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Simultaneous measurement of ^{89}Sr and ^{90}Sr in aqueous samples by liquid scintillation counting using the spectrum unfolding method

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Abstract

Two radiostrontium isotopes, ^{89}Sr and ^{90}Sr, were measured simultaneously by liquid scintillation counter coupling with a full spectrum DPM counting protocol. Strontium was separated from the aqueous media by extraction chromatography using Sr-spec resin. Individual count rates were evaluated from quench correlation curves for ^{89}Sr and ^{90}Sr related with SIS and tSIE quench indicators. The method exhibited a counting efficiency of 95% for ^{89}Sr and 92% for ^{90}Sr within their full energy channels and gave highly precise results when the sample was counted within 4 h after strontium separation. Lower limits of detection were 37 mBq/l for ^{90}Sr and 32 mBq/l for ^{89}Sr with a 60 min counting time. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Liquid scintillation counting; Full spectrum DPM; ^{89}Sr; ^{90}Sr

1. Introduction

The general analytical scheme for radiostrontium measurement, ^{89}Sr and ^{90}Sr from an environmental sample, requires sample preparation and isolation of the strontium followed by gas proportional counting (HASL 300, 1990). However, the measurement of radiostrontium activity by conventional methods is time-consuming because the analytical procedure for the separation of strontium is very long and the low counting efficiency of the gas proportional counter requires a long counting time for a sample of low-level activity. Recently, Dietz and Horwitz have developed extraction chromatography using a strontium selective binding resin (Sr-Spec™). It provides a simple and rapid separation method for strontium from an aqueous sample (Horwitz et al., 1991, 1992). In conventional counting of ^{89}Sr and ^{90}Sr activity by a gas proportional counter, the ^{90}Sr activity is determined by counting the ^{90}Y activity that is equilibrated with the ^{90}Sr activity. ^{89}Sr activity is determined by subtracting the amount of ^{90}Sr from the initial gross activity of ^{89}Sr, ^{90}Sr and ^{90}Y. But this method requires the yttrium to be separated before ^{90}Y activity counting is done and a sufficient period is required for an equilibrium state between ^{90}Sr and ^{90}Y. Dual channel liquid scintillation counting has also been used to determine the ^{89}Sr and ^{90}Sr activity simultaneously (Dietz et al., 1991; Piltingsrud and Stencel, 1972; Buchtela and Tschurlovits, 1975; Vajda et al., 1992). In this case,

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two discrete counting windows are selected on the basis of the ^{90}Sr and ^{89}Sr energies. Standards containing pure ^{89}Sr, pure ^{90}Sr and pure ^{90}Y were counted under the same counting window to determine the coefficients associated with the contribution of each isotope to the expected count. The activity of each radiostrontium isotope was calculated from a set of simultaneous equations describing the counts expected in each window. In this method, however, the optimization of the counting window is difficult with respect to the quenching level of the sample. Furthermore, limited counting efficiencies of each isotope defined by the discrete counting window should be applied in order to minimize the spillover counting.

Full spectrum liquid scintillation DPM counting protocol, developed by the Packard Instrument (Meriden, CT, USA), can be used to determine the activities of the individual radionuclides of a dual labeled sample. In this windowless counting method, which is called the spectrum unfolding method, the total energy distribution spectrum of a dual labeled sample is decomposed into each radionuclides spectra using the spectral index of the sample, SIS, parameter of each radionuclides. The counting efficiency of each nuclide is evaluated from the quench curve and is correlated with the transformed spectral index calculations, tSIE, quench parameters and then the DPM is calculated. This unique method is a relatively simple and easy liquid scintillation counting procedure for a dual labeled sample. In this paper, we describe the application of this method to the simultaneous measurement of radiostrontium, ^{89}Sr and ^{90}Sr from an aqueous sample and then examined its counting performance. In addition, the limitations of this counting method to evaluate the activity when the ingrown activity of daughter nuclide, ^{90}Y, is accumulated into the ^{89}Sr and ^{90}Sr energy region was also discussed.

