

Sample treatment techniques for the determination of environmental radiocarbon in a nuclear power station area

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(Received April 8, 1998)

This report describes the environmental sample treatment techniques for ¹⁴C measurement with liquid scintillation counter. The groundwater sample of about 80 liters was collected from well and inorganic carbon was removed by acidification and recirculated gas stripping with the extraction efficiency of more than 98%. The biological samples were freeze-dried and combusted to carbon dioxide in high pressure combustion unit with a combustion efficiency of nearly 99%. The ¹⁴CO₂ in the stack effluents was collected by an air bubbler with a collection efficiency of more than 99% for a sampling time of two weeks. Sampling of ¹⁴C in reduced form also has been done by passing the gases through a tube furnace with Pt/Al and Pd/Al catalyst. Active and passive sampling methods for atmospheric ¹⁴C measurements were compared in detail, and it could be concluded that the uncertainty associated with passive sampling method was quite acceptable for environmental monitoring. The CO₂ trapped in NaOH was precipitated as BaCO₃, and subsequently reconverted to CO₂ for environmental samples and transferred to Carbo-Sorb ETM for liquid scintillation counting. In case higher precision is the deciding factor, benzene synthesis would be employed with home-made benzene synthesizer.

Introduction

With the growth of the nuclear industry in Korea, there is an increasing concern with the radiological impact associated with the discharge of long-lived radionuclides. Carbon-14 is one of the most significant radionuclides in the group because of its long half-life and the ease with which it assimilates into biological system. Relative to other reactor systems, CANDU reactors generate and release significant amount of ¹⁴C. In Korea twelve nuclear power reactors are operating now including two PHWR reactors at Wolsong. The nuclear power plant at Wolsong consists of four CANDU-type power units of 700 MWe, respectively, two of which are now still under construction.

A program was commenced in the middle of 1995 to determine ¹⁴C in gaseous discharge and to follow up the local radiological impact of ¹⁴C releases. The objectives of the program are: (1) to develop and run a reliable sampling system for measuring radiocarbon on a routine basis, (2) to determine the annual emission of ¹⁴C in gaseous form, and (3) to follow the local impact due to ¹⁴C release by monitoring ¹⁴C concentration in the environmental air, water and vegetations. In this paper sample treatment techniques for the determination of environmental radiocarbon are briefly discussed.

Experimental

Sample preparation for liquid scintillation counting in this work basically relied on the direct CO₂ absorption method, and benzene synthesis method was used as a

standard tool only as the technique requires not only relatively larger samples but also complex preparation procedures.^{1,2}

CO₂ was directly absorbed in a mixture of commercially available CO₂ absorber (Carbosorb ETM) and a compatible scintillation cocktail (Permafluor VTM). The amount of CO₂ required to saturate 20 ml absorption mixture with 1:1 volume ratio is about 1.2 l at STP, so all the sampling systems for the environmental radiocarbon measurement except for stack gas monitoring were designed to get at least 0.1 mole of CO₂.

However, due to the limitation of the available sample amount in case of reduced carbon species in stack effluent gases, BaCO₃ gel suspension method was applied to ¹⁴C measurements. The sampling period varied from 2–4 weeks, and the total integrated sample gas volume was targeted to 6–8 m³.

Air sampling

Active techniques for sampling ¹⁴CO₂ in reactor stack effluents have been developed. Air was pulled through a bubbler containing sodium hydroxide solution. The optimum conditions for the concentration and volume of sodium hydroxides, type of the bubbler have been examined for the complete collection of CO₂. Sampling period was usually from 2–4 weeks, and the maximum air flow rate was about 400 ml/min for sampling of 8 m³ of air. The absorption of CO₂ in 200 ml of 2M NaOH solution was found to be more than 99.5% at the flow rate.

