

Chapter 2

Determination of Strontium-90 and Strontium-89 in Environmental Samples by Liquid Scintillation Counting

L. Salonen

Institute of Radiation Protection, P.O. Box 268, SF-00101, Helsinki 10, Finland.

INTRODUCTION

The simultaneous measurement of ^{89}Sr and ^{90}Sr using the liquid scintillation technique has been the topic of growing interest due to the need for a quick and accurate method for monitoring analysis with the increasing activities of the nuclear industry. The interest in using this technique, instead of the low-background β -counting, arises for many reasons. The main ones are the fully automatic and very reliable performance of the modern counters compared to the low-background beta counters, and the possibility of getting results quickly and with less work than with β counters. In laboratories where a great deal of strontium analysis is carried out, the saving in the labour costs is quite pronounced if the measurements are done by the liquid scintillation method. The high-background count rate of liquid scintillation counters has been the reason for the reduced use of this measuring technique as a common practice in laboratories. The higher price of the liquid scintillation counter compared to that of the low-background gas flow counters is soon compensated by the costs of the gas used in gas flow β counters.

In the method described here ^{89}Sr and ^{90}Sr are determined by counting the sample twice, once after separation of strontium and yttrium by Cerenkov counting and later after yttrium ingrowth by LS counting. Both counts may be performed after chemical separation of strontium and yttrium. Thus the result may be obtained quickly after separation if necessary.

The separation of ^{89}Sr and ^{90}Sr in the two counts is based on the differences in their counting efficiencies in the Cerenkov measurement. Because the maximum β energy of ^{89}Sr is only 540 keV, its Cerenkov-counting efficiency is only 1% but ^{90}Sr with a higher maximum β energy of 1460 keV has 40% counting efficiency. If the Cerenkov counting is performed soon after chemical separation, before the ingrowth of ^{90}Y -daughter of ^{90}Sr , the counts in the Cerenkov counting are mainly due to ^{89}Sr . The maximum β energy of ^{90}Y is 2270 keV thus having 60% counting efficiency in Cerenkov counting. In LS solution all three isotopes are counted with high efficiencies.

In recent years some papers have been published regarding the simultaneous determination of ^{89}Sr and ^{90}Sr by LS counting.¹⁻⁴ This paper's method is closest to Randolph's method, the difference being that all counts are collected in both counts with only one counting channel, whereas Randolph used two channels in the LS counting. The use of only one channel has simplified the method, no correction curves, formerly necessary because of overlapping β spectra of these isotopes, now being needed.

The most important difference between the method described in this paper and that described in earlier papers is the very low-background count rate thus making this method competitive with conventional low-background β counting methods. The low-background count rate was achieved by performing the measurements in plastic Mini-Vials and by keeping the sample volume as small as possible. The background count rate in Cerenkov counting is only 5 cpm and in scintillation counting 8 cpm. For the 20 ml plastic vials the corresponding backgrounds are 7 and 14 cpm. These values are really low compared with values reported in the other papers. Regan and Tyler¹ have reported 13 cpm background count rate in plastic vials for Cerenkov counting and Randolph² 28 cpm in glass vials. In scintillation counting backgrounds vary between 26 and 65 cpm. Since the low background count rates were achieved in Mini-Vials, their usability for precise work was tested carefully and found to be good.

APPARATUS AND MATERIALS

Instrumentation

All counts were performed at the temperature of $+13^{\circ}\text{C}$ using an LKB-Wallace Ultrobeta - 1210 Liquid Scintillation Counter. The chemical yields of the analysed samples were determined using a Varian Techtron Atomic Absorption Spectrophotometer, type AA-5.

Reagents and Radioactive Standards

All reagents needed for chemical separations were reagent grade (Packard Instrument Inc.). Insta-Gel³ was used as a scintillation solution; standardized solutions of ^{90}Sr , ^{90}Y and ^{89}Sr were obtained from Amersham-Searle.

Counting Vials

Plastic Mini-Vials of type MILLI-6 were obtained from Lumac. Zinsser plastic vials were used as their carriers. Both vials were cleaned before use by rinsing them with distilled water.

SAMPLE PREPARATION AND COUNTING

Chemical Separations

Radiostrontium was chemically separated from some air filter and human bone samples and then measured by LS counting. Human bone samples were also measured in a low background gas flow counter of ICN, OMNI/QUARD COUNTER, type AC-1. Air filter samples had been collected on glass fibre filters (Whatman GF-A). For these samples chemical separation was done using fuming nitric acid.⁶ An ion exchange procedure, where strontium is fractionally eluted from a cation exchange resin using ammonium lactate at pH 7, was used for bone samples. In both types of separation the procedure was continued in the normal manner to the step in which strontium is precipitated as a carbonate after the separation of strontium and yttrium. The time of separation was recorded as the start of ^{90}Y ingrowth. The carbonate precipitate was carefully washed to eliminate quenching in counting and then oven dried.

Sample Preparation for Counting

The carbonate precipitate was placed in a tarred Mini-Vial and dissolved in 1 ml of 1M hydrochloric acid. After weighing the vial again, a known portion (about 50 mg) of solution was removed for chemical yield determination by atomic absorption spectrophotometer.

The Mini-Vials were placed in carriers in the counter. Counting of Cerenkov radiation was started after 2 h cooling time in the counter.

