Participation in proficiency test for tritium strontium and caesium isotopes in seawater 2015 (IAEA-RML-2015-02)

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Abstract. A proficiency test (PT) exercise has proposed by the International Atomic Energy Agency (IAEA) 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 2012. In 2015 the exercise was referred to Proficiency Test for Tritium, Strontium and Caesium Isotopes in Seawater 2015 (IAEA-RML-2015-02) to analyse ^{3}H, ^{134}Cs, ^{137}Cs and ^{90}Sr in a seawater sample. OAP was one of the 17 laboratories from 15 countries from Asia-Pacific Region who joined the PT exercise. The aim of our participation was to validate our analytical performance for the accurate determination of radionuclides in seawater by developed methods of radiochemical analysis. OAP submitted results determining the concentration for the three elements i.e. ^{134}Cs, ^{137}Cs and ^{90}Sr in seawater to the IAEA. A critical review was made to check suitability of our methodology and the criteria for the accuracy, precision and trueness of our data. The results of both ^{134}Cs and ^{137}Cs passed all criteria which were assigned "Accepted" statuses. Whereas ^{90}Sr analysis did not pass the accuracy test therefore it was considered as "Not accepted" Our results and all other participant results with critical comments were published in the IAEA proficiency test report.

1. Introduction

Accurate and precise radiation monitoring is critical to determine the radionuclide level in the environment for assessment of the radiological impact and risk to the public and environment. This is especially important during nuclear power plant accidents. For instance the recent nuclear power plant accident happened in Japan, Fukushima on March 2011. It released radionuclides to the environment i.e. to the atmosphere, seawater, river and land. In such cases, nearby countries must monitor the situation by estimating radioactivity levels in the environment and the impact of the contamination on humans, animals and the environment to protect their countries. Moreover it is important to be able to share the radiological impact within regions. Those radiochemical laboratories should have the same standard and capability to determine radionuclides in environment in order to share and compare the radiological impact for comprehensive protection and preparedness. The International Atomic Energy Agency (IAEA) is an inter phase organisation who is deeply concerned about radioactive data quality. It has regularly conducted interlaboratory comparisons and proficiency tests on radionuclides in various samples. Due to the Fukushima accident, it recently organised a new proficiency test 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".

Office of Atoms for Peace (OAP) has a radiochemistry laboratory composed of gamma spectrometer, alpha spectrometer, liquid scintillation counter and gross alpha-beta counting system to carry out our radiation monitoring program by both radiochemical analysis and direct measurement. We also have a remote ambient gamma dose rate and radionuclides stations all around Thailand for establishment of radiation baseline information and assessment of the radiological impact on the environment in the case of any accidents. We however need to approve our radionuclide analysis method to assure data quality to be used as an accurate estimation for any nuclear and radiation circumstances. We have participated in a number of exercises supported by the IAEA. Lastly we were one of 17 laboratories from 15 countries from the Asia-Pacific Region who participated in the new exercise which was referred to Proficiency Test for Tritium, Strontium and Caesium Isotopes in Seawater 2015 (IAEA-RML-2015-02). We used our developed methods for the radionuclide analysis of ^{134}Cs, ^{137}Cs and ^{90}Sr. All participant results were published in the IAEA proficiency test report [1].

2. Experiment

2.1. PT sample description

The five litre proficiency test sample containing ^{134}Cs, ^{137}Cs, ^{90}Sr and ^{3}H was received from IAEA. The picture of PT sample can be seen from figure 1. The sample was of unknown activity and was determined in its ^{134}Cs, ^{137}Cs and ^{90}Sr activities. The results were submitted to the IAEA to evaluate accuracy and quality control.

2.2. ^{134}Cs and ^{137}Cs determination method

2.2.1. Chemicals and reference solution for ^{134}Cs and ^{137}Cs determination using AMP pre-concentration technique. Ammonium phosphomolybdate (AMP), CsCl, HCl and NaOH used were analytical grade. The ^{134}Cs and ^{137}Cs reference solution used to prepare calibration source was obtained from Eckert and Ziegler Isotope Product.

