

PRECISE DETERMINATION OF ^{89}Sr AND $^{90}\text{Sr}/^{90}\text{Y}$ IN VARIOUS MATRICES: THE LSC 3-WINDOW APPROACH

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ABSTRACT. A fast method is presented for determining radioactive isotopes of Sr in environmental and bioassay samples using extraction chromatography and liquid scintillation counting performed in a 3-window region under normal counting mode, which yields the best sensitivity values (E^2/B). Prior to application of radiochemical separation procedures, all samples are spiked initially with almost carrier-free ^{85}S tracer for calculation of the chemical recovery. After i) preconcentration of Sr via oxalic acid (soil, grass) or carbonate precipitation (urine, waste water) and ii) redissolution in nitric acid and purification using SrSpec resin, iii) LS counting is performed in a 3-window region, i.e. ranging from 0–10 keV (^{85}S spike); 10–300 keV, the maximum energy of ^{90}Sr on the LS scale (for $^{90}\text{Sr} + ^{89}\text{Sr}$); and 300–1200 keV (for $^{89}\text{Sr} + \text{ingrowing } ^{90}\text{Y}$). Constant quench conditions are obtained by preparing cocktail solutions consisting of a mixture of 2 mL toluene sulfonic acid (in which the Sr fraction is dissolved) and 18 mL Ultima Gold™ LLT scintillation liquid. This mixture results in highly reproducible β spectra, i.e. the counting efficiencies of the different isotopes remain constant and independent on the starting matrix taken for analysis. The respective counting windows were selected to obtain optimum sensitivity for the 2 radioactive Sr isotopes, i.e. to consider situations in which the activity of ^{90}Sr significantly exceeds that of ^{89}Sr and vice versa. Using low-level LS spectrometers such as the PerkinElmer Tri-Carb 2550TR/AB, detection limits for both Sr radioisotopes of <0.1 Bq/L are obtained in a 5×100 -min counting interval if 0.2-L water aliquots are processed. The 3-isotope/3-window approach was validated internally on various matrices and by participation in an intercomparison exercise on artificial reactor water samples (German Federal Inspectorate for Radiation Protection, BfS, intercomparison exercise 2004, lab code #75), which yielded identical results to the mean value of all participants (i.e. 1.7 ± 0.3 Bq/L for ^{89}Sr and 2.6 ± 0.3 Bq/L for ^{90}Sr).

INTRODUCTION

Monitoring of nuclear weapons testing fallout or accidentally released neutron fission or activation products around nuclear facilities is a major concern for environmental emission investigations. Of particular interest are activity measurements of highly toxic radioisotopes such as the pair $^{90}\text{Sr}/^{90}\text{Y}$ due to i) rather long residence time in the biosphere, ii) bio-availability for certain dietary products (Friedrich and Schönhofer 1996; Irlwick et al. 1999), and iii) high dose contribution after ingestion due to preferential fixation into the skeleton (e.g. ICRP 1988; Szabo 1993; Schönhofer et al. 1994; Mieltski et al. 2001). Furthermore, for determining radioisotopes in nuclear reactor waste or coolant water, short-lived ($T_{1/2} = 49$ days) ^{89}Sr has to be considered as well, especially since the activity of ^{89}Sr may exceed that of ^{90}Sr by up to a factor of 20 (e.g. Vogl and Gesewsky 1992). Since all of these 3 radionuclides decay by β emission solely, direct counting methods cannot be applied; rather, radiochemical separation methods have to be applied to isolate the triple ^{89}Sr , ^{90}Sr , ^{90}Y from the chemical matrix elements. This is necessary to avoid i) contribution from other radioisotopes to the total count rate and ii) to minimize self absorption of the particle radiation in the counting source. Furthermore, because β decay does not proceed on discrete energy levels such as α and γ radiation, (i.e. β spectra are continuously shaped), clear peak separation is not possible, even if quenching is reduced to a minimum in highly aromatic LS cocktails. Distinguishing between ^{89}Sr and ^{90}Sr in the same counting source therefore requires either separate counting of unsupported ^{90}Y (as a measure for ^{90}Sr) and the mixture of ^{89}Sr and ^{90}Sr (with regrowing ^{90}Y during counting) or application of modern LSC technology, where the 3 isotopes can be partially separated by the counting window setting. This work describes an optimized 3-window approach that allows a clear numerical separation between ^{89}Sr and ^{90}Sr including low-energy ^{85}S in the same spectrum. The addition of the latter

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isotope prior to the chemical separation procedure directly yields the chemical yield fraction, i.e. further laboratory steps to determine this parameter such as gravimetric or other analytical methods (e.g. via atomic adsorption or mass spectrometry) can be omitted. Chemical procedures are presented for cases in which the activity of ^{89}Sr significantly exceeds that of ^{90}Sr and vice versa.

