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Verification of Sr-90 Determination in Water and Spruce Needles Samples Using IAEA-TEL-2016-04 ALMERA Proficiency Test Samples

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***Abstract*—**Determination of ^{90}Sr in environmental samples has been widely developed with several radioanlytical methods and radiation measurement techniques since ^{90}Sr is one of the most hazardous radionuclides produced from nuclear reactors. Liquid extraction technique using di-(2-ethylhexyl) phosphoric acid (HDEHP) to separate and purify ^{90}Y and Cherenkov counting using liquid scintillation counter to determine ^{90}Y in secular equilibrium to ^{90}Sr was developed and performed at our institute, the Office of Atoms for Peace. The approach is inexpensive, non-laborious, and fast to analyse ^{90}Sr in environmental samples. To validate our analytical performance for the accurate and precise criteria, determination of ^{90}Sr using the IAEA-TEL-2016-04 ALMERA proficiency test samples were performed for statistical evaluation. The experiment used two spiked tap water samples and one naturally contaminated spruce needles sample from Austria collected shortly after the Chernobyl accident. Results showed that all three analyses were successfully passed in terms of both accuracy and precision criteria, obtaining "Accepted" statuses. The two water samples obtained the measured results of 15.54 Bq/kg and 19.76 Bq/kg, which had relative bias 5.68% and -3.63% for the Maximum Acceptable Relative Bias (MARB) 15% and 20%, respectively. And the spruce needles sample obtained the measured results of 21.04 Bq/kg, which had relative bias 23.78% for the MARB 30%. These results confirm our analytical performance of ^{90}Sr determination in water and spruce needles samples using the same developed method.

***Keywords*—**ALMERA proficiency test, Cherenkov counting, determination of ^{90}Sr, environmental samples.

I. INTRODUCTION

SR-90 is one of the most hazardous radionuclides due to its long physical half-life (E_{max} = 0.546 MeV, $T_{1/2}$ = 28.79 years) [1] and biological half-life (18 years), accumulation in bone tissue and its highly energetic decay product ^{90}Y (E_{max} = 2.280 MeV, $T_{1/2}$ = 64 h) [1] causing damage to bone marrow. It is present in the environment on global and local scales from intentional and unintentional releases from nuclear facilities, nuclear weapons testing and nuclear accidents. It is therefore one of the important isotopes to be monitored in environment in order to estimate the dose impact to humans. To determine ^{90}Sr in environmental samples and foodstuffs, radiochemical analysis has to be applied to purify samples before beta radiation measurement. In past decades, a great number of radiochemical analyses have been developed and applied for determination of ^{90}Sr in environmental samples as well as radiation measurement methods depending upon physical and chemical property of prepared sources [2]. For chemical separation, there are various radioanalytical methods to separate and purify ^{90}Sr and/or ^{90}Y such as selective precipitation, liquid-liquid extraction, extraction chromatography and ion exchange chromatography. In the measurement methods for beta counting, prepared beta sources could depend upon physical and chemical properties such as solid precipitate or liquid solution and their analyte/ isotopes, i.e. ^{90}Sr, ^{90}Y, or ^{90}Sr/^{90}Y. For example, ^{90}Sr radioactivity can be measured in solid form by gross beta counting using gas proportional counter and in liquid form (mixed with scintillator) using liquid scintillation analyser. For determining ^{90}Y activity in secular equilibrium to ^{90}Sr options such as the gross beta counting in solid form and advanced Cherenkov counting in a solution without a scintillator, using liquid scintillation counter (LSC) could be applied. Recently Cherenkov counting has a lot of interest to determine ^{90}Sr in environmental samples [3]. Not like gross beta counting with gas proportional counters, Cherenkov counting with LSC can discriminate beta energy therefore avoiding over counting other beta particles in samples. Moreover, the Cherenkov samples only produce acidic solution and therefore are cheap and easy for source preparation and waste treatment.

To determine ^{90}Sr via ^{90}Y daughter in environmental samples, the liquid-liquid extraction using HDEHP to prepare ^{90}Y liquid source and Cherenkov counting using LSC has been developed and applied at our institute, the Office of Atoms for Peace (OAP) [3]. However, the analytical methods needed to be verified for the accurate and precise criteria where recently the IAEA-TEL-2016-04 ALMERA proficiency test samples were used to determine the performance for statistic evaluation.

