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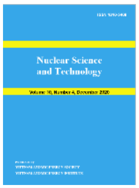

Determination of recovery efficiency of ^{137}Cs in seawaterusing co-precipitation method

Duong Duc Thang*, Vuong Thu Bac, Bui Dac Dung, Duong Van Thang, Doan Thuy Hau,
Le Dinh Cuong, Nguyen Van Khanh, Nguyen Thi Thu Ha, Cao Duc Viet,
Nguyen Huyen Trang, Nguyen Thi Oanh, Le Thị Hoa

Institute for Nuclear Science and Technology, 179 Hoang Quoc Viet – Cau Giay – Hanoi
** Email: ducthangb2k52@gmail.com, thangdd@vinatom.gov.vn*

Abstract: Recovery efficiency of ^{137}Cs in seawater samples with different volumes of 40, 50, 60, 80 and 100 liters using co-precipitation method by ferrocyanide compounds has been determined. ^{134}Cs nuclide was used as a tracer to determine recovery efficiency. The results showed that the recovery efficiency of ^{134}Cs ranged from 92.62% to 99.26% with mean value of (95.22 ± 2.61)% for different sample volumes. Average recovery efficiency for samples with a volume of 50 liters was (95.70 ± 2.50)% and uncertainty when determining ^{137}Cs in seawater samples were still less than 20%. Therefore, reducing the volume of sample to 50 liters still ensures reliability when determining ^{137}Cs in seawater samples by co-precipitation method, thereby reducing the chemical and time when analyze a large number of samples.

Keywords: *Recovery efficiency of ^{137}Cs, co-precipitation method, seawater, HPGe.*

I. INTRODUCTION

Huge amounts of anthropogenic radionuclides have been introduced into marine environment as global fallout from large-scale atmospheric nuclear-weapon testing, discharge from nuclear facilities and ocean dumping of nuclear wastes [1]. Their radiological and ecological effects are still of world concern [2]. ^{137}Cs is one of the most important anthropogenic radionuclides in the field of environmental radioactivity monitoring because of its long physical half-life of 30.02 years. It is a major fission product (fission yield is about 6–7%) from both plutonium and uranium [1]. ^{137}Cs in the ocean has been mainly derived from global fallout [1, 2, 3, 4, 5], together with close-in fallout from the Pacific Proving Ground nuclear explosions [3, 4], discharge of radioactive wastes from nuclear facilities and others [6, 7, 8].

The determination of activity concentration of radionuclides in seawater samples is a complicated issue, because their activity in seawater samples is very low, a large number of samples are required (about 200 - 400 liters) [9]. Currently, there are various processes in the world for preliminary enrichment of seawater samples on the field before laboratory analysis. A number of previous studies have successfully reduced seawater sample volume to 20 liters [10, 11] or 10 liters [12] to reduce chemical and sample processing time while still ensuring accuracy.

This paper presents the survey results on the recovery efficiency of ^{137}C in seawater samples by different volumes, determining

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the activity of ^{137}C and uncertainty by co-precipitation method in the field then analysis in the laboratory of Center for Environmental Radiation Monitoring and Impact Assessment (CERMIA), Institute for Nuclear Science and Technology (INST). Based on the results obtained, it is recommended to analyze ^{137}C in seawater samples with optimal volumes.

II. MATERIALS AND METHODS

Sampling and sample processing

The activity concentration of ^{137}Cs currently in the East Sea is quite small. It ranges from (1.16 ± 0.06) Bq/m^3 to (1.62 ± 0.15) Bq/m^3 [9], therefore, to determine ^{137}Cs, the enrichment method must be applied prior to analysis in the laboratory.

Seawater samples were taken on Co To island, Co To District, Quang Ninh province, the sampling locations are shown in Figure 1. Samples were taken at the time of high tide to avoid the influence from the mainland. In this study, we took samples of surface seawater with different volumes of 40, 50, 60, 80 and 100 liters, pretreated by co-precipitation method in the field (Figure 2) according to the procedure presented as shown below.

