Determination of $^{137}$Cs in large volume seawater using Cu-hexacyanoferrate cartridge filters

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Abstract. A simple method to determine $^{137}$Cs in seawater has been developed based on the use of a Cu-hexacyanoferrate scavenger. The Cu-hexacyanoferrate supported on cotton wound cartridge filter was used to absorb $^{137}$Cs from seawater by passing large volumes over the cartridge filters with flowrate of 240 L hr$^{-1}$. Results from the Cu-hexacyanoferrate method were proved acceptable for accuracy with bias below $\pm$ 20 % i.e. -9.16 to +18.55 % when compared with the traditional ammonium molybdophosphate pre-concentration method. This developed method is cost-effective and less time consuming. In addition it can be easily performed at sampling fields.

1. Introduction

Cs-137 is one of the fission products which has a long half life of 30 years. It can be released from a nuclear accident, nuclear waste discharge and atomic bomb test to the atmosphere and into the ocean. Therefore $^{137}$Cs is one of our monitored radionuclides in environmental samples especially in seawater. Caesium normally exists and migrates in monovalent state in an aquatic environment. The determination of $^{137}$Cs in the ocean can be applied to monitor a release of any radiological incident in the pacific region [1]. The classical ammonium molybdophosphate (AMP) pre-concentration method has been used routinely to determine $^{137}$Cs in seawater. This analysis passed the proficiency test exercise under the project “IAEA proficiency test exercise on Marine benchmark study on the possible impact of the Fukushima radioactive releases in the Asia-Pacific Region for Caesium Determination in Sea Water (RCA RAS/7/021)” [2]. Routinely seawater samples are collected from fields and brought to our laboratory. The samples are acidified to pH 1.6 and followed by adsorption of $^{137}$Cs on AMP as the scavenger. The precipitate samples are filtrated and dissolved with 10 M NaOH before gamma-ray measurement using HPGe detector. However the radiochemical method is laborious and time consuming. Moreover the method limits number of samples that can be brought to laboratory due to 20 L seawater per sample to be collected. A simple method to determine $^{137}$Cs in seawater has been developed based on hexacyanoferrate ion exchanger. Hexacyanoferrates have advantage of being selective of Cs (excluding Na and K). Moreover it is easily to prepare in three forms i.e. intrinsic, supported and composite [3]. Terada [4] and Su [1] used silica gel as supporting bed for Cu-hexacyanoferrate (in the following text abbreviation CuHCF) which exhibited stability in seawater when compared with other transit element such as Co, Ni and Zn [5]. Our work used also CuHCF but on cotton cartridge filters supporting bed which can be prepared easily and performed with large volume samples for high detection of contained Cs. The traditional AMP technique and developed method based on CuHCF are compared and described in this paper.
2. **Experiment**

2.1. **Seawater sample description**
Local sea water at Sriracha Fishery Research Station, Thailand (13°11' 03.8"N, 100°55' 43.7"E) which contained natural $^{137}$Cs was used for both of AMP pre-concentration and CuHCF filter methods. Seawater salinity was 35 ppt and its pH was 7.8.

2.2. **AMP pre-concentration method**

2.2.1. **Reagents and reference solution for AMP pre-concentration method**. AMP, CsCl, HCl and NaOH used were analytical grade. The $^{137}$Cs certified reference solution used to prepare calibration source was purchased from Eckert and Ziegler Isotope Product.

2.2.2. **Sample preparation and analysis for AMP pre-concentration method**. The AMP-concentration method was developed from Hirose and Phaopeng’s work [6-7]. Two hundred litre seawater samples in the field were pumped through a 1 µm filter into plastic containers. The samples were acidified with HCl to pH 1.6. Then 2.6 g of CsCl (caesium carrier) and 40 g of AMP were added. The samples were stirred for one hour and left overnight to allow the precipitate to settle. The precipitate samples were centrifuged and washed with 1 M HCl twice. The precipitate samples were dissolved with 10 M NaOH. The solutions were heated to remove ammonia. The precipitation step was repeated. The second precipitate samples were dissolved with 10 M NaOH. The solutions were transferred to calibrated containers (the same shape and type as prepared calibration source i.e. 100 ml transparent polypropylene bottle) and made up to the same volume as the calibration source i.e. 20 ml. The pictures of AMP pre-concentration method are shown in figure 1.