2. Experimental

2.1. Apparatus and materials

Tricarb-2700TR (Packard Instrument) was used for the measurement of liquid scintillation counting of radiostrontium. Data analysis and the calculation of activity was performed by using the full spectrum dual level DPM counting protocol developed by Packard Instrument. A ^{85}Sr standard (IPL, CA, USA) activity was used as a chemical yield tracer, this was measured by a gamma spectrometer coupled with a HPGe detector (EG&G ORTEC). A standardize solution of ^{90}Sr/^{90}Y, provided by Amersham (Buckinghamshire, UK), was used for calibrating the counting efficiency of ^{90}Sr and ^{90}Y related with the quenching index. Separation of ^{90}Sr and ^{90}Y was carried out with extraction chromatography utilizing a Sr-Spec (Eichrom Industries, IL, USA) column. Ultima Gold XR (Packard Instrument) scintillating solution was mixed with the sample solution in a 20 ml low-potassium glass vial (Wheaton NJ, USA).

2.2. Quench calibration for ^{89}Sr and ^{90}Sr measurement

To determine the individual activity of radiostrontium of a dual labeled sample, the counting efficiency of each radiostrontium isotope with a particular quench level must be measured. This was done by counting a quench series of reference standards for each radiostrontium. A known activity of ^{90}Sr (147 Bq) was separated from the ^{90}Sr/^{90}Y standardized solution using a Sr-spec column. The separation procedure, using a Sr-spec resin, has been described by Horwitz et al. (1992). Finally, 10 ml of 0.05 M HNO_3 eluent contaning the pure strontium element was collected in a 20-ml glass vial and heated until dryed to avoid chemical quenching due to the nitrate anion. Once complete dryness was established, different volumes of distilled water and cocktail solution portions were mixed to give a total volume of 20 ml. Quench calibration standard solutions were prepared in which the volume of distilled water and cocktail solution were varied in the range of 1:19 and 6:14 ml, respectively, to make a total of 20 ml. ^{90}Y was collected from the first elution stage from a Sr-spec column with 5 M HNO_3 as eluent. Diluted ^{89}Sr activity (151 Bq) was added directly to the water and cocktail solution mixture. The preparations of standard quench sets of ^{90}Y and ^{89}Sr were made as described above. The counting of the ^{90}Sr standards could be completed within 1 h after strontium separation when a counting terminator is used with the sample to obtain a %2s (2σ percent value of the counts) of 0.5%. This counting terminator terminates the sample count only after the 2σ value set for 0.5%. This count terminator allows us to set a minimum counting period with good statistical accuracy. A quench curve for ^{90}Y was used for the calculation of ^{90}Y activity contributing to the ^{90}Sr activity caused by the ingrowth of ^{90}Y after the ^{90}Sr separation.

2.3. Sample preparation and chemical yield determination

Six aqueous samples were collected from effluent waste storage tanks in a nuclear power plant in Korea. After filtration and acidification with 0.1 M HNO_3 solution, 1 l of sample was passed through the cation exchange column packed with 10 ml of Dowex resin (50WX8-200, Sigma) preconditioned with 0.1 M HNO_3. After rinsing with 50 ml of 0.1 M HNO_3 solution, 20 ml of 5 M HNO_3 was eluted and introduced into the Sr-spec column preconditioned with 5 M HNO_3. After washing with 10 ml of 5 M HNO_3 solution, strontium was stripped with 10 ml of 0.05 M HNO_3 solution and collected in a glass vial. A parallel procedure was done simultaneously with the same sample and a final eluent was collected in another vial for comparison measurement with a gas proportional counter. The flow rate for all procedures was kept at 1 ml/min. Prior to activity counting, 10 parallel experiments for ^{85}Sr separation were done for chemical recovery determination. Internal standard addition into the sample as a yield tracer was not desirable because the gamma activity of ^{85}Sr is severely affected the strontium beta spectrum. The average recovery of strontium was $94 \pm 2\%$ and this value was directly used for the activity calculation. After completely drying the final eluent, 3 ml of water and 17 ml of cocktail was added for liquid scintillation counting and stored in a dark cold chamber for 30 min before counting.