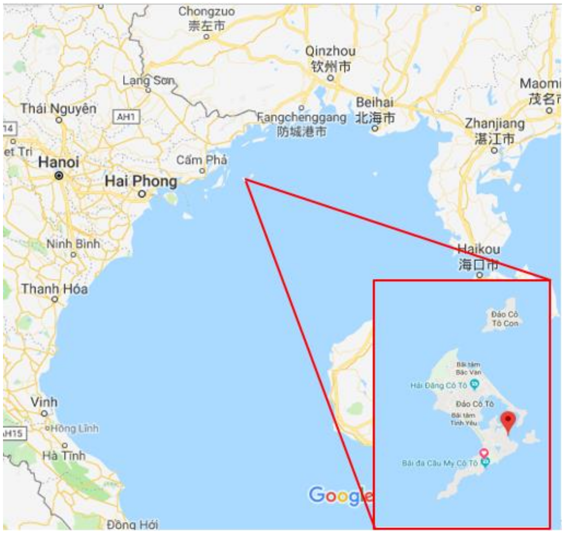


Fig. 1. Location of seawater sampling on Co To island.

Fig. 2. Sample treatment.

Result of analyzing seawater samples on Co To island in 2018 (State-level Scientific and Technological Program (KC.05.07/16-20)) shows that there is not ^{134}Cs in seawater on Co To island. Because ^{134}Cs and ^{137}Cs have same chemical properties. So ^{134}Cs is often used to determine the recovery efficiency for Cs in seawater samples. In this study, the ^{134}Cs radioactive solution was used as a tracer to determine the recovery efficiency for ^{137}Cs.

For a 100-liter seawater sample, the following procedure has been applied [9]:

- Pour the 100 L of seawater sample into the water tank, add (3.33 ± 0.05) Bq of ^{134}Cs tracer.

- Add 100ml of HCl (1:1) solution to adjust the pH to 2 ÷ 3.

- Add 10ml of CsCl solution (100 mg/ml), 15ml $BaCl_2$ (100mg/ml), mix well.

- Add 6 g of $NiCl_2$, 40 g of $CaCl_2$, 25 g of $K_4Fe(CN)_6$, mix well, leave for 3 hours.

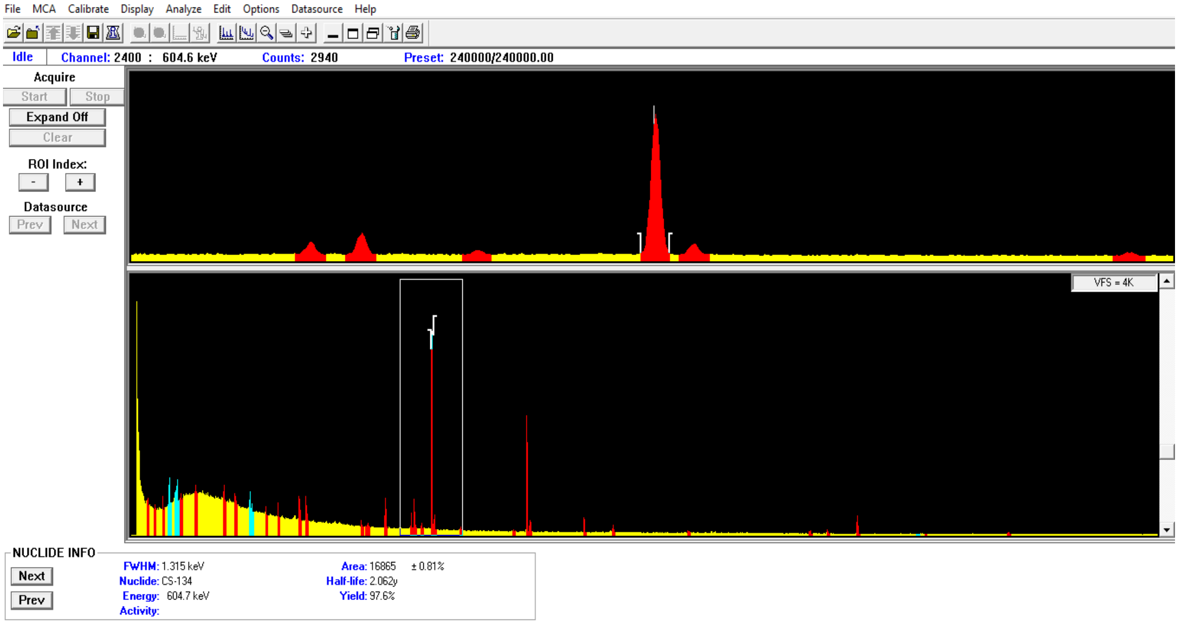
- Add to the sample 800 g NH_4Cl, 400 g Na_2CO_3, mix well, leave for 2 hours.

