Verification of ^{137}Cs determination in seawater using Cu-hexacyanoferrates filters

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Abstract. A rapid method to determine ^{137}Cs in seawater using Cu-hexacyanoferrates ion exchanger has been developed and verified for purpose of Thailand routine and emergency environmental radiation monitoring. The Cu-hexacyanoferrate supported cotton-wound cartridge filters were used to absorb ^{137}Cs from spiked synthesis seawater by passing various large volumes i.e. 200 L, 300 L and 400 L over the filters with slow flow rate at 240 L/hr. The filter samples were converted to ash through a heating step and directly measured with gamma ray analysis using HPGe detector. The result showed acceptable accuracy with bias below ± 25%, in the range from - 24.63% to + 3.29%. This developed method is cost-effective and easily to performed in sampling fields and can be optimised its accuracy with analysis time when it needed.

1 Introduction

Cs-137 is one of the fission products which can be released from a nuclear accident, nuclear waste discharge and atomic bomb test. It has a long half life of 30 years which can be dispersed as global fallout over the oceans. Therefore ^{137}Cs is regarded as important indicator of radioactive pollution in the marine environment and it is one of our monitored radionuclides in environmental samples especially in seawater. Caesium usually exists and migrates in monovalent state in an aquatic environment. The ^{137}Cs determination in seawater in the region can be applied to monitor a release of any radiological incident in the pacific region [1]. Routinely the classical ammonium molybdophosphate (AMP) pre-concentration method has been used to determine ^{137}Cs in seawater. Seawater samples are collected from the field and brought to our laboratory for Cs radiochemical separation.

Recently a rapid method to determine ^{137}Cs in seawater has been developed based on hexacyanoferrates ion exchanger. Hexacyanoferretes have advantage of being selective of Cs. In addition, it is easily to prepare in three forms i.e. intrinsic, supported and composite [2]. According to Gaur [3] Cu-hexacyanoferrates (in the following text abbreviation CuHCF) exhibited stability in seawater when compared with other transit element such as Co, Ni and Zn. CuHCF therefore has been widely used for caesium determination in seawater in different forms and supporters. Terada [4] and Su [1] used silica gel as supporting bed for CuHCF packed in small column for sample volume of 40 - 60 L with low flowrate at 20 - 30 L/hr. They found that sample volume had to be increased to obtain more ^{137}Cs activity but flowrate and amount of ion exchanger had to be optimised. Yii [5] used polyethylene filter as supporting bed for CuHCF for very large sample volume of 2000 L with fast flowrate at 900 L/hr. The results showed quite low Cs collection efficiency in a range of 55 - 66% due to the high flowrate. Our work therefore tried to optimise amount of ^{137}Cs detection, sample volume and flowrate to obtain accurate ^{137}Cs concentration in seawater. To verify our analytical performance CuHCF supported on cotton filters was used to absorb ^{137}Cs in various amount of spiked synthesis seawater i.e. 200 L, 300 L and 400 L with flowrate at 240 L/hr.

2 Experimental

2.1 Chemicals and standard for CuHCF filter method

$K_4[FeCN_6]$. $3H_2O$ and $Cu(NO_3)_2$. $3H_2O$ used were analytical grade. The synthetic sea salt was purchased from Marinium. The ^{137}Cs certified reference solution used to prepare the calibration source was obtained from Eckert and Ziegler Isotope Product.

2.2 CuHCF filter preparation

To determine total ceasium composing of dissolved and suspended forms [6], the 1-μm cotton-wound cartridge filters which had a stainless steel core were used. The filters were submerged in 3% $K_4[FeCN_6]$ solution for a few days. The filters were removed from the solution and were dried in an oven at 80ºC. The dried filters were soaked in 3% $Cu(NO_3)_2$ solution for at least one day. The filters were removed from the solution and washed with deionised water. The washed filters were dried at 80ºC. The dried filters were separately packed in plastic bags to be ready for using as Cs ion exchanger.

2.3 Spiked sea water preparation

The synthetic sea water samples were prepared using the synthetic sea salt dissolved in tap water at 35 ppt. The parallel sea water samples with volume of 200 L, 300 L and 400 L were prepared. The samples were spiked with the known activity solution of ^{137}Cs to obtain concentration of 0.191 ± 0.002 Bq/L.

2.4 CuHCF filter method

Sets of cartridge filter contained three filters i.e. pre filtered cotton-wound cartridge filter and the two CuHCF filters in series in filter housing were fabricated. The various amounts of seawater samples were pumped through the filter sets with flow rate at 240 L/hr. The CuHCF filter samples contained Cs were packed separately in plastic bag and labelled "A" and "B" as the first and second CuHCF filters respectively. The both filters were dried and ashed at 400°C for 15 hours. It should be noted that radiocaesium will be significantly loss at temperature above 400°C [7]. The ash samples were transferred into a calibrated container (the same shape and type as the prepared calibration source i.e. 100-ml transparent polypropylene bottle). The pictures of CuHCF filter method are shown in Figure 1.

Fig. 1. The CuHCF filter method; (A) Prepared CuHCF filters, (B) CuHCF filter set for ^{137}Cs absorption in seawater, (C) CuHCF filter samples after ashing and (D) Calibration source and samples for gamma-ray measurement.

