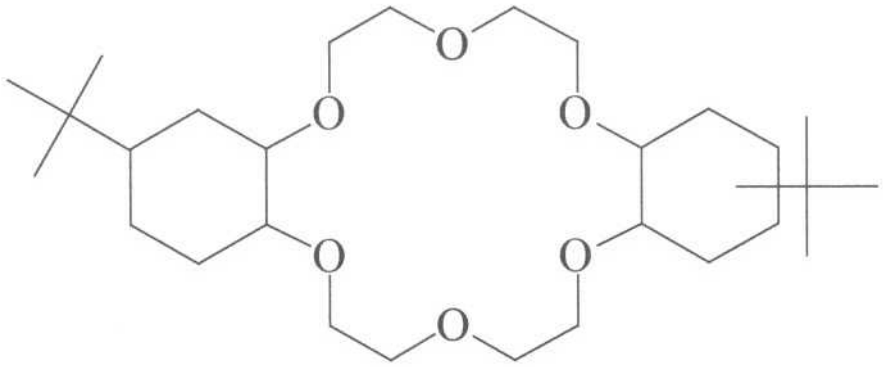
Sr resin: Determination of Sr-89 and Sr-90 in environmental and biological samples

- Sr resin
- Yield determination
- Sample preparation
- Separation
- Sample Prep for counting
- Counting
- Mostly based on a publication of the FS-AKU

  « Moderne Routine- und Schnellmethoden zur Bestimmung von Sr-89 und Sr-90 bei der Umweltüberwachung »

Sr Resin



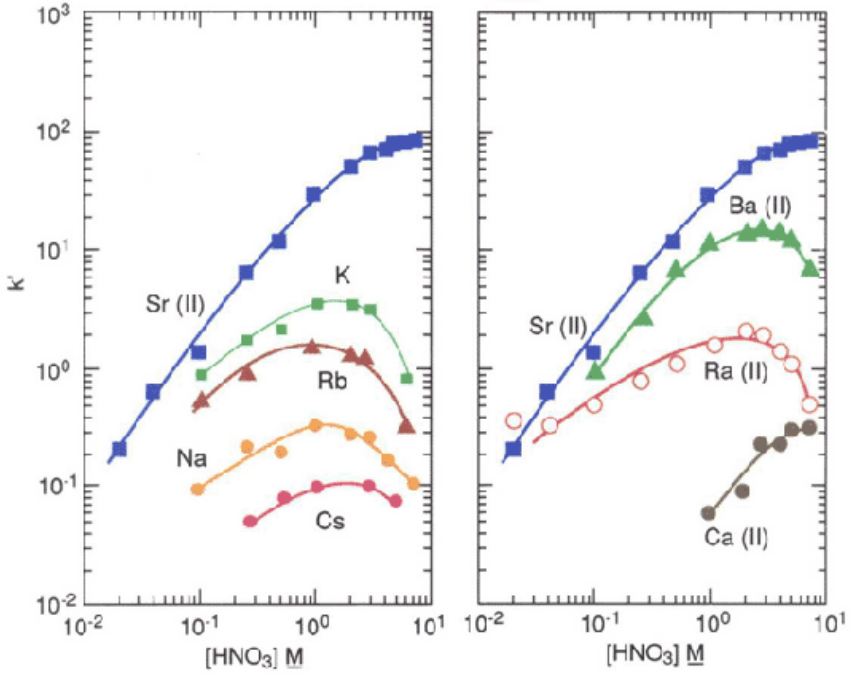
Diluent: 1-octanol

- 1.0M 4,4'(5')-di-t-butylcyclohexano 18-crown-6 in 1-octanol.
- 40% (w/w) loaded onto inert chromatographic support.
- Bed density of Sr Resin approximately 0.35 g/mL.
- Sr max. capacity: 21 mg / 2mL resin bed,
- Advised working capacity: max. 8 mg / 2mL resin bed (Opt.: 5 mg)

