# Study on the <sup>3</sup>H and <sup>14</sup>C Determination for the Environmental Sediment Samples with Combustion Method

Hae-Ri Kim<sup>a,b</sup>, Da-Young Kam<sup>a</sup>, Hye-Hyun Kim<sup>a</sup>, Jong-Myoung Lim<sup>a\*</sup>

<sup>a</sup> Environmental Radioactivity Assessment Team, Korea Atomic Energy Research Institute, 111, Daedeok-daero

989beon-gil, Yuseoung-gu, Daejeon, 34057, Republic of Korea

<sup>b</sup> Department of Environmental Engineering, Chung-Nam National University

\*Corresponding author: jmlim@kaeri.re.kr

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### 1. Introduction

The tritium and radiocarbon, which are pure bemitters with low energy (<sup>3</sup>H: Emax = 18.6 keV; <sup>14</sup>C: Emax = 156.5 keV), are major radionuclides which generate from near nuclear sites. Tritium and radiocarbon contamination in marine sediments near nuclear power plants can result from the release of radioactive materials through cooling water, wastewater, or gases. Marine sediments act as long-term reservoirs for these radionuclides, making them critical indicators of historical and ongoing nuclear activity impacts. These substances can accumulate in sediments, affecting ecosystems and increasing radiation risks to the environment and humans. The regular monitoring of tritium and radiocarbon in marine sediment samples is essential for understanding environmental changes, dating sediment layers, and assessing the impact of nuclear activities [1]. These isotopes serve as tracers for studying oceanic processes, carbon cycling, and the long-term effects of radioactive contamination on marine ecosystems. This study aims to establish analytical methods for tritium, including organically bound tritium (OBT), and radiocarbon in marine sediments. The established procedures and methods were applied to analyze tritium and radiocarbon in marine sediment samples collected from sites near nuclear power plants.

# 2. Methods and Results

# 2.1 Overview of analytical method

Fig. 1. presents the process for analyzing tritium (HTO) and organically bound tritium (OBT). A fresh sample undergoes combustion to measure overall tritium, followed by dehydration to extract free water for TFWT measurement. The dry matter is combusted to measure OBT. This systematic approach ensures a detailed analysis of the various forms of tritium present in the sample.

<sup>14</sup>C is a beta-emitting radionuclide with a half-life of 5730 years, naturally present at 0.2 Bq/g-C in living organisms. Its concentration peaked in the 1960s due to nuclear testing but has since returned to natural levels. <sup>14</sup>C analysis uses liquid scintillation counting for

environmental monitoring or accelerator mass spectrometry (AMS) for precise dating. Both methods require carbon extraction, often using combustion, and can be conducted alongside OBT analysis with different absorbents. The environmental sample is combusted to produce  $CO_2$ , which is absorbed into a 1 M NaOH solution. The resulting solution is then concentrated by forming CaCO<sub>3</sub> precipitates, which are subsequently dissolved to prepare the final measurement sample.



Fig. 1. Systematic approach of tritium analysis

### 2.2 Sample combustion

The dried sediment samples (about 10 g) were combusted in a purpose-designed tubular hightemperature furnace which consists of six quartz tubes. The combusting temperature can be controlled at 900°C. The quartz boats containing about dried sediment sample were loaded in the combusting zone of six quartz tubes, separately.

The 0.5 % platinum catalyst (Pt-Al<sub>2</sub>O<sub>3</sub>) which was held at 800 °C before sample combustion were used in the catalyst zone to accelerate oxidation of hydrogen and carbon compound to water and CO<sub>2</sub> respectively. Furthermore, to increase the oxidation of flue gas, a pure oxygen gas was introduced at 450 °C of the sample combustion temperature. The <sup>3</sup>H and <sup>14</sup>C were trapped in 10 mL of 0.01 M HNO<sub>3</sub> and in 20 mL of 1.5 M NaOH, respectively. The trapping efficiency of <sup>3</sup>H in first diluted nitric acid is typically over than approximately 95%, and <sup>14</sup>C co-trapping is also prevented effectively [2].

### 2.3 Radioactivity determination

The 8 or 10 mL of solutions containing trapped radionuclides were transferred into 20 mL polyethylene vials with scintillation cocktail. For scintillation of <sup>3</sup>H and <sup>14</sup>C in LSC, 12 mL of GoldStar<sup>TM</sup> and Permaflour (Perkin Elmer) were mixed with the sample, respectively. The measurement of the radioactivity was carried out in LSC (Quantulus 1220, Perkin Elmer). A low (5-200 keV) or high (70-500 keV) energy beta nuclides window was used for the measurement of <sup>3</sup>H and <sup>14</sup>C, respectively. All of the samples and blanks were kept in LSC for 24 h to eliminate chemiluminescence effect and measured for 60 min and ten cycles, and their averages and standard deviations were calculated. The counting efficiency corresponding quenching level [SQP(E)] measured by external source for <sup>3</sup>H and <sup>14</sup>C were presented in Fig. 2. As show in Fig. 2, the counting efficiency for <sup>3</sup>H ranged from 18 to 25 % while those for  $^{14}$ C ranged from 49 to 82 %.



Fig. 2. The counting efficiency calibration curve for  ${}^{3}H$  and  ${}^{14}C$  of liquid scintillation counter

#### 2.3 Extraction and recovery rate

To evaluate the recovery ratio of the combustion and LSC counting method across different radioactivity ranges, radioactive standard solutions were spiked into blank sea sand samples. The relative deviations between measured and spiked activities ranged from -14.3% to 4.0% for <sup>3</sup>H and from -10.7% to 0.3% for <sup>14</sup>C.



Fig. 3. The recovery rate of <sup>3</sup>H and <sup>14</sup>C with combustion and LSC counting method (n=15).

The validity of the <sup>14</sup>C measurement method, which involves extraction, precipitation, and re-desorption, was assessed using NIST SRM 4990C (Oxalic acid). The certified value of NIST SRM 4990C is 0.307 Bq/g-C, and the analysis yielded 0.289  $\pm$  0.012 Bq/g-C, with a relative error of 5.9% and a relative standard deviation of 4.3%, confirming the method's validity.

The minimum detectable activity (MDA) was also evaluated by the background counting statistics within a confidence interval of 95 % on the basis of Currie's definition. For tritium (<sup>3</sup>H) analysis using liquid scintillation counting (LSC), under a measurement condition of 600 minutes, the minimum detectable activity (MDA) for OBT is approximately 0.5 Bq/kgfresh. This is based on combusting about 8 g of dried sample, as shown in Fig. 3. For samples requiring a lower MDA, the analysis can be improved by increasing the amount of combusted sample, modifying the setup, or performing repeated combustion to enhance preprocessing conditions.



Fig. 3. The required sample amount and counting conditions for the determination of  ${}^{3}$ H by LSC

# **3.** Conclusions

This study developed and validated methods for analyzing tritium (<sup>3</sup>H) and radiocarbon (<sup>14</sup>C) in marine sediments. A systematic process, including drying, combustion, and dehydration, was established to measure HTO, OBT, and 14C. Recovery rates ranged from -14.3% to 4.0% for <sup>3</sup>H and -10.7% to 0.3% for 14C. Radiocarbon analysis was validated using NIST SRM 4990C, with a relative error of 5.9%. The minimum detectable activity (MDA) for OBT was approximately 0.5 Bq/kg-fresh, with potential for further improvement.

# REFERENCES

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