3. Results and discussion

3.1. Spectrum unfolding of dual labeled sample

The principle of the full spectrum dual label DPM counting method is based on the decomposition of the

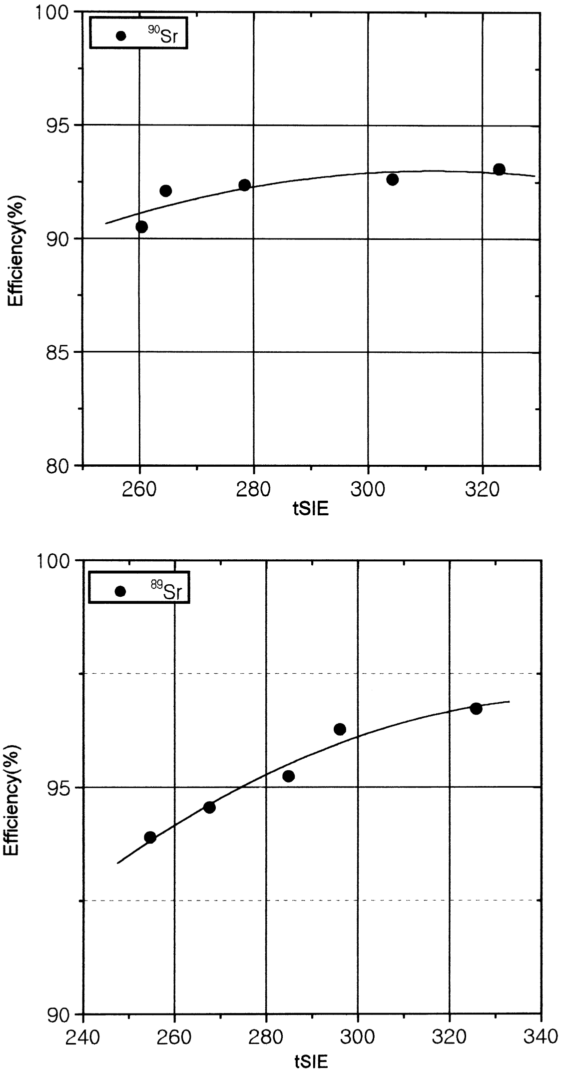

Fig. 1. Quench correlation curves of ^{90}Sr and ^{89}Sr for full spectrum DPM liquid scintillation counting.

composite spectrum into two components using an individual SIS index (Packard Instrument, 1989). The SIS index of each radionuclide in a mixed sample is predetermined by the quench correlation curves plotting SIS against tSIE quench parameter. If two radiostrontium isotopes exist in a single sample, the SIS of the total distribution, SIS_T, with a particular quench level can be described as follows

$$\mathrm{SIS_T} = \frac{\mathrm{SIS_{sr90}} \cdot N_{\mathrm{sr90}} + \mathrm{SIS_{sr89}} \cdot N_{\mathrm{sr89}}}{N_\mathrm{T}} \tag{1}$$

N_{sr90}	Accumulated counts from ^{90}Sr
N_{sr89}	Accumulated counts from ^{89}Sr
N_T	Total accumulated counts from sample ($N_{\mathrm{sr90}} + N_{\mathrm{sr89}}$)

