



# Verification of $^{137}\text{Cs}$ determination in seawater using Cu-hexacyanoferrates filters

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## 1. Introduction

Office of Atoms for Peace, Radiation monitoring group has carried out radiation monitoring program in Thailand for establishment of radiation baseline information and assessment of the radiological impact on the environment in case of any incidents. Cs-137 is one of the fission products which has a long half life of 30 years. It can be released from nuclear accident, nuclear waste discharge and atomic boom test to atmosphere and through ocean. Therefore it is one of our monitored radionuclides in environmental samples especially in seawater. Routinely the traditional AMP pre-concentration technique was used, however this technique which involves chemical separation, is laborious and time-consuming. A rapid method to determine  $^{137}\text{Cs}$  in seawater using Cu-hexacyanoferrates (CuHCF) ion exchanger has been therefore developed and verified for purpose of both routine and emergency environmental radiation monitoring. The CuHCF supported cotton-wound cartridge filters were prepared and used to absorb  $^{137}\text{Cs}$  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 result showed acceptable accuracy with bias below  $\pm 25\%$ , in the range from - 24.63% to + 3.29%. This developed method would be a better choice for  $^{137}\text{Cs}$  determination in seawater, since it is cost-efficient and less time consuming. In addition it can be easily performed in sampling fields

## 2. Experimental

### 2.1 CuHCF filter preparation



1- $\mu\text{m}$  cotton-wound cartridge filters having stainless steel core



Filter soaked  $\text{K}_4[\text{Fe}(\text{CN})_6]$  solution



Filter soaked  $\text{Cu}(\text{NO}_3)_2$  solution



Prepared CuHCF filters

### 2.2 Spiked sea water preparation

The synthetic sea water samples were prepared using the synthetic sea salt dissolved in tap water at 35 ppt. The samples were spiked with the known activity solution of  $^{137}\text{Cs}$  to obtain concentration of  $0.191 \pm 0.002$  Bq/L.

- Two 200 L spiked seawater samples
- Two 300 L spiked seawater samples
- Two 400 L spiked seawater samples

### 2.3 CuHCF filter method



Filter set



Ashed filter samples



Ashed samples in Calibrated containers

- The  $\text{CuFeCN}_6$  cartridges set was fabricated : pump > cotton cartridge > first  $\text{CuFeCN}_6$  filter (A) > second  $\text{CuFeCN}_6$  filter (B) > flow meter > outlet tube.
- The seawater samples were pumped through the cartridges with flow rate at 240 L/hr.
- The cartridges samples were ashed at  $400^\circ\text{C}$  for 15 hr and transferred to calibrated containers

### 2.4 Calibration source preparation for CuHCF filter method

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

### 2.5 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 ashed samples in calibrated containers were measured with the same gamma spectrometry system.

## 3. Results

The validation results of CuHCF filters method

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

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

$$E = \frac{[F] - [B]}{[F]}$$

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

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

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

When A is the final  $^{137}\text{Cs}$  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 1) difference in quality of prepared CuHCF filters and 2) unstable flowrate of seawater pass through the filters. However the collection efficiency in a range of 48.09 - 94.82% with flowrate at 240 L/hr agreed well with Yii's work and Ross.

For accuracy aspect, the repeated samples resulted various accuracy in a range from - 24.63% to + 3.29%. The negative bias presented the loss of caesium especially sample 2 200L with 48.09 % collection efficiency and -24.63 % bias. Unabsorbed radiocaesium on the filters could be explained with a combination of 1) low quality of prepared CuHCF filters and 2) 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 lost of CuHCF from the first cartridge and trapped on the second during filtering. This was possibly poor rinse of prepared cartridge with DI water before drying.

In conclusion the technique even using minimum 200 L samples was proved to be accepted with bias range below  $\pm 25\%$ . However its accuracy can be improved by enhancing quality of prepared CuHCF filters and lowering the flowrate.

## 4. Conclusion

- The developed  $\text{CuFeCN}_6$  filter technique gave acceptable results with bias range below  $\pm 25\%$  i.e. in the range from - 24.63% to + 3.29%.
- The minimum 200 L seawater samples can be adequate to perform the  $\text{CuFeCN}_6$  filter technique.
- The  $\text{CuFeCN}_6$  filter technique should be concerned about quality of unstable prepared  $\text{CuFeCN}_6$  cartridges since the repeated samples had significantly different Cs collection efficiencies.
- The  $\text{CuFeCN}_6$  filter technique could be optimised its accuracy with analysis time, depending upon situations such as routine monitoring and emergency accident.
- The  $\text{CuFeCN}_6$  filter technique was convenient, more cost efficient and less time consuming.