Sr Resin

Figures 2 and 3

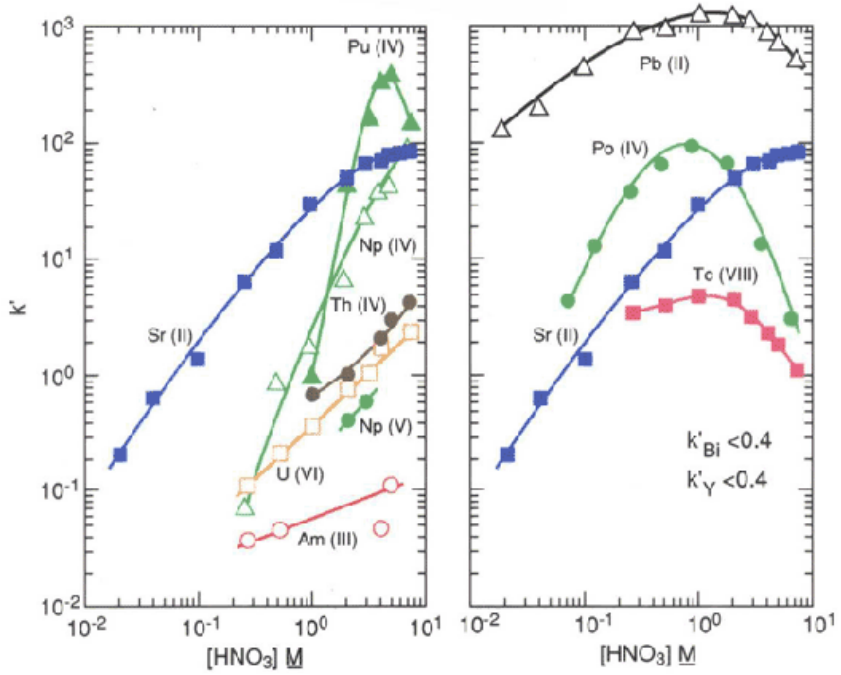
Acid dependency of k' for various ions at 23-25°C.
Sr Resin



Horwitz, et al., (HP292)

Figures 4 and 5

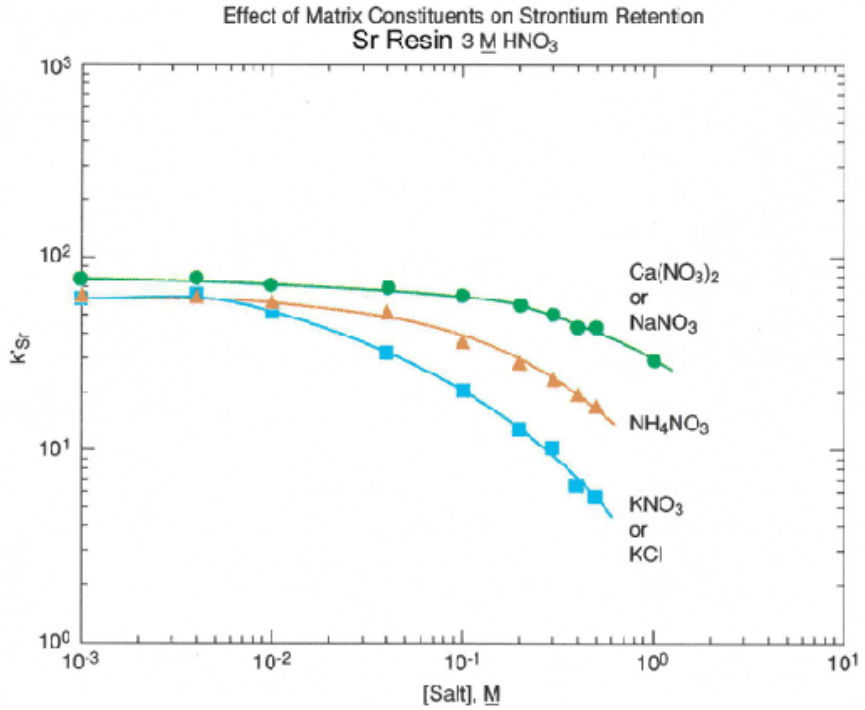
Acid dependency of k' for various ions at 23-25°C.
Sr Resin



Horwitz (HP199)

- Ø Good Sr uptake at high HNO_3 ; easy elution at low HNO_3
- Ø Good selectivity over alkaline and other earth alkaline
- Ø Very good selectivity for Pb (elution problematic, preferably Pb resin)