METHODS

Separation Procedure for ^{89}Sr and ^{90}Sr

The method for separating radioactive Sr isotopes in environmental samples (soil, grass, etc.) is similar to procedures based on extraction chromatography on SrSpec resin (Eichrom Technologies), which was initially introduced by Vajda et al. (1992) and is still among the most efficient rapid methods for determining ^{89}Sr and ^{90}Sr in environmental materials. At the Paul Scherrer Institute (PSI), a slightly modified method is used that reduces the effort for chemical yield determination simply by counting added ^{85}Sr besides ^{89}Sr and ^{90}Sr in a second β window or via ICP measurement of stable Sr before and after the extraction chromatographic step. This method eliminates the need for a second precipitation step (following the extraction of Sr) for gravimetric yield determination. The separation scheme is shown in Figure 1. Initially, after dry ashing and adding of a few Bq of ^{85}Sr tracer the environmental samples (~30-g aliquots) are leached while gently boiling in 8M nitric acid (~1 hr), and solid and liquid phases are then separated by centrifugation. Aqueous samples (e.g. waste water, urine) are also acidified with nitric acid and boiled for 1 hr to oxidize all organic components. Prior to the extraction of Sr, a preceding precipitation step is carried out for the environmental samples using oxalic acid at pH 5–6. This step is required because the distribution coefficient for Sr on SrSpec resin decreases significantly in the presence of large quantities of alkaline elements (particularly potassium; details in Horwitz et al. 1992). Scoping experiments revealed that for the aqueous samples, the highest precipitation yields for Sr were obtained via carbonate precipitation under alkaline conditions (i.e. increase of the pH to about 11 with NaOH, then addition of a few grams of Na_2CO_3 to a 0.5-L starting solution). The precipitates are dissolved while boiling in 20 mL 65% HNO_3 until the solid fraction has been destroyed completely (a clear, colorless solution should result). This solution is dried again, redissolved in 15 mL 3M HNO_3 , and passed through a commercially available SrSpec column. After passing through of the sample solution, the column is rinsed 4 times with 3M HNO_3 (washing step is important if traces of $^{133,140}\text{Ba}$ are present) to eliminate further radioisotopes. For routine analysis (e.g. environmental monitoring of fallout ^{90}Sr without short-lived ^{89}Sr), the Sr fraction is eluted with 10 mL 0.05M HNO_3 in a glass beaker, evaporated, dissolved in 2 mL 25 wt% toluene sulphuric acid, and finally transferred into a 20-mL LS vial. Before LS measurement, the counting cocktail is prepared by mixing the sample solution with 18 mL of a highly aromatic scintillation liquid such as Ultima Gold™ LLT to minimize chemical quenching. If ^{89}Sr is of major concern and in large excess over ^{90}Sr (for instance, after a nuclear accident), it is recommended to allow ^{90}Y to build up onto the column for 1 to 2 days and to analyze 2 cocktails separately (one with a pure ^{90}Y fraction counted in Cerenkov mode and the other mixed with a scintillation liquid for $^{89,90}\text{Sr}$ counting). For the latter cocktail, 3 counting windows have to be set to convolute the continuum β spectrum of i) ^{90}Sr (with ingrowing ^{90}Y), ii) ^{89}Sr , and iii) the added ^{85}Sr yield tracer into these 3 components (see Figures 2 and 3 for the single and composite β spectra of the Sr isotopes). In particular, the following settings were selected for optimized measurement precision of all radioisotopes:

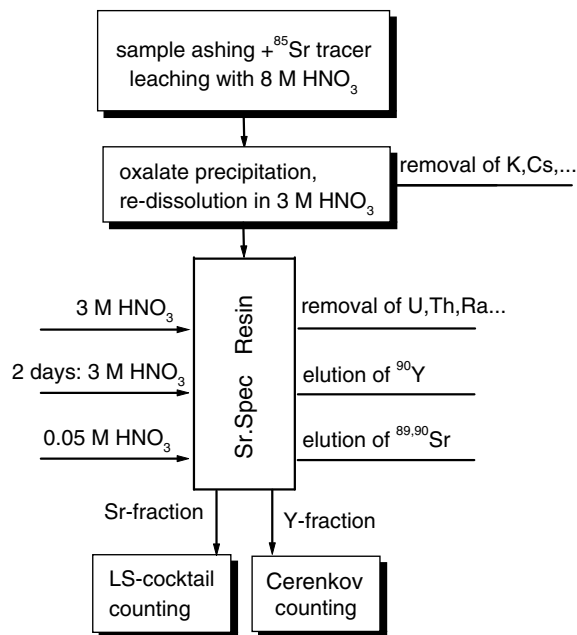


Figure 1 Flow chart showing the separation scheme for analysis of $^{89,90}\text{Sr}$ in environmental samples (soil, grass) via α/β LSC.

Window A: 0–12 keV: for ^{85}Sr chemical yield determination. The following isotopes are measured in this region: ^{85}Sr + ^{90}Sr (~50% and 10% efficiency in normal LS count mode) with a small contribution of high-energy ^{89}Sr and ^{90}Y (<2%).

Window B: 12–300 keV: window setting to the maximum β -emission energy of ^{90}Sr . All relevant isotopes are measured in this region: ^{90}Sr (~90% efficiency), ^{90}Y (~40%), ^{89}Sr (~50%), and ^{85}Sr (~10%).

Window C: 300–1200 keV: region for high-energy ^{89}Sr and ^{90}Y . Only these 2 isotopes are counted in this region: ^{89}Sr (about 50% efficiency) and ^{90}Y (about 60%).

After window setting, counting is carried out via low-level LSC, using a PerkinElmer Tri-Carb 2770 TR/SLL equipped with a BGO detection guard for coincidence/anticoincidence background suppression (for details: Cook 1995; Packard Instrument Publication 1995; Noakes and Valenta 1996).

Calculation of the ^{89}Sr and ^{90}Sr Activity Concentration

The following set of parameters is used for calculating the activity concentrations of ^{85}Sr , ^{89}Sr , and ^{90}Sr :

$t(0)$: time of the $^{90}\text{Sr}/^{90}\text{Y}$ separation on the SrSpec column followed by stripping of the Sr fraction;

$t(m)$: time of measurement;

Δt_m : time difference between measurement and $t(0)$;

Δt_{ref} : time difference between $t(0)$ and the reference date;

$A(0)_{^{90}\text{Sr}}$: activity of ^{90}Sr in the scintillation cocktail at $t(0)$;

$A(t)_{^{90}\text{Y}}$: activity of ^{90}Y in the scintillation cocktail at $t(m)$;

- $A(t)_{89}$: activity of ^{89}Sr in the scintillation cocktail at $t(m)$;
 $A(0)_{89}$: activity of ^{89}Sr in the scintillation cocktail at $t(0)$;
 $A(t)_{85}$: activity of the added ^{85}Sr tracer in the scintillation cocktail at $t(m)$;
 $A(0)_{85}$: activity of the added ^{85}Sr tracer in the scintillation cocktail at $t(0)$;
 $N(t)_m$: measured total net count rate at $t(m)$ in the respective counting windows (i.e. A, B, and C);
 $\epsilon_{90\text{Sr}}$: counting efficiencies of ^{90}Sr in the respective counting windows (i.e. A, B, and C);
 $\epsilon_{90\text{Y}}$: counting efficiencies of ^{90}Y in the respective counting windows (i.e. A, B, and C);
 ϵ_{89} : counting efficiencies of ^{89}Sr in the respective counting windows (i.e. A, B, and C);
 ϵ_{85} : counting efficiencies of ^{85}Sr in the respective counting windows (i.e. A, B, and C);
 λ_i : decay constant of the respective radionuclide (i), taken from Firestone and Shirley (1996): $\lambda_{90\text{Sr}} = 6.550 \times 10^{-5} / d$; $\lambda_{89\text{Sr}} = 1.372 \times 10^{-2} / d$; $\lambda_{85\text{Sr}} = 1.068 \times 10^{-2} / d$; $\lambda_{90\text{Y}} = 2.599 \times 10^{-1} / d$;
 Y_{chem} : chemical yield or recovery;
 V_{samp} : sample volume taken for analysis.

