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Measurement of ^{90}Sr in aqueous samples using liquid scintillation counting with full spectrum DPM method

M.H. Lee*, K.H. Chung, G.K. Choi, C.W. Lee

Nuclear Environment Research Division, Korea Atomic Energy Research Institute, P.O. Box 105, Yusung, Taejeon 305-353, South Korea

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Abstract

^{90}Sr activity was measured with the full spectrum DPM (FS-DPM) counting method after plotting the quench correction curves of ^{90}Sr and ^{90}Y, and the FS-DPM method was applied to determine the ^{90}Sr in liquid waste samples. The optimum regions of ^{90}Sr and ^{90}Y were set for measuring ^{90}Sr with the dual label DPM (DL-DPM) method. The 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}Sr/^{90}Y standardized solution measured with the FS-DPM protocols were close to the true activity. The concentrations of ^{90}Sr in the liquid waste samples measured with the FS-DPM counting method were compared with those obtained with conventional methods. © 2002 Published by Elsevier Science Ltd.

Keywords: Strontium-90; Liquid scintillation counting; Spectrum unfolding

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 (Goldin et al., 1959; Fourie and Ghijsels, 1969; Chieco et al., 1992) or Cerenkov counting with a liquid scintillation counter (Carmon, 1979; James, 1987; Walter et al., 1993; Poletiko et al., 1994; Torres et al., 1996) have been classically 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; the chemical separation step of ^{90}Y from ^{90}Sr is necessary as well. A waiting time of more than 2 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, direct measurements of ^{90}Sr or ^{90}Y by liquid scintillation counting with modern liquid scintillation spectrometry equipped with spectrum analysis have been developed (Piltingsrud and Stencel, 1972; Randolph, 1975; Amano and Yanase, 1990; Zhu et al., 1990; Tait and Weichen, 1993; Passo and Cook, 1994; Alvarez et al., 1995; Tinker et al., 1997; Heilgeist, 2000). Compared to gas-proportional counting, liquid scintillation counting of ^{90}Sr has merits such as high counting efficiency and energy discrimination. When ^{90}Sr is measured with a liquid scintillation counter, the dual label DPM (DL-DPM) method has been conventionally used for determining ^{90}Sr. Recently, the full spectrum DPM (FS-DPM) method developed by Packard Instrument Company (Kessler, 1989) has been used to determine the activities of a dual labeled sample such as ^{33}P–^{32}P (L'Annunziata, 1997). Hong et al. applied this method to determine the activities of ^{89}Sr and ^{90}Sr in aqueous samples (Hong et al., 2001). In this study, after we plotted the quench correction curves of ^{90}Sr and ^{90}Y, ^{90}Sr/^{90}Y activities in the standard solution were measured with the FS-DPM method. The advantages of the FS-DPM method for measuring ^{90}Sr activity were compared with those of the conventional DL-DPM method. Also, the FS-DPM method for measuring ^{90}Sr was applied to liquid waste samples so

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*Corresponding author. Tel.: +82-4286-82324; fax: +82-4286-31289.

E-mail address: mhlee1@kaeri.re.kr (M.H. Lee).

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the concentrations of ^{90}Sr measured with the FS-DPM counting method could be compared with those obtained with conventional methods.

2. Theoretical

The principle of the FS-DPM method is based on the decomposition of the composite spectrum into components using an individual SIS index. This method utilizes the SIS index of the double labeled material to "unfold" the separate pulse height spectra of the composite spectrum of the double labeled radionuclide sample. At a given level of quenching, each radionuclide has a very definite pulse height distribution and a unique SIS index can be calculated. The SIS index of each radionuclide in a mixed sample is predetermined by the quench correlation curves plotting the SIS against the transformed spectral index of external standard (tSIE) quench parameter. If ^{90}Sr and ^{90}Y exist in a single sample, the SIS of the total distribution, $\mathrm{SIS_T}$, with a particular quench level can be mathematically calculated as follows:

$$\mathrm{SIS_T} = \frac{\mathrm{SIS_{Sr90}}N_{\mathrm{Sr90}} + \mathrm{SIS_{Y90}}N_{\mathrm{Y90}}}{N_{\mathrm{T}}}, \quad (1)$$

where N_{Sr90} is the accumulated counts from ^{90}Sr, N_{Y90} the accumulated counts from ^{90}Y, N_{T} the total accumulated counts from sample ($N_{\mathrm{Sr90}} + N_{\mathrm{Y90}}$).

