Optimization of Pretreatment Procedures for Radio-Carbon Determination using Liquid Scintillation Counter

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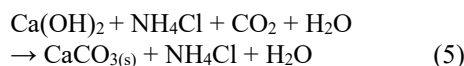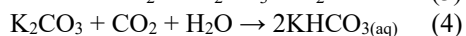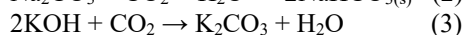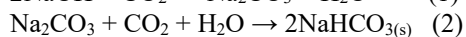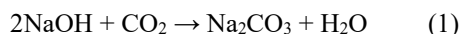*[*]heewonkim@kaeri.re.kr*

1. Introduction

^{14}C($T_{1/2}$ = 5730 yr, Decay energy = 0.156 MeV) is a naturally occurring radionuclide that exists in all environments at a concentration level of 0.2 Bq/g-C as a low-energy pure beta emitter. It is naturally produced by the nuclear reaction of neutrons and ^{14}N produced by the cosmic rays. In the northern hemisphere, the bomb-produced radiocarbon in air gradually decreased after recording its highest level of about 0.452 Bq/g-C (~200 pMC) in 1965, and as of 2020 it is at a level of about 0.22 Bq/g-C (~100 pMC). Around nuclear facilities, however, the concentration of ^{14}C per unit carbon has been reported above 0.2 Bq/g-C [1].

In this study, the pretreatment procedures, which include absorption in NaOH solution, concentration in $CaCO_3$ precipitation, CO_2 generation from $CaCO_3$, and CO_2 absorption in measuring solution for LSC were comprehensively optimized for determination of ^{14}C in air samples for the environmental monitoring program vicinity of the nuclear facilities. The performance tests of pretreatment processes were conducted with various standard gas and investigated composition and purity of $CaCO_3$ precipitation with XRD. Finally, the assessment of accuracy and precision of optimized procedures for ^{14}C activity measurement using LSC was evaluated with the analytical results of the NIST SRM 4990C (Oxalic Acid) samples.

2. Methods and Results

2.1. Selection of CO₂ trap solution

For the purpose of optimizing of CO_2 trapping solution on the field sampling, capability for CO_2 capturing of various solution (e.g., NaOH, KOH, and $Ca(OH)_2$+NH_4Cl) was investigated. The CO_2 standard gas of 3% and 50% (RIGAS, KOREA) were used for evaluation of trapping capability. The exhausted CO_2 from trapping solution was measured by CO_2/H_2O gas analyzer (LI-850, LI-COR). The chemical formula for the reaction of the substances with CO_2 is as following:

$$2NaOH + CO_2 \rightarrow Na_2CO_3 + H_2O \qquad (1)$$
$$Na_2CO_3 + CO_2 + H_2O \rightarrow 2NaHCO_{3(s)} \quad (2)$$
$$2KOH + CO_2 \rightarrow K_2CO_3 + H_2O \qquad (3)$$
$$K_2CO_3 + CO_2 + H_2O \rightarrow 2KHCO_{3(aq)} \quad (4)$$

$$Ca(OH)_2 + NH_4Cl + CO_2 + H_2O$$
$$\rightarrow CaCO_{3(s)} + NH_4Cl + H_2O \qquad (5)$$

Although KOH and NaOH have silmilar chemical properties, KOH require about 30% compared to NaOH to capture the same amount of CO_2[2]. If $Ca(OH)_2$+NH_4Cl was used, separation of $CaCO_3$ precipitates would be easier than other solutions because all precipitates produced by CO_2 absorption are $CaCO_3$. However, $Ca(OH)_2$+NH_4Cl solution is hard to control of stable reaction and has a lack capability for all CO_2 capture. In this study, although the disadvantage of producing large amounts of hydroxides during carbonate precipitation, considering for the economic and stable CO_2 capture ability, NaOH solution was chosen.
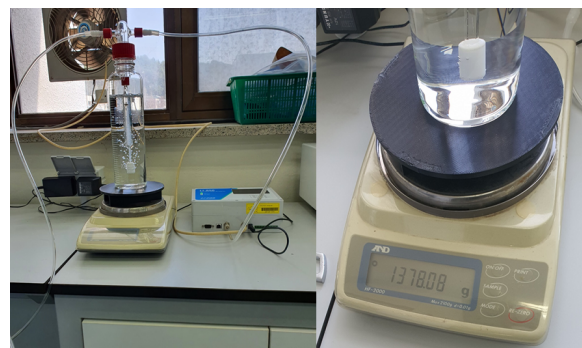

Fig. 1. Evaluation of CO_2 absorption amount for the NaOH solution using standard gas (3% and 50%) and gas analyzer.

2.2. Choice of trap solution volume and concentration

In the field campaign, CO_2 sampling conditions were set as followings:
- The concentration of CO_2 in the air : 450 ppm
- Air flow rate : 0.5 L/min
- Amount of CO_2 captured per month (theoretically) : about 0.43 mol
- Maintain pH above 9 until the end of the sampling

In order to optimize the trapping condition of NaOH solution, the volume and concentration conditions differently with 1.0 M, 1.5 M, 2.0 M and 1400 mL, 800 mL were tested with 50% CO_2 standard gas. The weight and pH of trapping solution and CO_2 concentration of exhausted gas were measured in the condition presented

in Table 1. For the sampling of about 0.43 mol of CO_2, the condition with 800 mL of 1.5 M NaOH solution is enough to capture the entire CO_2 in the air during 1-month period.

