Analytical Methods for Volatile Radionuclides in Radioactive Waste: High-Temperature thermal decomposition and Wet Digestion Approaches

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1. Introduction

The management strategy for decommissioning waste from nuclear facilities depends on radionuclide concentrations, therefore accurate quantification is essential. Among radionuclides, ^{3}H (E_{max}=18.6 keV, $T_{1/2}$=12.32 yr), ^{14}C (E_{max}=156.5 keV, $T_{1/2}$ = 5730 yr), and ^{129}I (E_{max}=194 keV, $T_{1/2}=1.57\times10^{7}$ yr) are representative volatile radionuclides. Because of their high mobility, diffusion potential, and management challenges during decommissioning, these radionuclides are of particular concern. The Korea Radioactive Waste Agency (KORAD) explicitly requires the determination of the concentrations of ^{3}H, ^{14}C, and ^{129}I as part of its acceptance procedure for decommissioning waste [1].

To analyze such volatile radionuclides, several techniques are commonly employed, including the combustion bomb, wet oxidation using a Teflon bomb, and high-temperature thermal decomposition. For the combustion bomb method, samples are oxidized under high temperature and pressure to extract water and carbon dioxide. The wet oxidation method uses the sulfuric acid to decomposes samples under nitrogen flow, thereby releasing water and carbon dioxide. The high-temperature combustion method involves injecting air or oxygen at temperatures above 600 °C to achieve complete combustion and to totally extract water, carbon dioxide, and iodine.

In this study we focused on optimizing the wet oxidation and high-temperature thermal decomposition methods for different waste sample matrices to separate the target radionuclides (e.g., ^{3}H, ^{14}C, and ^{129}I). In order to evaluate the analytical accuracy, the recovery yields for the spiked standard sources were calculated. Finally, based on the results for the various waste sample matrix, the optimal analytical methods were established.

2. Methods and Results

Concrete, sludge, metals, spent resins, concentrated liquid waste, plastics, rubber, and paper are representative types of radioactive waste generated during the operation or decommissioning. However, wastes such as plastics, rubber, and paper are composed of polymeric and combustible materials, which makes high-temperature incineration challenging. Therefore, non-combustible wastes are treated by high-temperature incineration, whereas combustible wastes are processed by wet oxidation.

2.1 High-temperature thermal decomposition

Experiments were performed using a Mini-Tube furnace (Figure. 1). The 0.5 % platinum catalyst (Pt-Al_2O_3) were used as the catalyst materials to accelerate oxidation of hydrogen and carbon compounds to water and CO_2 respectively. ^{3}H and ^{129}I were simultaneously trapped in an absorption solution consisting of 0.01 M HNO_3 with 0.01 M $NaHSO_3$ (20 mL), while ^{14}C was selectively collected in a downstream Cabosorb (Perkin Elmer) (20 mL). From the trapped solutions, 8 mL aliquots for ^{3}H and ^{129}I were mixed with 12 mL of Ultima Gold LLT, and 10 mL aliquots for ^{14}C were mixed with 10 mL of Permaflour (Perkin Elmer) [2]. Each mixture was subsequently measured by LSC for 20 minutes in triplicate.

Fig. 1. Thermal decomposition method with Mini-Tube furnace.

A preliminary experiment was conducted for the spiking sea sand samples with ^{3}H, ^{14}C, and ^{129}I standard sources on the sea sand, and radioactive concentrations were evaluated with measured counts by liquid scintillation counting (LSC). The results showed that the activities measured by LSC were consistently recovered at high yields compared to the spiked activities, with values of 105.1 ± 4.2% for ^{3}H, 98.0 ± 1.9% for ^{14}C, and 83.7 ± 4.0% for ^{129}I. Notably, when the flow rate was set at 30 mL/min, a recovery yield of 58.11 ± 11.69% was observed. Increasing the flow rate to 60 mL/min or higher effectively mitigated the issue of the previously low and highly variable recovery yields.

Subsequently, waste samples (soil 5 g, concrete 5 g, sludge 3 g, concentrated liquid waste 3 g, metal 1 g, and

resin 1 g) were spiked in the same manner and analyzed under the temperature profile shown in Figure 2. Air was introduced into the quartz tube up to 450 °C, after which O_2 gas was supplied at a flow rate of 60 cc/min.

