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Combustion/absorption process for the separation of ^{14}C and ^{3}H in radwastes released from nuclear power plants and their analysis

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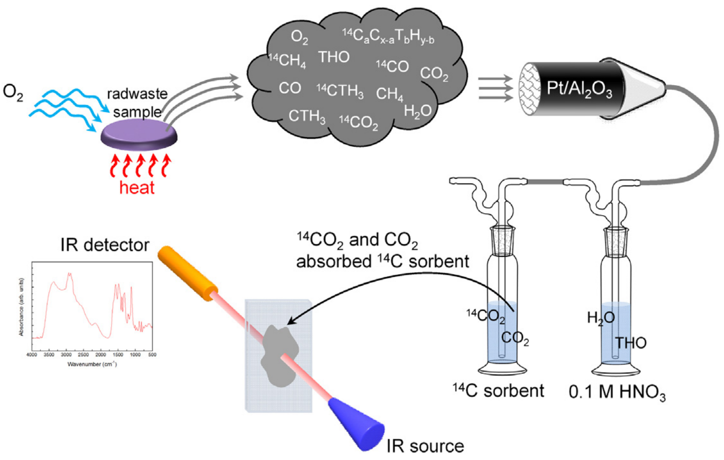
HIGHLIGHTS

- $^{14}CO_2$ and THO were produced by the combustion of radwaste samples.
- The radioactivity of $^{14}CO_2$ and THO absorbed sorbents were measured by LSC.
- The CO_2 absorption in the ^{14}C sorbent was analyzed using by FT-IR and a rheometer.
- The temperature and viscosity of the CO_2 absorbed ^{14}C sorbent was investigated.

GRAPHICAL ABSTRACT



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ABSTRACT

Radioactivities of ^{3}H and ^{14}C in spent radioactive ion exchange resins and spent radioactive lubricant oils released from nuclear power plants, has been determined using a combustion and sorption method (combustion method). The liquid scintillation counting (LSC) spectra showed that the interference of other radionuclides has not significantly affected the determination of radioactivities of ^{3}H and ^{14}C in the radwaste samples. The chemical structure of $^{14}CO_2$, which originated from the combustion of radwastes, trapped ^{14}C sorbent has been investigated using Fourier transform infrared spectroscopy (FT-IR). FT-IR study showed interesting results that peaks for uncoupled CO_2 and carbonic amide appeared at FT-IR spectra of CO_2 high-absorbed ^{14}C sorbents, while the peak for carbamate was only observed at the spectra of CO_2 low-absorbed sorbents. During the CO_2 sorption in ^{14}C sorbent, temperature and viscosity of the sorbent increased owing to decrease of enthalpy and increase of apparent molecular weight of the sorbent caused by the bonding formation between sorbent molecules.

1. Introduction

Radwastes containing ^{14}C and ^{3}H (tritium) are released from nuclear power plants during their normal operation or decommissioning. ^{14}C (E_{max}: 156 keV) and ^{3}H (E_{max}: 18.6 keV) are pure beta

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emitters. ^3H is produced in the reactor core mainly by ternary fission, and generated in the coolant by neutron capture in deuterium. ^{14}C is built up in the reactor owing to three neutron reactions: (n,p)-reactions with ^{14}N, (n,α)-reactions with ^{17}O, and (n,γ)-reactions with ^{13}C [1,2]. Their binding affinity toward molecules of the biological cell can cause mutation of the cell and/or death of the cell by their inhalation or ingestion as forms of HT, HTO, organically bound tritium (OBT), $^{14}CO_2$, etc. Inhaled or ingested ^3H and ^{14}C may accumulate in the body, and be incorporated into molecules of tissues, respectively [3]. Therefore, the clearance of radwastes containing ^3H and/or ^{14}C has been rigorously regulated not only by Nuclear Safety and Security Commission (NSSC) [4] but also by International Atomic Energy Agency (IAEA) [5] recommendations for clearance in Korea.

The combustion is a widely used technique to analyze samples precisely [6,7]. The combustion method for the analysis has been also applied to determine the radioactivities of ^3H and ^{14}C in the samples [8]. The method (also called the dry oxidation method) and the solubilization method are most widely used to determine the radioactivities of ^3H and ^{14}C in the samples. In comparison with the solubilization method, the combustion method has advantages of rapid analysis, analysis of various samples, dual (^3H and ^{14}C) analysis, excellent radioactive recovery (>97%), no loss of radioactivity by volatilization, no chemiluminescence interference, no color quench interference, etc [9]. To determine the radioactivities of ^3H and ^{14}C in the samples, the liberated decomposition products are fully oxidized with a catalyst (Pt-alumina) following the combustion of samples to ensure that ^3H and ^{14}C are present only as HTO and $^{14}CO_2$ which can be subsequently trapped using dilute acid solutions and ^{14}C sorbents respectively.

Sodium hydroxide [10] ethanolamine [11] and Carbo-Sorb® E [12] are commonly used as CO_2 trapping reagents. There are no absolutes to select the trapping agent. However, there will be the occasion when more than one trapping agent will be both suitable and available. In this case, the agent should be selected considering chemical/color quenching after mixing with LSC cocktail and CO_2 capacity. If the universal CO_2 trapping reagent is developed which reduces the quenching effects and improves its solubility in LSC cocktail dramatically, the reagent will be selected without hesitation. The beginning of the development of the universal CO_2 trapping reagent is understanding of the CO_2 trapping mechanism in the reagent and physical properties of the CO_2 trapped reagent.