Concentration of NaOH (M)	Amount of Captured CO_2 (mol)	
	800mL + 600mL	800mL
1	0.45	0.278
1.5	-	0.648
2	0.97	0.847

Table 1. Amount of captured CO_2 in various condition

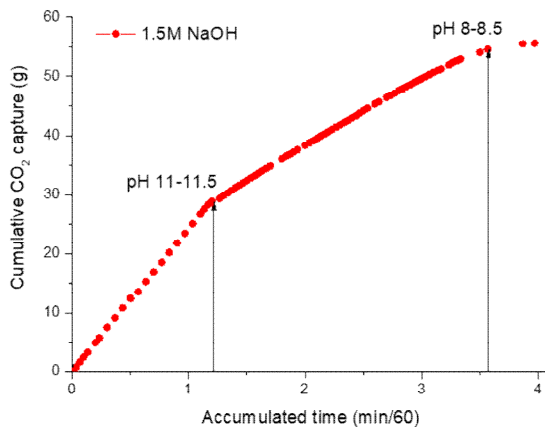Fig. 2. The cumulative amount of CO_2 and pH in 1.5M NaOH 800 mL with injected CO_2 standard gas.

Fig. 2 shows the cumulative amount of absorbed CO_2 and pH in 1.5M NaOH 800 mL with injected CO_2 standard gas. The concentration of CO_2 in exhausted gas was measured below 50 ppm until about 30 g of CO_2 absorbed in the trapping solution with pH 11-11.5. After then CO_2 concentration in exhausted gas increased simultaneously to about 2000 ppm showing a change in the increasing rate of trapping amount. Finally, after the CO_2 absorption of approximately 55 g, further weight change was not detected and the CO_2 concentration in exhaust gas was measured with similar to injected CO_2 concentration and the pH of the solution was dramatically decreased to about 8.0~8.5.

2.3. Design and apply of pretreatment procedures

Fig. 3 shows the pretreatment process of deriving $CaCO_3$ precipitation from NaOH solution with absorbed about 20 g of CO_2. For the concentration of CO_2 with $CaCO_3$, the $CaCl_2$ and NH_4Cl were selectively injected into the NaOH solution according to pH condition. In the solution, NH_4^+ reacts with OH^-, which removes hydroxide ions, and maintains the pH above 11.
Although the purified $CaCO_3$ precipitation was centrifuged and dried, impurity containing NaCl or $Ca(OH)_2$ etc. in some samples were founded from the XRD analysis. Thus, dissolution with demineralized water (DIW) steps were added in order to remove NaCl or $Ca(OH)_2$.
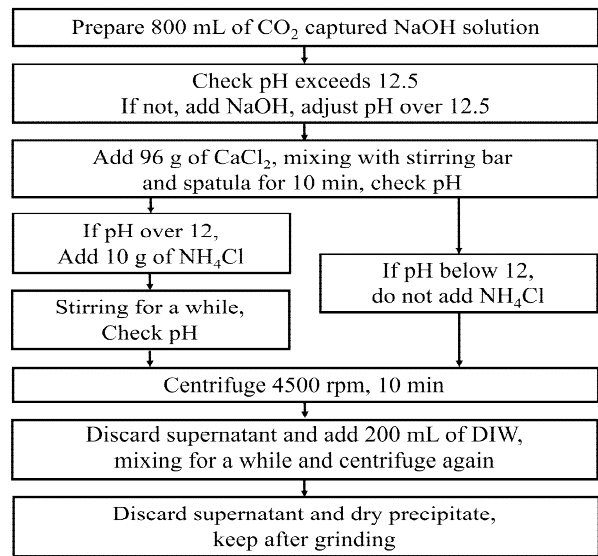

Fig. 3. Procedure of pretreatment

2.4 Analytical results of CRM samples

In order to verify the pretreatment procedure, ^{14}C of the standard samples (SRM-4990C, Oxalic acid powder) were analyzed with developed and optimized pretreatment procedures. The CO_2 gas was generated from the $CaCO_3$ precipitation with 6 M HCl using automatic instrument and absorbed in 10 mL of CarboSorb®. The ^{14}C activity was measured by LSC and the amount of absorbed CO_2 was quantitatively measured by balance. The analytical results (0.298±0.020 Bq/g-C) were in agreement with the certified activity (0.3068 Bq/g-C) of SRM 4990C.

3. Conclusion

The developed pretreatment processes in this study could increase the efficiency and purity of $CaCO_3$ for measuring the airborne (or environmental samples) radiocarbon. Furthermore, the optimal conditions containing CO_2 capture, purification, release, and absorption could be considered suitable due to the small volume of solution and easier treatment. Finally, based on the accuracy and precision of optimized procedure in this study, one may draw conclusions that the analytical results derived with optimal conditions were fairly reliable.

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