After Cerenkov counting, the sample was left in the counter to wait for ^{90}Y ingrowth. After a proper ingrowth period, 4 ml of Insta-Gel was added and the sample was recounted after about 12 hours cooling. To minimize contamination vials were always cleaned outside before placing them in the counter.

Table 1. Counting efficiencies of ⁸⁹Sr standard sample in Cerenkov counting as a function of time from sample preparation.

Time	Efficiency (%)	Time	Efficiency (%)
2 h	40.64	42 h	41.00
3 h	40.77	48 h	41.12
4 h	40.75	54 h	40.76
5 h	41.03	60 h	40.97
6 h	40.91	66 h	40.96
7 h	41.00	3 d	41.13
8 h	40.84	4 d	41.21
10 h	40.87	5 d	41.14
12 h	40.85	6 d	41.20
14 h	41.01	9 d	41.29
18 h	40.96	14 d	41.19
24 h	40.76	26 d	41.20
30 h	41.05	28 d	41.51
36 h	40.95	30 d	41.45
Mean		41.02 ± 0.21	

Table 2. Counting efficiencies and external standard channel ratios (ESCR) of ⁸⁹Sr standard sample measured in Insta-Gel scintillation solution as a function of time from sample preparation.

Time	Efficiency (%)	ESCR
4 h	93.89	0.86
12 h	95.14	0.81
24 h	94.98	0.79
36 h	95.07	0.77
2 d	95.28	0.78
3 d	95.00	0.79
4 d	95.15	0.79
5 d	94.89	0.78
6 d	95.36	0.77
7 d	95.02	0.77
Mean	94.98 ± 0.41	

The background sample for Cerenkov counting was prepared from the same hydrochloric acid as that used to dissolve the carbonate precipitate. The same background sample was later prepared for scintillation counting. The background count rates were the same whether they contained strontium or not.

Sample Counting

The stability of measurements performed in plastic Mini-Vials was carefully examined by preparing a series of standard samples and recounting them many times. Counting efficiencies in the Cerenkov measurement remained constant at least for one month as is shown in Table 1, in which the counting efficiencies of a ⁸⁹Sr standard sample are shown as a function of time.

Table 3. Variation of counting rates and external channel ratios (ESCR) of a background sample prepared in Insta-Gel scintillation solution as a function of time from sample preparation.

Time	Background counting rate (cpm)	ESCR
2 h	7.60	0.94
10 h	8.59	0.90
18 h	8.59	0.88
26 h	8.99	0.88
34 h	9.20	0.86
42 h	9.39	0.87
50 h	9.60	0.85
58 h	10.00	0.85
66 h	10.00	0.85
74 h	10.19	0.85
82 h	10.40	0.85
90 h	10.19	0.84
98 h	10.19	0.85
106 h	10.40	0.84

Variations in counting efficiencies are due to counting statistics. The background counting rates varied around 5 cpm in Cerenkov counting. No systematic fluctuation in background was observed as a function of time from sample preparation. The long-term stability of Cerenkov measurement is good because the determination of ^{90}Sr and ^{90}Y may also be done by counting the sample twice by Cerenkov technique.

About 12 h cooling time between addition of scintillation solution and starting the counting was observed to be necessary to achieve stable counting efficiencies. If the counting was started earlier, 1-2% lower counting efficiencies were obtained. In Table 2 are shown the counting efficiencies and the external standard channel ratios of a ^{90}Sr standard for which the first count was started after a 4 h cooling time. Later counting efficiencies remained constant for at least one week. The slow drifting of external standard channel ratios towards lower values happened for all samples recounted many times. The good stability of the scintillation counting method is valuable for some samples which have been counted after insufficient ingrowth time of ^{90}Y . These samples may be recounted later, again without errors caused by the unstable nature of the measurement.

The variation of background count rate in scintillation counting is shown in Table 3. This measurement was started after 2 h cooling time and then repeated using 8 h counting times over 5 d. Because background fluctuates towards higher values it is useful for environmental samples to measure the background before and then recount the samples in the same order and use the mean of two background count rates for correction. This counting mode is performed automatically on the Ultrobeta-1210 liquid scintillation counter.

CALIBRATION OF THE COUNTER

Optimizing the Counter for Low-level Measurement

Low minimum detectable activities were achieved by keeping the sample volume as small as possible and also by optimizing the counter for the measurement.

Optimizing the Ultrobeta-1210 liquid scintillation counter is simple. No manual gain adjustments and high-voltage adjustments are needed, because an automatic spectrum stabilizer provides the instrument with optimum measuring conditions. The counter has three counting channels which can operate simultaneously. Each