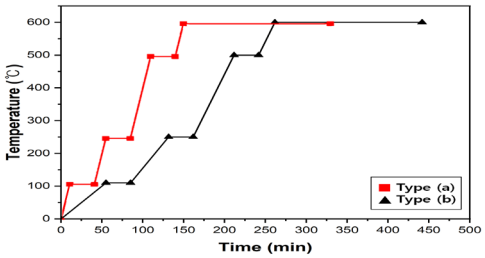

Fig. 2. Temperature profiles of the high-temperature combustion furnace: (a) soil, concrete, sludge, and metal; (b) resin and concentrated liquid waste

2.2 Wet oxidation

Experiments were performed using a custom-designed 3-neck flask digestor with 30% H_2SO_4 (Figure. 3). Combustible wastes (plastic, rubber, and paper) were each sampled at approximately 2 g, spiked with standard sources, and sealed in a closed vessel connected to the absorption solutions. For ^{3}H collection, 10 mL of 0.01 M HNO_3 was placed in the front trap, and for ^{14}C, 20 mL of Cabosorb was positioned in the rear trap [3]. Subsequently, 30% H_2SO_4 was injected into the sealed vessel via syringe, followed by continuous purging with N_2 gas while heating at 170 °C for 2 hours. After the reaction was completed, the trapped solutions were analyzed by liquid scintillation counting (LSC) using the same procedure as applied in the high-temperature thermal decomposition method.

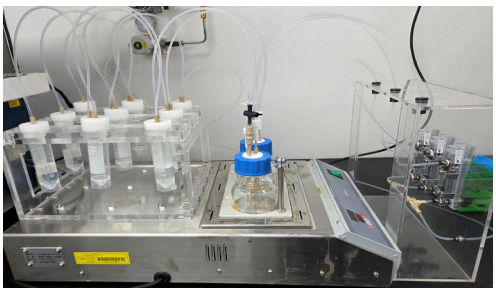

Fig. 3. Wet oxidation method with 3-neck flask digestor.

2.3 Analytical accuracy for the volatile radionuclides

When analyzing the ^{3}H absorption solution obtained from the high-temperature thermal decomposition method, ^{129}I was measured using ICP-MS in order to avoid spectral interference between ^{3}H and ^{129}I. Alternatively, the ROI of ^{3}H and ^{129}I in the LSC spectrum could be distinguished with a cutoff at channel 180. Accordingly, counting efficiencies were adjusted for each radionuclide's ROI. The recovery yields obtained under these conditions are presented in Table 1.

As shown in Table 1, application of high-temperature thermal decomposition and wet oxidation methods demonstrated that the recovery yields of ^{3}H and ^{14}C in all waste samples ranged from 94.1% to 110.4% and from 94.5% to 104.9%, respectively, indicating high recovery performance. For ^{129}I, the maximum recovery yield was 87.7%, and further optimization of parameters such as flow rate and residence time at elevated temperature is necessary to improve the recovery. In addition, the minimum detectable activity (MDA) of ^{3}H, ^{14}C, and ^{129}I ranged from 0.032 to 0.158 Bq/g, from 0.012 to 0.060 Bq/g, and from 0.007 to 0.034 Bq/g, respectively,

Table 1.Analytical results of volatile radionuclides for the wastes samples.

Recovery rate (Mean ± SD %)			
Sample	**^{3}H**	**^{14}C**	**^{129}I**
Soil	107.3±5.9	100.1±1.6	87.7±5.2
Concrete	101.1±2.1	95.1±3.4	85.1±4.4
Sludge	101.4±5.9	104.9±1.6	84.8±5.8
Metal	96.1±6.6	100.3±1.6	82.5±3.1
Resin	94.1±4.8	104.4±7.4	80.2±3.3
liquid waste	101.1±2.2	100.2±3.4	81.1±6.4
Plastic	98.9±1.7	98.4±0.1	-
Glove	98.6±2.2	98±1.6	-
Paper	110.4±5.9	94.5±7.4	-
MDA (Bq/g)	**0.032-0.158**	**0.012-0.060**	**0.007-0.034**

3. Conclusions

When high-temperature thermal decomposition and wet oxidation method were applied, high recovery yields were observed for ^{3}H and ^{14}C across the all types of waste samples. However, the analytical accuracy of ^{129}I was relatively lower than those of ^{3}H and ^{14}C. Although some adjustments are required in the measurement and pretreatment processes, applying both methods to analyze volatile nuclides in radioactive waste achieve an analytical accuracy of over 95% for ^{3}H and ^{14}C, and over 80% for ^{129}I. Therefore, the analytical method for volatile nuclides established in this study is expected to be used as an efficient analytical method for the treatment of radioactive waste generated during decommissioning and operation in the future.

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