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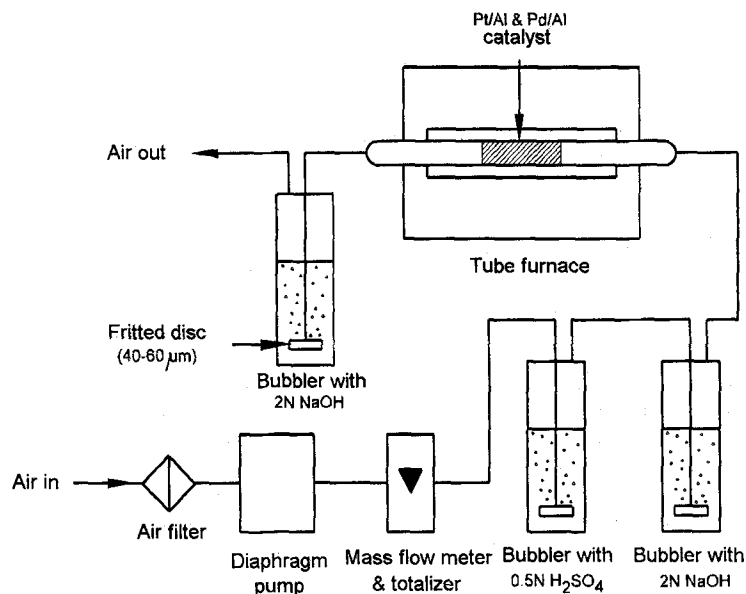


Fig. 1. Layout of the sampler for separating ^{14}C in CO_2 form and in reduced form (CO and hydrocarbon) from effluent gas sample

Table 1. Comparison of the results of air sampling methods

Period	Specific activities of atmospheric ^{14}C , dpm/g C			$\delta^{13}\text{C}$, ‰	
	active	passive	ratio (pass/act)	active	passive
test #1 (2/06–2/27)	16.0±0.7	15.9±0.7	0.994	-8.39	-17.30
test #2 (2/27–3/28)	16.7±1.1	15.9±1.2	0.952	-8.41	-18.80
test #3 (3/28–4/25)	17.5±1.1	16.6±1.1	0.948	-8.78	-16.68
test #4 (4/25–5/23)	19.9±1.1	18.8±1.1	0.945	-8.60	-16.21
test #5 (8/22–9/19)	16.5±1.1	16.4±1.1	0.994	-8.98	-15.50

A sampler for separating ^{14}C in CO_2 form and ^{14}C in reduced form from effluent gas was also developed³ and the layout is provided in Fig. 1. Air sample was passed through an assembly consisting of (1) first bubbler containing 0.5 N H_2SO_4 for the trapping of tritiated water; (2) second bubbler containing 2M NaOH for the absorption of $^{14}\text{CO}_2$; (3) a tube furnace maintained at 600 °C with Pd/Al and Pt/Al catalysts; (4) third bubbler containing 2M NaOH for absorbing the oxidized forms of ^{14}CO and hydrocarbon species. Gas chromatographic measurements were done to examine the collection efficiency of CO_2 in the bubbler and the conversion efficiency of hydrocarbons into CO_2 with an air standard containing about 400 ppm CO_2 and 100 ppm CH_4 . It was determined that the conversion efficiency exceeded 99.2%.

Samples of $^{14}\text{CO}_2$ in an open air can be collected by exposing NaOH solution in dishes or trays for two or four weeks, and this method is the simplest and least expensive to set up.⁴ The atmospheric CO_2 can be collected anywhere in the field, since it does not need

pump. A 600 ml of 2M NaOH was put into plastic tray, covered with stainless steel mesh to keep out insects, leaves and dusts. However, in winter season more concentrated NaOH solution of about 3M is recommended to prevent the solution from freezing. About nine litres of CO_2 were collected over a four-week period at normal temperature, and the CO_2 uptake rate remained almost constant during the whole period. At the end of period, the NaOH solution was transferred into a leak-proof polyethylene bottle and brought to the laboratory for further treatment.

Atmospheric $^{14}\text{CO}_2$ has been collected several times both with active and passive sampling methods at the same site and period, and the results are summarized in Table 1. The differences of specific ^{14}C activities measured with passive and active methods were maximum 5%, and passive values were generally lower than active ones. The average $\delta^{13}\text{C}$ values were measured to be -8.55 ± 0.18 and -17.25 ± 1.13 ‰ for active and passive samplings, respectively, which means that isotope fractionations have occurred in passive sampling.