The following general relationship holds for the net count rates (corrected for background scatter) in a 3-isotope system consisting of ^{85}Sr , ^{89}Sr , and ^{90}Sr (with ingrowing ^{90}Y), which are measured in 3 counting regions (i.e. in widows A, B, and C):

$$N(t)_m^A = N(t)_{85}^A + N(t)_{89}^A + N(0)_{90\text{Sr}}^A + N(t)_{90\text{Y}}^A \quad (1)$$

$$N(t)_m^B = N(t)_{85}^B + N(t)_{89}^B + N(0)_{90\text{Sr}}^B + N(t)_{90\text{Y}}^B \quad (2)$$

$$N(t)_m^C = N(t)_{85}^C + N(t)_{89}^C + N(0)_{90\text{Sr}}^C + N(t)_{90\text{Y}}^C \quad (3)$$

Decay of ^{90}Sr is neglected here, since the typical counting times of a few days and less are very short compared to the half-life of ^{90}Sr (i.e. 29 yr or $T_{1/2} [^{90}\text{Sr}] \gg \Delta t_m$), which means that radioactive decay of ^{90}Sr during this time period is about 1% or less. Considering the relationship between activity and counting rate for a β -emitting isotope (i) in a liquid scintillation counter yields:

$$A_i = N_i / \epsilon_i \quad (4)$$

Furthermore, considering the ingrowth of ^{90}Y during measurement according to the relationship between long-lived parent and short-lived progeny after complete removal of ^{90}Y at $t(0)$, i.e. for $\lambda_{90\text{Sr}} \ll \lambda_{90\text{Y}}$ and for the boundary condition $A(0)_{90\text{Y}} = 0$:

$$A(t)_{90\text{Y}} = A(0)_{90\text{Sr}} \cdot (1 - e^{-\lambda_{90\text{Y}} \Delta t_m}) \quad (5)$$

with the ingrowth term:

$$f_1 = (1 - e^{-\lambda_{90\text{Y}} \Delta t_m}) \quad (6)$$

The following set of expressions is obtained for Equations 1, 2, and 3:

$$N(t)_m^A = A(t)_{85} \cdot \epsilon_{85}^A + A(t)_{89} \cdot \epsilon_{89}^A + A(0)_{90\text{Sr}} \cdot \epsilon_{90\text{Sr}}^A + A(0)_{90\text{Sr}} \cdot f_1 \cdot \epsilon_{90\text{Y}}^A \quad (7)$$

$$N(t)_m^B = A(t)_{85} \cdot \epsilon_{85}^B + A(t)_{89} \cdot \epsilon_{89}^B + A(0)_{90\text{Sr}} \cdot \epsilon_{90\text{Sr}}^B + A(0)_{90\text{Sr}} \cdot f_1 \cdot \epsilon_{90\text{Y}}^B \quad (8)$$

$$N(t)_m^C = A(t)_{89} \cdot \epsilon_{89}^C + A(0)_{90Sr} \cdot f_1 \cdot \epsilon_{90Y}^C \quad (9)$$

Solving (9) for $A(t)_{89}$:

$$A(t)_{89} = \frac{N(t)_m^C}{\epsilon_{89}^C} + \frac{A(0)_{90Sr} \cdot f_1 \cdot \epsilon_{90Y}^C}{\epsilon_{89}^C} \quad (10)$$

Inserting $A(t)_{89}$ in (7) and (8), i.e.

$$N(t)_m^A = A(t)_{85} \cdot \epsilon_{85}^A + N(t)_m^C \cdot \frac{\epsilon_{89}^A}{\epsilon_{89}^C} - A(0)_{90Sr} \cdot f_1 \cdot \epsilon_{90Y}^C \cdot \frac{\epsilon_{89}^A}{\epsilon_{89}^C} + A(0)_{90Sr} \cdot (\epsilon_{90Sr}^A + f_1 \cdot \epsilon_{90Y}^A) \quad (11)$$

$$N(t)_m^B = A(t)_{85} \cdot \epsilon_{85}^B + N(t)_m^C \cdot \frac{\epsilon_{89}^B}{\epsilon_{89}^C} - A(0)_{90Sr} \cdot f_1 \cdot \epsilon_{90Y}^C \cdot \frac{\epsilon_{89}^B}{\epsilon_{89}^C} + A(0)_{90Sr} \cdot (\epsilon_{90Sr}^B + f_1 \cdot \epsilon_{90Y}^B) \quad (12)$$

and solving for $A(t)_{85}$ yields:

$$A(t)_{85} = \frac{N(t)_m^A}{\epsilon_{85}^A} + N(t)_m^C \cdot \frac{\epsilon_{89}^A}{\epsilon_{89}^C \cdot \epsilon_{85}^A} + A(0)_{90Sr} \cdot f_1 \cdot \frac{\epsilon_{90Y}^C \cdot \epsilon_{89}^A}{\epsilon_{89}^C \cdot \epsilon_{85}^A} - A(0)_{90Sr} \cdot \frac{(\epsilon_{90Sr}^A + f_1 \cdot \epsilon_{90Y}^A)}{\epsilon_{85}^A} \quad (13)$$

$$A(t)_{85} = \frac{N(t)_m^B}{\epsilon_{85}^B} + N(t)_m^C \cdot \frac{\epsilon_{89}^B}{\epsilon_{89}^C \cdot \epsilon_{85}^B} + A(0)_{90Sr} \cdot f_1 \cdot \frac{\epsilon_{90Y}^C \cdot \epsilon_{89}^B}{\epsilon_{89}^C \cdot \epsilon_{85}^B} - A(0)_{90Sr} \cdot \frac{(\epsilon_{90Sr}^B + f_1 \cdot \epsilon_{90Y}^B)}{\epsilon_{85}^B} \quad (14)$$

