Rapid Method for Low Level ^{90}Sr Determination in Seawater by Liquid Extraction Technique

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Abstract—Determination of low level ^{90}Sr in seawater has been widely developed for the purpose of environmental monitoring and radiological research because ^{90}Sr is one of the most hazardous radionuclides released from atmospheric during the testing of nuclear weapons, waste discharge from the generation nuclear energy and nuclear accident occurring at power plants. A liquid extraction technique using bis-2-etylhexyl-phosphoric acid to separate and purify yttrium followed by Cherenkov counting using a liquid scintillation counter to determine ^{90}Y in secular equilibrium to ^{90}Sr was developed to monitor ^{90}Sr in the Asia Pacific Ocean. The analytical performance was validated for the accuracy, precision, and trueness criteria. Sr-90 determination in seawater using various low concentrations in a range of 0.01 – 1 Bq/L of 30 liters spiked seawater samples and 0.5 liters of IAEA-RML-2015-01 proficiency test sample waste performed for statistical evaluation. The results had a relative bias in the range from 3.41% to 12.28%, which is below accepted relative bias of ± 25% and passed the criteria confirming that our analytical approach for determination of low levels of ^{90}Sr in seawater was acceptable. Moreover, the approach is economical, non-laborious and fast.

Keywords—Proficiency test, radiation monitoring, seawater, strontium determination.

I. INTRODUCTION

THE presence of ^{90}Sr in marine environments over the last several decades has increased mainly from atmospheric nuclear weapon tests in the 1950s and 1960s [1]. Moreover, it has been intentionally and accidentally released into ocean from nuclear reprocessing facilities. It has long physical half-life (E_{max} = 0.546 MeV, $T_{1/2}$ = 28.79 years) [2] and biological half-life (18 years) and has a high radiotoxicity due to its accumulation in bone and its highly energetic decay product ^{90}Y (E_{max} = 2.280 MeV, $T_{1/2}$ = 64 h) [2] which causes damage to bone marrow. This makes the presence of ^{90}Sr in the environment a significant health concern. Sr-90 is therefore one of the important isotopes in the marine environment to be monitored in order to estimate the dose impact to human [3].

To determine ^{90}Sr in environmental samples especially at low level concentrations, radiochemical analysis has to be applied to separate and purify ^{90}Sr or ^{90}Y from samples before beta radiation measurement. In most cases, radioanalytical methods are determined in ^{90}Sr via its daughter product ^{90}Y which have options of source preparation such as the gross beta counting in solid form using gas proportional counter and advanced Cherenkov counting in a solution using a liquid

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scintillation counter (LSC). Recently Cherenkov counting has been widely employed for determining ^{90}Sr via its daughter ^{90}Y in environmental samples [4]. Cherenkov counting with LSC, has advantage of avoiding over counting from the contaminated of low energy beta emitters in samples as only high energy beta particles (E_{max}> 800 keV) could produce Cerenkov light, i.e. ^{32}P, ^{36}Cl, ^{90}Y, and ^{89}Sr. Moreover, the samples used for Cherenkov counting are only acidic solution and therefore are economical and easy for source preparation and waste treatment.

Liquid extraction using bis-2-etylhexyl-phosphoric acid (HDEHP) to separate and purify yttrium has been developed for determining low concentration ^{90}Sr in seawater. Major et al. [5], Fukai et al. [6], and Borcherding and Nies [7] used HDEHP solution to extract yttrium in seawater and prepared the sources in form of precipitate Y_2O_3 for gross beta counting using a gas proportion counter which caused inaccurate recovery yield from the gravimetric method and overcounting from the gross beta measurement. Suomela et al. [8] developed ^{90}Sr determination in environmental samples, excluding seawater, which used HDEHP in toluene for yttrium separation and Cherenkov counting for the radiation measurement which was an effective method. Therefore, our work for low concentration ^{90}Sr determination in seawater was developed based on the liquid extraction and Cherenkov counting techniques [9]. The liquid extraction method using 10% HDEHP to prepare yttrium liquid source, and Cherenkov counting using LSC was carried out. The analytical method had been verified for accuracy, precision and trueness criteria which various low level ^{90}Sr concentrations in spiked synthetic seawater and the IAEA-RML-2015-01 proficiency test (PT) sample were used to determine the performance for statistical evaluation.