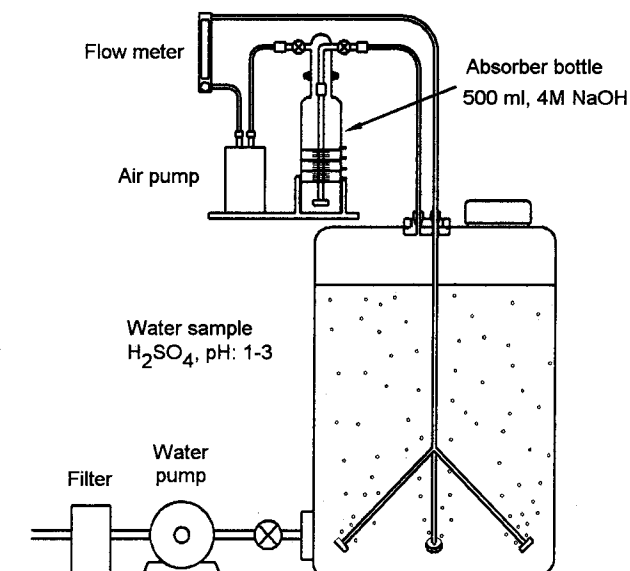


Fig. 2. Carbon dioxide evolution system for the extraction of dissolved carbonate species from natural water

A seasonal change of this effect also has been found showing somewhat larger fractionations at lower temperature. The possible error due to the isotopic fractionation in passive sampling was estimated to be maximum 2% in atmospheric ^{14}C measurement. So, it could be concluded that the uncertainty associated with passive sampling method was quite acceptable for environmental monitoring in view of uncertainties in the original natural ^{14}C content and in the absorption counting method.

Water sample treatment

Dissolved carbonate species in a ground water may be extracted by using direct precipitation method or gas evolution method. The precipitation method gives smaller isotopic fractionation, however, the presence of high concentration of sulfate ions may be a problem in this method and it takes longer time for the complete precipitation.^{5,6} Gas evolution method seems to be a better method since it is less time-consuming, less susceptible to contamination from atmospheric CO_2 and little affected by the sulfate ions. Possible isotope fractionation can be avoided in case the recovery of carbonates reaches nearly 100%.

In our country the contents of inorganic carbon species in the ground water ranges from 20 to 3000 ppm. However, the contents were in the range only from 40 to 60 ppm in public drinking waters around Wolsong power station area. In order to get about 0.1 mole of CO_2 maximum 100 litres of water were collected.

Initially tested gas purging system using pure N_2 gas was replaced with gas circulation system, because many gas bombs should be carried if different samples should be treated in a time. Figure 2 shows a modified gas stripping system with a small diaphragm pump to recirculate the air trapped above the sample water. The bubbler had a CorningTM coarse fritted disc, and inside the water tank there were three same discs for bubbling.

Laboratory studies were performed to examine the carbon dioxide recovery yields from water samples. One liter of conc. H_2SO_4 was added into 100 l of de-ionized water, which was then purged with CO_2 -free nitrogen gas to expel any dissolved carbon dioxide in the water. To produce 0.1 mole of CO_2 from an artificial ground water, 3.4 g of magnesium sulfate, 8.0 g of calcium chloride and 8.4 g of sodium bicarbonate were dissolved in 100 l of water.

The CO_2 gas purged with recirculated air was then bubbled through two bottles with 600 ml of 4M NaOH solution each connected in series. Purging gas flow rates and purging times were controlled to make the collection efficiency of evolved CO_2 at the first bubbler more than 98% and to minimize the time required. The optimum flow rate and purging time were found to be 4 l/min and 2 hours, respectively.

Samples for carbon isotope fractionation studies were collected in three fractions with evolution time. The evolution time for the first fraction was 1 hour, and second and third fractions were collected at intervals of 30 minutes, respectively. Carbon dioxide in each fraction was precipitated to form a barium carbonate.

