# Chemical Separation of Carbon -14 in Radwastes

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## 1. Introduction

Carbon-14 has a long half-life of 5730 years and decays by beta emission of 156KeV to the stable nuclide, Nitrogen-14[1]. Carbon-14 is produced mostly by the neutron activation of naturally occurring oxygen-17 in water molecules of the reactor coolant and Nitrogen-14 from nitrogen gas dissolved in the reactor coolant. Most of these carbon-14 are known to be discharged as gaseous wastes. The chemical forms of the gaseous emissions of carbon-14 from PWR stations range from 10~26% as $^{14}CO_2$ and 74~90% as $^{14}CH_4$ and other hydrocarbons, compared to about 95% as $^{14}CO_2$ and 5% as $^{14}CH_4$ and other hydrocarbons in BWR station gaseous emissions[2].

Knowles[3] reported that although the exact nature of these organic compounds was not identified, most of the carbon-14 was present as forms of organic species in a PWR primary coolant. Praudic[4] measured the contents of the total organic and inorganic carbon-14 in waste trench leachates of New York commercial LLW disposal site and found that 74 ~ 98% of carbon-14 was organic. In 1991, Dayal and Kirby reported that carbon-14 identified in LLW trench leachates from the Maxi Fiats site were carbonate and bicarbonate as inorganic carbon-14 and citric acid and palmitic acid as organic carbon-14[2].

Thus concentrated Boric acid waste solutions(CB) which has generated from domestic NPP were classified into organic and inorganic carbon-14 with wet oxidation method in order to grasping a existing ratio of organic carbon-14 from total one due to affecting an environment.

## 2. Methods and Results

### *2.1 Quench Calibration for Carbon-14 measurement*

The counting efficiency of carbon-14 with a particular quench level must be measured for determining the activity of carbon-14. 14,878Bq of carbon-14 (spec-check, Packard) was added to each 10 ㎖ vial with Carbo-sorb E(Packard) and permafluor E$^+$(Packard). The quenching agent, nitromethane was also placed into each vial in increasing amounts over the range 0~200. With increasing nitromethane volume, the efficiencies were lowered due to the increasing quenching level. The quench correction curves data produced by the instrument were stored in the liquid scintillation spectrometer. The counting efficiency of carbon-14 was evaluated from the quench curve and was correlated with tSIE and then DPM was calculated. In the real samples, the activities of carbon-14 were calculated by using this quench correction curve, depending upon the quenching in the scintillation cocktail[5].

### *2.2 Chemical separation of Carbon-14 from simulated CB solution*

For evaluating quantitatively organic and inorganic carbon-14, 3 types of simulated compound labeled by $^{14}C$, $Na_2{}^{14}CO_3$, alcohol (1-pentanol + 1,3-butanediol), and 14C-toluene were prepared. In order to measure the whole contents of carbon-14, 3 sorts of samples containing 1g of $H_3BO_3$ refluxed with 5g of $K_2S_2O_8$ and 0.5g of $AgNO_3$ used as oxidizing agent mixture and 3N $H_2SO_4$ solution was dropped to that slowly during heating up to 90~96℃ to convert organic and inorganic compounds of carbon-14 into $^{14}CO_2$. The generated $^{14}CO_2$ gas was adsorbed to Carbo-sorb trap (Packard) for counting carbon-14, and the result was shown in Figure 1. From Figure 1, $Na_2{}^{14}CO_3$ had the highest recovery rate, 93±1%, alcohol and toluene at the activity of above 100Bq were shown each 90±1 and 82±1% in the recovery rate with wet oxidation method. What the recovery rate of organic carbon is lower than that of inorganic one was because CO and hydrocarbon like methane in organic compounds were formed by being incompletely decomposed and do not adsorb to Carbo-sorb solution.

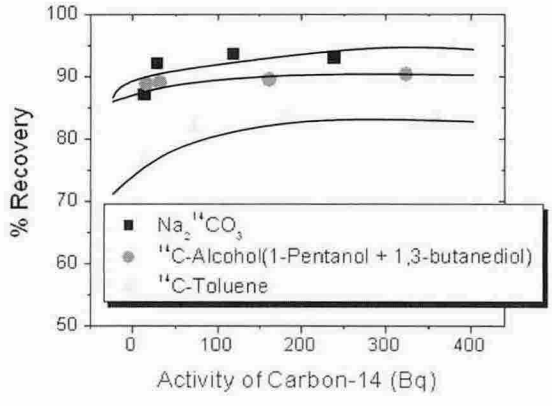


Figure 1. Recovery of carbon-14 in various $^{14}C$-labeled compounds with wet oxidation according to activity

