

Using UV irradiation for radiochemical analysis of C-14 in radioactive wastes

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1. Introduction

Disposal of radioactive waste requires radiological characterization. There are three primary approaches for assessing the concentration of radionuclides in radioactive waste: direct measurement, indirect measurement, and theoretical evaluation. Direct measurements include non-destructive or radiochemical analyses, while indirect measurements involve scaling coefficients, dose-radioactive conversion, and average radioactive concentration. Theoretical evaluation methods encompass radiation and decay calculations. Radiochemistry often entails sampling, sample production pretreatment, chemical separation, radiometry, and data interpretation. Radiochemical methods are beneficial for analyzing beta-ray and low-energy gamma-ray emission nuclides, but they are expensive and time-consuming. However, for beta nuclei such as H-3, C-14, and I-129, it is challenging to measure radioactive concentration non-destructively for medium- and low-level radioactive waste, necessitating the use of radioactive methods. H-3 and C-14 are significant radionuclides found in radioactive waste because they occur in nuclear power plants. H-3 and C-14 in radioactive waste exist in organic forms, and it is essential to physically extract trace amounts of these elements. Extraction methods vary and can be broadly classified into dry oxidation methods such as combustion and explosion combustion, and wet oxidation methods like microwave dissolution and Fenton processes. Wet oxidation is suitable for radioactive waste with high moisture content, as it can break down organic matter and compounds. Wet oxidation is an effective method for extracting H-3 and C-14 from organic compounds, collected in the form of water vapor and CO₂ gas, and measured using the Liquid Scintillation Factor Method (LSC). In this study, more efficient and environment-friendly C-14 analysis method was suggested by adopting the photochemical reactions via in-situ decomposition using UV light source. As an initial step for the demonstration of the feasibility of the proposed method, instead of using radioactive C-14 standards, non-radioactive inorganic and organic standards were investigated to evaluate the recovery of carbon as a preliminary study. These standards were oxidized with chemical oxidants such as

Formic acid (HCOOH), silver nitrate (AgNO₃) and potassium persulfate (K₂S₂O₈) under UV irradiations, and the generated CO₂ was collected in Carbo-Sorb E solution. Recovery yield of carbon was measured based on the gravimetric method. As an advanced oxidation process, our photocatalytic oxidation will be promising as a time-saving method with less secondary wastes for the quantitative C-14 analysis in low-level radioactive wastes.

2. Methods

2.1 Photochemical Equipment

The sample is placed in a 150mL beaker containing three openings, each of which serves to connect the sample injection port, measure temperature, and attach collection pipes. This apparatus was illuminated with a 100 W UV lamp to initiate a photochemical reaction, resulting in the desired outcome.

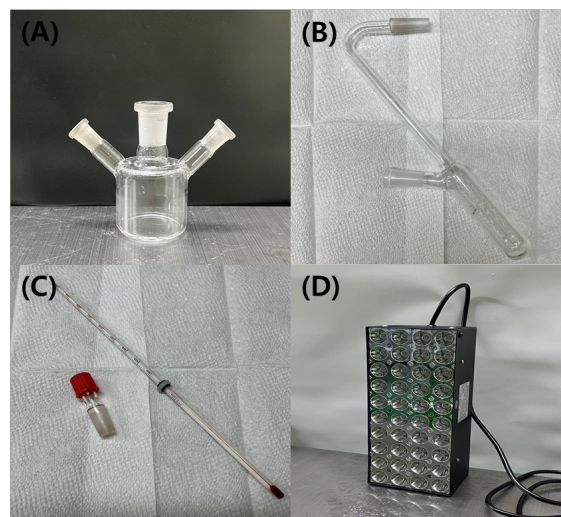


Fig. 1. Photochemical equipment. (A) 150 mL beaker. (B) A collection tube. (C) Thermometer. (D) UV lamp (100 W)

2.2 Reagent

Formic acid (HCOOH), silver nitrate (AgNO₃) and potassium persulfate (K₂S₂O₈) are used. Generally, the ratio of oxidant to catalyst is 10:1, and it uses 2.0 g of

potassium persulfate and 0.2 g of nitric acid. CO₂ is produced using an OH radical redox reaction using oxidants and catalysts. Put 100 mL of distilled water, 2.0 g of potassium persulfate, 0.2 g of nitric acid, and a magnetic stirring rod in a 150 mL beaker. Connect the collection tube to the thermometer and seal each inlet. Stir enough samples and reagents to dissolve in distilled water and irradiate with UV lamps.

Table I: Concentration

	Sample	Catalyst	Oxidizer
	HCOOH	AgNO ₃	K ₂ S ₂ O ₈
mol	8.00*10 ⁻⁷	1.18*10 ⁻³	7.40*10 ⁻³

3. Result

3.1 UV lamp effect

In the experiment to confirm the UV lamp effect, we compared the UV lamp effect, temperature effect, and stirring effect. Temperatures were set at 40°C and 50°C. UV lamp irradiation has proven to be more successful than other results.