Sr Resin

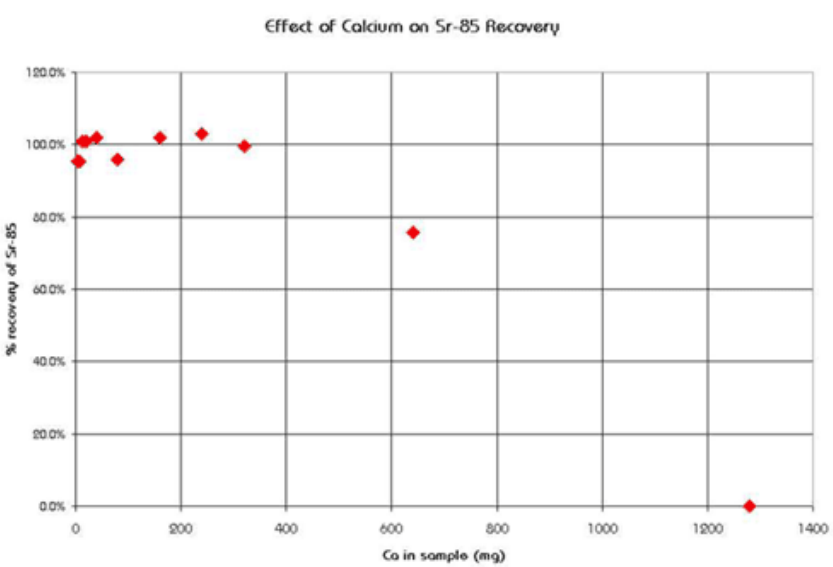


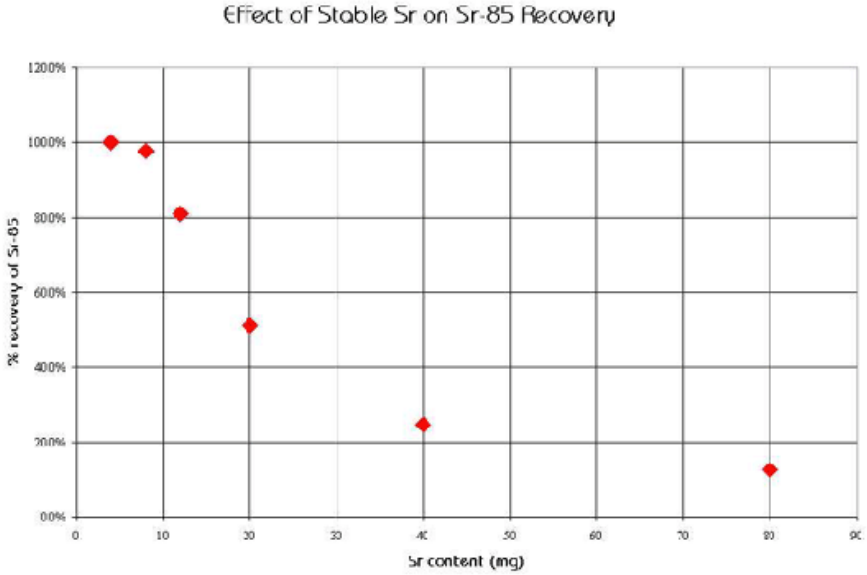
- Ø High impact of K/NH_4 ; elimination necessary when present in high concentration (ion exchange or co-precipitation: e.g. carbonate, phosphate, oxalate)
- Ø Moderate impact of Ca, nevertheless problematic when present in high concentration - column size needs to be adapted

Yield determination

Ø Stable Sr

- Natural Sr content might need to be determined upfront
- Adjust introduced Sr mass to column size / capacity





- Gravimetry
- AAS / ICP-AES / ICP-MS (• spectrometry)

Yield determination

- Ø Stable Y when Y-90 is measured after Y-ingrowth and elution
  - Pb-210/Bi-210 !
- Ø Sr-85
  - Half-life 50,5 days
  - Measurement via LSC (3 window method)
    - Calculation
    - Less contribution to background
  - Measurement via γ-spectrometry
    - § Usually several Bq
    - § Contribution to background! (LSC)

Comparison: Background vs Sr-85

FS-08-147-AKU

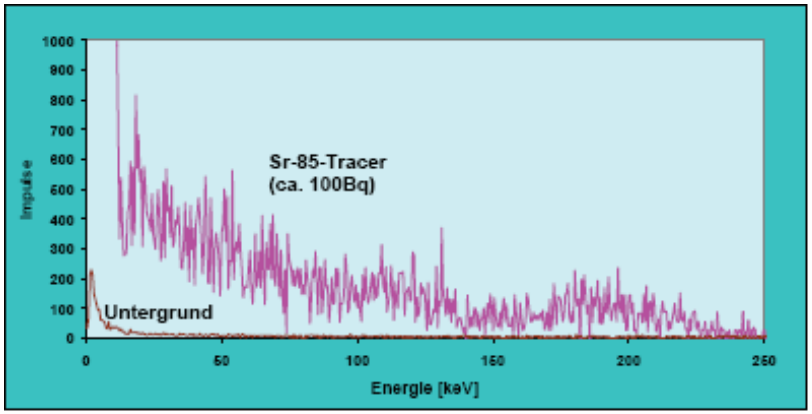


Abb. 3-3: Ausschnitt des Szintillationsspektrums in Abb. 3-2 mit Sr-85 (ca. 100 Bq) und Untergrund mit gleicher Messzeit.