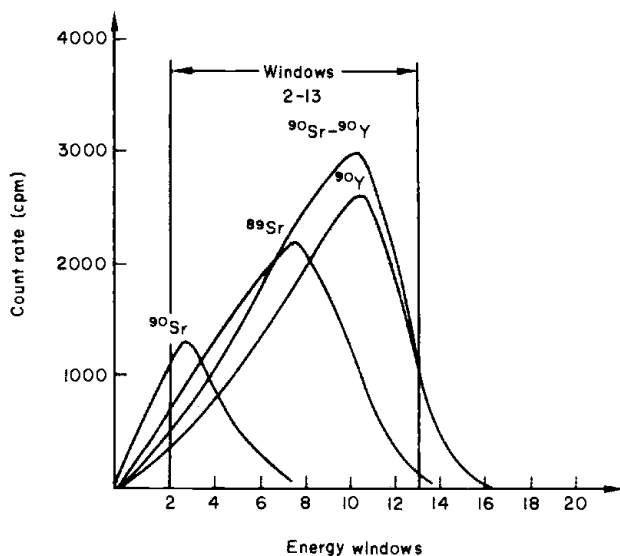


Fig. 1

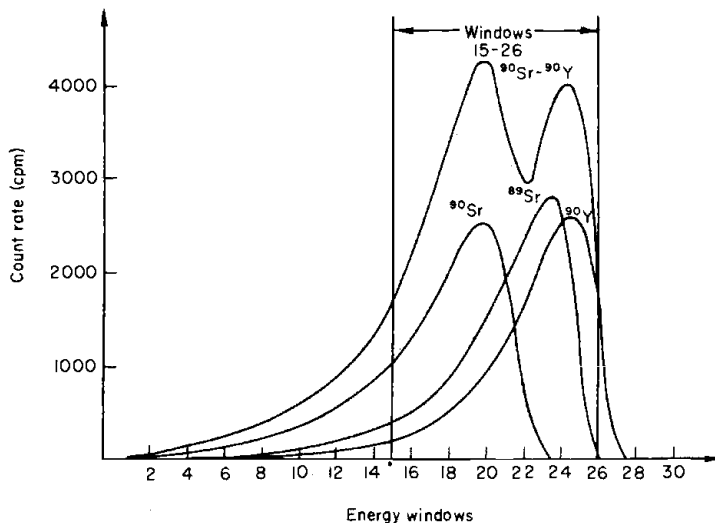


Fig. 2

of these counting channels has 33 fixed, logarithmically arranged windows in the energy range 1-2800 keV, which can be preselected with simple, plug-in diode pins.

The energy range covered by the counting window was selected so that highest figure of merit, E_r/B_s , was obtained. The energy spectrum of each isotope was measured in the solution used for counting to find the optimum window width. These spectra for Cerenkov counting are shown in Fig. 1 and for scintillation counting in Fig. 2. These spectra have not been measured for identical amounts of activity. The best figure of merit in Cerenkov counting was obtained when the counting channel contained windows from 2 to 13 and in scintillation counting from 15 to 26. Because the energy spectra of the various isotopes coincide to a great degree it was decided to collect counts on one channel only in both counts.

Table 4. Fractional counting efficiencies of various isotopes in Cerenkov and scintillation counting as measured by LKB-Wallac Ultrabeta-1210 Liquid Scintillation Counter.

Isotope	%	
	Counting efficiencies Cerenkov counting Windows 2-13	Scintillation counting Windows 15-26
^{90}Sr	0.8 ± 0.2	77.0 ± 0.4
^{90}Y	56.6 ± 0.5	91.4 ± 0.5
$^{90}\text{Sr}-^{90}\text{Y}$	57.4 ± 0.4	168.4 ± 0.4
^{89}Sr	40.8 ± 0.3	95.0 ± 0.5

Counting Efficiency Corrections

No variation in counting efficiencies between various standard samples was observed when the samples were measured in the windows shown in Figs 1 and 2.

Standard samples contained different amounts of strontium and hydrochloric acid and their water volumes varied between limits normally encountered in sample preparation. Thus no quench-correction curves are needed and the same counting efficiency correction percentages, shown in Table 4, may be used for every sample. The values of Table 4 have been calculated as a mean of several samples for which the counting has been repeated many times. Careful tests were performed to show that same counting efficiency percentages may be utilized for each sample. These tests were done for each isotope. For this reason ^{90}Sr and ^{90}Y were separated from each other. The counting efficiencies obtained for separated standard solutions of ^{90}Sr and ^{90}Y correlated well with the value for the $^{90}\text{Sr}-^{90}\text{Y}$ solution.

Some data from these tests are shown in Tables 5-8. The stability of counting was tested with all samples by counting many times. In Table 5 are shown variation of counting efficiencies for eight standard samples of ^{90}Y in Cerenkov measurement. These samples contained various amounts of strontium and hydrochloric acid and their water volumes also varied. The counting efficiencies are practically the same for all samples. Variations observed are mainly due to counting statistics and sample preparation. This Table shows that the stability of the counting window has been good. If the window had been unstable and some drifting had occurred, it would have been observed easily from the ^{90}Y standards whose energy spectra lie partially outside the window.

Table 5. Counting efficiencies of various ^{90}Y standard samples in Cerenkov counting as a function of time from sample preparation.