The individual count rates from total accumulated count rates can be evaluated as follows:

$$\mathrm{CPM_{Sr90}} = \frac{\mathrm{SIS_{Y90}} - \mathrm{SIS_T}}{\mathrm{SIS_{Y90}} - \mathrm{SIS_{Sr90}}} \times \mathrm{CPM_T}, \quad (2)$$

$$\mathrm{CPM_{Y90}} = \frac{\mathrm{SIS_T} - \mathrm{SIS_{Sr90}}}{\mathrm{SIS_{Y90}} - \mathrm{SIS_{Sr90}}} \times \mathrm{CPM_T}. \quad (3)$$

Therefore, individual DPM values can also be calculated from the efficiency calibration curves for ^{90}Sr and ^{90}Y related with a tSIE quench index.

3. Experimental

3.1. Apparatus and materials

A standardized solution of ^{90}Sr/^{90}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 a Sr-Spec resin (Eichrom Industries, IL, USA) column (Horwitz et al., 1992, 1993). 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 activity calculation were performed by using the FS-DPM protocol stored in the liquid scintillation counter.

3.2. Quench calibration for ^{90}Sr and ^{90}Y measurements

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}Sr/^{90}Y standardized solution using a Sr-Spec column. The column of Sr-Spec resin was conditioned with 20 ml of $6\,\mathrm{M \cdot HNO_3}$. The standardized solution was loaded into the column, followed by washing with 20 ml of $6\,\mathrm{M \cdot HNO_3}$. 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. Each sample (5 sets) 12 ml of 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 as used for ^{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 ± 3%. The quench correction curves were produced by the "count standards" protocol in the instrument and stored in the Packard liquid scintillation analyzer.

3.3. Determination of ^{90}Sr in liquid waste samples

After addition of 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 $0.1\,\mathrm{M \cdot HNO_3}$ solution, the sample solution was passed through the cation exchange column packed with 10 ml of AG 50-X8 cation exchange resin preconditioned with $0.1\,\mathrm{M \cdot HNO_3}$. After rinsing with 50 ml of $0.1\,\mathrm{M \cdot HNO_3}$ solution, 20 ml of $6\,\mathrm{M \cdot HNO_3}$ was eluted and introduced into the Sr-spec column preconditioned with $6\,\mathrm{M \cdot HNO_3}$. After washing with 10 ml of $6\,\mathrm{M \cdot HNO_3}$ solution, strontium was stripped with 20 ml of deionized water. The flow rate for all procedures was kept at 0.5 ml/min. Three hundred milligram of oxalic acid was added to the strip solution. Strontium oxalate was precipitated from the alkaline solution by adding 3 ml of 25% $\mathrm{NH_3}$. The precipitate was filtered through preweighed filter paper. The chemical recovery for strontium was determined by gravimetry. Samples were dissolved in 8 ml of $0.1\,\mathrm{M \cdot HCl}$ and mixed with 12 ml liquid scintillation cocktail. Strontium-90 was analyzed by liquid scintillation counting. For gas-proportional counting, a detailed description of the sample preparation for measuring ^{90}Y has been provided elsewhere (Hong et al., 1996).