Sample preparation

	typical sample size	Drying	ashing	leaching	extraction	precipitation
Aerosol		air/oven	depending on used filter, 450° C	6M HCl	/	
drinking water	1 - 3 L	/	/	/	(CEX)	Carbonate
waste water	1 - 10 L	Hotplate	wet ashing (HNO_3 / H_2SO_4)	/	/	Sulphate / carbonate
	1 - 3 L	/	/	/	extraction with Chelite P	Carbonate
Urine	0,5 - 1 L	/	(400°C/wet ashing)	/	/	Phosphate
vegetation	100 g	Drying oven	450° C	1M HNO_3	/	1.) CaOxalate (followed by oxalate destruction)
foodstuff	10g ash	Drying oven	450° C (slow increase)	8M HNO_3	/	/
Milk	1 - 5 L	(Lyophilisation /) drying oven	< 400° C	6M HCl or 8M HNO_3	/	Carbonate or Phosphate
	1 L	/	/	/	extraction with Chelite P or CEX	Carbonate
soil / sediment	30 - 100 g	Drying oven	< 400° C	6M HCl or 1M HNO_3	/	1.) CaOxalate (followed by oxalate destruction) 2.) Carbonate

Sample preparation

- Aerosol/filters
  - Drying in oven or air
  - Ashing (300°C then 450°C)
    - depending on filter type and volume
    - matrix removal / concentration
  - Extraction with 6M HCl
  - Evaporation and redissolution in 8M HNO_3
- Drinking water and « clean » surface water
  - Volume up to 300 L (depending on Ca concentration)
  - Preconcentration by evaporation
  - Precipitation as carbonates
    - Redissolution in 8M HNO_3
  - Also possible: preconcentration via cation exchange
    - Elution with 8M HNO_3

Sample preparation

- Waste water (Option 1)
  - Wet ashing with H_2SO_4 and HNO_3
    - $Sr/CaSO_4$ precipitates during dilution
  - Sulphates converted to carbonates
  - Carbonates dissolved in 8M HNO_3
- Waste water (Option 2)
  - Extraction of earth alkalines with Chelite P
    - in batch experiment (2 – 3 h)
  - Transfer of Chelite P in column, rinsing with deion. water
  - Elution of earth alkalines with 5M HNO_3
  - Volume reduction by evaporation
  - Carbonate precipitation
  - Carbonates dissolved in 8M HNO_3

Sample preparation

- Urine
  - Addition of Ca and conc. HNO_3 , boiling for 2 h
  - Optional: first drying and mineralization, then precipitation
  - Addition of HPO_4^{2-} (and Phenolphtalein)
  - Adjust to pH 9 using NH_4OH , precipitation
  - Redissolution of Ca-Phosphate precipitate in 8M HNO_3 / 0,5M $Al(NO_3)_3$
- Vegetation
  - Drying and homogenisation
  - Ashing 500°C
  - Leaching with 1M HNO_3
  - Ca/Sr-Oxalate precipitation at pH 5-6
  - Oxalate destruction (wet ashing or furnace)
  - Dissolution in 8M HNO_3

Sample preparation

- Milk (Precipitation)
  - 1 - 5 L fresh milk, drying and ashing (600° C)
  - Leaching with 8M HNO_3 (or 6M HCl), Filtration
  - Ca-Phosphate precipitation at pH10
  - Redissolution of Ca-Phosphate precipitate in 8M HNO_3
- Milk (Ion exchange)
  - Extraction of earth alkaline with Chelite P or Cation exchange resin
    - in batch experiment (2 – 3 h)
  - Transfer of Resin in column, rinsing with deion. Water
    - Removal of milk and milk fat, might need to be done at elev. temp.
  - Elution of earth alkaline with 5M HNO_3 (Chelite P) or NaCl solution (CEX)
  - Volume reduction by evaporation
  - Carbonate precipitation, followed by dissolution in 8M HNO_3

Sample preparation

Ø Soil/Sediment/Sludge (Option 1)

- 100 g dry sample
- drying and ashing (400° C)
- Leaching with 6M HCl, ΔT
- Dilution
- Filtration to remove precipitated sicilic acid
- Ca-Oxalate precipitation at pH 5.5
- Oxalate destruction at 400°C, then 700°C
- Redissolution in HNO_3/HCl
- Carbonate precipitation
- Redissolution in 8M HNO_3