Summarizing the efficiency ratios as follows:

$$k_1 = \frac{\epsilon_{89}^A}{\epsilon_{89}^C \cdot \epsilon_{85}^A}, l_1 = \frac{\epsilon_{90Y}^C \cdot \epsilon_{89}^A}{\epsilon_{89}^C \cdot \epsilon_{85}^A}, m_1 = \frac{(\epsilon_{90Sr}^A + f_1 \cdot \epsilon_{90Y}^A)}{\epsilon_{85}^A} \quad (15)$$

$$k_2 = \frac{\epsilon_{89}^B}{\epsilon_{89}^C \cdot \epsilon_{85}^B}, l_2 = \frac{\epsilon_{90Y}^C \cdot \epsilon_{89}^B}{\epsilon_{89}^C \cdot \epsilon_{85}^B}, m_2 = \frac{(\epsilon_{90Sr}^B + f_1 \cdot \epsilon_{90Y}^B)}{\epsilon_{85}^B} \quad (16)$$

Inserting the factor k , l , and m into (13) and (14), eliminating $A(t)_{85}$, and rearranging for $A(0)_{90Sr}$ yields:

$$A(0)_{90Sr} \cdot (f_1 \cdot l_1 - m_1 - f_1 \cdot l_2 + m_2) = \frac{N(t)_m^B}{\epsilon_{85}^B} - \frac{N(t)_m^A}{\epsilon_{85}^A} + N(t)_m^C \cdot (k_1 - k_2) \quad (17)$$

Finally, $A(0)_{90Sr}$ can be inserted into the rearranged Equation 9 for calculation of $A(t)_{89}$, or:

$$A(t)_{89} = \frac{N(t)_m^C - A(0)_{90Sr} \cdot f_1 \cdot \epsilon_{90Y}^C}{\epsilon_{89}^C} \quad (18)$$

and additionally by inserting $A(0)_{90Sr}$ as well as $A(t)_{89}$ into the rearranged expression (7):

$$A(t)_{85} = \frac{N(t)_m^A - A(t)_{89} \cdot \epsilon_{89}^A - A(0)_{90Sr} \cdot (\epsilon_{90Sr}^A + f_1 \cdot \epsilon_{90Y}^A)}{\epsilon_{85}^A} \quad (19)$$

Correcting decay of rather short-lived ^{85}Sr and ^{89}Sr to the separation date, i.e. solving for $A(0)_{85}$ and $A(0)_{89}$ at $t(0)$:

$$A(0)_{85,89} = A(t)_{85,89} \cdot e^{\lambda_{85,89} \cdot \Delta t_m} \quad (20)$$

Finally, considering the chemical yield or recovery, i.e. the ratio between initially added and actually measured ^{85}Sr , or $Y_{chem} = A(0)_{85} / A(0)_{85,add}$, considering furthermore the sample volume or quantity taken for analysis and correcting for radioactive decay of ^{89}Sr and ^{90}Sr at the reference date yields:

$$A(ref)_{89,90} = A(0)_{89,90} \cdot e^{\lambda_{89,90} \cdot \Delta t_{ref}} \cdot \frac{1}{Y_{chem} \cdot V_{samp}} \quad (21)$$

RESULTS AND DISCUSSION

Optimized Window Settings

While windows A and C should be in the fixed position for measuring the most precise count rate of the added low-energy ^{85}Sr tracer and the maximum emission energy of the isotope with the highest emission energy (^{90}Y), the setting of window B allows some flexibility. Window B can be fixed either at the end-point energy of ^{90}Sr (as in this study) or the end-point energy of ^{89}Sr at a higher channel number. The setting proposed here was selected for 2 major reasons:

1. The activity distribution between ^{89}Sr and ^{90}Sr can be immediately obtained for counting sources that are measured shortly after separation (because distinguishing both radioisotopes in 1 counting region without significant growth of ^{90}Y is not possible), i.e. this setting yields rapid results;
2. ^{89}Sr can still be measured with high precision for cases with $^{90}\text{Sr} > ^{89}\text{Sr}$, provided, however, that preparation and measurement of the counting source is done immediately after the separation step (ingrowth of ^{90}Y for initial counting should be minor).

Counting Mode Setting

Table 1 summarizes the counting efficiencies for ^{85}Sr , ^{89}Sr , ^{90}Sr , and ^{90}Y determined under low-level and normal count conditions for 3 PerkinElmer Tri-Carb LS spectrometers. It is clear that under normal count conditions, the isotopes ^{89}Sr , ^{90}Sr , and ^{90}Y are measured with maximum counting efficiencies of close to 100%, while the low-level count mode reduces these efficiencies by about a factor of 2 (see integrated values for total count window in the last 2 columns of Table 1). It is also interesting to note that for Tri-Carb 2770TR/AB (equipped with a Bi-Germanate [BGO] detector guard), the counting efficiency for the ^{85}Sr spike is much lower compared to the other LS spectrometers. This is due to the fact that decay of ^{85}Sr by electron capture (EC) is accompanied by γ radiation (at 514 keV). This radiation is partially absorbed in the detector guard material surrounding the cocktail vial. Since EC and γ emission proceed simultaneously, both signals are recognized as a coincidence pulse, i.e. the pulse processing electronics for BGO models reject this event in an identical manner as cosmic radiation-induced events are suppressed in order to reduce the background noise.

