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Participation in IAEA Proficiency Test to Analyse Cobalt, Strontium and Caesium in Seawater Using Direct Counting and Radiochemical Techniques

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***Abstract*—**Radiation monitoring in the environment and foodstuffs is one of the main responsibilities of Office of Atoms for Peace (OAP) as the nuclear regulatory body of Thailand. The main goal of the OAP is to assure the safety of the Thai people and environment from any radiological incidents. Various radioanalytical methods have been developed to monitor radiation and radionuclides in the environmental and foodstuff samples. To validate our analytical performance, several proficiency test exercises from the International Atomic Energy Agency (IAEA) have been performed. Here, the results of a proficiency test exercise referred to as the Proficiency Test for Tritium, Cobalt, Strontium and Caesium Isotopes in Seawater 2017 (IAEA-RML-2017-01) are presented. All radionuclides excepting ^{3}H were analysed using various radioanalytical methods, i.e. direct gamma-ray counting for determining ^{60}Co, ^{134}Cs and ^{137}Cs and developed radiochemical techniques for analysing ^{134}Cs, ^{137}Cs using AMP pre-concentration technique and 90Sr using di-(2-ethylhexyl) phosphoric acid (HDEHP) liquid extraction technique. The analysis results were submitted to IAEA. All results passed IAEA criteria, i.e. accuracy, precision and trueness and obtained 'Accepted' statuses. These confirm the data quality from the OAP environmental radiation laboratory to monitor radiation in the environment.

***Keywords*—**International atomic energy agency, proficiency test, radiation monitoring, seawater.

I. Introduction

RADIATION monitoring with reliable data and good data quality is critical to determine radiation and radionuclides in the environment for the assessment of the radiological impact and the risk to the public and environment. Especially, during a nuclear emergency situation, it is important to accurately determine radiation contamination data for a proper determination of the risk assessment on the public and environment to protect the Thai population. The need for this was highlighted following the nuclear power plant accident which happened in Japan, Fukushima on March 2011, where radionuclides were released into the environment, i.e. the atmosphere, seawater, river and land [1]. The data and ability of OAP to accurately determine radioactive concentrations in environmental samples are not only important for the Thai people but also contribute towards international efforts to monitor the environment. The IAEA is an inter phase organisation who is greatly concerned about radioactive data quality. It has therefore regularly conducted interlaboratory comparisons and proficiency tests on radionuclides in various samples. Since the Fukushima accident, it organised a new proficiency test (PT) in the frame of the IAEA Technical Cooperation project RAS/7/021 "Marine benchmark study on the possible impact of the Fukushima radioactive releases in the Asia-Pacific Region for Caesium Determination in Sea Water". Since then, the PT has been conducted annually.

The OAP has a radiation monitoring laboratory to carry out a radiation surveillance program in Thailand. All data would be used to establishment a radiation baseline information and assessment of the radiological impact on the environment in the case of any incidents. These tests allow the OAP to validate the data quality of our procedures and to ensure an accurate estimation for any nuclear and radiation circumstances. We have participated in a number of PT exercises organized by the IAEA. Lastly, the OAP was one of 74 laboratories from countries from the Asia-Pacific Region who participated in the new exercise which was referred to as the Proficiency Test for Tritium, Cobalt, Strontium and Caesium Isotopes in Seawater 2017 (IAEA-RML-2017-01). The results presented here were for the OAP developed methodologies applied for the radionuclide analysis of ^{60}Co, ^{134}Cs, ^{137}Cs and ^{90}Sr. All participant results were published in the IAEA proficiency test report [2].

II. Experimental

A. PT Sample Description

The proficiency test sample was 5-L of seawater containing ^{3}H, ^{60}Co, ^{134}Cs, ^{137}Cs, and ^{90}Sr which was received from the IAEA. The sample was of unknown activity and was used as test case for the determination of its ^{60}Co, ^{134}Cs, ^{137}Cs and ^{90}Sr activities. The analysis results were submitted to the IAEA to evaluate accuracy and quality control. The PT sample is shown in Fig. 1.



Fig. 1 5-L proficiency test samples contained in plastic bottle

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B. ^{60}Co Determination Method

Co-60 was determined by direct gamma-ray counting without further chemical treatment.

1. Calibration Source

With mix radionuclide standard in 1-L cylinder shape bottle, Eckert and Ziegler Isotope Product No.1954-6-2, contained multinuclides covering energy range from 59.5409 keV to 1836.0520 keV were used for efficiency calibration for direct gamma-ray counting techniques.