Sample No.	Sr/ mg	HCl conc/ N	Sample volume/ ml	Counting efficiencies (%)								Mean
				2 h	5 h	8 h	11 h	14 h	17 h	20 h	6 d	
1	60	1.2	1.0	56.41	56.73	56.71	55.96	56.35	56.67	56.84	56.66	56.54 ± 0.29
2	50	1.1	1.0	56.48	56.68	56.62	56.81	56.61	56.93	57.22	56.92	56.78 ± 0.23
3	30	1.0	1.0	56.98	56.73	56.36	56.25	56.66	56.55	57.00	56.90	56.68 ± 0.28
4	10	1.0	1.0	56.44	56.24	56.36	56.39	56.30	56.47	55.97	56.50	56.33 ± 0.17
5	30	1.0	0.94	56.52	56.60	56.52	56.54	56.27	56.67	56.68	56.68	56.56 ± 0.14
6	30	1.0	0.96	56.73	56.45	56.46	56.68	56.28	56.19	56.37	56.83	56.50 ± 0.23
7	30	1.0	1.00	56.61	56.57	56.14	56.48	56.67	56.54	56.47	56.74	56.53 ± 0.18
8	30	1.0	1.06	56.33	56.56	56.75	56.84	56.56	56.46	56.99	56.88	56.67 ± 0.23

Table 6. Counting efficiencies of various ^{90}Sr - ^{90}Y standard samples in Cerenkov counting as a function of time from sample preparation.

Sample No.	Sample volume/ ml	Counting efficiencies (%)				Mean
		1 d	1 d	2 d	3d	
1	0.96	57.41	57.41	57.37	57.20	57.35 \pm 0.10
2	0.97	57.39	57.44	57.37	57.40	57.40 \pm 0.03
3	1.02	57.37	57.43	57.57	56.77	57.29 \pm 0.35
4	1.02	57.30	57.53	57.68	57.42	57.48 \pm 0.16
5	1.02	57.04	57.08	57.20	57.10	57.11 \pm 0.07
6	1.03	57.60	57.35	57.37	57.51	57.46 \pm 0.12
7	1.06	57.28	57.19	57.31	57.03	57.20 \pm 0.13

Table 7. Counting efficiencies and external standard channel ratios of various ^{89}Sr standard samples in scintillation counting as a function of time from sample preparation.

Sample No.	Sr/ mg	E (%) R	Counting efficiencies (E) and external standard channel ratios (R)					Mean
			1 d	1 d	2 d	3 d	4 d	
1	50	E	95.29	94.97	94.66	94.39	94.89	94.84 \pm 0.34
		R	0.84	0.84	0.83	0.82	0.83	
2	40	E	95.56	95.13	94.90	94.89	95.19	95.19 \pm 0.27
		R	0.86	0.85	0.82	0.84	0.81	
3	30	E	95.20	94.72	95.13	94.66	95.37	95.37 \pm 0.31
		R	0.86	0.85	0.84	0.82	0.83	
4	20	E	94.94	94.77	95.11	94.31	95.47	95.47 \pm 0.43
		R	0.84	0.82	0.81	0.81	0.81	
5	10	E	94.60	94.52	04.03	93.72	95.19	94.41 \pm 0.57
		R	0.85	0.83	0.82	0.80	0.81	

In Tables 7 and 8 are shown the counting efficiencies for ^{89}Sr and ^{90}Sr - ^{90}Y standard samples measured in the scintillation solution. For both series of samples the first measurement was started after a half day cooling time, so no greater lowering in external standard channel ratios is observable. Constant counting efficiency correction percentages may be used for all samples although the external standard channel ratios vary between 0.7 and 0.9. When strong quenching agents were added to the sample, efficiencies were lowered by a few percent. In scintillation counting some samples deteriorated after 4-6 days from sample preparation giving a few percent lower efficiencies than earlier.

CALCULATIONS

The following two equations are obtained for the determination of ^{89}Sr and ^{90}Sr from the two counting results:

Table 8. Counting efficiencies and external standard channel ratios of various ^{90}Sr - ^{90}Y standard samples in scintillation counting as a function of time from sample preparation.

Sample No.	E % R	Counting efficiencies (E) and external standard channel ratios (R)				Mean
		1 d	2 d	3 d	4 d	
1	E	168.21	168.53	168.54	168.10	168.34 \pm 0.22
	R	0.81	0.82	0.81	0.80	
2	E	168.47	168.28	168.45	168.05	168.31 \pm 0.19
	R	0.82	0.81	0.80	0.80	
3	E	168.96	168.57	168.15	168.40	168.52 \pm 0.34
	R	0.72	0.72	0.72	0.74	
4	E	168.72	168.04	168.25	168.31	168.33 \pm 0.28
	R	0.71	0.73	0.72	0.73	
5	E	168.55	168.49	168.34	168.12	168.37 \pm 0.19
	R	0.70	0.72	0.73	0.72	
6	E	168.53	168.88	167.96	168.17	168.39 \pm 0.40
	R	0.71	0.72	0.73	0.74	

$$\underline{C} = \underline{E}_{90\text{Sr}} \times \underline{X} + \underline{E}_{90\text{Y}} \times \underline{G}_{\text{C}} \times \underline{X} + \underline{E}_{89\text{Sr}} \times \underline{D}_{\text{C}} \times \underline{Y}$$

$$\underline{C}_{\text{Sc}} = \underline{F}_{90\text{Sr}} \times \underline{X} + \underline{F}_{90\text{Y}} \times \underline{G}_{\text{Sc}} \times \underline{X} + \underline{F}_{89\text{Sr}} \times \underline{D}_{\text{Sc}} \times \underline{Y}$$

where \underline{X} = ^{90}Sr -activity of the sample (dpm)