II. EXPERIMENTAL

A. Sample Description

1. The PT Sample

The 5 liter IAEA-RML-2015-01 PT sample containing ^{134}Cs, ^{137}Cs, ^{90}Sr and ^{3}H was obtained from the IAEA, Fig 1.

2. The Spiked Synthetic Seawater Samples

The synthetic seawater samples were prepared with a salinity of 35% using synthetic sea salt. Three 30-liter repeated samples were spiked with the known activity solution of ^{90}Sr to obtain three level concentrations, i.e. 0.01 Bq/L, 0.10Bq/L and1 Bq/L.

Fig. 1 Five-liter proficiency test sample from IAEA

B. Reagent and Radioactivity Standards

HNO$_3$, HCl, NH$_4$OH, HDEHP, phenolphthalein, Y(NO$_3$)$_3$, sodium acetate, xylenolorange, KNO$_3$, NaOH, toluene and Titriplex III used were analytical grade. The equilibrium ^{90}Sr/^{90}Y reference solution was purchased from Eckert and Ziegler Isotope Product.

C. Method for Determination of ^{90}Sr in Secular Equilibrium to ^{90}Y

1. Analysis of the PT Sample

The three 0.5-liter aliquots were adjusted to pH 1-1.5 with conc. HCl then added to 10 mg of yttrium carrier. Yttrium in the solutions was extracted with 50 ml of 10% HDEHP in toluene. The HDEHP phases were washed twice using 50 ml of 0.08 M HCl. Yttrium was back extracted by 50 ml of 3 M HNO$_3$. Yttrium hydroxide was precipitated by adding NH$_4$OH into the solutions until pH 9-10. The precipitates were separated by centrifuging then dissolved with 1 ml of conc. HNO$_3$. The solution samples were transferred into 20 mL polyethylene LSC vials and diluted to 15 ml with DI water for the Cherenkov counting using LSC. After Cherenkov counting, yttrium recovery yields were determined by titrating the solutions with Titriplex III. The solutions were added to 1.5 g of sodium acetate and 100 mg of xylenolorange in KNO$_3$ and then diluted to 50 ml with DI water in Erlenmeyer flasks. Before titrating, the samples were adjusted to pH 5-6 with 6 M NaOH then titrated with Titriplex III until solution colour was changed from red to orange.

2. Analysis of the Spiked Synthetic Seawater Samples

The same radioanalytical method as those of the PT sample was applied, with only changing the used amount of 10% HDEHP from 50 ml to 250 ml at the yttrium extraction step since larger volumes, i.e. 30 liters of the samples were used.
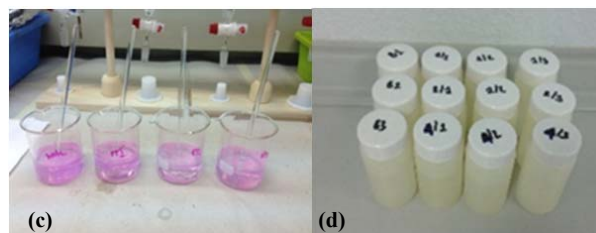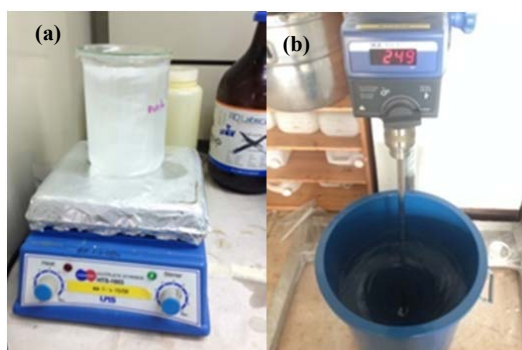

Fig. 2 Analysis of ^{90}Sr determination (a) The extraction of PT sample using 50 ml of 10% HDEHP, (b) The extraction of spiked seawater sample using 250 ml of 10% HDEHP, (c) Yttrium hydroxide precipitation step and (d) The concentrated yttrium solutions in the LCS vials for Cherenkov counting

D. Calibration Source Preparation

The secular equilibrium ^{90}Sr/^{90}Y reference solution (1.649 ±0.051 Bq in 15 ml of HNO$_3$ solution) was transferred to a 20 mL polyethylene vial for Cherenkov counting.