2.2.2. Sample preparation and analysis for ^{134}Cs and ^{137}Cs determination using AMP pre-concentration technique. The method for radiochemical analysis of caesium in seawater was developed from Hirose's technique [2-3]. The three repeated samples were prepared by taking five hundred grams of aliquots into separate beakers. The samples were acidified with HCl to pH 1.6. Then 0.26 g of CsCl (caesium carrier) and 4 g of AMP were added. The mixture was stirred for one hour and left overnight to allow the precipitate to settle. The precipitate samples were centrifuged at 3000 rpm, 5 min and washed with 1 M HCl twice. The precipitate samples were dissolved with 10 M NaOH. The solution was heated at 80°C, 15 min to remove ammonia. The precipitation step was repeated. The second precipitate samples were dissolved with 10 M NaOH. The solution was transferred to calibrated containers (the same shape and type as prepared calibration source i.e. 60 ml polypropylene bottle) and made up the same volume as the calibration source i.e. 20 ml. The pictures of AMP pre-concentration method are shown in figure 2.

2.2.3. Calibration source preparation for ^{134}Cs and ^{137}Cs determination using AMP pre-concentration technique. The reference solution which contained 1.077 ± 0.010 Bq of ^{134}Cs and 1.006 ± 0.005 Bq of ^{137}Cs was spiked into 20 ml of 1 M HCl in the calibrated container (60 ml polypropylene bottle).

2.2.4. Counting equipment and measurement for ^{134}Cs and ^{137}Cs determination using AMP pre-concentration technique. The gamma-ray spectrometry system, HPGe (Li) detector (CANBERRA) with MAESTRO software was used. The prepared calibration source was used to calibrate counting efficiency. The samples in calibrated containers were measured with the same gamma-ray spectrometry for 80000 s.

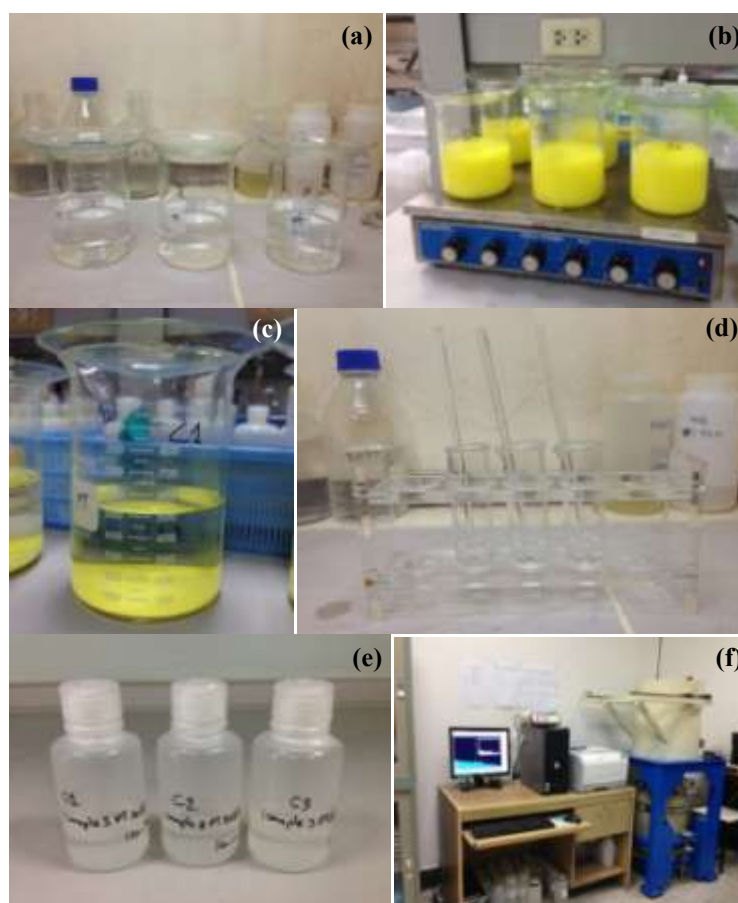**Figure 1.** The five litre proficiency test sample from IAEA.

Figure 2. ^{134}Cs and ^{137}Cs determination using AMP pre-concentration technique (a) The 500 gram aliquots in beakers, (b) Precipitating the aliquots by adding CsCl and AMP, (c) The AMP precipitates being left to settle, (d) Dissolving the AMP precipitate with NaOH, (e) The sample solutions in calibrated containers and (f) Gamma-ray spectrometer used for measuring in ^{134}Cs and ^{137}Cs activity in the samples.