\underline{Y} = ^{89}Sr -activity of the sample (dpm)

\underline{C}_{C} = net cpm in Cerenkov counting

$\underline{C}_{\text{Sc}}$ = net cpm in scintillation counting

$\underline{E}_{90\text{Sr}}$ = counting efficiency in Cerenkov counting

$\underline{E}_{90\text{Y}}$ = counting efficiency in Cerenkov counting

$\underline{E}_{89\text{Sr}}$ = counting efficiency in Cerenkov counting

$\underline{F}_{90\text{Sr}}$ = counting efficiency in scintillation counting

$\underline{F}_{90\text{Y}}$ = counting efficiency in scintillation counting

$\underline{F}_{89\text{Sr}}$ = counting efficiency in scintillation counting

\underline{G}_{C} = ingrowth factor for ^{90}Y from separation to midpoint of Cerenkov counting

$\underline{G}_{\text{Sc}}$ = ingrowth factor for ^{90}Y from separation to midpoint of scintillation counting

\underline{D}_{C} = decay factor for ^{89}Sr from separation to midpoint of Cerenkov counting

$\underline{D}_{\text{Sc}}$ = decay factor for ^{89}Sr from separation to midpoint of scintillation counting

From these two equations \underline{X} and \underline{Y} are easily calculated utilizing a small programmable calculator. When the ^{90}Sr and ^{89}Sr contents of the sample are known, the concentrations in the analysed sample material at the time of sampling are calculated from the following equations:

$$^{90}\text{Sr activity} = \frac{\underline{X}}{\underline{R} \times \underline{W} \times \underline{D}_{90\text{Sr}}} \text{ pCi g}^{-1}$$

$$^{89}\text{Sr activity} = \frac{\underline{Y}}{\underline{R} \times \underline{W} \times \underline{D}_{89\text{Sr}}} \text{ pCi g}^{-1}$$

where \underline{X} = ^{90}Sr activity of the sample (dpm)

\underline{Y} = ^{89}Sr activity of the sample (dpm)

\underline{R} = strontium chemical yield

\underline{W} = sample weight (g)

$\underline{D}_{90\text{Sr}}$ = decay factor for ^{90}Sr from sampling to separation

$\underline{D}_{89\text{Sr}}$ = decay factor for ^{89}Sr from sampling to separation

If ^{89}Sr is not present in the sample only one count is necessary for determining ^{90}Sr activity of the sample. Both counting techniques may be utilized. The strontium-90 activity of the sample may be calculated from the following equations, if the measurements are done after full ingrowth period of ^{90}Y :

$$^{90}\text{Sr activity} = \frac{\underline{C}}{\underline{E}_{90\text{Sr}-90\text{Y}} \times \underline{R} \times \underline{W} \times \underline{D}_{90\text{Sr}}} \text{ pCi g}^{-1}$$

$$\text{or } ^{90}\text{Sr activity} = \frac{\underline{C}_{\text{Sc}}}{\underline{F}_{90\text{Sr}-90\text{Y}} \times \underline{R} \times \underline{W} \times \underline{D}_{90\text{Sr}}} \text{ pCi g}^{-1}$$

In the counting conditions of this paper ^{90}Sr - ^{90}Y efficiencies gave the following values:

$$\underline{E}_{90\text{Sr}-90\text{Y}} = 57.4\% \quad \text{and} \quad \underline{F}_{90\text{Sr}-90\text{Y}} = 168.4\%$$

RESULTS

Results from samples with known ^{89}Sr - and ^{90}Sr -activities

Because the same counting efficiencies will be used for all samples in the counting method of this paper, it is possible to calculate what percentages of counts are due to ^{90}Sr , ^{90}Y and ^{89}Sr . These percentages have been calculated for various ^{90}Sr : ^{89}Sr ratios and for counts performed at various times from separation. These percentages are shown in Table 9, where the first 6 h measurement is based on Cerenkov counting and later measurements on scintillation counting. Table 9 shows, that the accuracies for ^{89}Sr activities with large ratios of ^{90}Sr : ^{89}Sr are much better than those for ^{90}Sr with low ratios of ^{90}Sr : ^{89}Sr .

Table 9. Percentage of ^{90}Sr , ^{90}Y and ^{89}Sr from total counts in measurement performed at various times from separation and for various ratios of ^{90}Sr : ^{89}Sr .

^{90}Sr : ^{89}Sr	Time	Percentage from total counts		
		^{90}Sr	^{90}Y	^{89}Sr
50:1	6 h	15.50	68.75	15.75
	1 d	66.47	31.91	1.62
	6 d	51.05	47.79	1.16
	21 d	45.45	53.71	0.84
30:1	6 h	14.02	62.21	23.76
	1 d	65.76	31.57	2.67
	6 d	50.65	47.43	1.92
	21 d	45.19	53.41	1.39
5:1	6 h	6.41	28.43	65.16
	1 d	58.02	27.86	14.12
	6 d	46.22	43.28	10.50
	21 d	42.25	49.94	7.81
1:1	6 h	1.78	7.88	90.34
	1 d	37.08	17.80	45.12
	6 d	32.55	30.47	36.98
	21 d	32.19	38.04	29.77
1:5	6 h	0.39	1.71	97.91
	1 d	13.22	6.35	80.43
	6 d	13.13	12.29	74.58
	21 d	14.69	17.37	67.94
1:30	6 h	0.07	0.29	99.64
	1 d	2.63	1.26	96.10
	6 d	2.78	2.60	94.63
	21 d	3.34	3.95	92.71
1:50	6 h	0.04	0.17	99.79
	1 d	1.60	0.77	97.63
	6 d	1.70	1.59	96.70
	21 d	2.07	2.44	95.49

