A Feasibility Study of the Quantification of C-14 by Photocatalytic Oxidation

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1. Introduction

The regulations of radioactive waste discharges and disposals require the radiochemical waste characterization for major radionuclides such as ^{3}H, ^{14}C, and ^{129}I, which provides important criteria for establishing disposal principles based on the concentration of radionuclides. Moreover, to identify the need for further treatment of radwastes or their suitability for storage, numerous analytical procedures have been developed for radionuclides of interest. Among those radionuclides, the determination of radioactive ^{14}C in low- and intermediate-level radwastes (LILW) has been getting more and more attention due to concerns about the radiological impacts to the environment. As ^{14}C is a pure beta emitter with a half-life of 5,730 years, it should be chemically separated from other radionuclides present in LILW for accurate quantification. Compared to non-volatile radionuclides, the successful analysis of ^{14}C relies mainly on how efficiently organic or inorganic carbon in radwastes is converted to gaseous carbon dioxide through an oxidation reaction. Although several methods have been developed for the radiochemical analysis of ^{14}C in LILW, for example, combustion, wet oxidation, and acid stripping techniques [1], it is still a challenge to determine the accurate radioactivity of ^{14}C effectively. In terms of processing time, complicated procedures including the decomposition of a sample along with the purification of ^{14}C might be considered a major obstacle to the practical application. In this study, advanced oxidation process (AOP) based on the UV light source was adopted as a promising technique for the quantification of ^{14}C in LILW via *in situ* decomposition of samples. As an initial step to demonstrate the feasibility of the proposed method, various radioactive ^{14}C standards were investigated to evaluate the recovery of ^{14}C: ^{14}C-labeled methanol (^{14}CH$_3$OH), lauric acid (CH$_3$(CH$_2$)$_{10}$^{14}COOH), sodium carbonate (Na$_2$^{14}CO$_3$), and toluene (C$_6$H$_5$^{14}CH$_3$). These compounds were oxidized with chemical oxidants such as H$_2$O$_2$ or K$_2$S$_2$O$_8$ under photocatalytic conditions, and the generated ^{14}CO$_2$ was collected in Carbo-Sorb E solution. The individual solution was then mixed with a scintillation cocktail and counted using a liquid scintillation counter (LSC).

2. Methods and Results

2.1 Photocatalytic oxidation

Photocatalytic oxidation of organic or inorganic carbon was carried out in an immobilized batch reactor. Fig. 1 describes a schematic diagram of the UV photo-reactor. A cylindrical photo-reactor made of borosilicate glass with capacity of about 250 mL was employed with water circulation arrangement to maintain the temperature below 30°C. The UV lamp (131 mm arc length) was mercury 450 W with the wavelength range of 280 ~ 400 nm. It was inserted symmetrically into the reactor and immersed directly in the solution. In a preliminary study for the optimization of photocatalytic reaction, non-radioactive lauric acid was chosen as the target organic compound, and mixed with K$_2$S$_2$O$_8$/AgNO$_3$ or H$_2$O$_2$ oxidant in an acidic solution. To evaluate the effect of reaction parameters on the decomposition of lauric acid, the corresponding lauric acid in aqueous solution was extracted with HPLC grade ethyl acetate (EtOAc) and then analyzed using GC-FID with an external standard of myristic acid. In the case of radioactive compounds, the resulting gaseous ^{14}CO$_2$ was trapped by Carbo-Sorb E solution with a supply of nitrogen carrier gas, followed by the measurement of its radioactivity using LSC.

2.2 Quench calibration for C-14 measurement

To determine the counting efficiency from the quench levels obtained during ^{14}C counting, 14,878 Bq of a ^{14}C standard (Packard) were each placed into 10 scintillation vials. Subsequently, both 10 mL of Carbo-Sorb E and 10 mL of Permafluor E+ were added to the above vials. As a quenching agent, nitromethane (CH$_3$NO$_2$), was finally added in the range of 0 ~ 200 μL. A quench indicator, in which the gamma activity of ^{133}Ba was used as a standard to monitor external quenching prior to application, was adjusted to the transformed spectral index of external

standard (tSIE/AEC) mode. In the resulting quench correction curve, as the amount of CH_3NO_2 was increased, we confirmed that the quench level was increased while the counting efficiency was decreased. Furthermore, an increase in the counting efficiency was observed with an increase in the tSIE.
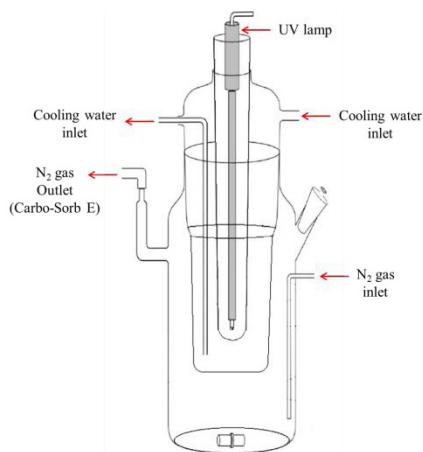

Fig. 1. Schematic diagram of UV photo-reactor.

2.3 Minimum detectable activity (MDA)

The MDA (Bq/g) for radioactive ^{14}C samples is determined as follows [2]:

$$MDA = \frac{2.71 + 4.65\sqrt{C_b T_b}}{E_{ff} \times V_s \times T_s \times 60} \quad (1)$$

Where E_{ff} is the counting efficiency of LSC, V_s is the sample weight (g), C_b is the background count rate, T_s is the sample counting time, and T_b is the background counting time. As shown in Eq. (1), the MDA can be decreased by increasing the counting efficiency, sample weight, and sample counting time. Using these parameters and the maximum allowable weight of simulated samples, MDA of ^{14}C for the proposed photocatalytic oxidation can be calculated from Eq. (1). Table 2 provides MDA results for different amount of simulated ^{14}C resins, which were obtained using the LSC parameters shown in Table 1. When the maximum 20 g of sample was applied, MDA of the ^{14}C radionuclide was 8.6×10^{-4} Bq/g.

Table 1. LSC parameters for the calculation of MDA

Radionuclide	E_{ff}	C_b (cpm)	T_b (min)	T_s (min)
^{14}C	0.91	1	30	30

Table 2. MDA of ^{14}C for different amount of simulated resins

Sample	Weight (g)	MDA (Bq/g)
Simulated resins	5	3.4×10^{-3}
	10	1.7×10^{-3}
	20	8.6×10^{-4}

2.4 C-14 measurement

From the result of recovery rate for various inorganic and organic ^{14}C standards, it was identified that the overall recoveries of ^{14}C were above 90%. However, toluene was found to be difficult to decompose due to the absence of an activating group such as hydroxyl on benzene ring.

3. Conclusion

UV-assisted photocatalytic reaction was optimized and evaluated using various ^{14}C standards for the application to determine the ^{14}C concentration in LILW. During the photocatalytic oxidation, inorganic and organic ^{14}C compounds were found to be efficiently oxidized and separately recovered with yields above 90%. Furthermore, the corresponding data were compared with those of reported wet-oxidation method.

REFERENCES

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