Table 1 LSC counting efficiencies for ^{85}Sr , ^{89}Sr , ^{90}Sr , and ^{90}Y determined under low-level and normal count conditions for 3 Tri-Carb LS spectrometers. Cocktail composition: 2 mL toluene sulphonic acid (25%) + 18 mL Ultima Gold LLT.

Isotope	Counting efficiency (%) window A 0–12 keV		Counting efficiency (%) window B 12–300 keV		Counting efficiency (%) window C 300–1200 keV		Counting efficiency integral 0–1200 keV (%)	
	normal	low level	normal	low level	normal	low level	normal	low level
	Tri-Carb 2200							
^{85}Sr	57.0	43.1	7.8	1.9	0.0	0.0	64.8	45.0
^{89}Sr	1.6	1.4	53.5	21.8	45.2	26.6	100.3	49.8
^{90}Sr	7.1	5.9	91.3	46.8	0.0	0.0	98.8	52.7
^{90}Y	0.2		35.3		64.3		99.8	
Tri-Carb 2550								
^{85}Sr	61.7	44.7	7.7	1.8	0.0	0.0	69.4	46.5
^{89}Sr	2.0	1.8	51.2	21.2	47.0	18.7	100.2	41.7
^{90}Sr	6.7	5.6	90.2	44.3	0.0	0.0	96.9	49.9
^{90}Y	0.3		33.4		66.5		99.9	
Tri-Carb 2770								
^{85}Sr	27.8	21.1	2.6	0.5	0.0	0.0	30.4	21.6
^{89}Sr	2.0	1.6	53.1	21.7	42.8	13.3	97.9	36.6
^{90}Sr	6.8	5.5	89.9	40.2	0.0	0.0	96.7	45.7
^{90}Y	0.5		35.4		61.6		97.5	

The most important parameter affecting the counting sensitivity in gross α/β proportional and LS counters is the counting efficiency (E) divided by the square root of the background count rate (B) (cf. Equation 26); this quantity is often expressed in the literature as E^2/B . The values obtained here for background count rates and counting sensitivity are listed in Tables 2 and 3. It is obvious that for the high-energy β -emitting isotopes, normal count conditions yield significantly higher counting performance values; therefore, low-level settings are not recommended in this investigation.

Table 2 Background (blank) count rates for 3 different PerkinElmer LS spectrometers.

Counter	Blank count rate (cpm) window A 0–12 keV		Blank count rate (cpm) window B 12–300 keV		Blank count rate (cpm) window C 300–1200 keV	
	normal	low level	normal	low level	normal	low level
	Tri-Carb 2200	6.6	4.5	13.9	5.4	6.4
Tri-Carb 2550	6.2	3.7	12.9	4.8	7.2	1.6
Tri-Carb 2770	2.2	1.5	4.6	1.6	2.9	0.7

Table 3 Compilation of counting sensitivities (E^2/B) for 3 PerkinElmer LS spectrometers.

Isotope	Counting window	Tri-Carb 2200		Tri-Carb 2550		Tri-Carb 2770	
		normal	low level	normal	low level	normal	low level
		^{85}Sr	A	490	410	610	540
^{89}Sr	B+C	480	150	520	190	1220	530
^{90}Sr	B	600	410	630	400	1760	1000
^{90}Y	B+C	490		500		1250	

Case Studies

Two cases are discussed below with i) ^{90}Sr in excess over ^{89}Sr or both radionuclides in comparable quantity (in terms of activity) and ii) ^{89}Sr in excess over ^{90}Sr . Significant excess of ^{90}Sr is typical for present-day environmental samples (e.g. soil, grass) because fallout ^{89}Sr has decayed completely. On the other hand, considerable excess of ^{89}Sr (compared to ^{90}Sr) may arise in operating nuclear power plants (e.g. in reactor coolant waters) if short-lived ^{89}Sr is close to saturation with respect to production/decay while long-lived ^{90}Sr is far away from its saturation level (typical situation for fuel elements that were replaced recently).

Case (i) $^{90}\text{Sr} > ^{89}\text{Sr}$, $^{90}\text{Sr} \approx ^{89}\text{Sr}$. For this situation (i.e. $^{90}\text{Sr}/^{89}\text{Sr}$ ranging from 100 to 0.1), it is suitable to use the method presented here because the counting efficiencies for ^{90}Sr and ^{89}Sr in window B are comparable, but all counting efficiencies have different values in the different counting windows. Therefore, the linear equation system (3 equations, 3 components, different coefficients) yields a meaningful solution. This case is depicted graphically in Figures 2 and 3, which show the smoothed spectra for ^{85}Sr , ^{90}Sr , and ^{90}Y (Figure 2) and for ^{85}Sr and ^{89}Sr (Figure 3). The composite spectra (^{85}Sr , ^{90}Sr , and ^{90}Y in Figure 2; all 4 isotopes in Figure 3) are additionally shown. All spectra were obtained by separate measurements of each isotope, and the composite spectrum was generated mathematically by integrating the counts of all isotopes in the respective channel. For comparable activities, the peaks of both high-energy isotopes (^{89}Sr , ^{90}Y) remain poorly resolved, while the peak of ^{90}Sr (which emits β radiation at considerably lower energy) can still be discerned in the composite spectrum. This is advantageous when visually monitoring sample quenching and potential electronic shifting using the counting window settings as proposed here.