4. Results and discussion

4.1. Optimum region in the conventional dual labeled DPM method

Measuring ^{90}Sr activity with the conventional DL-DPM method requires the setting of counting regions with lower level (LL) and upper level (UL) pulse height discriminators. To find appropriate LL and UL discriminator settings for ^{90}Sr and ^{90}Y of double level, we counted a known activity of ^{90}Sr over in a wide range of counting regions starting at a LL discriminator setting of zero and progressively increasing the UL discriminator. This procedure was repeated with a known activity of ^{90}Y. The counting efficiency values for the ^{90}Sr and ^{90}Y in the various counting regions were then plotted against each other as illustrated in Fig. 1. The optimum section is where there is minimum change in efficiency of the ^{90}Sr and ^{90}Y for any slight changes in counting settings. These conditions are found in the "knee" of the curve. A counting region (LL–UL) of 0–350 keV was selected as the optimum region of ^{90}Sr, which occurs in the knee of the curve. The discriminator settings for a region of ^{90}Y are defined by selecting the LL discriminator setting of 350 keV, which is the upper limit for ^{90}Sr. The UL discriminator setting of ^{90}Y was selected as 2000 keV, because no pulses from this double label can reach beyond 2000 keV for the least quenched sample. Therefore, the counting region of ^{90}Y was defined by the LL and UL settings of 350–2000 keV.

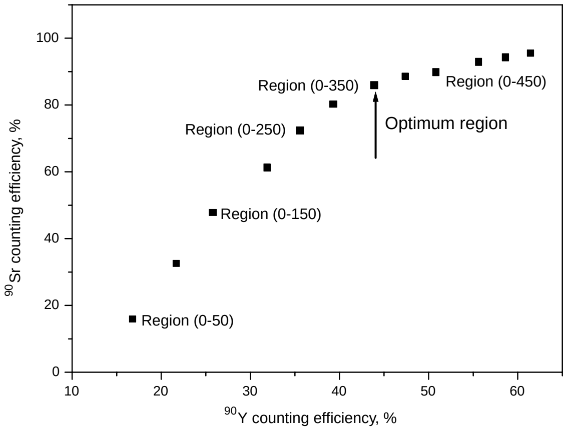

Fig. 1. Counting efficiency values for the ^{90}Sr and ^{90}Y in the various counting regions.

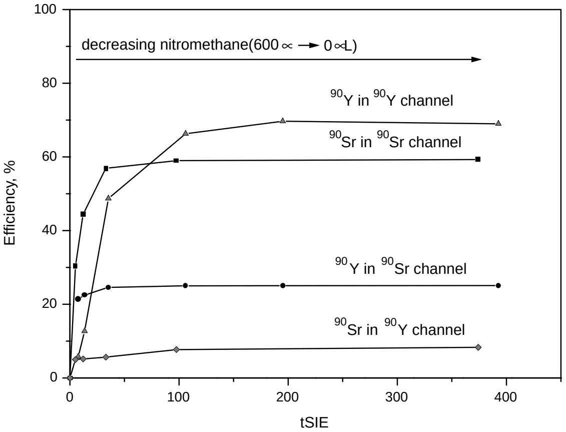

Fig. 2. Dual label efficiency curves using tSIE.

Using tSIE as the quench indicating parameter and two sets of quenched standards for ^{90}Sr and ^{90}Y in the DL-DPM data mode, we show the typical quench correction curves in Fig. 2. With increasing nitromethane volume, the efficiencies became lower due to the increasing of the quenching level. The quench correction curves data produced by the instrument were stored in the liquid scintillation spectrometer. In the real samples, the activity of ^{90}Sr in the DL-DPM mode is calculated using these quench correction curves, depending upon quenching in the scintillation cocktail.

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

In order for one 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 must be stored in the liquid scintillation counter. Quench correction curves for FM-DPM of ^{90}Sr and ^{90}Y plotted with tSIE and SIS are shown in Fig. 3. 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. 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