In order to obtain quantitatively the contents of inorganic carbon-14 from total one, $^{14}CO_2$ was generated by dropping 0.1~3M HCl at room temperature to 3 kinds of simulated samples for activity counting. Figure 2 showed the process finding only the condition of converting $CO_3^{2-}$ and $HCO_3^-$ into $^{14}CO_2$. That is, according to dropping HCl to samples, organic alcohol and toluene labeled by $^{14}C$ were difficult to resolve into $^{14}CO_2$, but

$Na_2{}^{14}CO_3$ was easily decomposed. This point will be able to apply to extract selectively inorganic carbon-14 from unknown radwastes. Figure 2 represented the recovery of inorganic carbon-14s were obtained from each simulated samples by using 0.5M HCl at room temperature. In every concentrations, 238Bq added $Na_2{}^{14}CO_3$ was indicated to 93±1% of activity, but the recovery was less than 0.3% for alcohol(325Bq) and toluene(360Bq).

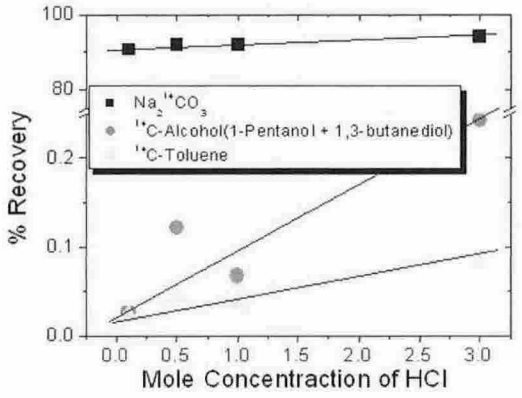


Figure 2. Recovery of carbon-14 in simulated organic and inorganic samples

*2.3 Determination of Carbon-14 in NPP CB solution with wet oxidation*

Total carbon-14 from domestic PWR stations (KR, YK, and UJ) were evaluated with wet oxidation. Inorganic carbon-14 in CB solution was also investigated by means of the method introduced in Figure 2, and shown in Table 1. From Table 1, the contents of total and inorganic carbon-14 in CB were 8.3~1380.5Bq/g and $5.0\times10^{-3}$~6.622Bq/g respectively, and the existence ratio of inorganic carbon–14 was 0.051~2.145% in total one. The contents of organic carbon-14 in domestic CB solution was above 97.86%. In Figure 3, inorganic carbon-14 was in direct proportion to total amount of carbon-14 of each NPP CB solutions

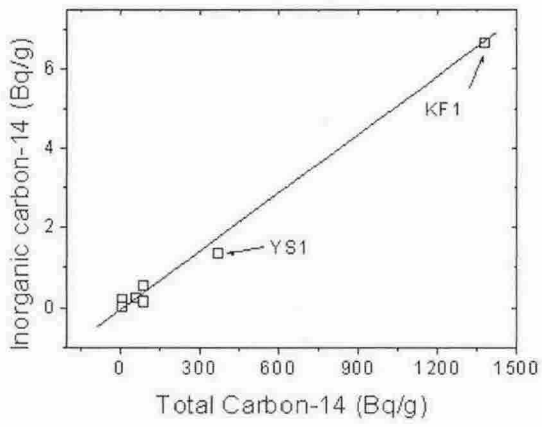


Figure 3. Correlation of total carbon-14 and inorganic carbon-14 of domestic PWR CB solutions

## 3. Conclusion

From simulated concentration bottom solutions, the oxidation condition of organic carbon-14 and the condition of selectively $^{14}CO_2$ generation from inorganic one were investigated. And also, chemical separation properties were evaluated with CB solutions from domestic PWR stations; the existence ratio of inorganic compounds was the max. 2.145% and 0.595% as average in total carbon-14 and the major carbon-14 in CB was mostly organic carbon-14 on the whole.

## REFERENCES

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[3] G. K. Knowles, CONF-791049-13, pp87, 1979.
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[5] M. H. Lee, Applied Radiation and Isotopes, pp257, 2002.

Table 1. Carbon-14 determination of CB solution in NPP with wet oxidation method

| Sample ID | Activity of Carbon-14 (Bq/g) | | Inorganic/organic | Inorganic/Total Carbon-14 (%) |
|---|---|---|---|---|
| | total | Inorganic | | |
| UT1 | 8.3 | 0.178 | 2.132 | 2.145 |
| KT1 | 9.9 | $5.0\times10^{-3}$ | 0.053 | 0.051 |
| YF2 | 62.1 | 0.232 | 0.374 | 0.373 |
| UF1 | 87.4 | 0.133 | 0.152 | 0.152 |
| YF1 | 87.9 | 0.530 | 0.603 | 0.603 |
| YS1 | 371.4 | 1.330 | 0.091 | 0.358 |
| KF1 | 1380.5 | 6.622 | 0.480 | 0.480 |