- Add to the sample 40 ml of $FeCl_3$ 15%, mix well, leave for 12 hours.

- Discard the sample supernatant by siphon, pour the precipitated substance into 5 L beaker.

For the process of precipitation of seawater samples with a volume of 40, 50, 60 and 80 liters, the amount of chemicals as well as ^{134}Cs to be used will increase or decrease proportionally to the volume of seawater samples.

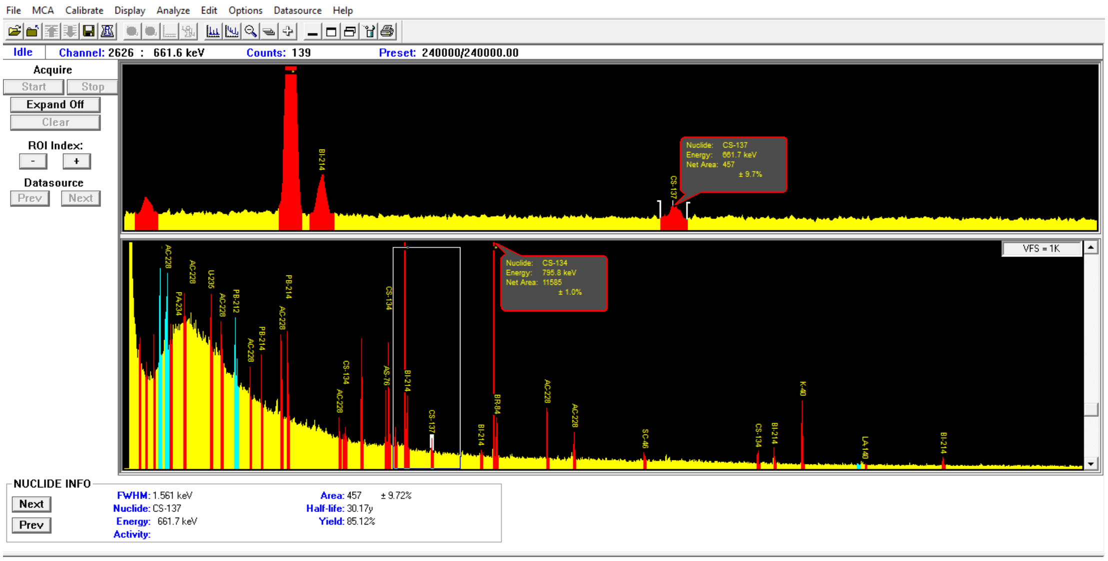
After pretreatment on the site, the precipitate is transferred to the laboratory. The precipitate was filtered thought paper filter, dried to dryness at 105^{0}C and put into the measuring box. Typical gamma spectra of seawater samples are shown in Figures 3 and 4.



Idle Channel: 2400 : 604.6 keV Counts: 2940 Preset: 240000/240000.00

FWHM: 1.315 keV
Nuclide: CS-134
Energy: 604.7 keV
Activity:
Area: 16865 ± 0.81%
Half-life: 2.062y
Yield: 97.6%

Fig. 3. The gamma spectrum represents the peak of 604.7 keV of ^{134}Cs.



Idle | Channel: 2626 : 661.6 keV | Counts: 139 | Preset: 240000/240000.00

NUCLIDE INFO

FWHM: 1.561 keV
Nuclide: CS-137
Energy: 661.7 keV
Activity:
Area: 457 ± 9.72%
Half-life: 30.17y
Yield: 85.12%

Fig. 4. The gamma spectrum represents the peak of 661.7 keV of ^{137}Cs.