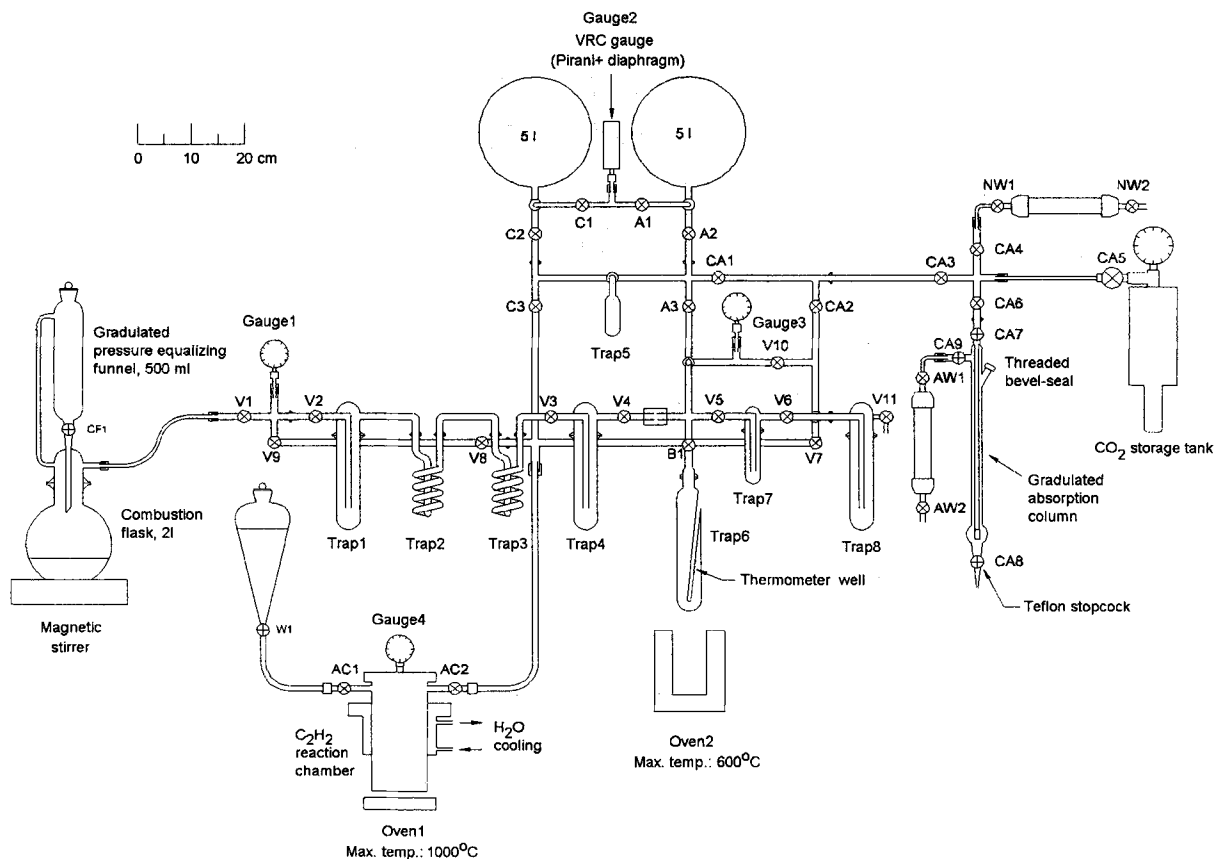


Fig. 3. Benzene synthesis system

The first fraction contained 70% of total carbon content in the water sample, and the second and the third fraction contained about 26 and 4%, respectively. A small portion of each fraction was analyzed to evaluate $\delta^{13}\text{C}$ values, which were measured to be -7.9 , -3.0 and $+0.4\%$ for the first, second and third fraction, respectively. The result clearly indicated that gas evolution method generates isotopically lighter carbon at the beginning of the purging process and heavier isotopes at the end. If complete recovery of organic carbon is not attained, isotope fractionation may be a problem for the accurate monitoring of radiocarbon in water samples.

