

Accurate Measurement of ^{90}Sr in Aqueous Samples with Full Spectrum DPM Method by Liquid Scintillation Counting

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Abstract

The conventional dual label DPM (DL-DPM) and full spectrum DPM (FS-DPM) counting method for determination of ^{90}Sr was comparing under the aspect of the accuracy and detection limits, and the FS-DPM method was applied to determine the ^{90}Sr in liquid waste samples. In liquid scintillation counting, the activity concentrations of ^{90}Sr and ^{90}Y were calculated from quench correlation curves related with SIS and tSIE quench indicators. Direct measurement of purified ^{90}Sr with spectrum unfolding techniques could overcome the disadvantages of the DL-DPM method. The activities of ^{90}Sr in the $^{90}\text{Sr}/^{90}\text{Y}$ standardized solution measured with the FS-DPM protocol were close to the true activity. The measurement of ^{90}Sr in the liquid waste samples with the FS-DPM counting method was easier and faster than that with the DL-DPM method, since optimization of counting regions is not necessary.

1. Introduction

In the determination of ^{90}Sr by counting the ^{90}Y activity that equilibrated with ^{90}Sr activity,

beta counting with a gas proportional counter [1-3] or Cerenkov counting with a liquid scintillation counter [4-8] has been generally used for the measurement of ^{90}Sr . However, these determinations of ^{90}Sr are time-consuming and laborious because a sufficient period (2 ~ 4 weeks) is demanded for reaching an equilibrium state between ^{90}Sr and ^{90}Y as well as chemical separation step of ^{90}Y from ^{90}Sr is necessary. A waiting time of more than two weeks for the determination of ^{90}Sr is not acceptable in an emergency situation.

To overcome the disadvantages of the conventional measurement of ^{90}Sr , the direct measurements of ^{90}Sr or ^{90}Y by liquid scintillation counting with modern liquid scintillation spectrometry equipped with spectrum analysis have been developed [9-18]. Comparing the liquid scintillation counting and the gas proportional counting, low counting efficiency of a gas proportional counter requires a long counting time for a low-level activity sample. Also, the measurement of ^{90}Sr with a proportional counter has the demerits such as lack of spectral information and lack of energy discrimination using counting windows. Among the liquid scintillation counting methods of ^{90}Sr , a spectrum unfolding method was developed for analysis of mixtures of ^{90}Sr , ^{89}Sr and ^{90}Y with expensive computer and relatively elaborate and expensive auxiliary counting equipment [18]. Recently, simple spectrum unfolding method was developed by Packard Instrument Company (Meriden, CT, USA). Hong et al applied this method to determine the activities of ^{89}Sr and ^{90}Sr in aqueous samples [19]. In this study, comparing with the dual label DPM (DL-DPM) method, advantages of the full spectrum DPM (FS-DPM) method for determining ^{90}Sr were described. Also, the FS-DPM method on measuring ^{90}Sr was applied to liquid waste sample after validating on the standard solution of ^{90}Sr .

2. Experimental

2.1 Apparatus and materials

A standardized solution of $^{90}\text{Sr}/^{90}\text{Y}$, provided by Amersham, 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 Sr SpecTM (Eichrom Industries, IL, USA) column [20,21]. The ^{85}Sr tracer was obtained from Amersham. Radioisotopes dilution was made by weight. A liquid scintillation counter (Tricarb-2770) was used for the measurement of radiostrontium. Data analysis and the calculation of activity were performed by using the FS-DPM protocol stored in the liquid scintillation counter.