2. Sample Preparation and Analysis

1-L aliquots were transferred to a 1-L bottle as the same geometry type as the calibration source.

3. Counting Equipment and Measurement Method

The gamma-ray spectrometry system, HPGe (Li) detector (CANBERRA) with MAESTRO software was used. The calibration source was used to calibrate counting efficiency. The sample in the calibrated container was measured with the same gamma-ray spectrometry system for 80000 s.

C. ^{134}Cs and ^{137}Cs Determination Methods

Cs-143 and ^{137}Cs were determined by two methods, i.e. direct gamma-ray counting technique without further chemical treatment and AMP pre-concentration technique.

1. Chemicals and Calibration Sources

Ammonium phosphomolybdate (AMP), CsCl, HNO_3 and NaOH used were analytical grade. Mix radionuclides obtained from the National Physical Laboratory (NPL), NPL no. X09083 in 2 mm thick coin shape compressed filter paper, was used as calibration source for prepared samples from AMP pre-concentration technique. The mix radionuclide standard in 1-L bottle, Eckert and Ziegler Isotope Product No.1954-6-2, was used for efficiency calibration for the sample from direct gamma-ray counting technique.

2. Sample Preparation and Analysis

For the direct counting technique, the same sample as those of ^{60}Co determination was used to measure ^{134}Cs and ^{137}Cs.

In terms of the AMP pre-concentration technique, the method for radiochemical analysis of caesium in seawater was developed from Hirose's technique [3], [4]. A 500-gram aliquot was transferred into a beaker. The sample was acidified with 14 M HNO_3 to pH 1.6. Then 0.26 g of CsCl (caesium carrier) and 4 g of AMP were added to the sample. The mixture was stirred for one hour and left overnight to allow the precipitate to settle. The precipitate sample was filtered using 5B filter paper. The precipitate sample was dried under IR lamp. The pictures of caesium determination method with AMP pre-concentration technique are shown in Fig. 2.

3. Counting Equipment and Measurement Method

The gamma-ray spectrometry system, HPGe (Li) detector (CANBERRA) with MAESTRO software, was used.

For direct counting technique, the same measurement method as those of ^{60}Co determination was applied.

In terms of AMP pre-concentration technique, The NPL no. X09083 calibration source was used for calibrating counting efficiency. The sample source was measured with the same gamma-ray spectrometry system for 80000 s.

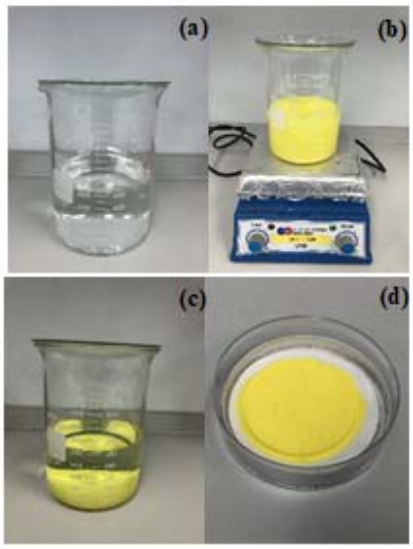


Fig. 2 Analysis of ^{134}Cs and ^{137}Cs with AMP pre-concentration technique (a) The 500 ml aliquot, (b) The AMP precipitation (c) The precipitate after settling down and (d) The caesium-AMP precipitate samples for direct gamma-ray counting using gamma-ray spectrometer

D. ^{90}Sr Determination Method

Sr-90 analysis was developed from [5]-[8]. Liquid extraction technique using HDEHP to separate and purify yttrium and Cherenkov counting to determine ^{90}Y in secular equilibrium with ^{90}Sr was applied.

1. Chemicals and ^{90}Sr Reference Solution

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 secular equilibrium ^{90}Sr/^{90}Y reference solution used to prepare calibration source was purchased from Eckert and Ziegler Isotope Product.

2. Sample Preparation and Analysis

The three 0.5-L aliquots were acidified to pH 1-1.5 with conc. HCl was then added to 10 mg of yttrium carrier. Yttrium in the solutions was extracted with 50 ml of 10% HDEHP in toluene. The toluene phases were washed twice with 50 ml of 0.08 M HCl. In yttrium separation step, yttrium was extracted by 50 ml of 3 M HNO_3. Yttrium was purified by hydroxide precipitation where the solutions were added with NH_4OH until pH 9-10. The precipitates were separated by centrifuging and dissolved with 1 ml of conc. HNO_3. The purified samples were transferred into 20 mL polyethylene LSC vials and then diluted with DI water to a 15 ml volume for the Cherenkov counting using LSC. After the Cherenkov measurement, chemical recovery yields were determined by titrating the solutions with Titriplex III. The solutions were added to 1.5 g of sodium acetate pulsed 100 mg of xylenolorange mixed with

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KNO_3 and then diluted with DI water to a 50 ml volume. Before the titration, the samples were adjusted to pH 5-6 with 6 M NaOH and then titrated with Titriplex III until the solution colour was changed from red to orange.