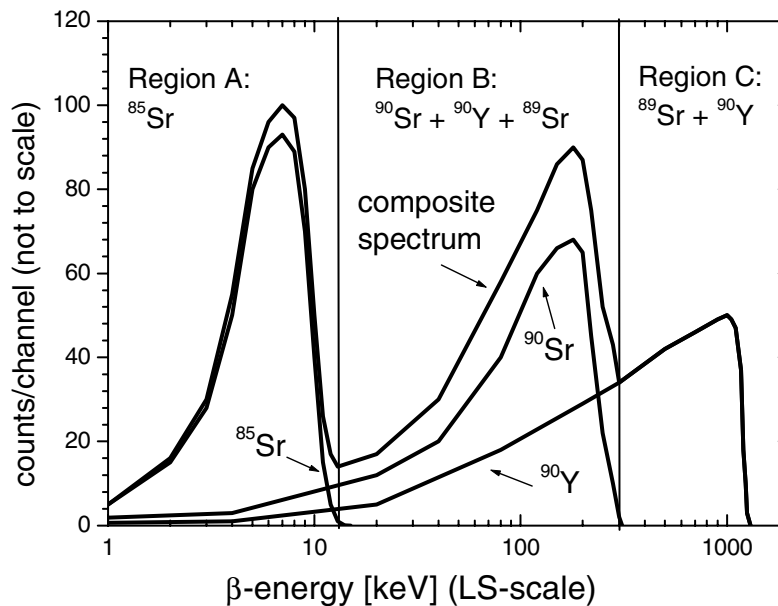


Figure 2 LSC β spectra of ^{85}Sr , ^{90}Sr and ^{90}Y (obtained from separate isotope measurements). The composite spectrum (superposition) of all 3 isotopes is also shown. Three counting windows (i.e. region A: ^{85}Sr ; region B: ^{90}Sr ; region C: ^{90}Y) were selected to allow most precise measurement of each of the 3 isotopes.

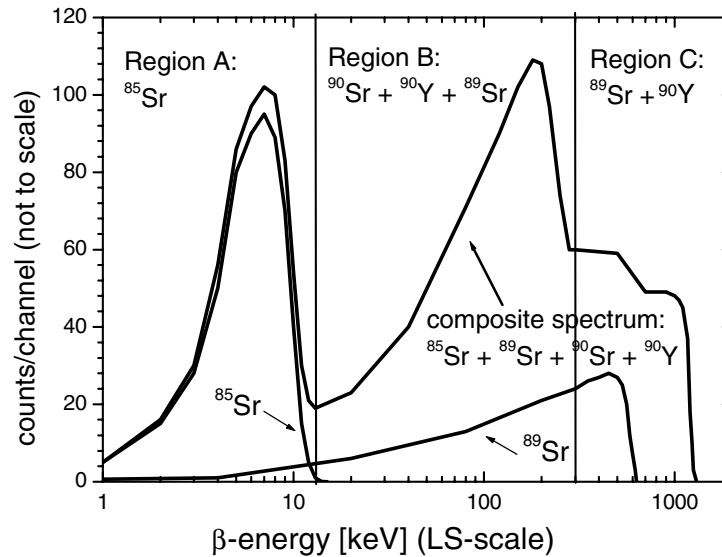


Figure 3 LSC β spectra of ^{85}Sr and ^{89}Sr (obtained from separate isotope measurements). The composite spectrum (superposition) of these isotopes including ^{90}Sr and ^{90}Y from Figure 2 is additionally shown. It is clear that for comparable activities of ^{89}Sr and ^{90}Sr , clear peak separation between all isotopes is almost impossible.

Case (ii) $^{90}\text{Sr} \ll ^{89}\text{Sr}$. For this case, it is advantageous to additionally measure the ^{90}Y that rebuilds on the SrSpec column after a first purification for 2 reasons: 1) the ingrowth of ^{90}Y in the Sr fraction cannot be accurately measured in presence of a large quantity of ^{89}Sr ; and 2) determination of $A(0)_{\text{Sr}90} + A(0)_{\text{Sr}89}$ via counting directly after the separation (i.e. without regarding build-up of ^{90}Y) may give a systematically wrong result because of luminescence contribution from freshly prepared cocktail samples that were exposed to light shortly before the assay was initiated. For such extreme low $^{90}\text{Sr}/^{89}\text{Sr}$ activity ratios, it is recommended to allow partial ingrowth of ^{90}Y onto the SrSpec resin after loading Sr onto the column and a first purification step with 3M HNO_3 . The column is then set aside for 1–2 days and the partially regrown fraction of ^{90}Y is again eluted with 3M HNO_3 . The elution solution is directly rinsed into a cocktail vial, which is taken for counting high-energy ^{90}Y via Cerenkov light emission. The ingrowth/decay relationship of ^{90}Y after the first extraction on the SrSpec column is illustrated schematically in Figure 4. While the activity of ^{90}Sr between the first (t_0) and second (t_1) milking does not change in a detectable manner (i.e. $A[t]_{90\text{Sr}} = A[0]_{90\text{Sr}}$), initially removed ^{90}Y grows on the column again but then decays parent unsupported during Cerenkov measurement after a second stripping from the SrSpec column. The Cerenkov measurement of decaying ^{90}Y as a function of time (Δt_m) yields the initial activity of ^{90}Sr that is fixed on the column, $A(0)_{90\text{Sr}}$. The most precise result for this quantity is obtained via regression analysis of the measured ^{90}Y activity as a function of time, which is shown in Figure 5 for a typical soil aliquot of 30 g with a ^{90}Sr activity concentration of 8 Bq/kg. The chemical yield for this sample was 80% and the detector efficiency for low-level Cerenkov counting was about 60%, which gives an initial ^{90}Y net count rate of about 7 cpm. If the assay is carried out with modern LS counters, such as the Tri-Carb 2770SLL/BGO (with a background count rate as low as 2.5 cpm for Cerenkov window setting between 1–25 keV), the decay of ^{90}Y can be easily followed over 2–3 half-lives (i.e. about 1 week) to obtain $A(0)_{90\text{Sr}}$ with high accuracy.