2.2 Quench calibration for ^{90}Sr and ^{90}Y measurement

The counting efficiency of each ^{90}Sr and ^{90}Y with a particular quench level must be measured for determining the individual activity of ^{90}Sr and ^{90}Y . Quench calibration was done by counting a quench series of reference standards for ^{90}Sr and ^{90}Y . A known activity of ^{90}Sr was separated from the $^{90}\text{Sr}/^{90}\text{Y}$ standardized solution using a Sr Spec column. The column of Sr Spec resin was conditioned with 20 ml of 6 M HNO_3 . The standardized solution was loaded to the column followed by washing with 20 ml of 6 M HNO_3 . The passing and washing solutions, containing ^{90}Y , were collected and evaporated to dryness to avoid chemical/color quenching due to the nitrate anion. Strontium-90 was stripped with 8 ml of deionized water and collected in a 20 ml low diffusion polyethylene vial. To each sample (5 sets) 12 ml liquid scintillator (Ultima Gold LLT, Packard Instrument) was added into five liquid scintillation counting vials. The quenching agent nitromethane was then placed into each vial in increasing amounts over the range of 0-600 μL . A set of quenched standards of ^{90}Y was prepared by the same method of ^{90}Sr . Prior to activity counting, 5 parallel experiments for ^{85}Sr separation were done for chemical recovery determination. The average recovery of strontium was $96 \pm 3 \%$. This value was directly used for the activity calculation. The quench correction curves were produced by the "Count Standards" protocol in the

instrument and stored in the Packard liquid scintillation analyzer.

2.3 Determination of ^{90}Sr in liquid waste samples

Adding 50 mg of a stable Sr carrier into the liquid waste sample (300 ml), the sample was evaporated to dryness on a hotplate. After the evaporate was dissolved in 0.1 M HNO_3 solution, the sample solution was passed through the cation exchange column packed with 10 ml of AG 50-X8 cation exchange resin preconditioned with 0.1 M HNO_3 . After rinsing with 50 ml of 0.1 M HNO_3 solution, 20 ml of 6 M HNO_3 was eluted and introduced into the Sr-spec column preconditioned with 6 M HNO_3 . After washing with 10 ml of 6 M HNO_3 solution, strontium was stripped with 20 ml of deionized water. The flow rate for all procedures was kept at 0.5 ml/min. 300 mg of oxalic acid was added to the strip solution. Strontium oxalate was precipitated from alkaline solution by adding 3 ml of 25 % NH_3 . The precipitate was filtered through pre-weighed filter paper. The chemical recovery for strontium was determined by gravimetry. Samples were dissolved in 8 ml of 0.1 M HCl and mixed with 12 ml liquid scintillation cocktail. Strontium-90 was analyzed by liquid scintillation counting. For gas-proportional counting, detailed description of the sample preparation for measuring ^{90}Y has been well described elsewhere [22].

3. Results and discussion

3.1 Measurement of ^{90}Sr standard solution with spectrum unfolding method

Spectrum unfolding method developed by Packard Instrument Company can be used to determine the activities of dual labeled sample such as ^{89}Sr - ^{90}Sr [19] and ^{33}P - ^{32}P [23]. The principle of the FS-DPM counting method is based on the decomposition of the composite into two components using an individual SIS (Spectral Index of the Sample) [24]. The SIS index of each radionuclide in a mixed sample is predetermined by the quench correlation

curves plotting SIS against tSIE quench parameter. In order to be able to calculate CPM and DPM over the entire quench range, SIS versus tSIE and efficiency versus tSIE correlation curves for ^{90}Sr and ^{90}Y have to be stored in the liquid scintillation counter. Quench correction curves for full spectrum DPM of ^{90}Sr and ^{90}Y plotted with tSIE and SIS were shown in Fig. 1. Individual DPM in the full spectrum protocol can be calculated from the net CPM and the efficiency calibration curves for ^{90}Sr and ^{90}Y . DPM calculations are performed at maximum efficiency levels for ^{90}Sr and ^{90}Y , according to quenching in the scintillation cocktail. No spillover corrections are required as spectrum unfolding gives the actual CPM for ^{90}Sr and ^{90}Y .

Direct measurement of purified ^{90}Sr with spectrum unfolding techniques easily overcomes the disadvantages of the DL-DPM method. As shown in Fig. 2, regionless counting in the FS-DPM method avoids error due to incorrect selection of optimum regions in the DL-DPM method. As the zero spillover concept maximizes the counting efficiencies for ^{90}Sr and ^{90}Y , counting efficiencies of the FS-DPM method (63 %) are higher at each quench level than those of the DL-DPM (59 %). At a counting time of 100 min, the detection limit of ^{90}Sr (25.63 mBq/sample) in the FS-DPM mode calculated from the Curie equation [25] is a little lower than that (27.37 mBq/sample) in the DL-DPM mode due to high counting efficiency.