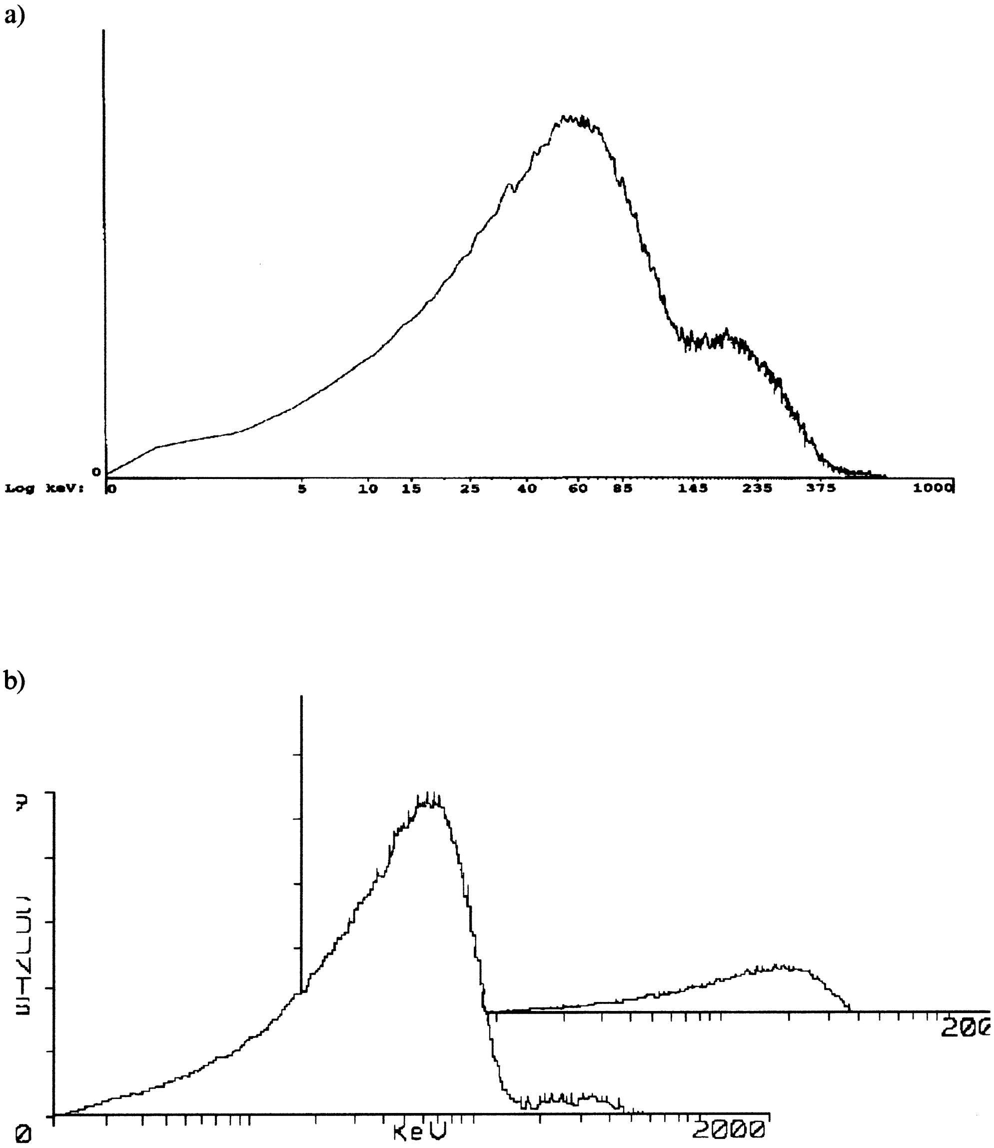

Fig. 2. Unfolded spectrum of ^{90}Sr and ^{89}Sr (b) from mixture spectrum (a) by full spectrum DPM counting method.

Table 1
^{90}Sr and ^{89}Sr measurment in reference aqueous samples[a]

Standard sample no.	^{90}Sr (Bq/l)		^{89}Sr (Bq/l)		Activity ratio ^{90}Sr:^{89}Sr
	Added	Measured	Added	Measured	
1	71.5	70.7 ± 2.65[b]	1.84	2.96 ± 1.18	39:1
2	35.8	35.2 ± 2.07	1.84	1.92 ± 1.14	20:1
3	7.15	7.12 ± 1.43	3.68	3.55 ± 1.19	2:1
4	3.58	3.60 ± 1.33	0.37	0.39 ± 1.09	9:1
5	0.36	0.34 ± 1.23	0.37	0.36 ± 1.08	1:1
6	0.36	0.31 ± 1.23	0.74	0.71 ± 1.10	1:2
7	7.15	6.89 ± 1.43	36.8	37.1 ± 1.97	1:5
8	3.58	2.97 ± 1.31	36.8	37.5 ± 1.98	1:10

[a] Counting time: 60 min.
[b] 2σ.

Where, the $\mathrm{SIS_T}$ is a function of the SIS of the individual distributions, $\mathrm{SIS_{sr90}}$, SIS_{sr89}, and the fractional counts of each radionuclide. The individual count rates from total accumulated count rates can be evaluated as follows

$$\mathrm{CPM_{sr90}} = \frac{\mathrm{SIS_{Sr89}} - \mathrm{SIS_T}}{\mathrm{SIS_{Sr89}} - \mathrm{SIS_{sr90}}} \cdot \quad \mathrm{CPM_T} \qquad (2)$$

$$\mathrm{CPM_{sr89}} = \frac{\mathrm{SIS_T} - \mathrm{SIS_{sr90}}}{\mathrm{SIS_{sr89}} - \mathrm{SIS_{sr90}}} \cdot \quad \mathrm{CPM_T} \qquad (3)$$