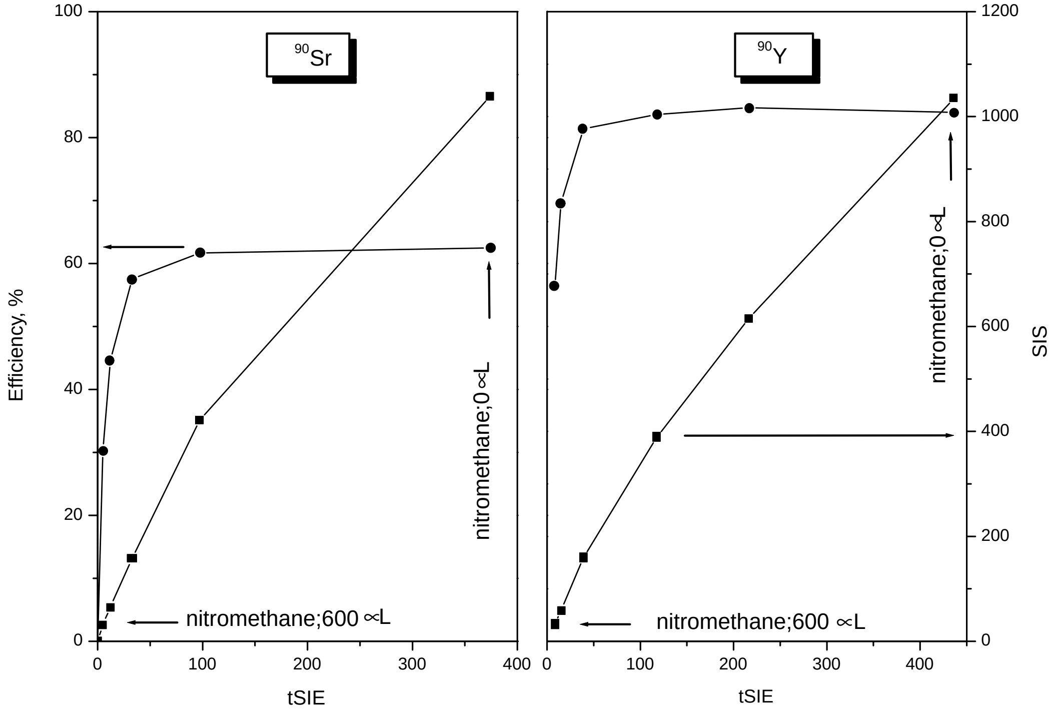

Fig. 3. Quench correlation curves of ^{90}Sr and ^{90}Y for FS-DPM.

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 (Curie, 1968) is a little lower than that (27.37 mBq/sample) in the DL-DPM mode due to high counting efficiency.

To validate the reliable measurement of ^{90}Sr with the spectrum unfolding method, we measured known activities of ^{90}Sr/^{90}Y 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. 4, ^{90}Sr activities measured with the FS-DPM method were very close to the true ^{90}Sr standard activity. Also, it is interesting to check the ^{90}Sr standard activity with ^{90}Y in-growth. Prior to measuring ^{90}Sr activity, ^{90}Sr was separated from ^{90}Y in the equilibrated ^{90}Sr/^{90}Y standard solution with extraction chromatography (Horwitz et al., 1992, 1993). The typical spectra of ^{90}Sr and ^{90}Y in the FS-DPM counting mode are shown in Fig. 5. As presented in Table 1, the activities of ^{90}Sr measured with the FS-DPM protocol were close to the expected value, regardless of ^{90}Y in-growth. Therefore, measurement of ^{90}Sr with the spectrum unfolding protocol is a more accurate and reliable method, compared with conventional methods, since the FS-DPM method is independent of ^{90}Y in-growth.

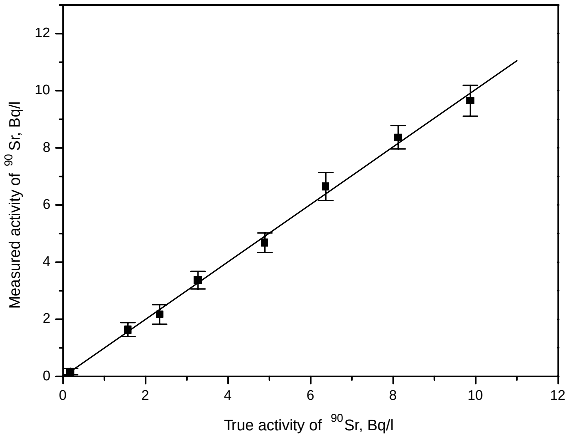

Fig. 4. Plots of ^{90}Sr activities measured with FS-DPM in cocktails of known activities.