3. Calibration Source Preparation

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

4. Counting Equipment and Measurement Method

A liquid scintillation counter was made from the PerkinElmer model Tri-Carb 3180 TR/SL. QuantaSmart software was used for the Cherenkov counting. The 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}Sr and ^{90}Y have very different Cherenkov counting efficiencies i.e. about 1%, and 60% efficiencies for ^{90}Sr and ^{90}Y respectively [9]. Cherenkov counting from ^{90}Sr therefore could be negligible which means that the prepared ^{90}Sr/^{90}Y calibration source could be directly used to determine Cherenkov counting efficiency from ^{90}Y Cherenkov counting. The samples were then counted at the same condition and using the system as those of the calibration source. The pictures of ^{90}Sr determination method are shown in Fig. 3.

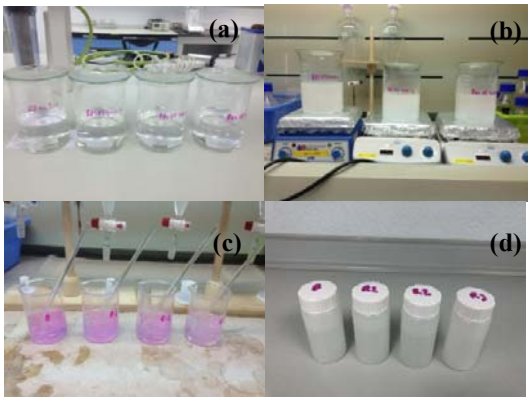


Fig. 3 Analysis of ^{90}Sr (a) The 500 ml aliquots and blank sample (DI water) (b) Liquid extraction using 10% HDEHP in toluene (c) Yttrium hydroxide precipitation and (d) The concentrated yttrium samples in 20 mL polyethylene vials for Cherenkov counting

E. Data Evaluation of Proficiency Test

Results were analysed according to IAEA criteria using different statistical evaluation such as accuracy, precision and trueness [10], [11] as follows:

The Accuracy, was determined from **relative bias (RB)** which $Value_{Measured}$ was compared with $Value_{Taget}$ as a percentage according to (1).

$$RB = \frac{Value_{Measured} - Value_{Target}}{Value_{Target}} \times 100 \quad (1)$$

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

If the relative bias was equal to or less than the Maximum Accepted Relative Bias (MARB) value, the result was considered "Accepted" for accuracy. The MARB in relation to the level of the radioactivity and the complexity of radioanalytical methods used for the evaluation can be seen from Table I.

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

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

The precision was compared to the Limit of Accepted Precision (LAP) which is shown in Table I. The result was scored as "Pass" when:

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

The trueness, T, was scored as "Pass" when:

$$|RB| \leq \frac{Value_{Measured}}{Value_{Target}} 2.58\, P \quad (4)$$

The resulting final score can be summarised according to the detailed evaluation as follows:

- "Accepted (A)" when accuracy, precision and trueness were "Passed".
- "Not Accepted (N)" when the accuracy was "Failed".
- "Warning (W)" when accuracy was "Passed", but either precision or trueness was "Failed".

TABLE I
MARB AND LAP FOR EACH ANALYTE

Nuclide	MARB	LAP
^{60}Co	20	20
^{134}Cs	20	20
^{137}Cs	20	20
^{90}Sr	25	25

III. Results and Discussion

The analysis results of ^{60}Co, ^{134}Cs, ^{137}Cs and ^{90}Sr are shown in Tables II and III.

TABLE II
RESULTS OF ^{60}CO, ^{134}CS AND ^{137}CS ANALYSIS

Nuclide	Activity concentration (Bq/kg)	
	Direct gamma counting technique	Radiochemical technique
^{60}Co	0.150 ± 0.013	-
^{134}Cs	0.168 ± 0.013	0.173 ± 0.014
^{137}Cs	0.278 ± 0.016	0.298 ± 0.017

Since the ^{134}Cs and ^{137}Cs determination had two methods, i.e. direct gamma counting technique and radiochemical technique, the results from the two techniques had quite similar values. The direct counting technique gave slightly lower values than those of the radiochemical one. In terms of ^{90}Sr analysis, the three repeated results had quite similar values which should indicate good precision. However, performance evaluation can be analysed according to the data

evaluation criteria as seen from Table IV.