Sample preparation

Ø Soil/Sediment/Sludge (Option 2)

- 30 g dry sample
- drying and ashing (400° C)
- Leaching with 1M HNO_3, ΔT
- Dilution
- Ca-Oxalate precipitation at pH5.5 in presence of Na-Citrate
- Oxalate destruction by wet ashing (conc HNO_3, H_2O_2)
- Redissolution in 3M HNO_3

Separation

- Ø Loading solution in general in 8M HNO_3 or 3M HNO_3
  - Depending on matrix and phosphate concentration also 0,5M in $Al(NO_3)_3$
- Ø Volume of the loading solution depending on
  - Column size
  - Sr content
  - Matrix (Ca content)
- Ø Column sizes generally used:
  - 2 mL prepacked (0,65g resin) e.g. water samples, urine samples
  - 5 mL prepacked (1,6g resin) e.g. waste water, some food stuff
  - 8 mL prepacked (2,6 g resin) e.g. milk, soil
  - Up to 10 - 15 mL (3 - 5 g resin) all matrices
    - own packing from bulk Sr resin
    - MPLC setups

MPLC

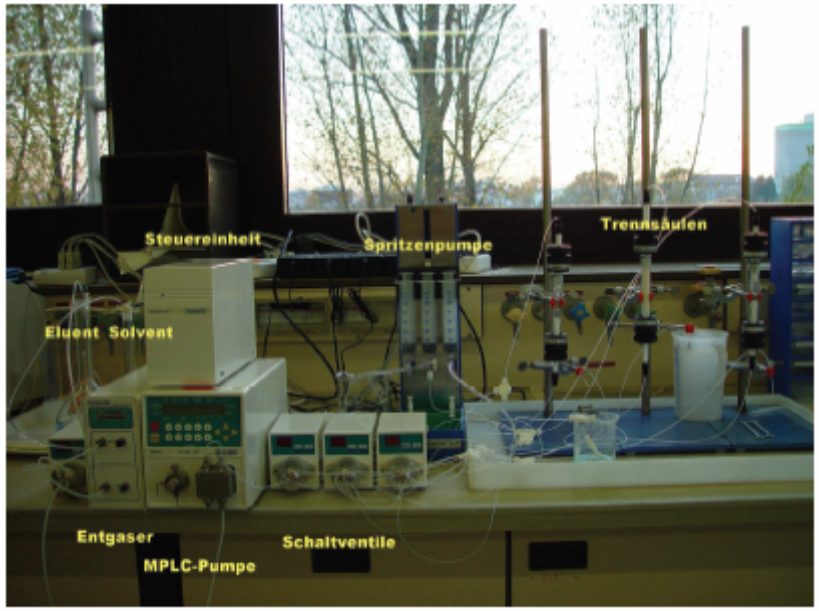


Abb. 2-4: Ansicht der 3-Säulen-MPLC-Anlage im Isotopenlabor der BfG

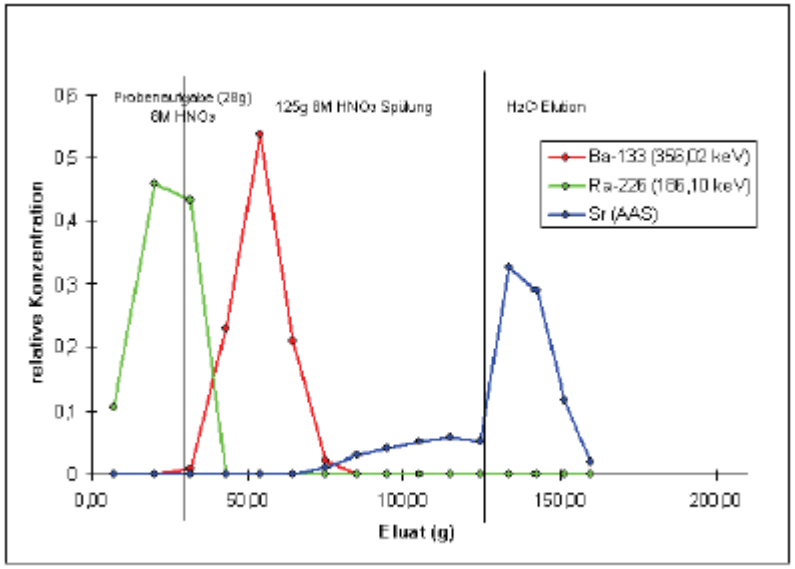


Abb. 2-2: Elutionskurve zur Charakterisierung der MPLC-Anlage

- Automatized separation
- Good characterization of system necessary (e.g. elution volumina)