2.3. ^{90}Sr determination method

2.3.1. Chemicals and reference solution for ^{90}Sr determination using ion exchange chromatographic technique. $Sr(NO_3)_2$, $Ba(NO_3)_2$, $Y(NO_3)_3$, $Ca(NO_3)_2$, NaOH, HCl, EDTA, NaCl, Na_2CO_3, HNO_3, $(NH_4)_2SO_4$, sodium acetate buffer solution used were analytical grade. The cation resin used was Dowex 50WX8 hydrogen form. The ^{90}Sr certified reference solution used to prepare calibration source was purchased from Eckert and Ziegler Isotope Product.

2.3.2. Sample preparation and analysis for ^{90}Sr determination using ion exchange chromatographic technique. The method for radiochemical analysis of strontium in seawater was developed from EPA-600/4-80-032 [4] and EMSL-LV-0539-17 [5]. A one kilogram aliquot of PT sample was used. $Sr(NO_3)_2$, $Ba(NO_3)_2$, and $Ca(NO_3)_2$ were added into the sample as carriers. To pre-concentrate strontium the sample was alkalised to pH 10 with NaOH and added with 3 N Na_2CO_3 to form carbonate precipitate. Strontium was separated using cation exchange chromatography. The Dowex 50WX8 hydrogen form was used. The loading solution was prepared by dissolving the carbonate precipitate with HCl and adding EDTA and sodium acetate buffer solution at pH 3.8. The resin was conditioned with 4 N NaCl and 5% NaOH. The resin was applied with the loading solution and then washed with 2% EDTA. Strontium fraction was eluted with 1.5 N HCl. $SrCO_3$ was formed by precipitating the strontium fraction with Na_2CO_3. The $SrCO_3$ precipitate was kept for 2 weeks for yttrium-ingrowth.Y-90 in equilibrium with ^{90}Sr was separated in hydroxide form. The $SrCO_3$ precipitate was dissolved with HNO_3 and then added with $Y(NO_3)_3$ and NaOH in order to form hydroxide precipitate. Its filtrate contained strontium fraction was used to determine strontium gravimetric yield by precipitating $SrCO_3$. Whereas the hydroxide precipitate was reprecipitated into oxalate form by adding HCl and sat. $(NH_4)_2C_2O_4$. The yttrium oxalate sample was filtrated and placed into planchet for measuring with gas proportional counter. Yttrium gravimetric yield was determined by weighting the sample. The pictures of ion exchange chromatographic technique are shown in figure 3.

2.3.3. Calibration source preparation for ^{90}Sr determination using ion exchange chromatographic technique. The ^{90}Sr certified reference solution which had activity 1.042±0.008 Bq was used to prepare yttrium oxalate calibration source using a short procedure of sample separation.

2.3.4. Counting equipment and measurement for ^{90}Sr determination using ion exchange chromatographic technique. Low background proportional counter, Berthold LB 770 with UMS programme was used. The prepared calibration source was used to determine counting efficiency. The sample was measured with the gas proportional counter for 100 min.
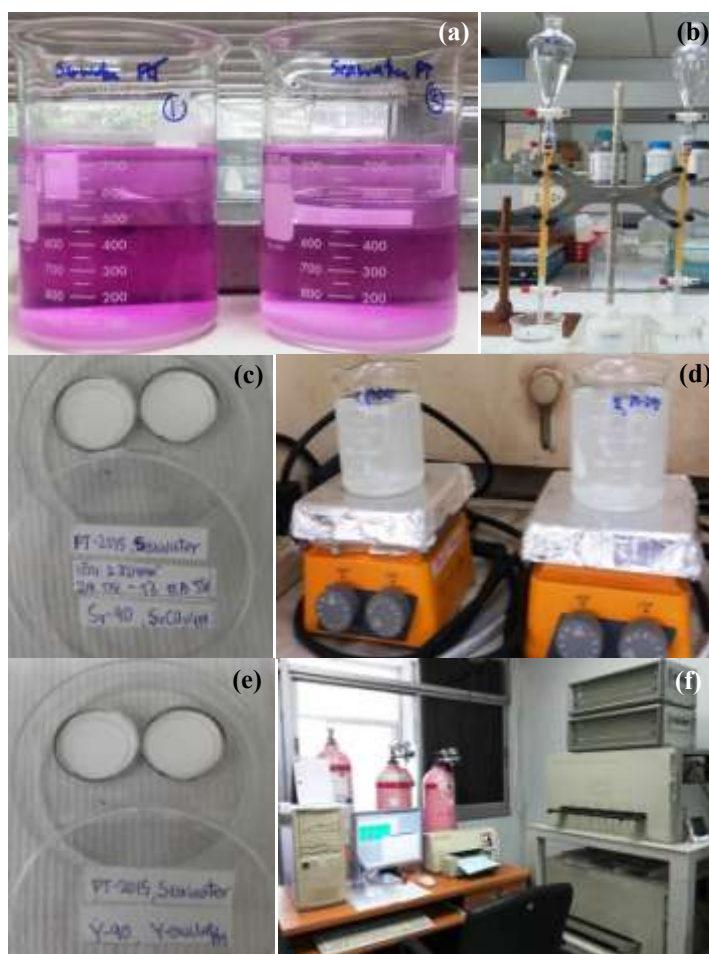
Figure 3. ^{90}Sr determination using ion exchange chromatographic technique (a) The one kilogram aliquot being precipitated as carbonate foam, (b) Ion exchange chromatography used to separate strontium, (c) SrCO$_3$ precipitates being kept for yttrium-ingrowth, (d) Precipitating yttrium in oxalate form, (e) Purified yttrium oxalate for activity measurement and (f) Gas proportional counter used for measuring in ^{90}Y activity in samples.