4.3. Application to liquid waste sample

To check its general applicability, the FS-DPM and DL-DPM liquid scintillation methods were used to measure the ^{90}Sr in liquid waste samples collected from three different liquid waste storage tanks at nuclear power plants. Measurement of ^{90}Sr by the liquid scintillation counter began directly from the chemical

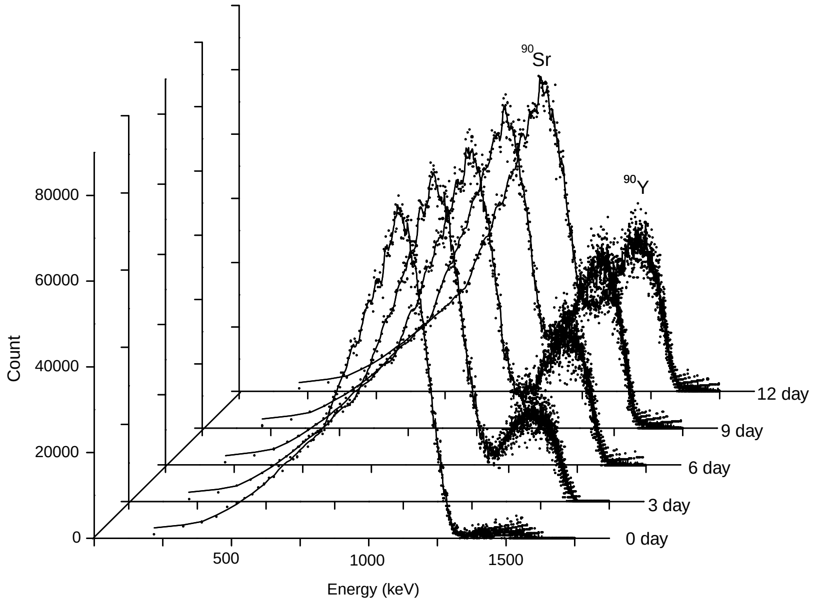

Fig. 5. Spectra of ^{90}Sr and ^{90}Y in FS-DPM counting mode with time after separation of ^{90}Sr.

Table 1
^{90}Sr activities in the standard solution measured with FS-DPM with the passing of time after ^{90}Sr separation

Time after	Expected value (Bq/ml)		Measured value with FS-DPM (Bq/ml)	
^{90}Sr separation	^{90}Sr	^{90}Y	^{90}Sr	^{90}Y
0 day	183.6	0	182.9 ± 7.7	0
3 day	183.6	99.4	180.1 ± 10.1	69.4 ± 6.2
6 day	183.6	145.0	182.9 ± 8.5	113.2 ± 8.4
9 day	183.6	165.9	184.0 ± 9.8	140.9 ± 9.2
12 day	183.6	175.5	181.5 ± 8.7	157.2 ± 8.5
15 day	183.6	179.9	184.8 ± 6.4	165.1 ± 7.9

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. No significant difference was observed in the liquid scintillation counting and the gas-proportional counting. However, compared with the gas-proportional method, the FS-DPM method has advantages such as high chemical yield and spectral energy discrimination using Spectraworks™ spectrum analysis software, as shown in Fig. 6, though the figure of merit (E^2/B) in the scintillation counting was worse than that in the proportional counting (scintillation counting, 1044; proportional counting, 2304) due to the high background (scintillation counting, 3.8 cpm; proportional counting, 1.0 cpm). Also, the difference between the activities of ^{90}Sr measured with the FS-DPM method and DL-DPM method was negligible, considering the error range of concentration of ^{90}Sr. However, the measurement of ^{90}Sr with the DL-DPM counting method requires the setting of optimum counting regions of ^{90}Sr and ^{90}Y before measuring ^{90}Sr.