To validate reliable measurement of ^{90}Sr with spectrum unfolding method, known activities of $^{90}\text{Sr}/^{90}\text{Y}$ were measured with the FS-DPM protocol. Without chemical separation of ^{90}Sr from ^{90}Y , the activity of the ^{90}Sr standardized solution was measured directly by the liquid scintillation counter. As shown in Fig. 3, ^{90}Sr activities measured with the FS-DPM method were very close to the true ^{90}Sr standard activity. It is interesting to compare the ^{90}Sr standard activities measured with the DL-DPM protocol and those with the FS-DPM protocol. Prior to measuring ^{90}Sr activity, ^{90}Sr were separated from ^{90}Y in the equilibrated $^{90}\text{Sr}/^{90}\text{Y}$ standard solution with extraction chromatography [20,21]. As presented in Table 1, the activities of ^{90}Sr measured with the FS-DPM protocol were close to the expected value, regardless of

passing time of ^{90}Sr separation. On the contrary, when the activity of ^{90}Sr was measured with DL-DPM protocol in a few days after separation of ^{90}Sr , the concentrations of ^{90}Sr were overestimated, comparing with the expected value, because ^{90}Y ingrowth in the ^{90}Sr region with increasing time contributed to the activity of ^{90}Sr , as shown in Fig. 4. Therefore, measurement of ^{90}Sr with the spectrum unfolding protocol is more accurate and reliable than that with the dual DPM protocol, since this method is independent of ^{90}Y ingrowth.

The activities of ^{90}Y measured in the DL-DPM and FS-DPM protocol were a little lower than the expected value. In the calculating the counting efficiency of ^{90}Y , the loss of ^{90}Y in the sample preparation and the column operation for chemical separation of ^{90}Y should have been compensated for getting reliable data of ^{90}Y . However, directly measured the purified ^{90}Sr from chemical separation before ^{90}Y ingrowth, it is not necessary to get accurate activity of ^{90}Y in the determination of ^{90}Sr .

3.2 Application to liquid waste sample

To check its general applicability, the FS-DPM and DL-DPM liquid scintillation method were used to measure ^{90}Sr in liquid waste sample collected from three different liquid waste storage tanks at nuclear power plants. Measurement of ^{90}Sr by the liquid scintillation counter began directly from chemical purification of ^{90}Sr . The results are presented in Table 2, which includes the results from the conventional gas-proportional counting method after ^{90}Y milking. Determining ^{90}Sr in the liquid waste samples, ^{89}Sr could interfere with the accuracy of ^{90}Sr measurements. However, it is implied that ^{89}Sr did not contain in these liquid waste samples, because ^{90}Y , which beta energy ($E_{\text{MAX}} = 2.282 \text{ MeV}$) overlaps with ^{89}Sr ($E_{\text{MAX}} = 1.492 \text{ MeV}$), was found to be below to the detection limit (0.085 Bq/l).

No significant difference was observed in the liquid scintillation counting and the gas-proportional counting. However, the measurement of ^{90}Sr in the liquid waste sample with the

FS-DPM counting method was easier and faster than that with the DL-DPM method, because optimization of counting regions is not necessary, as noted previously. Also, comparing with the gas-proportional method, the FS-DPM method has advantages of spectral energy discrimination using a Spectraworks™ spectrum analysis software, as well as high chemical yield and counting efficiency, though the higher background (scintillation counting; 3.8 cpm, proportional counting; 1.0 cpm) of liquid scintillation counter reduces its sensitivity in measuring the sample containing low-level ⁹⁰Sr activity.