Separation – example 2 mL column

- 10 – 20 mL loading solution
- Sr content: 5 mg (« working capacity »)
- 10 mL rince with 8M HNO_3 (eliminates matrix, Ba, Y, K)
- In case of presence of Pu(IV), Np(IV) or Ce(IV) rince with 10 mL 3M HNO_3 / 0,05M oxalic acid
- 5 mL rince with 8M HNO_3 (eliminates traces of Ba and K)
- Sr elution with 10 mL H_2O or 0.05M HNO_3

Separation – example 2 mL column
Option Y-90 elution

- In case a determination via Y-90 is prefered (e.g. via Cerenkov counting)
- Possibility: no Sr-90 elution, let stand column and allow for Y-90 ingrowth, elute Y
- Problem: need to be sure of absence of Pb-210
  - ingrowth of Bi-210 (high energy beta emitter: $E_{\beta,max}$ = 1,2 meV)
  - Co-eluted with Y-90
- Better: elute Sr-90 and allow for Y-90 ingrowth, then reload onto fresh Sr column
- Additional advantages:
  - Sr-89 determination in Sr eluate via Cerenkov counting
  - Y yield determination via stable Y

Separation – example 10 mL column

- 50 - 100 mL loading solution
- Sr content 20 mg (« working capacity »)
- 50 - 80 mL rince with 8M HNO_3 (eliminates matrix, Ba, Y, K)
- In case of presence of Pu(IV), Np(IV) or Ce(IV) rince with 40 - 50 mL 3M HNO_3 / 0,05M oxalic acid
- 20 mL rince with 8M HNO_3 (eliminates traces of Ba and K)
- Sr elution with 100 mL H_2O or 0.05M HNO_3
- Evaporation or Sr-Carbonate precipitation

Sample preparation for counting

Ø LSC counting - 10 mL elution volume (2 mL column)

- Sr-85 tracer: direct measurement γ and/or LSC
- Stable Sr – via spectrometry: aliquot for yield, rest LSC (choice of cocktail!)
- Stable Sr – via gravimetry: carbonate precipitation, weighing, redissoloution in aqueous 12,5% touluensulphonic acid (1 -2 mL) and scintillation cocktail (18 – 19 mL) • low quench! , LSC

Ø LSC counting - Larger elution volumes (5 – 15 mL columns)

- Preconcentration by Sr-Carbonate precipitation
- Yield via spectrometry: redissolution in acid, aliquotage for spectro/LSC
- Yield via gravimetry: weighing, redissoloution in aqueous 12,5% touluensulphonic acid (1 -2 mL) and scintillation cocktail (18 – 19 mL), LSC
- Yield via Sr-85 tracer: γ counting of filter or LSC sample (redissoloution in aqueous 12,5% touluensulphonic acid (1 -2 mL) and scintillation cocktail (18 – 19 mL))

Sample preparation for counting

- Cerenkov counting
  - Direct measurement of sample
  - Yield:
    - Via Sr-85: γ-spec of sample or by LSC after addition of scintillation cocktail
    - Via spectrometry : aliquotage
    - Y-90 measurement: 100% yield of elution assumed or Y via spectrometry
- GPC counting
  - In general gravimetry
  - Evaporation of Sr eluate
  - Sr oxalate or carbonate precipitation
  - Y oxalate or hydroxide precipitation / in general conversion to oxide
  - Optional for yield determination: redissolution of source and spectrometry