If ^{89}Sr is contained in the sample, it could interfere with the accuracy of the measurement of ^{90}Sr with the FS-DPM method, because ^{89}Sr, which has beta energy ($E_{\mathrm{MAX}} = 1.492\,\mathrm{MeV}$), has a possibility of overlapping with ^{90}Y ($E_{\mathrm{MAX}} = 2.282\,\mathrm{MeV}$). Fortunately, it is implied that ^{89}Sr does not appear in these liquid waste samples, because ^{90}Y was found to be below the detection limit (0.085 Bq/l). However, for the accurately determining ^{90}Sr in liquid waste samples, the purified ^{90}Sr solution must be directly checked as regards the activity of ^{89}Sr by Cerenkov counting with a liquid scintillation counter (Walter et al., 1993; Poletiko et al., 1994) before measuring ^{90}Sr with FS-DPM method. Therefore, if the Cerenkov radiation of ^{89}Sr is measured in the purified ^{90}Sr solution from liquid waste samples, the

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

	Liquid scintillation counting				Gas-proporational counting	
Sample	Dual DPM	Full spectrum DPM				
number	^{90}Sr (Bq/l)	^{90}Sr (Bq/l)	^{90}Y (Bq/l)	Chemical yield (%)	^{90}Sr (Bq/l)	Chemical yield (%)
Y1	7.7±1.9	8.5±1.2	<LLD[a]	87	6.9±1.2	80
Y2	9.1±1.7	8.3±1.4	<LLD	82	8.6±1.8	72
W1	0.23±0.06	0.33±0.05	<LLD	85	0.30±0.07	84
W2	0.36±0.07	0.35±0.07	<LLD	91	0.29±0.01	79
K1	0.70±0.09	0.62±0.09	<LLD	76	0.54±0.08	77
K2	0.57±0.05	0.67±0.15	<LLD	85	0.68±0.11	83

[a] Detection limit (0.085 Bq/l).

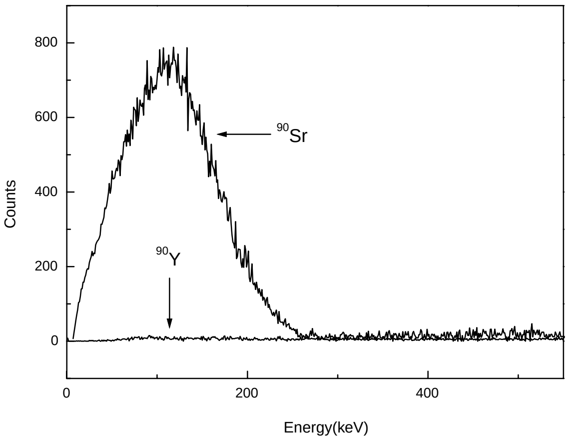

Fig. 6. Typical liquid spectra of ^{90}Sr and ^{90}Y in the waste sample (Y1).

determination of ^{90}Sr must be done by simultaneous measurement of ^{89}Sr and ^{90}Sr with the FS-DPM method (Hong et al., 2001).

5. Conclusion

In this work, compared to the DL-DPM method, the FS-DPM counting method was applied to measure the ^{90}Sr standardized solution and liquid waste samples. Measurement of ^{90}Sr activity with FS-DPM protocol is a more accurate and reliable method, compared with DL-DPM method, since the FS-DPM method has merits such as regionless counting, high counting efficiency and low detection limit. The activities of ^{90}Sr in the ^{90}Sr/^{90}Y standardized solution measured with the FS-DPM protocols were close to the true activity. From the results of ^{90}Sr activity in the liquid waste samples, no significant difference was observed between the FS-DPM method and the conventional counting methods.

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References

Alvarez, A., Navarro, N., Salvador, S., 1995. New method for ^{90}Sr determination in liquid samples. Radioanal. Nucl. Chem. Art. 191, 315.

Amano, H., Yanase, N., 1990. Measurement of ^{90}Sr in environmental samples by cation-exchange and liquid scintillation counting. Talanta 37, 585.

Carmon, B., 1979. The use of Cerenkov radiation for the assay of radiostrontium in aqueous solutions. Int. Appl. Radiat. Isot. 30, 97.

Chieco, N.A., Bogen, D.C., Knutson, E.O., 1992. EML Procedures Manual, 27th Edition.. US Department of Energy, New York.