E. Measurement of ^{90}Y, Counting Instrument and Software

LSC was performed using a PerkinElmer, Tri-Carb 3180 TR/SL. QuantaSmart software was used for the Cherenkov counting. The prepared calibration source was counted for 30 min in energy range of 0 - 50 keV to determine Cherenkov counting efficiency from ^{90}Y. Please note that ^{90}Y has about 60% efficiency in Cherenkov counting, whereas ^{90}Sr has only 1% Cherenkov counting efficiency [10]. Cherenkov counting from ^{90}Sr is therefore insignificant, and the calibration source, ^{90}Sr/^{90}Y solution, could be directly used for determining Cherenkov counting efficiency from ^{90}Y. The samples were counted at the same condition as those of the calibration source.

F. Data Evaluation

Results were analysed according to IAEA criteria using different statistical evaluation, i.e. accuracy, precision and trueness [11] as follows:

1. Accuracy

The first step in producing a score for a result measured value, Value$_{Measured}$, was the estimation of bias. The relative bias (RB) was between the measured value and the target value calculated as a percentage according to the following equation:

$$RB = \frac{Value_{Measured} - Value_{target}}{Value_{target}} \times 100 \qquad (1)$$

Value$_{target}$ and its associated uncertainty, unc$_{target}$, were the known values received from IAEA and the data of spiked sample preparation.

If RB is equal to or less than the Maximum Accepted Relative Bias (MARB), the result is obtained "Accepted" for accuracy. In this case, the MARB was 25%, determined based on level of the radioactivity and the complexity of radioanalytical method.

2. Precision and Trueness

The precision (P) was calculated according to (2).

$$P = \sqrt{\left(\frac{unc_{target}}{Value_{target}}\right)^2 + \left(\frac{unc_{Measured}}{Value_{Measured}}\right)^2} \times 100 \qquad (2)$$

The precision was compared to the Limit of Accepted Precision (LAP) which was 25%. Result was scored as "Pass" for precision when:

$$P \leq LAP \qquad (3)$$

Result for trueness was scored as "Pass" when:

$$|Bias_{relative}| \leq \frac{Value_{Measured}}{Value_{taget}} 2.58\,P \qquad (4)$$

3. The Resulting Final Score from the Test

The final score can be summarised according to the detailed evaluation shown in Table I.

TABLE I
PERFORMANCE EVALUATION CRITERIA

Accuracy	Precision	trueness	Final score	Accuracy
Pass	Pass	Pass	Accepted	Pass
Pass	Fail	Pass	Warning	Pass
Pass	Pass	Fail	Warning	Pass
Fail	Pass/Fail	Pass/Fail	Not accepted	Fail

III. RESULTS AND DISCUSSION

The analysis results of the spiked and PT samples can be seen from Table II. Individual analysis for each sample looked close together. It should be noticed that the PT samples had significantly higher chemical recovery when compared with those of spiked samples. This was expected as working with large volume of 30 liters possibly had higher process loss, i.e. sample solution attached on large area of container wall. However, the chemical recoveries of the spiked samples seemed fairly high i.e. 66.08%, 63.77% and 65.81% for activity concentration of 0.01, 0.1, and 1 Bq/kg, respectively. The detection limits were 2 mBq/L and 0.097 Bq/L for using 30 liters of the spiked samples and 0.5 liter of the PT samples respectively.

The performance evaluation of the spiked and PT samples can be seen from Table III.

All results passed accuracy, precision and trueness criteria which were assigned "accepted" status. However, it should be noted that all samples had similar relative bias in a range of 15%. These positive biases represented overestimated results, which were opposite to the assumption to have some loss during chemical separation steps. These possibly could be explained by an error from recovery yield determination. As the recovery yield was determined from the metal titration using Titriplex III (Na_2-EDTA. $2H_2O$). The end point which solution colour would change from red to orange, was not perfectly observed. However, the relative biases were still within the MARB which obtained the "Accepted" status. The method could be improved for the recovery yield determination step. Mass spectroscopy such as AAS and ICP, would be a better choice to determine accurate yttrium recovery yield but perhaps the cost for analysis is expensive.