Bomb combustion of organic samples

Biological samples such as rice, pine needle, vegetables were collected in polyethylene bags. Samples were rinsed with 1% hydrochloric acid to remove contaminants on surface and dried in a forced convection

drying oven. Milk, meat and fish samples were collected in an ice box and freeze-dried at approximately -50°C . The dried materials were powdered by using a mixer and pelletized to hold the sample together, allowing complete combustion to take place.

Samples were combusted in a high pressure combustion unit. The combustion unit, PHONONTM, is designed to combust organic material under pressure of oxygen in the range of 100–200 psi. Large samples of up to 50 g of material can be combusted and samples of as low as 5% carbon may be dealt with. Inside there is a water tray to trap the oxidized nitric and sulfuric oxide gases.

The CO_2 generated was passed through a gas regulator into a bubbler containing 150 ml of 3M NaOH solution outside of the combustion chamber. About 2.8 g of cellulose equivalent to 0.1 mole CO_2 was used as a test material, and the total recovery including the combustion efficiency was found to be nearly 99% and very reproducible.

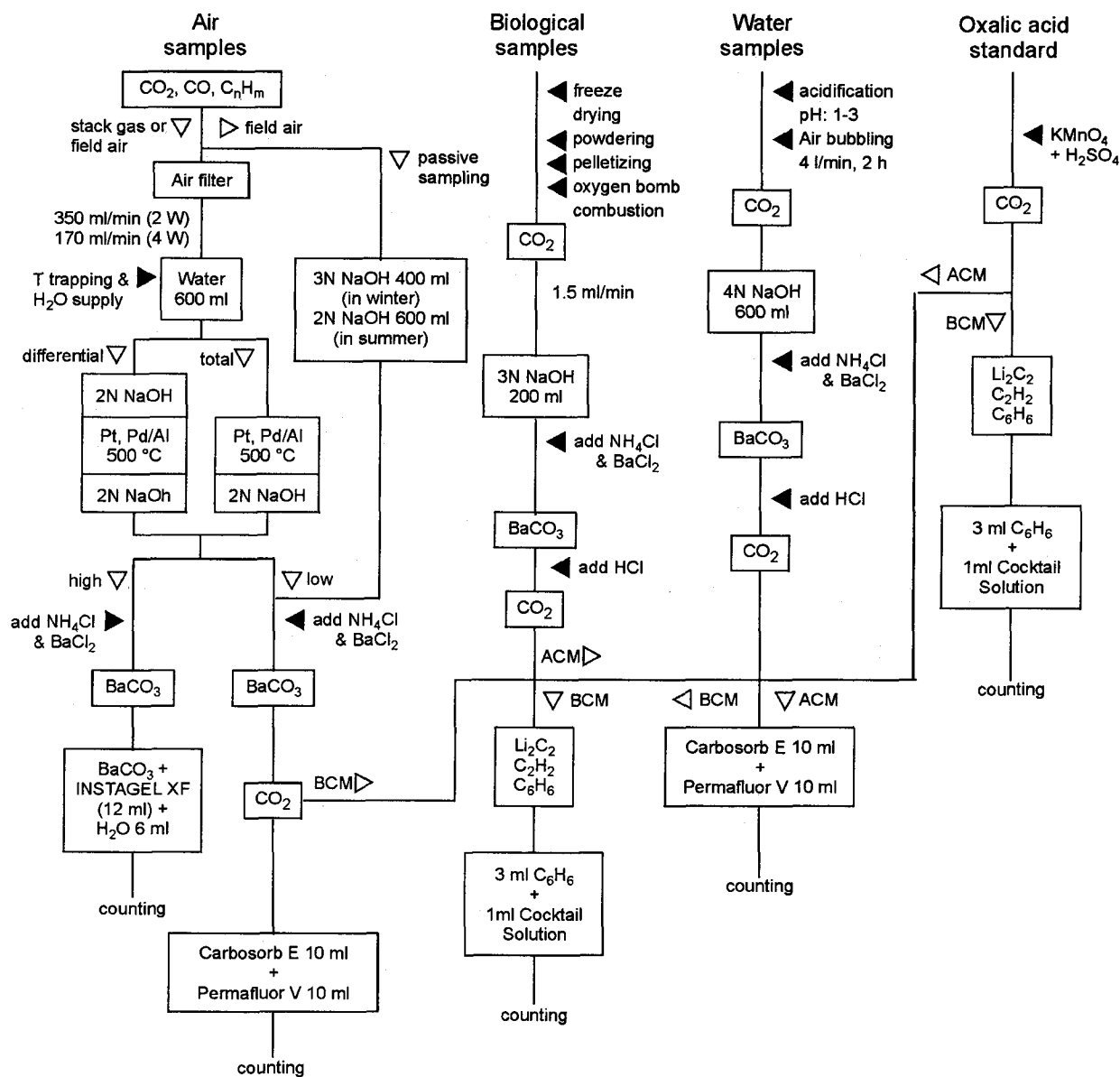


Fig. 4. Schematic diagram for the sampling and analysis of environmental samples

Benzene synthesis

Installation for benzene synthesis is schematically shown in Fig. 3. The benzene synthesizer is an integrated sample conversion system for the conversion of carbonaceous samples to benzene for liquid scintillation counting.⁷⁻⁹ This home-made system incorporated most of the recent developments in benzene synthesis and was designed to be capable of stoichiometric yields of up to 95%.

The starting material was usually BaCO₃, which was converted to CO₂ by wet combustion with perchloric

acid. Carbon dioxide was passed through water removal traps into 5-liter storage reservoir. A reaction yield was checked from the pressure and CO₂ was introduced into the reaction chamber with hot lithium metal to form lithium carbide. Pre-boiled distilled water was passed into the chamber and acetylene was formed. The acetylene was passed through purification traps into another storage reservoir and subsequently onto a Cr catalyst. The catalyst acts to trimerize the acetylene into benzene which was then collected for counting. Chemical yields for benzene synthesis are shown in Table 2.