2.2.3. **Calibration source preparation for AMP pre-concentration method**. The $^{137}$Cs certified reference solution which contained 0.385±0.002 Bq of $^{137}$Cs activity, was spiked into 20 ml of 1 M HCl in the calibrated container (100 ml transparent polypropylene bottle).

![Figure 1](image-url). The AMP pre-concentration method (a) Filtrated seawater samples, (b) Precipitating AMP in the seawater samples, (c) Samples after precipitation and (d) Calibration source and samples for gamma-ray measurement.
2.3. **CuHCF filter method**

2.3.1. **Reagents and standard for CuHCF filter method.** K₄[FeCN₆] and Cu(NO₃)₂ used were analytical grade. The ¹³⁷Cs certified reference solution used to prepare the calibration source was purchased from Eckert and Ziegler Isotope Product.

2.3.2. **CuHCF filter preparation.** The 1 µm cotton wound cartridge filters which had stainless steel core were used. The filters were soaked in a K₄[FeCN₆] solution (containing 10 g of K₄[FeCN₆]/300 ml of deionised water) for two days. The filters were removed from the solution and were dried in an oven at 80°C. The dried filters were submerged in Cu(NO₃)₂ solution (containing 10 g of Cu(NO₃)₂/300 ml of deionised water) for at least one day. The filters were removed from the solution and rinsed with deionised water. The washed filters were again dried at 80°C. The dried filters were packed in plastic bags and ready to be used as Cs ion exchanger.

2.3.3. **CuHCF filter method.** Sets of cartridge filter composed of three filters i.e. pre filter cotton wound cartridge filter and the two CuHCF filters in series in filter housing were fabricated. The various amount of seawater samples were pumped through the filter sets with flow rate of 240 L hr⁻¹. The CuHCF filter samples contained Cs were packed in plastic bag and labelled “A” and “B” as the first and second CuHCF filters respectively and brought back to the laboratory. The both filters were dried and ashed at 400°C for 15 hours. The ash samples were transferred into calibrated containers (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 2.

2.3.4. **Calibration source preparation for CuHCF filter method.** The ¹³⁷Cs certified reference solution which contained 0.943±0.005 Bq of ¹³⁷Cs, was spiked into ashed CuHCF filter in the calibrated container (100 ml transparent polypropylene bottle).

2.3.5. **Calculation of ¹³⁷Cs collection efficiency and ¹³⁷Cs activity concentration.** The ¹³⁷Cs collection efficiency onto the ion exchanger of each sample was calculated from the activity of filter A (front filter) and B (back filter) described below [1].

\[
E = \frac{[F] - [B]}{[F]} \tag{1}
\]

When E is the absolute collection efficiency. \([F]\) and \([B]\) are the activity of ¹³⁷Cs in the front and back filters respectively.

And the final ¹³⁷Cs activity concentration in seawater samples is referred to equation (2).

\[
A = \frac{[F]}{E \times V} \tag{2}
\]

When A is the final ¹³⁷Cs activity concentration in seawater samples. V is the volume of seawater samples.
Figure 2. The CuHCF filter method (a) Prepared CuHCF filters, (b) CuHCF filter set for $^{137}$Cs absorption in seawater, (c) CuHCF samples after ashing and (d) Calibration source and samples for gamma-ray measurement.

2.4. Counting equipment and measurement
Gamma-ray spectrometry system, coaxial HPGe detector (CANBERRA) with MAESTRO was used. The detector was shielded by low background lead. The prepared calibration sources for both AMP solution and CuHCF ash were used to calibrate counting efficiencies at 661.657 keV. Then the both AMP solution samples and CuHCF ash samples in calibrated containers were measured with the same gamma-ray spectrometry system.

3. Results and discussion
The results of AMP pre-concentration and CuHCF filter methods are compared and discussed in this section. The method to determine activity concentration of $^{137}$Cs in seawater samples using AMP pre-concentration method passed the proficiency test exercise, “IAEA proficiency test exercise on Marine benchmark study on the possible impact of the Fukushima radioactive releases in the Asia-Pacific Region for Caesium Determination in Sea Water (RCA RAS/7/021)”, for accuracy, precision and trueness criteria with -1.00 % bias [2]. The same method was applied to determine $^{137}$Cs in seawater in this analysis and result is shown in table 1. It obtained 0.026 mBq L$^{-1}$ of the detection limit. The result of three samples was precise with 2.55 % relative standard deviation (RSD).