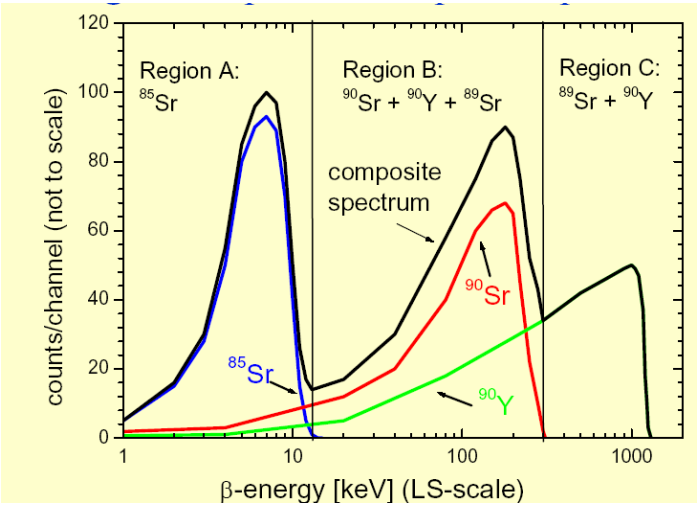
Counting

- LSC - no presence of Sr-89
  - Use of Sr-85 as yield tracer – 3 window method
    - 1st window Sr-85, 2nd window Sr-90, 3rd window Y-90 (plus control for Sr-89)
    - Yield and Sr-90 in one measurement
    - Allows result control by repeated measurements (Y-90 ingrowth)
    - Low Sr-85 activity, low contribution to Sr-90 background
  - Use of Sr-85 as yield tracer – yield via g-spectrometry
    - Elevated Sr-85 activity necessary
    - Considerable background contribution
    - One or two window method
    - High energy windows – diminuation of Sr-85 contribution to background

Counting

- Ø LSC - no presence of Sr-89
  - Use of stable Sr as yield tracer – 2 window method
    - 1st window Sr-90, 2nd window Y-90 (plus control for Sr-89)
    - Yield and Sr-90 in two different measurements
    - Allows result control by repeated measurements
    - No contribution of Sr-85 to background
- Ø Remark on LSC counting with multiple windows methods
  - Calibration!
  - Quench needs to be stable
  - Maths...

Example 3 window method – Sr-85 tracer
Eikenberg, Vetter presentation UGM Bratislava
Window A: Sr-85
Window B: Sr-89/90 and Y-90
Window C: Sr-89 and Y-90



Counting

- LSC – presence of Sr-89
  - Use of Sr-85 as yield tracer – 3 window method
    - 1st window Sr-85, 2nd window Sr-90, 3rd window Sr-89 (and Y-90)
    - Yield and Sr-89 and Sr-90 in one measurement
    - Control via repeated measurements
    - Measurement should be performed rapidly after elution
    - Low Sr-85 activity, low contribution to Sr-89/90 background

- LSC – presence of Sr-89
  - Use of Sr-85 as yield tracer – yield via γ-spectrometry
    - Elevated Sr-85 activity necessary, Considerable background contribution
    - Two or three window method
      - 2 windows: Sr-90 and Sr-89 (plus Y-90)
      - 3 windows: Sr-90, Sr-89 and Y-90
    - High energy windows – diminuation of Sr-85 contribution to background

Counting

- LSC – presence of Sr-89
  - Use of stable Sr as yield tracer
    - Two or three window method
      - 2 windows: Sr-90 and Sr-90
      - 3 windows: Sr-90, Sr-89 and Y-90
    - Yield and Sr-90 in two different measurements
    - Allows result control by repeated measurements
    - No contribution of Sr-85 to background

Example 3 window method – no Sr-85

Window A: Sr-89/90 and Y-90

Window B: Sr-89 and Y-90

Window C: Y-90

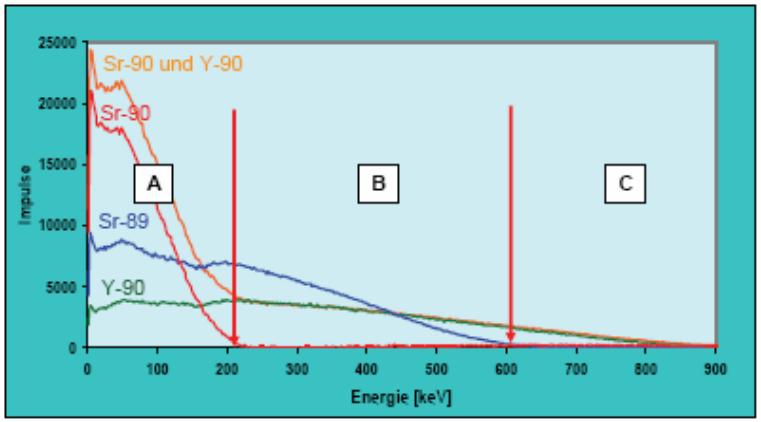


Abb. 3-1: Szintillationsspektren der Einzelnuklide Sr-89, Sr-90, Y-90 sowie der Nuklidmischung Sr-90 und Y-90 im radioaktiven Gleichgewicht.