Table 2. Steps and yields for benzene synthesis

Stepwise reactions	Reaction yield, %	Cumulative yield, %
Carbon combustion (1) $C+O_2 \rightarrow CO_2$ $BaCO_3+2HClO_4 \rightarrow CO_2+H_2O + \dots$	~100	~100
Carbide production (2) $2CO_2+10Li \rightarrow Li_2C_2+4Li_2O$	~100	~100
Acetylene production (3) $Li_2C_2+2H_2O \rightarrow C_2H_2+2LiOH$	95-98	95-98
Benzene production (4) $3C_2H_2 \rightarrow C_6H_6$	90-97	85-95

The maximum capacity of CO_2 treated in the system is about 0.4 moles, which would yield approximately 5 ml of benzene assuming an overall conversion yield of 85%. Sampled CO_2 or the environmental radiocarbon monitoring would usually amount to about 0.1 moles, which would be expected to yield about 1.25 ml benzene. The synthesized benzene was transferred from the trap to a pre-weighed low potassium glass vial of 7 ml. For the benzene counting method measurements were performed with a mixture of 3 ml benzene and 1 ml of scintillation cocktail (5 g of butyl-PBD in 100 ml of scintillation-grade toluene). If the sample yielded less than 3 ml, the difference was made up with an additional amount of non-radioactive benzene.

Conclusions

Simple and reliable sample treatment techniques for the environmental radiocarbon monitoring have been developed, and a flow diagram for the sampling and analysis of environmental samples is shown in Fig. 4. Sampling systems for environmental samples were designed considering the direct absorption of regenerated CO_2 in an absorber, Carbosorb ETM. However, as the available sample amount of non- CO_2 species in stack gases is limited, $BaCO_3$ gel suspension method was applied to stack gas monitoring.

The final step of a sample treatment procedure was to recover pure $BaCO_3$ precipitate, and in most cases the overall recoveries from environmental samples were proven to be more than 98% without any measurable contamination during the procedure. Benzene conversion yields were examined to be from 85-95%, and benzene synthesizer will only be used for a standardization in liquid scintillation counting and to measure small changes in background level of ^{14}C activity.

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