

# Verification of Sr-90 determination using ALMERA proficiency test samples

S. Visetpotjanakit, and N. Nakkaew

Radiation Monitoring Group, Bureau of Technical Support for Safety Regulation, Office of Atoms for Peace, Thailand

## 1. Introduction

Determination of <sup>90</sup>Sr in environmental samples has been widely developed with several radioanalytical methods and radiation measurement techniques since <sup>90</sup>Sr is one of the most hazardous radionuclides produced from nuclear reactors. Liquid extraction technique using bis-2-ethylhexyl-phosphoric acid to separate and purify <sup>90</sup>Y and Cherenkov counting using liquid scintillation counter to determine <sup>90</sup>Y in secular equilibrium to <sup>90</sup>Sr were developed and performed at our institute, the Office of Atoms for Peace. The approach is inexpensive, non-laborious and fast to analyse <sup>90</sup>Sr in environmental samples. To validate our analytical performance for the accurate and precise criteria, determination of <sup>90</sup>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 found all three analysis were successfully passed both in terms of accuracy and precision criteria obtaining "Accepted" statuses. These results could confirm our analytical performance of <sup>90</sup>Sr determination in water and spruce needles samples using the same developed method.

## 2. Experimental

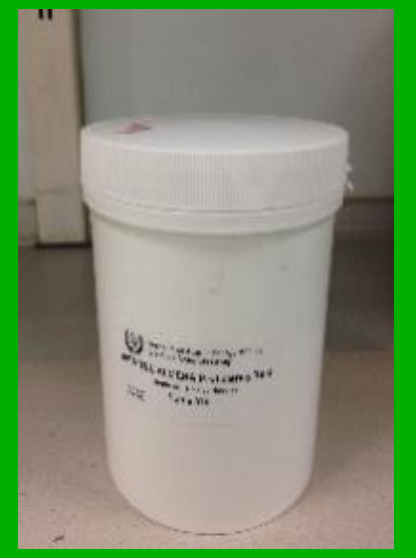
### 2.1 ALMERA Proficiency test samples



Sample 01  
spiked water



Sample 02  
spiked water



Sample 04  
natural contaminated  
spruce needles

### 2.2 Radiochemical method

#### Analysis of sample 01 and 02 :

- The 50 gram aliquots were evaporated until dry and then ashed at 610°C for 15 hr.
- The ashed samples were dissolved with 50 ml of 1 M HCl and boiled for 30 min and then filtrated to remove undissolved residual.
- The filtrated samples were added with citric acid and adjusted to pH 1 with 6 M NH<sub>4</sub>OH .
- 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.
- Yttrium in the organic phases was back extracted by 50 ml 3 M HNO<sub>3</sub>.
- The yttrium solutions were precipitated in form of yttrium hydroxide by adding NH<sub>4</sub>OH until a pH 9-10 was achieved.
- The yttrium hydroxide precipitates were dissolved with 1 ml of conc. HNO<sub>3</sub> and then were transferred into 20 mL polyethylene vials and diluted to 15 ml with DI water for Cherenkov counting using LSC.

#### 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.



Aliquots of  
sample 01 and 02



Aliquots of  
sample 04



Liquid extraction  
using 10% HDEHP  
in toluene



The samples in vials for  
Cherenkov counting

### 2.3 Determination of chemical recovery yield

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<sub>3</sub> were added to the samples.
- The samples were adjusted pH 5-6 with 6 M NaOH then titrated with Titriplex III until solution colour was changed from red to orange.

### 2.4 Calibration source preparation

The reference solution which was contained 1.649 ± 0.051 Bq of equilibrium <sup>90</sup>Sr/<sup>90</sup>Y in 15 ml of HNO<sub>3</sub> solution, was transferred into 20 mL polyethylene vials for Cherenkov counting using LSC.

### 2.5 Measurement of Y-90, counting instrument and software

Liquid scintillation counter 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 <sup>90</sup>Y. Please note that <sup>90</sup>Sr has only about 1% Cherenkov counting efficiency and <sup>90</sup>Y has 60% efficiency in Cherenkov counting. Therefore Cherenkov counting from <sup>90</sup>Sr could be negligible which means the calibration source i.e. <sup>90</sup>Sr/<sup>90</sup>Y solution could be directly used to determine Cherenkov counting efficiency from <sup>90</sup>Y Cherenkov counting. The samples were then counted at the same condition as those of the calibration source.

## 3. Result

### 2.1 ALMERA Proficiency test samples

Table 1. Results of <sup>90</sup>Sr analysis

Sample	Individual activity concentration (Bq/kg)			Mean activity concentration (Bq/kg)
	01	02	03	
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 2. Results of <sup>90</sup>Sr analysis

Sample	Target value	Target unc	MARB	Mean value	Mean unc	Rel bias	Accuracy	P	Precision	Final score
01	14.7	0.5	15	15.54	1.18	5.68	P	8.29	P	P
02	20.5	0.5	20	19.76	1.01	-3.62	P	5.65	P	P
03	17.0	2.0	30	21.04	1.16	23.78	P	13.00	P	P

#### Data Evaluation of Proficiency Test Precision

Results were analysed according to IAEA criteria using different statistical evaluation i.e. relative bias and precision .

#### Accuracy

$$\text{Relative bias} = \frac{\text{Value}_{\text{Measured}} - \text{Value}_{\text{target}}}{\text{Value}_{\text{target}}} \times 100$$

If the absolute value of relative bias ≤ the Maximum Accepted Relative Bias (MARB) value, the result is considered "Accepted" for accuracy.

#### Precision

$$P = \sqrt{\left(\frac{\text{unc}_{\text{target}}}{\text{Value}_{\text{target}}}\right)^2 + \left(\frac{\text{unc}_{\text{Measured}}}{\text{Value}_{\text{Measured}}}\right)^2} \times 100$$

If both P ≤ MARB and the relative bias ≤ k × P (k is coverage factor i.e. 2.56), the result is considered "Accepted" for precision. If one of these conditions is not met the result is assigned "Not accepted" for precision.

#### Summarised Final Score

"Accepted (A)" Both accuracy and precision are "Accepted".  
 "Not Accepted (N)" The accuracy is "Not accepted".  
 "Warning (W)" Accuracy is "Accepted", but precision is "Not accepted".

The evaluation showed the three results passed both accuracy and precision criteria and were assigned "accepted" status.

However, the two water samples had a significantly low relative bias i.e. 5.68% and -3.62% for sample 01 and 02 respectively when compare 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 loss due to imperfect chemical separation in the present of highly contained interference. The overestimated result was possibly due to an inaccurate recovery yield determination. As the recovery yield was determined from the metal titration using Titriplex III (Na<sub>2</sub>-EDTA. 2H<sub>2</sub>O). The end point which solution colour would change from red to orange, was not clearly observed. This resulted in over titration then the overestimate result. However the relative bias was still within the MARB which obtained the "Accepted" status. Not like the 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.

## 4. Conclusion

- The developed method for determination of <sup>90</sup>Sr in the IAEA-TEL-2016-04 ALMERA proficiency test samples composing of 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 i.e. sample 01 having 5.68% bias for 15% MARB, sample 02 having -3.63% bias for 20% MARB and sample 04 having 23.78% bias for 30% MARB.
- Sample 04 had significantly higher relative bias than those of sample 01 and 02 due to over chemical recovery yield from the metal titration affected by complexes matrix of highly organic matter in the sample.
- In case of the determination of highly organic matter contained samples, the more accurate results could be obtained by determination of chemical recovery yield using a mass spectroscopy technique such as AAS and ICP but analysis cost will be expensive.