2.5 Calibration source preparation for CuHCF filter method

The ashed CuHCF filter in the calibrated container (100-ml transparent polypropylene bottle) was added with the certified reference solution containing 38.188± 0.977 Bq of ^{137}Cs.

2.6 Counting equipment and measurement

Gamma-ray spectrometry system, HPGe detector (CANBERRA) with MAESTRO was used. The prepared calibration source was used to calibrate counting efficiencies. Then the CuHCF ash samples in calibrated containers were measured with the same gamma spectrometry system.

3 Results and discussion

The verification results of CuHCF filter analysis are shown Table 1.

Table 1. The validation results of CuHCF filter method.

Sample	Sample volume (L)	Efficiency of Cs collection	Activity (Bq/L)	Accuracy (%)
Sample 1 200L	200	85.97	0.156 ± 0.004	- 18.65
Sample 2 200L	200	48.09	0.144± 0.004	- 24.63
Average 200 L	**200**	**67.03**	**0.150 ± 0.004**	**- 21.64**
Sample 1 300L	300	72.39	0.172 ± 0.005	- 10.24
Sample 2 300L	300	87.48	0.161 ± 0.004	- 16.01
Average 300 L	**300**	**79.94**	**0.167 ± 0.005**	**- 13.13**
Sample 1 400L	400	94.82	0.161 ± 0.004	- 15.71
Sample 2 400L	400	52.99	0.198 ± 0.005	+ 3.29
Average 400 L	**400**	**73.91**	**0.180 ± 0.005**	**- 6.21**

The ^{137}Cs collection efficiency onto the ion exchanger of each sample shown in Table 1. was calculated from the activity of filter A (front filter) and B (back filter) described below [1].

$$E = \frac{[F] - [B]}{[F]} \qquad (1)$$

When E is the absolute collection efficiency. [F] and [B] are the ^{137}Cs activity in the front and back filters respectively.

And the final ^{137}Cs concentration activity in seawater samples is referred to the following equation.

$$A = \frac{[F]}{E \times V} \qquad (2)$$

When A is the final ^{137}Cs concentration activity in seawater samples. V is the volume of seawater samples.

Differences in Cs collection efficiencies of each repeated samples can be possibly due to the two main reasons i.e. difference in quality of prepared CuHCF filters and unstable flowrate of seawater pass through the filters [1]. First quality of prepared CuHCF filters were not identical i.e. various amount of CuHCF supported on filters. Second seawater passing through filter controlled by an outlet valve was not perfectly constant at 240 L/hr during sample collection. These could potentially affect different Cs collection efficiencies between each sample. It should be noted that the collection efficiency in a range of 48.09 - 94.82% with flowrate at 240 L/hr agreed well

with Yii [5] and Ross [8]. Yuii's work obtained 66 - 55% efficiency with higher flowrate at 900 L/hr and Ross suggested a very low flowrate at 60 - 120 L/hr to obtain efficiency more than 90%. For accuracy aspect, the repeated samples resulted various accuracy with bias between - 18.65 and - 24.63 for 200 L samples, between - 10.24 and - 16.01 for 300 L samples and between - 15.71 and + 3.29 for 400 L samples. The negative bias presented the loss of caesium especially sample 2 200 L with 48.09% collection efficiency and - 24.63% bias. Unabsorbed radiocaesium on the filters could be explained with a combination of low quality of prepared CuHCF filters and the high flowrate passing through the filters at 240 L/hr. It should be noted that sample 2 400 L had positive bias i.e. + 3.29 but quite low collection efficiency. It can be an effect of the loss of CuHCF from the first cartridge and trapped on the second one during filtering. This was possibly poor rinse of prepared filter with DI water before drying. In conclusion the repeated samples for 200 L, 300 L and 400 L with different Cs collection efficiencies had fairly acceptable accuracies in a range of ± 25%. This means that the two CuHCF filters in series were suitable to absorb caesium in the seawater samples and the minimum 200 L seawater samples can be adequate to perform the CuHCF filter method within accuracy of ± 25%. The accuracy can be improved with enhancing the quality of prepared CuHCF filters and lowering the flowrate. However reducing flowrate effects longer filtration time and then limits number of samples that can be processed within a certain time period. The method should be optimised for accuracy and time needed. For example, routine monitoring method when time is not strictly limited may lower flowrate to obtain higher accuracy. In case of emergency situations when time is limited this method i.e. at less 200 L sample volume and flowrate at 240 L/hr seems to be sufficient to perform the determination of contaminated caesium in seawater within ± 25% bias.

4 Conclusion

A rapid method to determine ^{137}Cs in seawater which is cost-effective and less time consuming, has been developed based on CuHCF ion exchanger. This method was verified using known activity spiked samples with various volumes i.e. 200 L, 300 L and 400 L and the performing flowrate at 240 L/hr. The results were shown accuracies were in the acceptable range of ± 25% bias i.e. - 24.63% to + 3.29%. It means that the minimum 200 L samples can successfully perform ^{137}Cs determination in seawater with bias range of ± 25%. It should be noted that most sample results had negative bias due to loss of unabsorbed caesium which can be improved by enhancing quality of prepared CuHCF filters and reducing flowrate. Therefore this method could be optimised its accuracy with analysis time, depending upon situations such as routine monitoring and emergency accident.

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