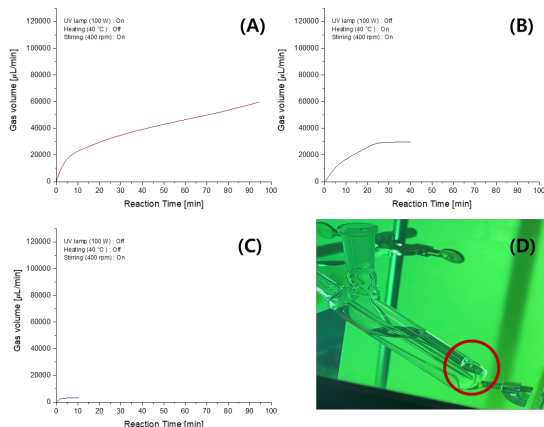


Fig. 3. Using UV lamp comparison results. (A) Result of the using stirrer and UV lamp. (B) Result of the stirrer and heating on 40 °C. (C) Result of the using only stirrer. (D) CO₂ bubble generation.

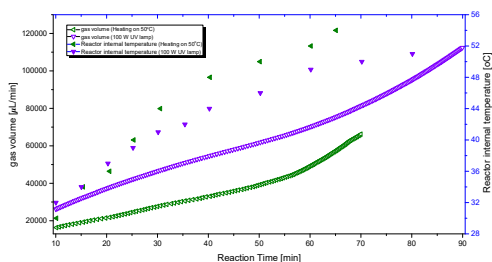


Fig. 4. Result of the using UV lamp on 50 °C.

3.2 Dependence on distance

It tested the separation distance between the reactor and the UV light at 0 cm, 2.5 cm, 5 cm, and 10 cm. It discovered that the response was only successful when the UV lamp was positioned within 5 cm. The reactor-UV lamp distance of 10 cm result verified that the beginning reaction was slow and the entire cumulative volume was small.

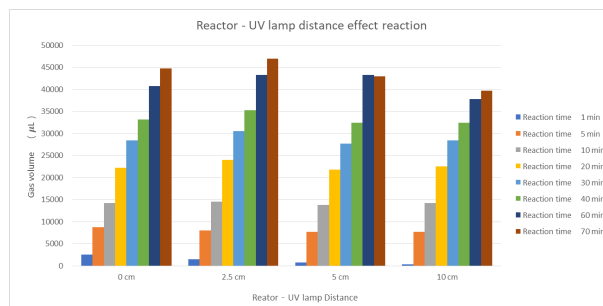


Fig. 5. Reactor-UV lamp distance effect results.

3.3 Dependence on UV lamp power

The UV lamp power experiment compared the reaction time at 100 W, 75 W, and 50 W, and found that the UV lamp was most efficient when the power of the UV lamp was 100 W. The higher the power of the UV lamp, the faster the initial reaction occurs, so using a high-power UV lamp will be able to analyze it more efficiently.

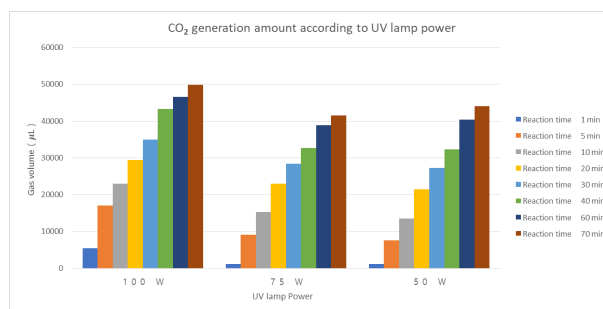


Fig. 6. UV lamp power reaction results.

3.4 Dependence on concentration

As the concentration of samples, catalysts, and oxidants decreased, the reaction according to the concentration slowed down. However, considering the number of mol, it was confirmed that even a very small amount of the reaction would occur.

Table 2: Formic acid concentration

Dilution	Sample		
	HCOOH		
	[mol]	Bubble generation (Initial)	Reaction term±S.D. (5 min, average)
		[#/min]	[sec]
1	8.00×10^{-7}	60	6.40±2.19
1/2	8.00×10^{-8}	0.34	37.67±0.58
1/100	8.00×10^{-9}	0.20	-
1/1000	8.00×10^{-10}	0.23	-

Table 3: Silver nitrate concentration

Dilution	Catalyst		
	AgNO ₃		
	[mol]	Bubble generation (Initial)	Reaction term±S.D. (5 min, average)
		[#/min]	[sec]
1	1.18×10^{-3}	60	6.40±2.19
1/2	5.90×10^{-4}	0.95	13.11±2.54
1/4	3.01×10^{-4}	0.52	13.85±2.51
1/20	5.90×10^{-5}	0.40	22.83±2.23
1/200	5.90×10^{-6}	0.17	-

Table 4: Potassium persulfate concentration

Dilution	Oxidizer		
	K ₂ S ₂ O ₈		
	[mol]	Bubble generation (Initial)	Reaction term±S.D. (5 min, average)
		[#/min]	[sec]
1	7.40×10^{-3}	60	6.40±2.19
1/2	3.70×10^{-3}	2.61	10.84± 1.03
1/4	1.85×10^{-3}	1.88	13.00±0.79
1/20	3.70×10^{-4}	0.38	48.33±2.31
1/200	3.70×10^{-5}	0.20	-

4. Conclusion

The bubble generation is affected by the concentration of the sample, irradiation, power and distance of the UV lamp. Easier, safer, and more eco-friendly C-14 analysis will be possible. UV lamp should be as close as possible to the reactor, because the CO₂ production strongly depends on the distance. We found the optimal conditions for the bubble generation reaction, we plan to optimize further with simulated samples, which are known to be different to decompose into CO₂. We also plan to use C-14 in the form of ¹⁴CO₂ from

actual radioactive samples using the method described above and analyze it using LSC.

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