Samples with known ^{90}Sr - and ^{89}Sr -contents were analysed for some ^{90}Sr : ^{89}Sr ratios. Results are shown in Tables 10-12. In Table 10 are shown the results for samples for which the ^{90}Sr : ^{89}Sr ratios were 30:1, 1:0.7 and 1:30. For these samples Cerenkov counting was performed 5 h after separation. Scintillation solution was added one day after separation and samples were counted several times. Results from these repeated counts are for two samples shown in Table 11, which shows the good stability of the counting system and also shows that counting efficiencies of ^{90}Sr and ^{90}Y have been determined accurately. In Table 12 are the results for eight parallel samples which were measured by Cerenkov counting after 4 h from separation and again in scintillation counting solution after 3 days. The results of these three Tables show that this method gives accurate results for ^{89}Sr with all tested ratios, but not for ^{90}Sr in the ratio of 1:30. This is understandable on the basis of the values in Table 9. Further experiments will be done to determine for what range of values of the ^{90}Sr : ^{89}Sr ratio the method is useful for the required accuracies in ^{90}Sr determinations. If the values of Table 9 are calculated for the ratio of 1:20, more than 10% of counts are due to ^{90}Sr and ^{90}Y together in the scintillation measurement performed after full ingrowth of ^{90}Y . This looks enough for moderate accuracy by this counter which has shown to be a very stable instrument. For the environmental samples the

Table 10. Test results for samples of known activities of ^{90}Sr and ^{89}Sr for two counts performed at various times from separation and for different ratios of ^{90}Sr : ^{89}Sr .

^{90}Sr : ^{89}Sr ratio	Sample no.	Time	^{90}Sr added/dpm	^{90}Sr found/dpm	Difference (%)	^{89}Sr added/dpm	^{89}Sr found/dpm	Difference (%)
30:1	1	2 d	59 790	59 636	- 0.2	2 101	2 029	- 3.4
		6 d		58 864	- 1.6		2 097	- 0.2
30:1	2	2 d	59 820	59 634	- 0.3	2 102	2 057	- 2.1
		6 d		58 706	- 1.9		2 143	+ 1.9
1:0.7	1	2 d	20 110	19 828	- 1.4	14 600	14 404	- 1.3
		6 d		19 783	- 1.6		14 408	- 1.3
1:0.7	2	2 d	20 450	20 146	- 1.5	14 860	14 530	- 2.2
		6 d		20 009	- 2.1		14 543	- 2.1
1:30	1	2 d	357	258	- 27.7	11 530	11 629	+ 0.8
		6 d		300	- 16.0		11 614	+ 1.7
1:30	2	2 d	354	279	- 21.2	11 420	11 472	+ 0.4
		6 d		352	- 0.6		11 465	+ 0.4

Table 11. Test results for two parallel samples with known ^{90}Sr and ^{89}Sr activities from several measurements performed at various times from separation.

Sample No.	^{90}Sr activity added/dpm	^{90}Sr and ^{89}Sr activities found/dpm						
		2 d	3 d	3.5 d	4 d	5 d	5.5 d	6 d
1	$^{90}\text{Sr} = 20\ 110$	19 828 - 1.4%	19 865 - 1.2%	19 814 - 1.5%	19 840 - 1.3%	19 842 - 1.3%	19 809 - 1.5%	19 783 - 1.6%
	$^{89}\text{Sr} = 14\ 600$	14 404 - 1.3%	14 400 - 1.4%	14 405 - 1.3%	14 384 - 1.5%	14 459 - 1.0%	14 583 - 0.1%	14 408 - 1.3%
2	$^{90}\text{Sr} = 20\ 450$	20 146 - 1.5%	20 097 - 1.7%	20 238 - 1.0%	20 051 - 2.0%	20 048 - 2.0%	20 034 - 2.0%	20 009 - 2.1%
	$^{89}\text{Sr} = 14\ 860$	14 530 - 2.2%	14 536 - 2.2%	14 520 - 2.3%	14 541 - 2.1%	14 541 - 2.1%	14 543 - 2.1%	14 546 - 2.1%

developed method looks very promising because of its simplicity and stability compared to low background β counters. In environmental samples the ^{90}Sr : ^{89}Sr ratios are rarely near to 1:20, and when this is the situation it is possible to separate ^{90}Y from ^{90}Sr and ^{89}Sr after Cerenkov counting and then measure ^{90}Y in liquid scintillation solution with about 100% efficiency and high accuracy.

Results from environmental samples

Some air filters and human bone samples were analysed by this method. Results from air filter analysis are shown in Table 13 and from human bone samples in Table 14. Air filter collections were from two different time periods: from the end of the year 1976 and from the beginning of the year 1977. Several parallel, three-monthly collections were done at the same location in Finland. The amount of air drawn through these filters was about 100 000 m³. Radiochemical separations

Table 12. Test results for eight parallel samples with known activities of ^{90}Sr and ^{89}Sr .

