

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

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INTRODUCTION

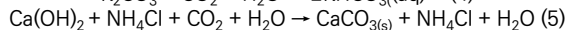
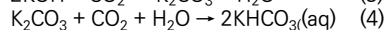
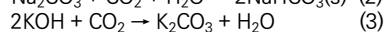
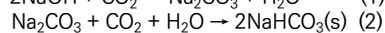
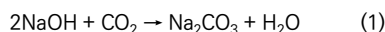
¹⁴C($T_{1/2}$ = 5730 yr, Decay energy = 0.156 MeV) is a naturally occurring radionuclide that exists in all environments at a concentration level of 0.2 Bq/g-C as a low-energy pure beta emitter. It is naturally produced by the nuclear reaction of neutrons and ¹⁴N produced by the cosmic rays. In the northern 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 ¹⁴C 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 CaCO₃ precipitation, CO₂ generation from CaCO₃, and CO₂ absorption in measuring solution for LSC were comprehensively optimized for determination of ¹⁴C 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 CaCO₃ precipitation with XRD. Finally, the assessment of accuracy and precision of optimized procedures for ¹⁴C activity measurement using LSC was evaluated with the analytical results of the NIST SRM 4990C (Oxalic Acid) samples.

METHOD AND RESULTS

2.1. Selection of CO₂ trap solution

For the purpose of optimizing of CO₂ trapping solution on the field sampling, capability for CO₂ capturing of various solution (e.g., NaOH, KOH, and Ca(OH)₂+NH₄Cl) was investigated. The CO₂ standard gas of 3% and 50% were used for evaluation of trapping capability. The exhausted CO₂ from trapping solution was measured by CO₂/H₂O gas analyzer (LI-850, LI-COR). The chemical formula for the reaction of the substances with CO₂ is as following:



Although KOH and NaOH have similar chemical properties, KOH require about 30% compared to NaOH to capture the same amount of CO₂[2]. If Ca(OH)₂+NH₄Cl was used, separation of CaCO₃ precipitates would be easier than other solutions because all precipitates produced by CO₂ absorption are CaCO₃. However, Ca(OH)₂+NH₄Cl solution is hard to control of stable reaction and has a lack capability for all CO₂ capture. In this study, although the disadvantage of producing large amounts of hydroxides during carbonate precipitation, considering for the economic and stable CO₂ capture ability, NaOH solution was chosen.

2.2. Choice of trap solution volume and concentration

In the field campaign, CO₂ sampling conditions were set as followings:

- The concentration of CO₂ in the air : 450 ppm
- Air flow rate : 0.5 L/min
- Amount of CO₂ captured per month (theoretically) : about 0.43 mol
- Maintain pH above 9 until the end of the sampling

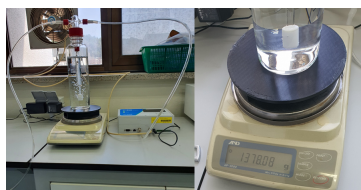


Fig. 1. Evaluation of CO₂ absorption amount for the NaOH solution using standard gas (3% and 50%) and gas analyzer.

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% CO₂ standard gas. The weight and pH of trapping solution and CO₂ concentration of exhausted gas were measured in the condition presented in Table 1. For the sampling

of about 0.43 mol of CO₂, the condition with 800 mL of 1.5 M NaOH solution is enough to capture the entire CO₂ in the air during 1 month period.

Fig. 2 shows the cumulative amount of absorbed CO₂ and pH in 1.5M NaOH 800 mL with injected CO₂ standard gas. The concentration of CO₂ in exhausted gas was measured below 50 ppm until about 30 g of CO₂ absorbed in the trapping solution with pH 11–11.5. After then CO₂ concentration in exhausted gas increased simultaneously to about 2000 ppm showing a change in the increasing rate of trapping amount. Finally, after the CO₂ absorption of approximately 55 g, further weight change was not detected and the CO₂

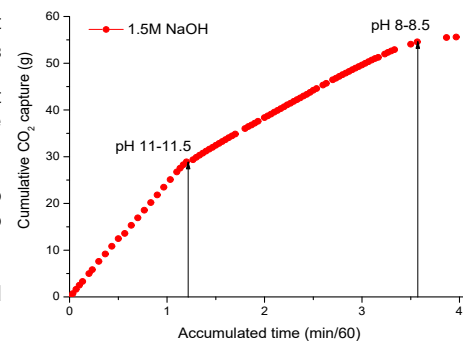
concentration in exhaust gas was measured with similar to injected CO₂ concentration and the pH of the solution was dramatically decreased to about 8.0~8.5.

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 CO₂ in various condition

2.3. Design and apply of pretreatment procedures

Fig. 3 shows the pretreatment process of deriving CaCO₃ precipitation from NaOH solution with absorbed about 20g of CO₂. For the concentration of CO₂ with CaCO₃, the CaCl₂ and NH₄Cl were selectively injected into the NaOH solution according to pH condition. In the solution, NH₄⁺ reacts with OH⁻, which removes hydroxide ions, and maintains the pH above 11.



Although the purified CaCO₃ 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.

2.4 Analytical results of CRM samples

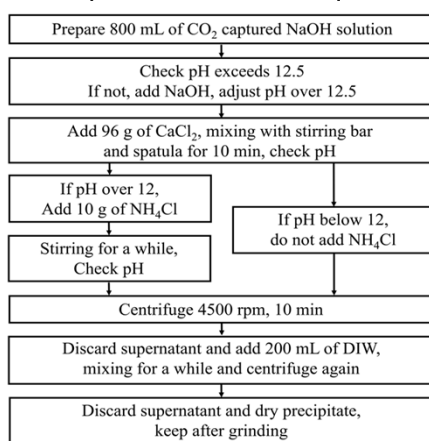


Fig. 3. Procedure of pretreatment

In order to verify the pretreatment procedure, ¹⁴C of the standard samples (SRM-4990C, Oxalic acid powder) were analyzed with developed and optimized pretreatment procedures. The CO₂ gas was generated from the CaCO₃ precipitation with 6 M HCl using automatic instrument and absorbed in 10 mL of Carbo-Sorb®. The ¹⁴C activity was measured by LSC and the amount of absorbed CO₂ 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.

CONCLUSION

The developed pretreatment processes in this study could increase the efficiency and purity of CaCO₃ for measuring the airborne (or environmental samples) radiocarbon. Furthermore, the optimal conditions containing CO₂ 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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