The samples were measured on a low background gamma spectrometer with CANBERRA's HPGe GC5019 detector with energy resolution and relative efficiency at the peak of 1332.5 keV of ^{60}Co of 1.8 keV and 50%, respectively. The spectrometer is calibrated using the IAEA RGU-1, IAEA-RGTh-1 and IAEA-soil 6 reference samples of comparable geometry.

The activity of ^{134}Cs and ^{137}Cs in the precipitation samples were determined, respectively, through gamma rays of energy 604.7 keV and 661.7 keV with a time of 240000 seconds to ensure the counting statistical error below 10%.

The recovery efficiency of ^{134}Cs is determined by the formula 1:

$$HS\ (\%) = \frac{Cs-134_{bd}}{Cs-134_{kt}} \times 100\% \qquad (1)$$

Where HS is recovery efficiency (%), $Cs-134_{bd}$ is the initial activity of ^{134}Cs used as the tracer (Bq), $Cs-134_{kt}$ is measured activity of ^{134}Cs in precipitation (Bq).

The recovery efficiency of ^{134}Cs was used to determine ^{137}Cs activity in seawater samples. The radioactivity concentration of ^{137}Cs was calculated as follows (IAEA, International Atomic Energy Agency, 1989):

$$A_{Cs-137} = \frac{100 \times N}{t \times \varepsilon \times \gamma \times V \times HS} \qquad (2)$$

Where A_{Cs-137} is the activity concentration of ^{137}Cs in seawater sample (Bq/m^3), N is the net peak area in the sample spectrum, t is the live time of the sample spectrum collection in seconds, ε is the detector efficiency of the gamma-ray, γ is the emission probability of the gamma line corresponding to the peak energy, *V* is the volume of the measured sample (m^3), HS is the recovery efficiency of ^{134}Cs (%).

III. RESULTS AND DISCUSSION

10 water samples with the different volumes have been analyzed. The recovery efficiency of ^{137}Cs in those samples were calculated and presented in the Table I.

Table I. Recovery efficiency of ^{137}Cs in seawater samples by different volumes.

Sample	Volume (L)	Recovery efficiency (%)
M1	40	92.62 ± 2.29
M2	40	99.26 ± 2.47
M3	50	98.50 ± 2.24
M4	50	94.54 ± 2.17
M5	50	93.15 ± 2.27
M6	50	93.41 ± 2.25
M7	50	98.92 ± 2.26
M8	60	93.93 ± 2.03
M9	80	93.39 ± 1.93
M10	100	94.48 ± 3.25

Table I shows that the recovery efficiency varies from (92.62 to 98.92)% with an average of (95.22 ± 2.61)%. In which, the recovery efficiency of ^{137}Cs in different volumes of 40, 50, 60, 80 and 100 liters are (95.94 ± 3.32)%, (95.70 ± 2.50)%, (93.93 ± 2.03)%, (93.39 ± 1.93)%, (94.48 ± 3.32)%, respectively. The recovery efficiency of ^{137}Cs in different volume of seawater samples tends to decrease when the volume increases.

The average recovery efficiency of the sample volumes of 40 and 50 liters are quite similar, but for our method, the volume of 50 liters is optimal. Because the precipitates obtained from 40-liter samples are approximately the same as the amount to be measured, while the precipitation volume of 50-liter samples is always greater than the amount to be measured. This makes the recovery efficiency of the sample volume of 50 liters stable and has less uncertainty.