2.4. Data Evaluation
The PT results judged were based on IAEA criteria using different statistic evaluation criterion such as accuracy, precision and trueness as follow [1, 6-7];

2.4.1. Accuracy. The relative bias (RB) was the first step in producing a score for a result Value Analyst. RB between the Analyst's value and the IAEA target value was calculated and expressed as a percentage according to equation (1).

$$Bias_{relative} = \frac{Value_{Analyst} - Value_{IAEA}}{Value_{IAEA}} \ X \ 100\% \tag{1}$$

The absolute value of the relative bias was compared to the Maximal Accepted Relative Bias (MARB) which were 20% for both ^{134}Cs and ^{137}Cs and 25% for ^{90}Sr. Value analysts were scored as "Pass" for accuracy when:

$$|Bias_{relative}| \leq MARB \tag{2}$$

2.4.2. Precision and trueness. The precision, P, was calculated according to equation (3).

$$P = \left(\left(\frac{unc_{IAEA}}{Value_{IAEA}} \right)^2 + \left(\frac{unc_{Analyst}}{Value_{Analyst}} \right)^2 \right)^{1/2} X\ 100\% \tag{3}$$

The precision P was compared to the Limit of Accepted Precision (LAP) which were 20% for both ^{134}Cs and ^{137}Cs and 25% for ^{90}Sr. Value analysts were scored as "Pass" for precision when:

$$P \leq \text{LAP} \tag{4}$$

Value analysts results for trueness were scored as "Pass" when:

$$|Bias_{relative}| \leq \frac{Value_{Analyst}}{Value_{IAEA}} 2.58\ P \tag{5}$$

2.4.3. Final evaluation. The final score can be summarised according to the detailed evaluation as follow:

"Accepted" when all three tests were passed.

"Not Accepted" when the accuracy test was failed.

"Warning" when accuracy test was passed but either precision or trueness test was failed.

3. Results and discussion

The IAEA assigned values were shown in table 1 and our reported results of three radionuclides can be seen in table 2 and 3.

Table 1. IAEA assigned values.

^{134}Cs activity concentration (Bq kg^{-1})	^{137}Cs activity concentration (Bq kg^{-1})	^{90}Sr activity concentration (Bq kg^{-1})
0.1544±0.0006	0.2044±0.0013	0.1009±0.0007

Table 2. Results of ^{134}Cs and ^{137}Cs analysis.

Radionuclide	Sample weight (kg)	Individual activity concentration (Bq kg^{-1})			Mean activity concentration (Bq kg^{-1})
		1	2	3	
^{134}Cs	0.5	0.174±0.008	0.144±0.007	0.161±0.008	0.160±0.008
^{137}Cs	0.5	0.214±0.010	0.181±0.009	0.212±0.009	0.202±0.009

Table 3. Results of ^{90}Sr analysis.

Radionuclide	Sample weight (kg)	Activity concentration (Bq kg^{-1})
^{90}Sr	1.0	0.840±0.110

For ^{134}Cs and ^{137}Cs results the three individual analysis looked close together. For ^{90}Sr result only one analysis was performed and its activity was quite high when compared with those of ^{134}Cs and

^{137}Cs activities. However the evaluation in those results shown in detail in statistical view is presented in table 4.

Table 4. Performance evaluation.