TABLE II
RESULTS OF ^{90}SR ANALYSIS

Sample	Volume (L)	Individual						Mean	
		Act (Bq/L)	%Y	Act (Bq/L)	%Y	Act (Bq/L)	%Y	Act (Bq/L)	%Y
PT 2015	0.5	0.1165±0.0086	86.49	0.1209±0.0089	86.49	0.1025±0.0077	89.19	0.1133±0.0084	87.39
SP 0.01	30	0.0085±0.0005	64.91	0.0119±0.0007	66.67	0.0104±0.0006	66.67	0.0103±0.0006	66.08
SP 0.1	30	0.1077±0.0050	66.09	0.1126±0.0052	59.13	0.1055±0.0049	66.09	0.1086±0.0051	63.77
SP 1	30	1.1030±0.0469	64.10	1.0981±0.0467	64.10	1.0623±0.0452	69.23	1.0878±0.0463	65.81

TABLE III
PERFORMANCE EVALUATION OF THE SAMPLES

Sample	PT 2015	SP 0.01	SP 0.1	SP 1
Target value	0.1009	0.0099	0.0993	0.9913
Target unc	0.0007	0.0003	0.0031	0.0306
MARB	25	25	25	25
Mea value	0.1133	0.0103	0.1086	1.0878
Mea unc	0.0084	0.0006	0.0051	0.0463
Rel bias	12.28	3.41	9.38	9.74
Accuracy	P	P	P	P
P	7.47	6.66	5.58	5.25
Precision	P	P	P	P
Valuemeasured x 2.58P / Valuetaget	21.63	17.76	15.75	14.87
Tureness	P	P	P	P
Final score	P	P	P	P

For spiked sample results, the performance of three concentration levels was proved to be successful using this analytical method which can be confirmed to determine activity concentration at low level in a range of 0.01 – 1 Bq/L in 30-liter seawater.

In aspect of volume differences, comparing between results of PT and spiked samples at low concentration of about 0.1 Bq/L, such a small volume of 0.5-liter PT sample could be used to determine ^{90}Sr as accurate as the higher volume of 30-liter spiked sample. This means that, at concentration of 0.1 Bq/L, volume of seawater between 0.5 and 30 liters can be used to determine ^{90}Sr with this method.

It is important to note that the yttrium samples were fairly purified as can be seen from yttrium activity decay with time in Fig. 3.

The activity can be calculated according to (5) and (6).

$$A = A_0 e^{-\lambda t} \qquad (5)$$
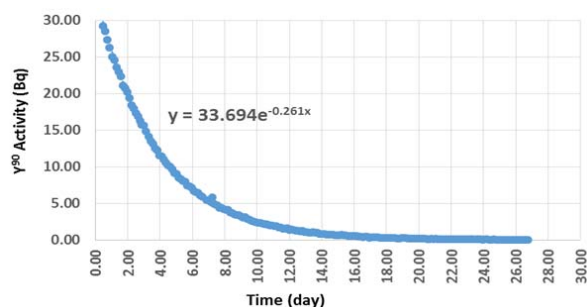
$$\lambda = \frac{ln2}{t_{\frac{1}{2}}} \qquad (6)$$

Fig. 3 ^{90}Y activity vs. time after separation of 1 Bq/L spiked sample (≈30 Bq/sample)

When yttrium half-life is 64 h, decay constant (λ) is theoretically equal to 0.260. The measured decay constant of the sample can be determined from the activity decay curve, i.e. 0.261 which is very closed to the theoretical one. This can be confirmed that the radioanalytical method was effective to perform yttrium separation in seawater samples.

IV. CONCLUSION

The determination of low level ^{90}Sr concentration in 0.5-liter IAEA-RML-2015-01 proficiency test sample, i.e. 0.1 Bq/L and 30-liter spiked seawater samples, i.e. 0.01, 0.1 and 1 Bq/L using the liquid extraction technique, 10% HDEHP and Cherenkov counting measurement was proved to be successful with a short source preparation of a few hours. All results passed accuracy, precision and trueness criteria and obtained "Accepted" status with relative bias in range from 3.41% to 12.28%, below accepted relative bias of ± 25%. This confirmed that ^{90}Sr determination in seawater especially with small volume of 0.5 L can be used to analyse low concentration of 0.1 Bg/L in seawater with such cases of radiological incident. Also, this method can be applied for radiation monitoring when the activity is very low, down to 0.01 Bq/L using 30 L of seawater. However, the analysis results can be improved in accuracy by determining a higher accurate recovery yield from mass spectroscopy techniques such as AAS and ICP, but the cost of the analysis would increase.

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