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Table 1. Comparison of $^{90}\text{Sr}/^{90}\text{Y}$ activities in the standard solution measured with DL-DPM and FS-DPM with the passing of time after ^{90}Sr separation

Time after ^{90}Sr separation	Expected value (Bq)		Dual DPM Measured value (Bq)		Full spectrum DPM Measured value (Bq)	
	^{90}Sr	^{90}Y	^{90}Sr	^{90}Y	^{90}Sr	^{90}Y
	0 day	183.6	0	181.0 ± 7.8	0	182.9 ± 7.7
3 day	183.6	99.4	187.8 ± 9.1	56.6 ± 6.2	180.1 ± 10.1	69.4 ± 6.2
6 day	183.6	145.0	191.5 ± 8.2	94.9 ± 7.9	182.9 ± 8.5	113.2 ± 8.4
9 day	183.6	165.9	196.7 ± 8.7	112.9 ± 6.1	184.0 ± 9.8	140.9 ± 9.2
12 day	183.6	175.5	202.8 ± 9.9	134.1 ± 8.5	181.5 ± 8.7	157.2 ± 8.5
15 day	183.6	179.9	203.1 ± 9.0	150.4 ± 7.5	184.8 ± 6.4	165.1 ± 7.9

Table 2. ^{90}Sr activity measured with liquid scintillation counting and gas proportional counting in liquid waste samples collected from nuclear power plants

Sample number	Liquid scintillation counting				Gas-proportional counting	
	Dual DPM	Full spectrum DPM		Chemical yield (%)	^{90}Sr (Bq)	Chemical yield (%)
	^{90}Sr (Bq)	^{90}Sr (Bq)	^{90}Y (Bq)			
Y1	7.7 ± 1.9	8.5 ± 1.2	< N. D.	92	6.9 ± 1.2	82
Y2	9.1 ± 1.7	8.3 ± 1.4	< N. D.	87	8.6 ± 1.8	74
W1	0.23 ± 0.06	0.33 ± 0.05	< N. D.	89	0.30 ± 0.07	83
W2	0.36 ± 0.07	0.35 ± 0.07	< N. D.	91	0.29 ± 0.01	79
K1	0.70 ± 0.09	0.62 ± 0.09	< N. D.	90	0.54 ± 0.08	75
K2	0.57 ± 0.05	0.67 ± 0.15	< N. D.	85	0.68 ± 0.11	82

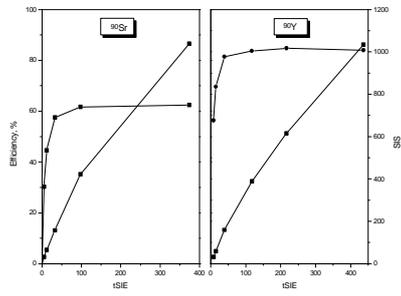


Fig. 1. Quench correlation curves of ^{90}Sr and ^{90}Y for FS-DPM method

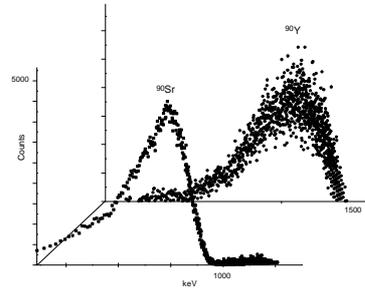


Fig. 2. Separation of ^{90}Sr and ^{90}Y in FS-DPM counting with spectrum unfolding techniques

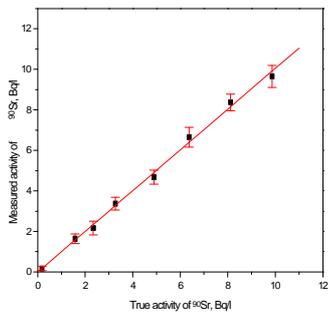


Fig. 3. Plots of ^{90}Sr activities measured with FS-DPM method in cocktails of known activities of ^{90}Sr

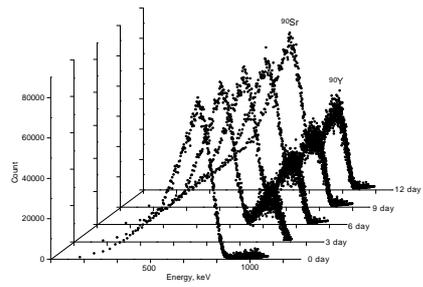


Fig. 4. Typical spectra of ^{90}Sr and ^{90}Y in FS-DPM counting mode with time after separation of ^{90}Sr