Curie, L.A., 1968. Limits for qualitative and quantitative determination: application to radiochemistry. Anal. Chem. 40, 586.

Fourie, H.O., Ghijsels, J.P., 1969. Radiostrontium in biological material: a precipitation and extraction procedure eliminating the use of fuming nitric acid. Health Phys. 17, 687.

Goldin, A.S., Velten, R.J., Frishkorn, G.W., 1959. Determination of radioactive strontium. Anal. Chem. 31, 1490.

Heilgeist, M., 2000. Use of extraction chromatography, ion chromatography and liquid scintillation spectrometry for rapid determination of strontium-89 and strontium-90 in food in cases of increased release of radionuclides. Radioanal. Nucl. Chem. Art. 245, 249.

Hong, K.H., Cho, Y.H., Kim, S.B., Lee, M.H., Lee, C.W., 1996. Analysis of ^{89}Sr, ^{90}Sr in soil sample using crown ether/

chloroform solvent extraction method. J. Korean Assoc. Radiat. Prot. 21, 9.

Hong, K.H., Cho, Y.H., Lee, M.H., Choi, G.S., Lee, C.W., 2001. Simultaneous measurement of ^{89}Sr and ^{90}Sr in aqueous samples by liquid scintillation counting using the spectrum unfolding method. Appl. Radiat. Isot. 54, 299.

Horwitz, E.P., Chiarizia, R., Dietz, M.L., 1992. A novel strontium-selective extraction chromatographic resin. Sol. Extr. Ion Exch. 10, 313.

Horwitz, E.P., Chiarizia, R., Dietz, M.L., Diamond, H., 1993. Separation and preconcentration of actinides from acidic media by extraction chromatography, analyt. Chim. Acta 281, 361.

James, E.M., 1987. Measurement of ^{90}Sr in reactor wastes by Cerenkov counting of ^{90}Y. Appl. Radiat. Isot. 38, 953.

Kessler, M.J. (Ed.), 1989. Liquid scintillation analysis. Science and Technology, Packard Instrument Co.

L'Annunziata, M.F., 1997. Tri-Carb LSC Application Note. CIA-003, Packard Instrument Company.

Passo, C.J., Cook, G.T., 1994. Handbook of Environmental Liquid Scintillation Spectrometry. A compilation of Theory and Methods. Meriden, Cambera.

Piltingsrud, H.V., Stencel, J.R., 1972. Determination of ^{90}Y, ^{90}Sr and ^{89}Sr in samples by use of liquid scintillation beta spectroscopy. Health Phys. 23, 121.

Poletiko, C., Lemerchier, R., Leiba, B., Llug, P., 1994. Mesurement of strontium-90 by the Cerenkov counting technique. J. Radioanal. Nucl. Chem. Art. 178, 131.

Randolph, R.B., 1975. Determination of strontium-90 and strontium-89 by Cerenkov and liquid-scintillation counting. Int. J. Appl. Radiat. Isot. 26, 9.

Tait, D., Weichen, A., 1993. Use of liquid scintillation counting for fast determination of ^{89}Sr and ^{90}Sr in milk. Sci. Total Environ. 130/131, 447.

Tinker, R.A., Smith, J.D., Cooper, M.B., 1997. Determination of strontium-90 in environmental samples containing thorium. Analyst 122, 122.

Torres, J.M., Garcia, J.F., Llaurado, M., Rauret, G., 1996. Rapid determination of strontium-90 in environmental samples by single Cerenkov counting using two different color quench curves. Analyst 121, 1737.

Walter, K., Trautmann, N., Herrmann, G., 1993. Simultaneous determination of strontium-90 and strontium-89 by Cerenkov-radiation and liquid-scintillation counting: a re-evaluation for low-level counting. Radiochim. Acta 62, 207.

Zhu, S., Ghods, A., Veselsky, J.C., Mirna, A., Schelenz, R., 1990. Interference of ^{91}Y with the rapid determination of ^{90}Sr originating from the Chernobyl fallout debris. Radiochim. Acta 51, 195.