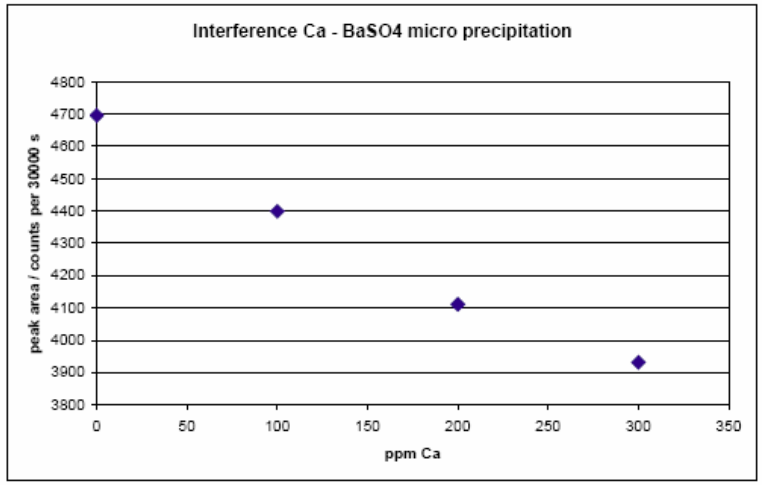
Interferences

- Interference of Ca – Micro-precipitation
  - Lower yield in presence of high Ca concentrations



Ca Interferenz – Peakfläche – Mikromitfällung

  - Little impact on resolution

	FWHM (keV)	Standardabweichung	Vergleich gegen 0 ppm
0 ppm Ca	62	6	
100 ppm Ca	60	1	0,97
200 ppm Ca	56	17	0,91
300 ppm Ca	64	1	1,04

Ca Interferenz – FWHM – Mikromitfällung

	FWTM (keV)	Standardabweichung	Vergleich gegen 0 ppm
0 ppm Ca	139	24	
100 ppm Ca	141	8	1,01
200 ppm Ca	132	8	0,95
300 ppm Ca	141	16	1,01

Ca Interferenz – FWTM – Mikromitfällung

Conclusion

- Choice and validation of a non-normative method
- Determination of performance data
- Uncertainty budget
- Meets internal acceptance criteria => Method validated
- Validation folder examined by two external auditors and accreditated