TABLE III
RESULTS OF ^{90}SR ANALYSIS

Nuclide	Individual activity concentration (Bq/kg)			Mean activity concentration (Bq/kg)
	1	2	3	
^{90}Sr	0.310 ± 0.018	0.256 ± 0.015	0.261 ± 0.016	0.276 ± 0.016

TABLE IV
PERFORMANCE EVALUATION

Nuclide	^{60}Co	^{134}Cs[a]	^{137}Cs[a]	^{134}Cs[b]	^{137}Cs[b]	^{90}Sr
Target value	0.1613	0.1946	0.3082	0.1946	0.3082	0.2754
Target unc	0.0006	0.0008	0.0019	0.0008	0.0019	0.0019
MARB	20	20	20	20	20	25
Mea value	0.150	0.168	0.278	0.173	0.298	0.276
Mea unc	0.013	0.013	0.016	0.014	0.017	0.016
Rel bias	–7	-14	-10	-11	-3	0
Accuracy	P	P	P	P	P	P
LAP	20	20	20	20	20	25
Precision	P	P	P	P	P	P
P	8.5	8.2	5.6	7.6	5.6	6.0
$\frac{\text{ValueMeasured2.58 P}}{\text{ValueTarget}}$	20	19	14	17	13	15
Trueness	P	P	P	P	P	P
Final score	P	P	P	P	P	P

[a]results from direct gamma counting technique and [b]results from radiochemical method.

All results passed the three criteria i.e. accuracy, precision and trueness which obtained "Accepted" scores. It could be concluded that the direct gamma counting to determine ^{60}Co, ^{134}Cs and ^{137}Cs, AMP pre-concentration technique to determine ^{134}Cs and ^{137}Cs and liquid extraction technique to determine ^{90}Sr were verified.

In the case of caesium determination, the two techniques gave slightly different values. The direct gamma counting technique seemed to obtain lower values and accuracies than those of radiochemical ones. These may be due to highly different counting efficiencies when using a 1-L cylinder shape bottle (Eckert and Ziegler Isotope Product No.1954-6-2) for direct counting technique and 2 mm thick coin shape compressed filter paper (NPL no. X09083) for AMP pre-concentration technique. For instance, the counting efficiencies of ^{137}Cs at 661.657 keV were 0.00274 and 0.02515 for the 1-L bottle and the filter paper, respectively. It could be assumed that the filter paper calibration source gave potentially better counting efficiency and better accuracy. However, the performance of the two techniques was validated, and we obtained the results within the MARB (±20%).

For ^{90}Sr determination, the liquid extraction technique using HDEHP and Cherenkov counting measurement was proven to be successful to analyse ^{90}Sr. From Table III, the three repeated results had similar activity concentration values which gave mean values of 0.276 ± 0.016 Bq/kg. And this mean value was very accurate, obtaining 0 % RB from MARB of 25%. Possibly the liquid extraction technique to separate and purify ^{90}Y was fairly selective. Also, the Cherenkov counting measurement to determine ^{90}Y was effective due to less interfering from other beta particles.

IV. CONCLUSION

The determination of ^{60}Co, ^{90}Sr and ^{134}Cs and ^{137}Cs in IAEA-RML-2017-01 proficiency test samples, i.e. 5-L seawater was proven to be successful, where all results passed accuracy, precision and trueness criteria and obtained "Accepted" status. To determine ^{60}Co, ^{134}Cs and ^{137}Cs, the direct gamma counting technique used was satisfactory to obtain an "Accepted" score which could be applied for emergency situations when time is limited. Also the AMP pre-concentration technique to analyse ^{134}Cs and ^{137}Cs was greatly effective with slightly higher accuracy due to higher counting efficiency when using small geometry source. In terms of ^{90}Sr analysis via its daughter ^{90}Y, liquid extraction technique to separate and purify ^{90}Y and Cherenkov counting to measure ^{90}Y was greatly successful with 0 % RB. It could be concluded that our methodology to analyse ^{60}Co, ^{134}Cs and ^{137}Cs using direct gamma counting was validated. Moreover, radiochemical techniques such as AMP pre-concentration technique to analyse caesium and liquid extraction technique to determine ^{90}Sr via its daughter ^{90}Y were verified. These results confirm the data quality from the OAP environmental radiation laboratory to monitor radiation in environment.

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