Sample No.	^{90}Sr added/ dpm	^{90}Sr found/ dpm	Difference (%)	^{89}Sr added/ dpm	^{89}Sr found/ dpm	Difference (%)
1	10 235	10 302	+ 0.65	1 157	1 147	- 0.86
2	10 233	10 314	+ 0.79	1 157	1 143	- 1.21
3	10 298	10 302	+ 0.53	1 164	1 170	+ 0.51
4	10 226	10 306	+ 0.78	1 156	1 143	- 1.12
5	10 280	10 304	+ 0.24	1 162	1 172	+ 0.86
6	10 192	10 228	+ 0.36	1 152	1 156	+ 0.35
7	10 335	10 387	+ 0.51	1 169	1 157	- 1.03
8	10 281	10341	+ 0.59	1 163	1 172	+ 0.77

Table 13. ^{90}Sr , ^{89}Sr , ^{141}Ce and ^{95}Zr activities in air during two periods at the same location in Finland.

Sample No.	Collection time	^{90}Sr activity-3 $\mu\text{Bq m}^{-3}/\text{pCi m}^{-3}$	^{89}Sr activity-3 $\mu\text{Bq m}^{-3}/\text{pCi m}^{-3}$	^{141}Ce activity-3 $\mu\text{Bq m}^{-3}/\text{pCi m}^{-3}$	^{95}Zr activity-3 $\mu\text{Bq m}^{-3}/\text{pCi m}^{-3}$
1	October-December 1976	3.22 (87.0×10^{-6})	192 (5.24×10^{-3})	260 (7.09×10^{-3})	280 (7.6×10^{-3})
2		3.45 (94.1×10^{-6})	164 (4.47×10^{-3})	280 (7.64×10^{-3})	300 (8.18×10^{-3})
3		3.02 (82.4×10^{-6})	175 (4.77×10^{-3})	250 (6.82×10^{-3})	240 (6.55×10^{-3})
1	January-March 1977	4.40 (120×10^{-6})	86.2 (2.35×10^{-3})	81 (2.21×10^{-3})	120 (3.27×10^{-3})
2		4.47 (122×10^{-6})	82.5 (2.25×10^{-3})	85 (2.32×10^{-3})	140 (3.82×10^{-3})
3		3.73 (102×10^{-6})	70.8 (1.93×10^{-3})	70 (1.91×10^{-3})	110 (3.00×10^{-3})
4		4.11 (112×10^{-6})	90.0 (2.45×10^{-3})	59 (1.61×10^{-3})	94 (2.56×10^{-3})

and counts of these samples were done in July 1977. Results of these analyses show that ^{90}Sr and ^{89}Sr activities with parallel air filter samples vary between rather narrow limits, whereas activity levels for two collection periods are different. For this reason ^{141}Ce and ^{95}Zr activities measured on samples from the same filters using γ spectroscopy have been added to the Table. These filters were measured using only moderate precision counting statistics. In Cerenkov counting, net counting rates varied from 2 to 5 cpm. In scintillation counting net counts were between 9 and 14 cpm. Low yields (about 30%) for chemical separations might also have caused variation in the measured concentrations.

Human bone samples were from the years 1969-71, thus containing only ^{90}Sr . These samples were measured by three counting techniques. Firstly the carbonate precipitate was measured after full ingrowth of ^{90}Y by low-background gas flow counter and later by liquid scintillation counter. The counter used had about 0.5 cpm background counting rate and 65% counting efficiency for the sample containing 50 mg strontium carbonate. All samples were recounted by β counter, after rotating the sample 90° around its axis. It was observed that this counting method decreased the variation between parallel standard samples. Variances in these two counts might be as high as 20%.

Table 14. ^{90}Sr content of human bones in Finland as measured by three counting techniques.

Age/y	Cerenkov ^{90}Sr counting/ pCi g^{-1} Ca	Liquid scintillation counting/pCi g^{-1} Ca	Low-background ^{90}Sr β counting/pCi g^{-1} Ca
14	3.97 \pm 0.28	3.81 \pm 0.13	3.76 \pm 0.09
20	3.20 \pm 1.02	2.98 \pm 0.44	2.73 \pm 0.13
25	1.01 \pm 0.24	1.01 \pm 0.10	1.04 \pm 0.04
40	0.425 \pm 0.137	0.434 \pm 0.068	0.645 \pm 0.034
43	0.736 \pm 0.148	0.759 \pm 0.140	0.666 \pm 0.031
59	0.835 \pm 0.159	0.807 \pm 0.070	0.948 \pm 0.034
60	0.467 \pm 0.528	0.425 \pm 0.222	0.510 \pm 0.046

Results from the three counting methods are, after allowing the statistical deviations at the 95% confidence level, the same for all samples. Differences between results from β counting and liquid scintillation counting are bigger than those between the two counts by liquid scintillation counter. The counting statistics were quite poor for liquid scintillation counting because only 6-7 h counting times were used. The net counting rate varied between 0.3 and 6 cpm for Cerenkov counting and between 0.8 and 15 cpm for scintillation counting. By β counter the samples were counted by better statistics when 1000 min counting times were used. No systematic errors seemed to occur in results from different counters.