In this study, the separation of ^3H and ^{14}C in spent radioactive lubricant oils and spent radioactive ion exchange resins was carried by using a combustion method to analyze the nuclides in the samples which are produced in Korea nuclear power plants. The resins and the oils originate from purification systems and pumps, respectively [13]. To determine radioactivities of ^3H and ^{14}C in samples, produced HTO and $^{14}CO_2$ during the combustion of samples were trapped in the dilute HNO_3 solution and the $^{14}CO_2$ sorbent (Carbo-Sorb® E), respectively. Each nuclide trapped sorbent was respectively mixed with LSC cocktail to determine the radioactivity concentration of ^3H and ^{14}C in the samples by using a liquid scintillation counter. Our combustion method to determine the radioactivities of ^3H and ^{14}C in radwaste samples is based on the Warwick group's method [14]. To investigate the reaction mechanism of CO_2 and ^{14}C sorbent, various amount of CO_2 trapped ^{14}C sorbents were studied by Fourier transform infrared (FT-IR) spectroscopy and their physical properties were analyzed by viscosity and temperature data of the sorbents. The obtained experimental results has demonstrated that both 1:1 and 2:1 for amine:CO_2 stoichimetry are possible in the liquid ^{14}C sorbent during trapping CO_2. CO_2 could be also trapped physically in the highly viscous ^{14}C sorbent.

2. Materials and methods

2.1. Reagents and chemicals

All reagents and solvents were of AR grade and used without further purification unless otherwise noted. 70% HNO_3, Carbo-Sorb® E, and Gold Star Multi-Purpose Liquid Scintillation Cocktail were purchased from Merck, PerkinElmer, and Meridian, respectively. 0.5% Pt on alumina pellet, sea sand (30–50 mesh), and quartz wool were bought from Elemental Microanalysis, Samchun Pure Chemical, and Grace Davison Discovery Science, respectively. Deionized water (DI water) was obtained using a Milli-Q Direct 8 water system (18.2 MΩ cm). 0.1 M HNO_3 was prepared by the dilution of 70% HNO_3 with DI water.

2.2. Combustion of samples

Low-level radioactive ion exchange resins and lubricant oils were supplied from Korea nuclear power plants as samples in this study. The combustion furnace for determination of radioactivities of ^3H and ^{14}C in samples consists of three zones; a sample oxidation zone, a temperature buffer zone, and a catalysis zone (Fig. 1). A sample boat including ca. 1 g of sample was placed in a silica glass tube withinin the sample oxidation zone of the furnace, and heated using preset temperature profiles (Fig. 2) with air purge (>99.99%, 30 mL/min). After the temperature of the sample oxidation zone has reached higher than 500 °C, oxygen (>99.99%, 30 mL/min) was purged into the combustion furnace system to burn the incompletely combusted sample. The formed gases pass through the 0.5% Pt/alumina catalyst pellets packed column to enhance the complete oxidation of the gases to H_2O (THO) and CO_2 ($^{14}CO_2$). H_2O (THO) and CO_2 ($^{14}CO_2$) are trapped in bubblers containing 20 mL of 0.1 M HNO_3 and 20 mL of ^{14}C sorbent (Carbo-Sorb® E) respectively. The furnace recovery was obtained by spiking diluted standard reference materials of ^3H (Standard Reference Material 4926E, National Institute of Standards & Technology) and ^{14}C (carbon-14 Standard Solution, National Physical Laboratory) in the samples.

2.3. Determination of ^3H and ^{14}C in samples

Ca. 8 g of H_2O (including THO) vapor trapped 0.1 M HNO_3 solution in the bubbler was transferred to a 22 mL plastic LSC vial, and mixed with 12 mL of Gold Star Multi-Purpose Liquid Scintillation (LSC) Cocktail. Ca. 5 g of CO_2 (including $^{14}CO_2$) gas trapped ^{14}C sorbent solution in the bubbler was mixed with 15 mL of Gold Star Multi-Purpose LSC Cocktail in a 22 mL plastic LSC vial. Radioactivities of ^3H and ^{14}C in the vials were determined by a Quantulus™ 1220 Ultra Low Level Liquid Scintillation Spectrometer (PerkinElmer). The radioactivities (A_s) of ^3H and ^{14}C in the samples were calculated by the following equation:

$$A_s = \frac{(C_s - C_B)}{60} \cdot \frac{100}{\varepsilon} \cdot \frac{1}{m_s} \cdot \frac{(m_f - m_t)}{m_b} \cdot \frac{100}{R} \tag{1}$$

where A_s, C_s, C_B, ε, m_b, m_f, m_t, m_s and R are the radioactivity concentration in the sample, the sample count rate, the background count rate, the counting efficiency for LSC, the mass of the bubbler solution taken for analysis, the final bubbler mass, the bubbler tare mass, the mass of sample and the furnace recovery, respectively. The minimum detectable activity (MDA) was obtained using the following formula:

$$\mathrm{MDA} = \frac{2.71 + 4.65\sqrt{C_B \cdot t_B}}{t_s \cdot 60 \cdot \frac{\varepsilon}{100} \cdot \frac{R}{100} \cdot m_s \cdot \frac{m_b}{(m_f - m_t)}} \tag{2}$$

where t_B and t_s are the background counting time and the sample counting time, respectively. The counting efficiency for LSC was