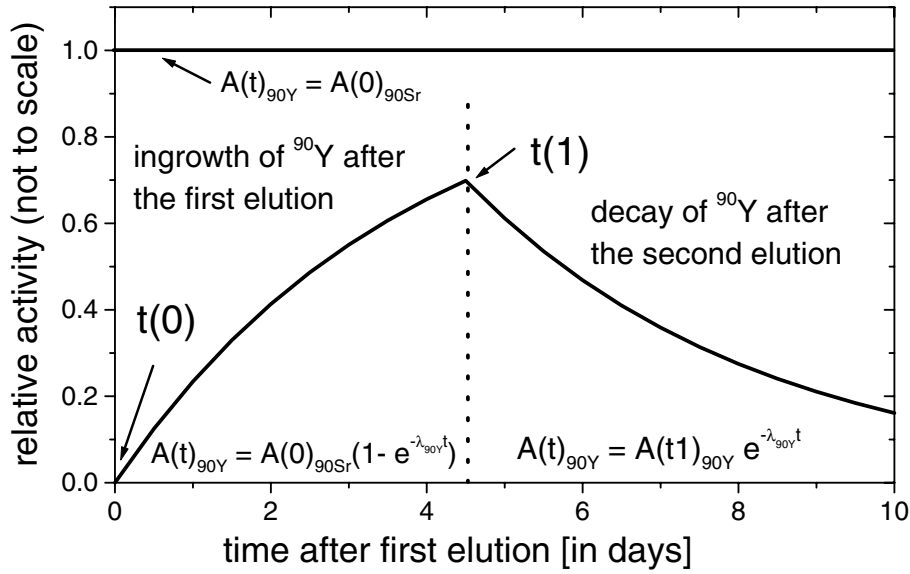


Figure 4 Schematic illustration of the build-up of ⁹⁰Y on SrSpec column after a first elution and decay during Cerenkov counting after the second extraction.

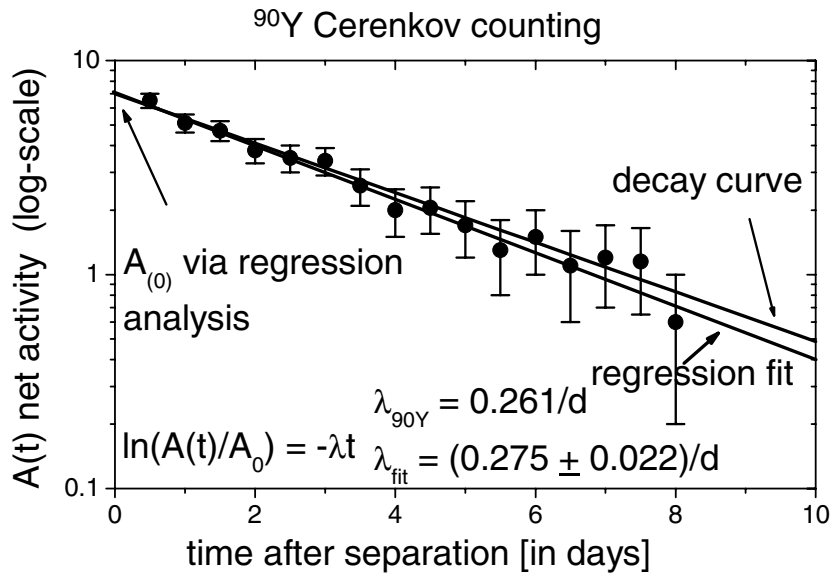


Figure 5 Decay of unsupported ⁹⁰Y eluted from a SrSpec column with time (net count rate, semi-log scale). The initial activity $A(0)_{90Y} = A(0)_{Sr}$ is obtained via regression analysis through the data.

Regarding that $A = N/\epsilon$ and considering the ingrowth/decay of ⁹⁰Y (as schematically shown in Figure 4), the following relation holds for the activity of ⁹⁰Sr that is fixed on the SrSpec column:

$$A(0)_{90Sr} = \frac{N(t)_{90Y} \cdot e^{\lambda_{90Y} \Delta t_m}}{\epsilon_{90Y, Cer} \cdot (1 - e^{-\lambda_{90Y} \Delta t_1})} \quad (22)$$

As soon as the ^{90}Y fraction has been collected, ^{89}Sr and ^{90}Sr are stripped off the column (with 10 mL 0.05M HNO_3), and this fraction is evaporated, dissolved in 2 mL 25 wt% toluene sulphuric acid, transferred into a 20-mL LS vial, and mixed with 18 mL Ultima Gold LLT (see details in the section “Separation Procedure for ^{89}Sr and ^{90}Sr ”). For this cocktail, the net count rate in window B+C (i.e. sum of ^{89}Sr , ^{90}Sr , ingrowing ^{90}Y , and a small fraction of ^{85}Sr) is as follows:

$$N(t)_m^{B+C} = N(t)_{85Sr}^{B+C} + N(t)_{89Sr}^{B+C} + N(0)_{90Sr}^{B+C} + N(t)_{90Y}^{B+C} \quad (23)$$

It has to be noted that this time windows B+C should be summarized because calculation of ^{90}Sr in the presence of large excesses of ^{89}Sr may not yield a precise result in the 3-window approach (but calculation of ^{85}Sr in the low-energy window A can still be performed with high-precision, independent of the $^{89}Sr/^{90}Sr$ activity ratio). In Equation 23, replacing $N(0)_{85Sr}$ by $A(0)_{85Sr} \cdot \epsilon_{85Sr}$, $N(0)_{90Sr}$ by $A(0)_{90Sr} \cdot \epsilon_{90Sr}$, and considering that growing $N(t)_{90Y}$ depends solely on $A(0)_{90Sr}$ (Equations 5, 6), $N(t)_{89Sr}$ can be calculated precisely by inserting $A(0)_{90Sr}$ obtained from the Cerenkov count of ^{90}Y (Equation 22):

$$N(t)_{89Sr}^{B+C} = N(t)_m^{B+C} - \epsilon_{85Sr}^{B+C} \cdot A(0)_{85Sr} - A(0)_{90Sr} (\epsilon_{90Sr}^{B+C} + \epsilon_{90Y}^{B+C} \cdot f_1) \quad (24)$$

The calculated net count rate for ^{89}Sr now enables determination of the ^{89}Sr activity via the relationship $A = N/\epsilon$. Additionally, correcting decay for the elution time of the Sr fraction, the activity of ^{89}Sr (at $t = 0$) is finally calculated as follows:

$$A(0)_{89} = \frac{N(t)_{89}^{B+C} \cdot e^{\lambda_{89} \cdot \Delta t_m}}{\epsilon_{89}^{B+C}} \quad (25)$$

Correcting for the chemical yield (i.e. losses of the analyte during the radiochemical procedure), as well as to a reference date, can be done using Equation 21.

