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Application of a wet oxidation method for the quantification of ^{3}H and ^{14}C in low-level radwastes

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HIGHLIGHTS

- The wet oxidation method was developed and verified with various radioactive standards.
- The sources were HTO, $^{14}CH_3OH$, $^{14}CH_3(CH_2)_{10}COOH$, $NaH^{14}CO_3$, and $C_6H_5{}^{14}CH_3$.
- The chemical yield of ^{14}C and ^{3}H were 82–97 % and 98%, respectively.
- The wet oxidation method will be applied to RI solid waste for clearance.

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ABSTRACT

Wet oxidation methods are utilized to separate and quantify ^{3}H and ^{14}C radionuclides in inorganic and organic radwastes generated at nuclear facilities. Because ^{3}H and ^{14}C are pure beta emitters with half-lives of 12.3 and 5,730 years, respectively, these radionuclides should be chemically separated from other radionuclides present in radwastes for accurate quantification. In particular, a collection technique for ^{14}C radionuclide in radwastes is needed because it is converted into $^{14}CO_2$ gas by an oxidation reaction.

To confirm the recoveries of ^{3}H and ^{14}C, various standard radioactive sources were used to verify the proposed method. Because the majority of ^{3}H radionuclides are distributed in tritiated water (HTO), only tritiated water was used as a standard for ^{3}H radionuclides. Additionally, ^{14}C-labeled methanol ($^{14}CH_3OH$), lauric acid ($^{14}CH_3(CH_2)_{10}COOH$), sodium bicarbonate ($NaH^{14}CO_3$), and toluene ($C_6H_5{}^{14}CH_3$) were used as ^{14}C standards. The compounds were oxidized with chemical oxidants and then separated. The individual species were mixed with a scintillation cocktail and counted using a liquid scintillation counter. The recoveries of ^{14}C and ^{3}H were 82–97% and 98%, respectively. The wet oxidation method will be applied to RI wastes for clearance.

1. Introduction

Radwastes generated in Korea can be divided into two types: RI (radioisotope) waste, which is generated in educational settings, medical institutes, and various industries, and LILWs (low- and intermediate-level radioactive wastes), which are generated during the operation and decommissioning of nuclear power plants. In Korea, the generation of RI waste from educational and medical institutes and industries has increased by approximately 10% every year. In July, 2007, open radiation sources of RI waste generated from these institutes and industries totaled 5,065 drums (each containing 200 l of waste). However, the number of drums has decreased in the past several years due to clearance, and approximately 4,000 drums have been stored temporarily. The clearance of radwastes in Korea is regulated by Nuclear Safety and Security Commission (NSSC) Notice No. 2012-59, which specifies the regulated radionuclides and concentration limits (a total of 100 Bq/g) in radwaste packages (). Nevertheless, the clearance of radwastes is not governed only by domestic regulations but also by International Atomic Energy Agency (IAEA) recommendations for clearance (IAEA, 1996; IAEA, 2004), including regulatory limits for each radionuclide, that are stricter than domestic regulations for clearance. According to IAEA recommendations, the Korea Institute of Nuclear Safety (KINS) requests the results of radionuclide inventories for the clearance of RI wastes, which include several beta- and gamma-emitting radionuclides with a short half-life. In particular, since ^{3}H and ^{14}C in the RI waste drums, which have long half-lives of 12.3 y and 5,730 y, constitute 43.2% and 46.5%, respectively, a suitable analytical method for radionuclides should be developed in accordance with the IAEA recommendations for clearance, which state that the contents of ^{3}H and ^{14}C in RI wastes should be less than 100 and 1 Bq/g, respectively.

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In the present study, radiochemical methods for the separation and quantification of ^{3}H and ^{14}C radionuclides from RI wastes were reviewed and tested to investigate the distribution of radionuclide inventories in Korean RI wastes. Thus, a wet oxidation technique was developed as a separation method for radionuclides and then tested using various standard radioactive sources to confirm the application feasibility to the chemical separation method. In Additional, the minimum detectable activities of the radionuclides were determined to evaluate whether the method meets the IAEA recommendations.

2. Experimental

2.1. Radiochemical analysis of ^{3}H and ^{14}C radionuclides

To apply the wet oxidation method, 5 g of $K_2S_2O_8$ and 0.5 g of $AgNO_3$ as primary oxidants were added to a 200 mL round-bottomed flask, which was quickly connected to a distillation apparatus. Then, about 1 mL ^{3}H and ^{14}C standards were added into the flask. Using a dropping funnel, approximately 20 mL of 16 wt% H_2SO_4 was added into the flask at a rate of 0.5 mL/min. After the additions of the acid, the temperature of the reactor was slowly increased to 96 °C and held at that temperature for 3 h (Park et al., 2006; Hornibrook, 1995; Balonov et al., 2004; Caron and Benz, 2002; Magnusson, 2002; Ahn et al., 2011). Two types of oxidants were used in the oxidation reaction. Specifically, potassium persulfate, a strong oxidant, reacts with organic compounds according to the following equations:

$$K_2S_2O_8 \xrightarrow{H_2O} 2K^+ + S_2O_8^{2-} \quad (1)$$

$$S_2O_8^{2-} + 2H_2O \xrightarrow[Ag]{} 2SO_4^{2-} + 2H^+ + 2OH^* \quad (2)$$

$$^{14}C_nH_m + (4n+m)OH^* \rightarrow n^{14}CO_2 + (2n+m)H_2O \quad (3)$$

Reactions (1)–(3) represent the mechanism of the decomposition of ^{14}C-labeled organic compounds by OH* radicals. In addition, sulfuric acid, which was used as a supporting oxidant, reacts with organic materials to produce $^{14}CO_2$ as presented in Reactions (4) and (5)