| Table 1. AMP pre-concentration method result. |
|-----------------------------------------------|
| Sample volume (L) | Sample | Activity (mBq L$^{-1}$) |
|-------------------|--------|------------------------|
| 200               | sample 1 | 0.782±0.059          |
|                   | sample 2 | 0.748±0.058          |
|                   | sample 3 | 0.749±0.059          |
|                   | average | 0.760±0.059          |

For the CuHCF filter method, the parallel results with various amounts of seawater volume i.e. 200 L, 300 L and 600 L are presented in table 2. The detection limits of $^{137}$Cs activity were 0.016 mBq L$^{-1}$, 0.010 mBq L$^{-1}$ and 0.005 mBq L$^{-1}$ for sample volumes 200 L, 300 L and 600 L respectively.
Table 2. CuHCF filter method results.

| Sample volume (L) | Sample | Efficiency of Cs collection | Activity (mBq L⁻¹) |
|-------------------|--------|-----------------------------|-------------------|
| 200               | sample 1 | 79.05                       | 0.837±0.080       |
|                   | sample 2 | 52.08                       | 0.698±0.101       |
|                   | average  | 65.57                       | 0.768±0.091       |
| 300               | sample 1 | 57.58                       | 0.901±0.077       |
|                   | sample 2 | 89.86                       | 0.831±0.060       |
|                   | average  | 73.72                       | 0.866±0.069       |
| 600               | sample 1 | 68.33                       | 0.889±0.057       |
|                   | sample 2 | 74.31                       | 0.762±0.050       |
|                   | average  | 71.32                       | 0.826±0.079       |

The Cs collection efficiencies of each repeated sample were not stable. This can be effected by combined sources i.e. unequal quality of prepared CuHCF filters (different amount of ion exchanger onto cotton wound in each cartridge), some loss of CuHCF and unstable flowrate of seawater during filtration [1]. However the repeated samples with the different Cs collection efficiencies gave quite similar ¹³⁷Cs activity concentration. Their repeated activity concentrations had 12.80 %, 5.72 % and 10.87 % RSD for 200 L, 300 L and 600 L respectively. The RSD of the three results were quite high as expected due to the low-level activity concentration and only two repeated samples used.

The average activity concentrations were close together i.e. 0.768 mBq L⁻¹, 0.866 mBq L⁻¹ and 0.826 mBq L⁻¹ which were 0 %, + 12.76 % and + 7.55 % bias for 200 L, 300 L and 600 L respectively as referred to the AMP pre-concentration method result from the PT exercise [2]. Even the minimum and maximum activity concentrations i.e. 0.698 mBq L⁻¹ for sample 2 200L and 0.901 mBq L⁻¹ for sample 1 300L, obtained bias in the range of – 9.16 % to + 18.55 %. It can be therefore concluded this method gave the accepted result as the PT exercise judged ± 20 % bias for ¹³⁷Cs determination was accepted for accuracy. This also means that the minimum 200 L seawater would be adequate to perform the CuHCF filter method and therefore 300 L and 600 L seawater is not necessary. However it should be noted that the CuHCF filter method gave higher bias than those of AMP pre-concentration method due to the unstable filter quality and flowrate during filtration.

4. Conclusion

The simple method to determine ¹³⁷Cs in seawater based on CuHCF scavenger was compared with the classical AMP pre-concentration method. The developed CuHCF filter method gave accepted results as the ¹³⁷Cs activity concentration in seawater samples obtained % bias within the range of ± 20 i.e. - 9.16 to + 18.55 when compared with the AMP method as referred to the IAEA proficiency test exercise RCA RAS/7/021. In addition, it was found the minimum 200 L seawater can be adequate to perform the CuHCF filter method as well as higher volumes i.e. 300 L and 600 L. This means the method can be easily and shortly performed at sampling fields within an hour when using 200 L sample with flowrate of 240 L hr⁻¹. However some concern in the CuHCF method was found surrounding the quality of unstable prepared CuHCF filters since the repeated samples had significantly different Cs collection efficiencies. Also the different Cs collection efficiency could be improved by constantly regulating and controlling flowrate during filtration. Perhaps this method can be optimised to obtain higher accuracy and Cs collection efficiency by improving quality of prepared CuHCF filters and lowering the flowrate during filtration.
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