II. EXPERIMENTAL

A. PT Sample Description

Three proficiency test (PT) samples were obtained from the IAEA. The details are described below:

- Sample 01: 500 g spiked water containing ^{134}Cs, ^{137}Cs, ^{22}Na, and ^{90}Sr in a 500 mL high-density polyethylene bottle
- Sample 02: 500 g spiked water consisting of ^{241}Am, ^{90}Sr, and ^{89}Sr in a 500 mL high-density polyethylene bottle
- Sample 04: 120 g natural contaminated spruce needles

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sample from Austria collected shortly after the Chernobyl accident containing ^{137}Cs, ^{90}Sr, and ^{40}K in a 200 mL high-density polyethylene bottle

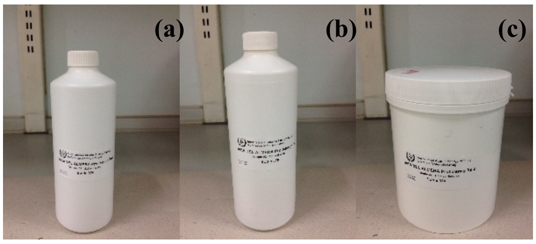

Fig. 1 The PT samples (a) Sample 01: spiked water, (b) Sample 02: spiked water, and (c) Sample 04: natural contaminated spruce needles

B. Reagent and Radioactivity Standards

HDEHP, HNO_3, HCl, NH_4OH, citric acid, 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 used to prepare calibration source was obtained from Eckert and Ziegler Isotope Product.

C. Sample Preparation and Determination of ^{90}Sr in Secular Equilibrium to ^{90}Y

The method for radiochemical analysis of strontium in environmental samples was developed from Suomela et al. [4]. For each PT sample, three 50-gram aliquots were prepared.

1. Analysis of Sample 01 and 02

The aliquots were evaporated until dry and then ashed at 610 ºC for 15h. The ashed samples were dissolved with 50 ml of 1 M HCl and boiled for 30 min. The samples were filtrated to remove undissolved residual. The filtrated samples were added with citric acid and adjusted to pH 1 with 6 M NH_4OH before yttrium separation by liquid extraction technique. First, the yttrium in the solution samples was extracted with 50 ml of 10% HDEHP in toluene. The organic phases were washed with 50 ml of 0.08 M HCl. Finally, yttrium was back extracted by 50 ml 3 M HNO_3. The yttrium solutions were precipitated in form of yttrium hydroxide by adding NH_4OH until a pH 9-10 was achieved. The yttrium hydroxide precipitates were separated by centrifuging then dissolved with 1 ml of conc. HNO_3. The concentrated yttrium solution samples were transferred into 20 ml polyethylene vials and diluted to 15 ml with DI water for Cherenkov counting using LSC. After Cherenkov counting, yttrium recovery yields were determined by titrating the solutions with Titriplex III. The solutions were diluted to 20 ml with DI water in Erlenmeyer flasks. 1.5 g of sodium acetate and 100 mg of xylenolorange in KNO_3 were added to the samples. Before titrating the samples were adjusted pH 5-6 with 6M NaOH then titrated with Titriplex III until solution colour was changed from red to orange.

2. Analysis of Sample 04

The same radioanalytical method as those of sample 01 and 02 was applied, but only skipping the first step for evaporation.

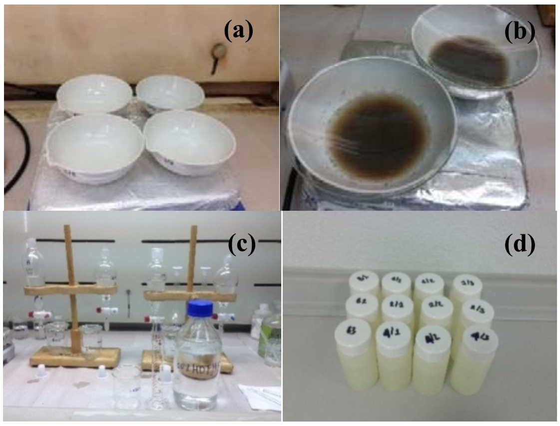

Fig. 2 Analysis of ^{90}Sr determination (a) The aliquots of sample 01 and 02, (b) The aliquots of sample 04, (c) Liquid extraction using 10% HDEHP in toluene, and (d) The concentrated yttrium samples in 20 mL polyethylene vials for Cherenkov counting

D. Calibration Source Preparation

The reference solution which contained 1.649 ± 0.051 Bq of equilibrium ^{90}Sr/^{90}Y in 15 ml of HNO_3 solution, was transferred into 20 ml polyethylene vials for Cherenkov counting using LSC.

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

LSC was made from PerkinElmer, Tri-Carb 3180 TR/SL. QuantaSmart software was used for the Cherenkov counting. The calibration source was counted for 30 min in energy range from 0 to 50 keV in order to determine Cherenkov counting efficiency from ^{90}Y. Please note that ^{90}Sr has only about 1% Cherenkov counting efficiency, and ^{90}Y has 60% efficiency in Cherenkov counting [5]. Therefore, Cherenkov counting from ^{90}Sr could be negligible which means the calibration source, i.e. ^{90}Sr/^{90}Y solution could be directly used to determine Cherenkov counting efficiency from ^{90}Y Cherenkov counting. The samples were then counted at the same condition as those of the calibration source.