Measurement Uncertainty and Detection Limit Calculations

Calculation of the measurement uncertainty can be performed using the law of error propagation for the following parameters: i) counting statistics and ii) uncertainties of the quantity as well as the activity concentration of the added ^{85}Sr spike, provided, however, that counting is carried out under identical quench conditions (i.e. the counting efficiency has to remain constant with time in all windows; i.e. calculation of the uncertainty budget via non-correlated uncertainties). This can be easily checked by observation of the ^{85}Sr peak in window A, the end-point β energy of ^{90}Y in window C, and by the spectrum index parameter from measurement of an external standard.

The minimum detectable concentration (MDC) at the 95% (2σ) confidence probability level was calculated analyzing blank samples using the following equation (according to Seymour et al. 1992):

$$MDC[(Bq)/(kg)] = \frac{2.71 + 2 \cdot K \sqrt{2 \cdot I_0}}{t \cdot Y_{chem} \cdot \epsilon \cdot V_s} \quad (26)$$

where $K = 1.65$ = statistical value for a $2\text{-}\sigma$ confidence level; I_0 = total background counts of a blank sample in time t ; t = counting time; Y_{chem} = chemical recovery; ϵ = counting or detector efficiency; and V_s = sample volume taken for analysis (all parameters in Table 4). The development of the detection limit as a function of measurement time is given in Figure 6 (soil sample as an example). It is obvious that within hours and for sample quantities of ~ 30 g, the detection limits drop clearly below the average environmental level of ^{90}Sr from nuclear weapons fallout in soils from northern Switzerland. The MDC is slightly higher for ^{90}Y if build-up time on the SrSpec column is rather short (here 2 days) and due to the lower detector efficiency compared to the LS cocktail measurement of ^{89}Sr and ^{90}Sr . Furthermore, with time the MDA of ^{90}Sr reaches the lowest values among the 3 isotopes due to continuous ingrowth of ^{90}Y in the sample cocktail.

Table 4 Set of parameters used for the calculation of the minimum detectable activities (MDAs) of ^{89}Sr , ^{90}Sr (scintillation cocktail, normal count mode), and ^{90}Y (Cerenkov measurement, low-level counting) in soil samples measured via LSC (using a Tri-Carb 2770).

Isotope	Parameter			
	I_0/t (cpm)	Y_{chem} (%)	ϵ (%)	V_s (kg)
^{89}Sr	9.7	80	98	0.03
^{90}Sr	6.8	80	97	0.03
^{90}Y	2.5	80	62	0.03

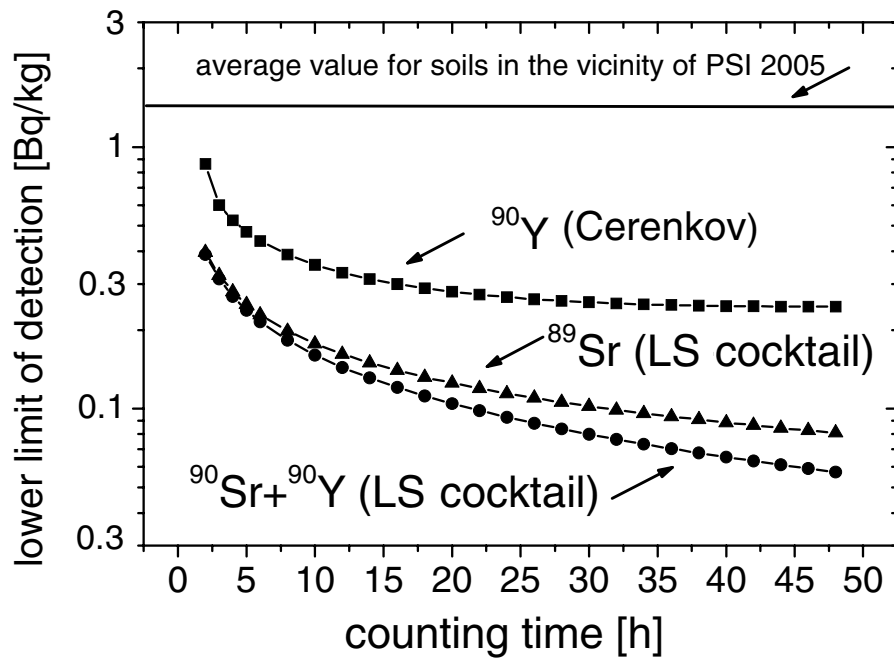


Figure 6 Lower limit of detection with time for ^{89}Sr , ^{90}Sr (scintillation cocktail), and ^{90}Y (as a measure for ^{90}Sr) via Cerenkov counting.

CONCLUSION

LSC is a highly practicable technique for determining ^{89}Sr alongside ^{90}Sr because LS spectrometry allows analytical convolution of β spectra if 3 counting windows are set at defined end-point energies of β emitters (here ^{85}Sr as yield tracer, ^{90}Sr and ^{90}Y). This is of high advantage over ionization counters that measure gross count rates solely. The method for simultaneous determination of ^{89}Sr and ^{90}Sr enables, in addition, determination of the chemical yield in the same spectrum, i.e. further steps (such as gravimetric yield determination) or further optical methods (such as AAS or ICP-OES) are no longer required. To precisely distinguish between ^{89}Sr and ^{90}Sr especially if ^{89}Sr is in excess over ^{90}Sr , it is, however, advantageous to also perform a Cerenkov measurement of ^{90}Y that grows in on a SrSpec extraction chromatography column after a first purification of the Sr fraction. Application of LSC for environmental determination of ^{89}Sr and ^{90}Sr is sufficiently sensitive within short counting times of a few hours. For instance, using the method described above, detection limits for ^{90}Sr of <0.5 Bq/kg are reached in <2 hr counting time if ~ 30 -g soil aliquots are taken for analysis, i.e. a value that is below typical environmental levels of ^{90}Sr in most parts of the Northern Hemisphere. Therefore, for cases requiring several environmental samples to be processed, LS spectrometry allows high sample throughputs even if low detection limits should be obtained.

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