Individual DPM can be also calculated from the efficiency calibration curves for each radiostrontium related with a tSIE quench index. Quench correlation curves for full spectrum DPM of ^{89}Sr and ^{90}Sr plotted with tSIE and SIS were shown in Fig. 1. With increased water volume, the quench level was higher. A graphic representation of the unfolded spectrum of each radiostrontium is shown in Fig. 2. The activity ratio of ^{90}Sr to ^{89}Sr was 4.8 (^{90}Sr: 7.2 Bq, ^{89}Sr: 1.5 Bq) and the counting time was 20 min. The resulting decomposed spectrum of ^{90}Sr and ^{89}Sr is shown in Fig. 2b and the measured activity was 7.5 Bq and 1.3 Bq, respectively. The ^{90}Y ingrowth occurs promptly after the ^{90}Sr separation. Since this situation also occurred in the preparation of the ^{90}Sr standards quench set, the resulted SIS index of the ^{90}Sr standard also contains the ^{90}Y contribution. As a result, the unfolded ^{90}Sr spectrum included a ^{90}Y contribution as shown in Fig. 2b corresponding to an ingrowth amount in the first 2 h after strontium separation. Although, it was a very minute contributor to the ^{90}Sr spectrum during the first several hours after separ-

Table 2
^{90}Sr and ^{89}Sr measurement performed by full spectrum DPM liquid scintillation counting and gas proportional counting in liquid samples collected from effluent waste storage tanks in a nuclear power plant

Sample No.	Full spectrum DPM counting				Gas-proportational counting			
	^{90}Sr (Bq/l)	^{89}Sr (Bq/l)	Chemical yield[a] (%)	t[b] (min)	^{90}Sr (Bq/l)	^{89}Sr (Bq/l)	Chemical yield (%)	t (min)
1	2.37 ± 1.28[c]	–[f]	94	60	2.42 ± 0.99	–	86[d] 94[e]	300
2	4.65 ± 1.35	1.12 ± 1.12	92		4.88 ± 1.13	1.08 ± 0.67	83 90	
3	0.16 ± 1.21	–	93		0.22 ± 0.78	–	90 91	
4	0.94 ± 0.91	0.56 ± 1.07	95		0.85 ± 0.99	0.54 ± 0.71	77 88	
5	1.35 ± 1.23	0.31 ± 1.09	93		1.67 ± 0.99	0.37 ± 0.66	81 89	
6	11.3 ± 1.53	1.85 ± 1.14	94		10.8 ± 1.11	1.78 ± 0.61	102 93	

[a] Determined by ^{85}Sr gamma counting.
[b] Counting time.
[c] 2σ.
[d] Determined by $SrSO_4$ precipitate weight.
[e] Determined by $Y_2(C2O_4)_3$ precipative weight.
[f] Not detected.

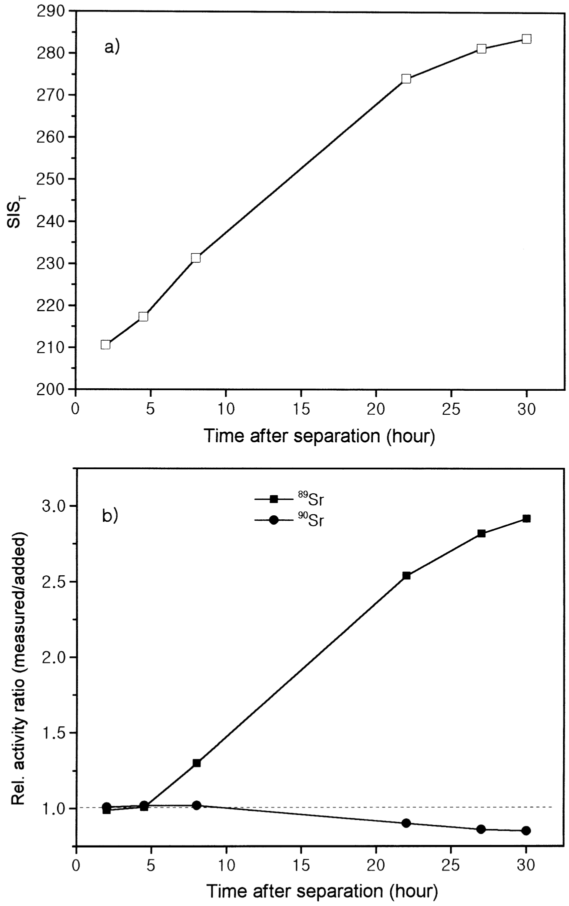

Fig. 3. A plot for SIS$_T$ (a) and the ratio of measured and added activity (b) with time after strontium separation.

ation, a lengthy period of ^{90}Y ingrowth limits the accuracy of the unfolded value of each radiostrontium.