Counting

- Cerenkov counting
  - Nuclides with $E_{\beta,max}$ > 500 meV (Sr-89 and Y-90)
  - Light emission at approx. 400 nm
  - Measurement with LS counter
  - Direct measurement of eluate
  - No scintillation cocktail needed, no mixed rad.waste
  - Very little interference from Sr-90 ε << 3%

Example of Sr-89 Cerenkov spectrum

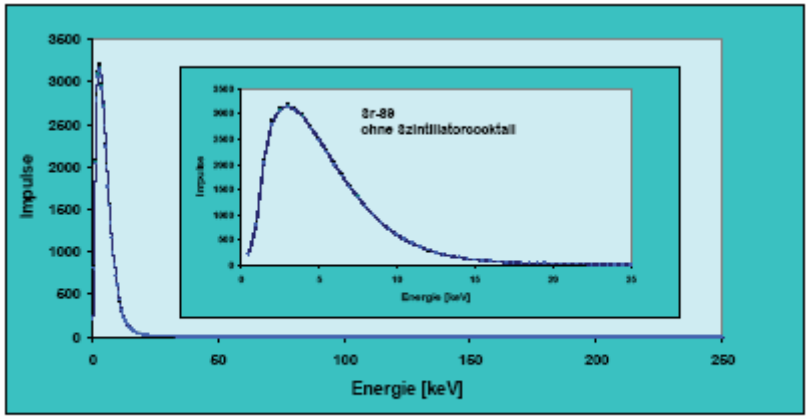


Abb. 3-4: Čerenkov-Spektrum von Sr-89

Counting

- GP counting
  - No spectrum, no energy window setting
  - No discrimination of radionuclides
  - Sr-90 direct, better via Y-90 ingrowth
    - multiple measurements
    - Y-90 measurement
  - Calculation of Sr-89 activity possible
  - Uncertainties
  - Very good calibration needed
  - Advantage: many samples at the same time (screening)
  - Improved DL when Y-90 in/near equilibrium

Typical detection efficiencies

Counting	Nuclide	type of sample	typical detection efficiency
Cerenkov	Y-90	liquid	0,80
	Sr-89	liquid	0,28
	Sr-90	liquid	< 0,003
GPC	Y-90	$Y_2(C_2O_4)_3$	0,54
	Sr-89	$SrCO_3$	0,51
	Sr-90	$SrCO_3$	0,41
LSC*	Y-90	liquid	0,99
	Sr-89	liquid	0,99
	Sr-90	liquid	0,97
	Sr-85	liquid	0,3 - 0,7 +

* mean of three different TriCarb LSC counter, 2mL toluenesulphonic acid / 18 mL UGLLT, integral 0 - 1200 keV, normal count mode

+ strongly depending on counter used

Nuclide	detection efficiency window A / % (0 - 12 keV)	detection efficiency window B / % (12 - 300 keV)	detection efficiency window C / % (300 - 1200 keV)
Y-90	0,3	33,4	66,5
Sr-89	2,0	51,2	47,0
Sr-90	6,7	90,2	0,0
Sr-85	61,7	7,7	0,0

Example TriCarb2550, 2mL toluenesulphonic acid / 18 mL UGLLT, normal count mode

Nuclide	detection efficiency window A / % (0 - 12 keV)	detection efficiency window B / % (12 - 300 keV)	detection efficiency window C / % (300 - 1200 keV)
Y-90	0,5	35,4	61,6
Sr-89	2,0	53,1	42,8
Sr-90	6,8	89,9	0,0
Sr-85	27,8	2,6	0,0

Example TriCarb2770, 2mL toluenesulphonic acid / 18 mL UGLLT, normal count mode

Typical yields and detection limits

	mass / volume of sample	typically obtained yield in %	approx. detection limit for Sr-89	approx. detection limit for Sr-90
Aerosol	52000 m^3	80 - 90	1,6 µBq/m^3	0,64 µBq/m^3
drinking water	1 - 2 L	80 - 100	0,1 Bq/L	0,01 Bq/L
drinking water	120 L	80 - 90		0,1 mBq/L
waste water	0,5 L	80 - 90	0,4 Bq/L	0,04 Bq/L
Urine	0,5L	70 - 90		0,04 Bq/L
vegetation	0,8 kg	60 - 80	0,1 Bq/kg FM	0,025 Bq/kg FM
foodstuff	0,8 kg	60 - 80	0,1 Bq/kg FM	0,025 Bq/kg FM
Milk	1 L	50 - 90		0,007 Bq/L
soil / sludge	5 - 30 g	50 - 80		0,1 Bq/kg

Summary

- Characteristics Sr resin
- Importance of preliminary matrix elimination
- Matrix, Sr content and column size
- Yields in general between 60 and 100 %
- Different types of counting with different advantages
- No mentioning of other applications
  - Pb-210/Po-210 determination
  - Ba/Ra separation
  - Radiopharmacy
- No mentioning of MS methods
  - Sr isotope ratios
  - Dating of soil samples and silicates, oil industry, origin of cheeses