F. Data Evaluation of PT

Results were analyzed according to IAEA criteria using different statistical evaluation such as relative bias and precision [6]-[7] as follow:

The relative bias (RB) was the first step in producing a score for a result $Value_{Measured}$. RB was calculated as a percentage according to (1):

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

where $Value_{target}$ and its associated uncertainty, unc_{target}, were the values provided by the IAEA.

If the relative bias is equal to or less than the Maximum Accepted Relative Bias (MARB) value, the result is considered "Accepted" for accuracy. The MARBs were determined from each measurer and level of the radioactivity and the complexity of radioanalytical methods was considered.

The precision, P (expressed as a percentage), was related to the combined uncertainty as described in (2):

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

Based on good laboratory practice principles, the expanded relative combined uncertainty is expected to cover the relative bias:

$$Relative\ bias \leq k \times P \qquad (3)$$

with k as the coverage factor, which is equal to 2.56 at the 95% confidential level. If both P ≤ MARB and the relative bias ≤ k×P, the result is considered “Accepted” for precision. If one of these conditions is not met, the result is assigned “Not accepted” for precision.

The resulting final score can be summarized according to the detailed evaluation as follow:

- “Accepted (A)” when both accuracy and precision are “Accepted”.
- “Not Accepted (N)” when the accuracy is “Not accepted”.
- “Warning (W)” when accuracy is “Accepted”, but precision is “Not accepted”.

III. RESULTS AND DISCUSSION

The analysis results of the three samples and the performance evaluation can be seen from Tables I and II.

TABLE I
RESULTS OF ^{90}SR ANALYSIS

Sample	Individual activity concentration (Bq/kg) 1	2	3	Mean activity concentration (Bq/kg)
01	17.23±1.26	16.10 ±1.21	13.28 ±1.05	15.54 ±1.18
02	20.62 ±1.05	20.06±1.02	18.59 ±0.95	19.76 ±1.01
04	20.84±1.18	22.98 ±1.25	19.31±1.06	21.04 ± 1.16

TABLE II
PERFORMANCE EVALUATION

Sample	01	02	04
Target value	14.7	20.5	17.0
Target unc	0.5	0.5	2.0
MARB	15	20	30
Mea value	15.54	19.76	21.04
Mea unc	1.18	1.01	1.16
Rel bias	5.68	-3.62	23.78
Accuracy	P	P	P
P	8.29	5.65	13.00
Precision	P	P	P
Final score	P	P	P

The three individual analyses of each sample looked close together. Also, the evaluation showed the three results which passed both accuracy and precision criteria and they were assigned to “accepted” status. However, it should be noted that the two water samples had a significantly low relative bias, i.e. 5.68 and -3.62 for sample 01 and 02, respectively, when compared with the sample 04 i.e. 23.78. Sample 04 was spruce needles which had complex matrix. Surprisingly, the radioactivity analysis gave the overestimated result, highly positive bias which was the opposite to the assumption to have some losses due to imperfect reaction from interference. The overestimated result was possibly due to an inaccurate recovery yield determination as the recovery yield was determined from the metal titration using the Titriplex III (Na_2-EDTA. $2H_2O$). The end point, where solution colour would change from red to orange, was not clearly observed. This caused over titration, and then the overestimated result. However, the relative bias was still within the MARB which obtained the “Accepted” status. Not like spruce needles sample, to determine yttrium recovery yield for the water samples by the titration was fairly accurate with sharp end point due to less interference.

The determination of ^{90}Sr using liquid extraction technique, 10% HDEHP in toluene, could conclude that the yttrium separation step was successful. However, the method could be improved with the titration step to determine yttrium recovery yield. Possibly reduction of sample amounts would potentially decrease interference, thereby obtaining a clearer end point, but it will increase the minimum detectable activity concentration (MDC). Alternatively, mass spectroscopy, such as AAS and ICP, would be a choice to determine accurate yttrium recovery yield. However, the cost for analysis is expensive. The determination of ^{90}Sr in highly organic matter contained samples would have to balance between detection limit, accuracy, and cost of analysis.

IV. CONCLUSION

The determination of ^{90}Sr in the IAEA-TEL-2016-04 ALMERA PT samples, i.e. the two water samples and one spruce needles sample using liquid extraction technique and Cherenkov counting measurement, was proved to be successful which passed both accuracy and precision criteria and obtained “Accepted” status. The two water samples had relative bias 5.68% and -3.63% for the MARB 15% and 20%. However, the spruce needles had significantly higher relative bias, i.e. 23.78% for the MARB 30% due to inaccurate yttrium recovery yield determination by metal titration using triplex III. The over titration was due to non-sharp end point caused by highly organic matter contained in the samples. In such cases, the reduction of sample amount would obtain clearer end point and therefore improve accuracy of result but will obtain a higher MDC. Alternatively, accurate yield recovery could commonly be determined by a mass spectroscopy technique such as AAS and ICP with a high cost of analysis.

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