Minimum detectable activities

Minimum detectable activities (MDA) have been calculated from the equation:

$$\text{MDA} = \frac{3 \text{ B}}{\underline{E} \times \underline{t} \times 2.22} \text{ pCi/sample}$$

where B = background counting rate (cpm); \underline{E} = counting efficiency; \underline{t} = counting time (min).

These values have been calculated only for the simplified situation when the sample contains one strontium isotope. The following values were obtained for 400 min counting time:

Cerenkov counting	$\text{MDA}_{^{90}\text{Sr}} = 0.26 \text{ pCi/sample}$
	$\text{MDA}_{^{89}\text{Sr}} = 0.37 \text{ pCi/sample}$
Liquid scintillation counting	$\text{MDA}_{^{90}\text{Sr}} = 0.12 \text{ pCi/sample}$
	$\text{MDA}_{^{89}\text{Sr}} = 0.21 \text{ pCi/sample}$
Low-level β counting	$\text{MDA}_{^{90}\text{Sr}} = 0.08 - 0.30 \text{ pCi/sample}$
	$\text{MDA}_{^{89}\text{Sr}} = 0.09 - 0.36 \text{ pCi/sample}$

Detection limits vary for different types of β counters between rather wide limits depending on their backgrounds and sensitivities. MDA_{90Sr} for β counters has been calculated on the basis of ^{90}Y . Comparison shows that the Wallac Ultrabeta-1210 liquid scintillation counter is quite competitive with low-background β counters, when the same counting times are used.

DISCUSSION

In this work the usability of liquid scintillation counting for environmental analysis of ^{90}Sr and ^{89}Sr was carefully examined. The first results are very promising because the same detection limit was achieved as by utilizing low-background β counters. Because the stability of the liquid scintillation counter used was very good, it appears that more accurate results will be obtained by liquid scintillation counting than by the conventional β counters which are quite unstable instruments. This is due to the fact that this type of simultaneous determination of two isotopes is very sensitive to the instability of the instrument. In addition the geometric and self-absorption factors in Geiger counting cause errors, which can never be corrected exactly.

The fluctuation of the background counting rate after sample preparation in liquid scintillation counting might cause errors in results if very low activities are measured quickly after sample preparation.

These errors may be eliminated by starting the counting later and by counting the background before and after the sample. This counting mode has given very good results in low-level tritium counting performed for years using this type of liquid scintillation counter. The background counting rate has been very constant in long-term tritium experiments and also in this work. It appears that variation in the background counting rate will not be the weak point of this method. Another possibility is to modify the proposed method so that the sample is measured twice by Cerenkov counting, because its background is very stable. On the other hand very few additional counts will be obtained in the second Cerenkov counting for low-activity samples, so that the liquid scintillation measurement seems to be a better alternative.

Low detection limits were achieved in this work by performing the measurements in plastic Mini-Vials and by utilizing only a small amount of Insta-Gel as scintillation solution. It might be that these limits will be lowered if Insta-Gel is a constituent of another commercial cocktail, thus with lower background tending to make the liquid scintillation counting method a preferred method in environmental radiostromtium analysis.

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DISCUSSION

A.R. WARE: You have described a LSC technique for the measurement of ^{90}Sr and ^{89}Sr in environmental samples and have stated that the system is better than conventional low-level β -counters. What in your opinion would be the sensitivity of the technique taking into account the background count rate and the quantity of sample which is counted? Could the technique measure 1 pCi l^{-1} of ^{90}Sr in milk, and with what accuracy?

L. SALONEN: Minimum detectable activities by LSC technique are practically the same as measured by β -low-background gas flow counter with 0.5 cpm background and with 35% efficiency for ^{90}Y and 28% efficiency for ^{89}Sr . Since the LSC sample is able to take more than 60 mg Sr, the same efficiencies may be used as shown in Table 4. Thus 1 pCi l^{-1} ^{90}Sr in milk may be measured; accuracy depends on the counting time. The LSC technique looks to be better than conventional β -counting methods especially in the simultaneous determination of ^{90}Sr and ^{89}Sr due to the good reproducibility of the measurement.

NOTE ADDED IN PROOF BY THE EDITORS

The method proposed by Dr. Salonen clearly gives a greater efficiency for measurement of ^{90}Sr and ^{89}Sr in environmental samples but on many occasions very low levels of activity need to be measured. The limit of detection of any method is often expressed as three times the standard deviation of the background count and this is used in this paper. In order to convert this limit of detection into activity in Curies, the efficiency of the detector is also important.

In the method proposed the efficiency of counting is higher than for low-level β -counters but the background is not only higher but, in the cocktail used, varies with time. In Table 14 the authors clearly indicate that at a level of 1 pCi g^{-1} the low-background β -counter is the most precise technique and this will also give a lower limit of detection.

In addition, Table 3 shows that if samples are not counted at a fixed time after placing them in the counter, the background will vary from sample to sample. The practice of counting backgrounds before and after counting a batch of samples will thus add to the uncertainty in the background and hence further increase the limit of sensitivity.

The method gives an efficient counting system at high levels of activity but cannot compete with the low-background β -counters at levels of ^{90}Sr below 1 pCi g^{-1} Ca.