$$^{14}C_nH_m + \frac{n}{2}H_2SO_4 \rightarrow nH_2O + \frac{n}{2}SO_2 + m^{14}C \quad (4)$$

$$^{14}C + 2H_2SO_4 \rightarrow 2H_2O + 2SO_2 + {}^{14}CO_2 \quad (5)$$

After the sample was oxidized according to Reactions (1)–(5), the evolved $^{14}CO_2$ in N_2 gases were trapped in 10 mL of Carbo-Sorb E and 10 ml of Permaflour E+. Permaflour E+ as a cocktail was added to the carbo-sorb E solution to increase the volume of trapping solution of $^{14}CO_2$. Although the cocktail should be added to ^{14}C extracts before radiation counting after chemical separations, the cocktail was added before the chemical separations because it was not affected for counting efficiencies. The principal ingredient of Carbo-Sorb E contains an amine group, and carbon dioxide readily reacts with compounds containing amines. The absorption reaction of carbon dioxide can be described as follows:

$$^{14}CO_2 + RNH_2 \rightarrow RNH_2^{+}{}^{14}COO^- \quad (6)$$

$$RNH_2^{+}{}^{14}COO^- + \begin{bmatrix} RNH_2 \rightarrow RNH^{14}COO^- + RNH_3^+ \\ H_2O \rightarrow RNH^{14}COO^- + H_3O^+ \\ OH^- \rightarrow RNH^{14}COO^- + H_2O \end{bmatrix} \quad (7)$$

$$RNH^{14}COO^- + H_2O \rightarrow RNH_2 + H^{14}CO_3^- \quad (8)$$

As shown in Eq. (6), the Carbo-Sorb E solution contains an amine and reacts with ^{14}C-labeled carbon dioxide to form a zwitterion, which reacts with H_2O to form a stable carbonate compound, as indicated in Reaction (8). Approximately 6–8 mL of distillate was distilled in a condenser after 3 h of refluxing, and 5 ml of the distillate was mixed with only 14 mL Ultima gold LLT scintillation agent which the volume has a good efficiency for radiation counting. Total volume for ^{3}H was 19 mL. The ^{3}H and ^{14}C extract solutions were allowed to stand for at least 24 h in a dark room to reduce interference with radiation counting. The radioactivities of ^{3}H and ^{14}C radionuclides were counted directly with a liquid scintillation analyzer (Packard, 2500 TR/AB, Alpha and Beta Liquid Scintillation Analyzer). The apparatus for the separation of ^{3}H and ^{14}C is shown in Fig. 1.

2.2. Verification of analytical method using standard radioactive sources

To confirm the reliability and the effectiveness of the wet oxidation method, various standard radioactive sources were subjected to the same oxidation procedure. Because ^{3}H is primarily distributed in tritiated water (HTO, Eckert & Ziegler), only tritiated water was used as a standard for ^{3}H radionuclides. To verify the reliability and the efficiency of ^{14}C separation, ^{14}C-labeled methanol ($^{14}CH_3OH$, Perkin-Elmer), lauric acid ($^{14}CH_3(CH_2)_{10}COOH$, Sigma), sodium bicarbonate ($NaH^{14}CO_3$, Eckert & Ziegler), and toluene ($C_6H_5{}^{14}CH_3$, Sigma) were used as ^{14}C standards in the wet oxidation method.

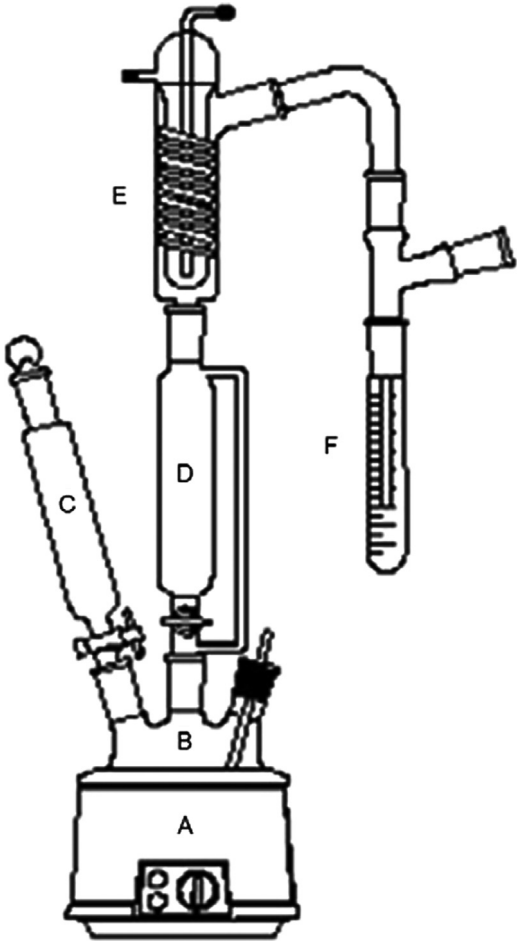

Fig. 1. Apparatus for the wet oxidation method to separate ^{3}H and ^{14}C radiochemically; A—heating mantle, B—200 ml round-flask with 3 tubes, C—H_2SO_4 feeding funnel, D—HTO receiver, E—reflux condenser and F—^{14}C trapping solution, mixture of 10 ml of Carbo-Sorb and 10 ml of Permafluor.