Radio-nuclide	Analyst Value (Bq kg^{-1})	Analyst Uncert. (Bq kg^{-1})	IAEA Value (Bq kg^{-1})	IAEA Uncert. (Bq kg^{-1})	RB (%)	P (%)	Trueness Limit (%)	Accuracy	Precision	Trueness	Final Score
^{134}Cs	0.160	0.008	0.1544	0.0006	3.4	4.9	13	Pass	Pass	Pass	Accepted
^{137}Cs	0.202	0.009	0.2044	0.0013	-1.0	4.5	12	Pass	Pass	Pass	Accepted
^{90}Sr	0.840	0.110	0.1009	0.0007	730	14	291	Fail	Pass	Fail	Not accepted

For determining caesium by the AMP precipitation technique, working in laboratory was quite simple. The procedure mainly involved precipitation steps to catch caesium in water media. Due to AMP being selective caesium scavenger and the simple separation steps the process loss was suitably negligible to obtain accurate and precise results. In addition for radioactivity measurement the use of prepared calibration source which had the same shape and type as sample containers potentially help to obtain correct counting efficiency, consequently obtaining the accurate final activities. Therefore the result of ^{134}Cs and ^{137}Cs passed the three tests which resulted in being assigned the status Accepted. However the result of ^{90}Sr did not pass accuracy test therefore it was considered as not accepted. Its relative bias was found to be very high i.e. 730 %. This may be due to two main possibilities. Firstly, the sample might contain contaminated ^{134}Cs and ^{137}Cs and this raised gross beta activity when using gas proportional counter. Secondly, the efficiency calculated from prepared calibration source was underestimated. Possibly the calibration source and sample had different precipitate thicknesses. The precipitate sample seemed to be thinner than those of calibration source. For measuring beta particle, the self-absorption difference needed to be corrected in order to determine proper efficiency, consequently obtaining an accurate final activity.

4. Conclusion

Our method for radiochemical analysis for caesium determination using AMP precipitation fully succeeded in ^{134}Cs and ^{137}Cs analysis since the results passed the three tests i.e. accuracy precision and trueness and then acquired the status Accepted. The AMP precipitation technique was proved to be suitable for determining ^{134}Cs and ^{137}Cs in seawater since AMP as scavenge was selective for caesium and the separation steps was not complicated. Also the other successful key was to use sample container having the same shape and type as prepared calibration source. This potentially helped to obtain corrected counting efficiency, hence obtaining the accurate final activities. In the case of ^{90}Sr the ion exchange chromatographic technique used resulted the inaccurate ^{90}Sr activity. To improve the analysis both aspects, radiochemical technique and radioactivity measurement should be considered. For the radiochemical technique, delicate separation steps must be used to remove other radionuclides from the final precipitate sample in order to avoid over beta particle counting using gas proportional counter. For measurement aspect, the different self-absorption between calibration source and sample has to be corrected in order to obtain accurate efficiency and therefore the calculated ^{90}Sr activity in the sample should be correct.

References

[1]   Harms A V, Osvath I and Osborn D 2016 *IAEA-RML-2015-02 Proficiency Test for Determination of Radionuclides in Seawater* (Vienna: IAEA)
[2]   Hirose K, Aoyama M, Igarashi Y and Komura K 2008 Improvement of ^{137}Cs analysis in small volume seawater samples using the Ogoya underground facility *J. Radioanal. Nucl. Ch.* **276**

         pp 795-798

[3]   Phaopeng N 2013 *The Measurement of Cs-137 Radioactivity in Seawater and the Oyster (Crassostrea belcheri) from the lower Gulf of Thailand for Radiation Dose Assessment in the General Public* (Bangkok: Kasetsart University)

[4]   Herman L K and Earl L W 1980 *Prescribed Procedures for Measurement of Radioactivity in Drinking Water* (OHIO: EPA)

[5]   EPA 1979 *Radiochemical Analytical Procedures for Analytical of Environmental Samples* (Nevada: EPA)

[6]   Shakhashiro A, Sanaone U, Trinkl A, Makarewicz M, Yonezawa A C, Kim C K, Kis-Benedek G, Benesch T. and Schorn R 2007 *Report on the IAEA-CU-2006-04 ALMERA Proficiency Test on the Determination of Gamma Emitting radionuclides, IAEA/AL/170* (Vienna: IAEA)

[7]   Pham M K, Osvath I and Sanchez-Cabeza J 2010 *Proficiency Test Determination of Radionuclides in Fish Flesh Samples IAEA/AQ/13* (Vienna: IAEA)