3.2. Accuracy and detection limit

An accuracy and counting performance test was done for the various known mixed activity samples, the results are given in Table 1. The most accurate results were obtained in the range of 20:1 to 1:5 ratios of ^{90}Sr to ^{89}Sr activities. The reason for poor accuracy, when one of the strontium isotopes is predominant, is assumed to be due to the total SIS index of the mixture is not resolved enough into the two component spectra corresponding to their contribution. This was more serious when the high energy ^{89}Sr predominantly existed in the sample.

The lower limit of detection (LLD) was calculated on the standard deviation of the background count rate with 95% condifence using

$$\mathrm{LLD} = \frac{4.65(B)^{1/2}}{t\,E\,Y\,V}$$

where, t is the count time, E is the counting efficiency, Y is the chemical recovery, V is the sample volume and B is the background counts (Prichard et al., 1992). The background count rates within the full energy region (^{90}Sr: 0–550 keV, ^{89}Sr: 0–1500 keV) with a counting time of 60 min was 9.8 cpm for ^{90}Sr, 7.9 cpm for ^{89}Sr; and the LLD was 37.4 mBq/l and 32.2 mBq/l, respectively. This is three times lower than the acceptable value (117 mBq/l) for either ^{90}Sr or ^{89}Sr by the ANSI N 13.30 (ANSI, 1989). The counting sensitivity (E^2/B) was 845 for ^{90}Sr and 1142 for ^{89}Sr. These values were much higher than the values from either of the dual channel liquid scintillation counting or the Cherenkov counting method. High E^2/B resulted from utilizing full channel counting that offers the maximum counting efficiency, 92% for ^{90}Sr and 95% for ^{89}Sr, whereas the discrete channel counting method gives limited counting efficiency (Tinker et al., 1997).

As already noted, the limitation of full spectrum DPM counting methods for simultaneous measurement of ^{89}Sr and ^{90}Sr was caused by the ingrowth of ^{90}Y from ^{90}Sr. This induced build-up of total counts, SIS$_T$ is also increased with time. That results in the decrease of ^{90}Sr counts and the increase of ^{89}Sr counts with time, as expected in Eqs. (2) and (3). Fig. 3 shows the time-variable SIS$_T$ and the relative ratio of measured and added activity. This result indicates that the samples should be counted immediately after strontium separation. The measured activities were within a 5% error range when the sample was counted within 4 h of strontium separation. The degree of deviation of ^{89}Sr activity from the reference value with time was more severe than the ^{90}Sr case because the build-up counts due to ^{90}Y contributes more to the ^{89}Sr energy region, 0–1500 keV.

3.3. Liquid waste analysis

^{90}Sr and ^{89}Sr was determined in liquid waste sample collected from six different liquid waste storage tanks at a nuclear power plant. The results are summarized in Table 2, which includes the results from the conventional gas proportional counting method. Gas proportional counting of radiostrontium was done with a $SrSO_4$ precipitate for ^{89}Sr measurement and a $Y_2(C_2O_4)_3$ precipitate for ^{90}Sr measurement (Hong et al., 1996). No significant difference was observed between the values from the two methods but the activity of each radiostrontium was determined more rapidly by applying the full spectrum DPM counting method.

4. Conclusions

In this paper, we examined the performance of the full spectrum DPM liquid scintillation counting method for simultaneous measurement of radiostrontium. The results of this study demonstrate that the full spectrum DPM counting technique provides a simple, rapid and sensitive method for simultaneous measurement of low-level activity of radiostrontium from aqueous media. Optimization of the counting region was no longer required. But limitations were due to the time variable count rates owing to the ingrowth of ^{90}Y. The most accurate results were achieved when the sample was counted within the first 4 h after strontium separation. With adequate sample preparation steps prior to counting, this method may be applied to all kinds of environmental samples. The method may also be useful in the measurement of ^{90}Sr activity in the sample containing only ^{90}Sr. If quench correlation curves for ^{90}Sr and ^{90}Y are prepared, ^{90}Sr activity will be stripped from the mixture spectrum of ^{90}Sr and ^{90}Y. That will eliminate the error due to the ^{90}Y activity ingrown after strontium separation.

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