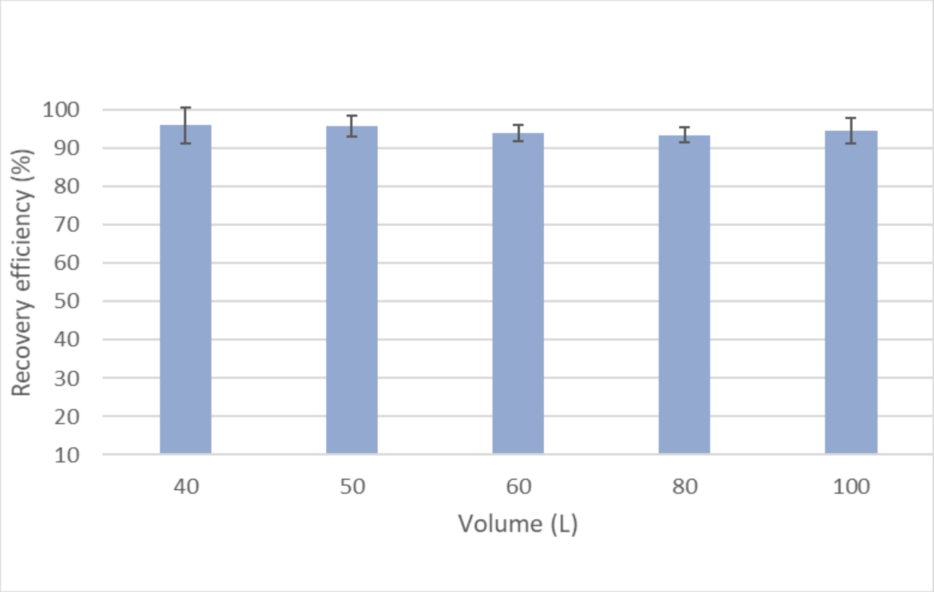


Fig. 5. The recovery efficiency of ^{137}Cs versus sample volume.

Figure 5 and Table I shows that the recovery efficiency of ^{137}Cs in seawater by different sample volumes is quite similar and greater than 90%. The recovery efficiency of the smaller volume seawater samples are greater a bit than those of the larger volume samples.

Activity concentrations of ^{137}Cs in different seawater samples with different volumes calculated by formula 2 are shown in Table II.

Table II shows that the activity concentration of ^{137}Cs are in the range of (1.12 ± 0.23) Bq/m^3 to (1.69 ± 0.21) Bq/m^3 with an average of (1.42 ± 0.22) Bq/m^3, with uncertainty less than 20%. The activity concentration of ^{137}Cs in different seawater volumes of this study is similar to previous publication [9].

Table III presents a comparison of the recovery efficiency of ^{137}Cs in seawater in this study with some results published before.

Table II. Activity concentration of ^{137}Cs in seawater samples.

Sample	Volume, L	Activity concentration ^{137}Cs (Bq/m^3)
M1	40	1.12 ± 0.23
M2	40	1.19 ± 0.19
M3	50	1.68 ± 0.17
M4	50	1.42 ± 0.28
M5	50	1.46 ± 0.20
M6	50	1.69 ± 0.21
M7	50	1.14 ± 0.23
M8	60	1.56 ± 0.23
M9	80	1.61 ± 0.21
M10	100	1.29 ± 0.19

Table III. The comparison of the recovery efficiency.

Volume, L	Recovery efficiency (%)			
10	93	±	3	K. Hirose [10]
20	99			Nakano [11]
20	90	÷	95	J. Kamenik [12]
40	92.62	÷	99.26	This work
50	93.15	÷	98.92	This work
60	93.93	±	2.03	This work
80	93.39	±	1.93	This work
100	94.48	±	3.25	This work

From Table III, we find that the recovery efficiency of ^{137}Cs in seawater in this study is quite good and as similar as results of other papers.

IV. CONCLUSIONS

In this study, we achieved the initial goal of determining the recovery efficiency of ^{137}Cs

in seawater with different volumes from 40, 50, 60, 80 and 100 liters. The recovery efficiency of ^{137}Cs in seawater samples varied from 92.62% to 99.26% with an average of (95.22 ± 2.61)% and relatively good repeatability.

The average recovery efficiency for samples with a volume of 50 liters is (95.70 ± 2.50)% and the uncertainty when determining the activity concentration of ^{137}Cs is still less than 20%. Therefore, it is possible to reduce the sample volume to 50 liters while maintaining reliability when determining the activity concentration of ^{137}Cs in seawater samples by the co-precipitation method, thereby reducing chemicals and time when analyzing many samples at the same time.

ACKNOWLEDGMENTS

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