

Optimization of C-14 Separation Technique by using ^{14}C Labelled Na_2CO_3 and CH_3COONa

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1. Introduction

This study has been focused on determining the analytical method of ^{14}C in terms of both organic and inorganic ^{14}C contents in reactor coolant water from PWRs. The purpose was to offer data that can serve as a basis for reliable estimates of the total ^{14}C inventory in the reactor coolant system. To establish the evaluation of recovery efficiency of ^{14}C , various experimental tests were carried out using known standard ^{14}C solution. And also, the yield of recovery shows 112% in Na_2CO_3 solution of inorganic form and 99% in CH_3COONa solution with organic form. The results have been used to obtain a rough partial mass balance with respect to ^{14}C produced in the reactor coolant.

2. Process Water

2.1 Sampling and sample description

Test samples for analyzing a wide range of process systems were prepared three different standard chemical solution such as inorganic form ($\text{Na}_2^{14}\text{CO}_3$), organic form ($\text{CH}_3^{14}\text{COONa}$). To evaluate the recovery yield of ^{14}C , purchased the 1mCi of $\text{Na}_2^{14}\text{CO}_3$ And 0.25mCi of $\text{CH}_3^{14}\text{COONa}$. Total volume of standard solution is 1.45 ml. And also, the activity of $\text{Na}_2^{14}\text{CO}_3$ has 185Bq in 1M- Na_2CO_3 with 1 liter solution. An activity of $\text{CH}_3^{14}\text{COONa}$ has 46.25Bq in 1M- CH_3COONa with 1 liter solution. The total number of samples processed was 6 samples where the ^{14}C concentration in both water phase was determined. Generally, 100ml of process water was collected in pre-evacuated 100 or 20 ml gas pipettes. These samples were initially processed and measured individually.

2.2 Analytical Method

The method used was based on the same principle as the ion exchange resins with the chemical treatment optimized for 100 ml of process water. A schematic outline of the system with relevant parameters is seen in Figure 1. The method was optimized using ^{14}C -labelled $\text{Na}_2^{14}\text{CO}_3$ and sodium acetate ($\text{CH}_3^{14}\text{COONa}$) with obtained recoveries of $> 96\%$ for both compounds. The loss of sodium acetate during acid stripping (resulting in

an overestimation of the inorganic ^{14}C content) was determined to be 1.2%.

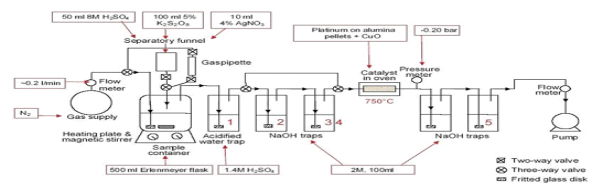
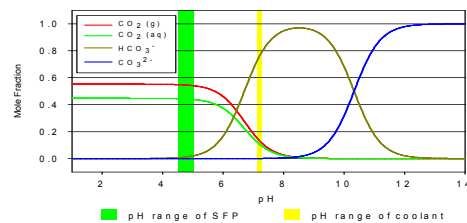


Figure 1. Schematic overview of the system used for extracting ^{14}C from process water

2.3 Behavior of CO_2 in liquid phase according to pH

As shown following figure2, behavior of CO_2 changes HCO_3^{-2} and CO_3^{-2} depending on pH in liquid phase. So the variation of pH under the chemistry condition in reactor coolant system becomes the key parameter to control the effluent radio carbon dioxide.



2.4 Procedure for ^{14}C extraction

Fig.2. CO_2 Behavior in the liquid by the pH Change

2.4 Procedure for ^{14}C extraction

The gas pipettes were mounted onto the system as shown above Figure 1 and the volume of process water transferred to the sample container by applying an overpressure using N_2 at the upper inlet of the pipette. For samples containing gas and water phase, the sample was purged with N_2 for 20minutes to collect any volatile compounds before transferring the water volume to the sample container. The inorganic ^{14}C -species were extracted from the water by adding 20ml of 8M H_2SO_4 and purging the water volume with N_2 for 1 hour. After the acid stripping was completed, the organic species were oxidized by adding 2×50 ml of $\text{K}_2\text{S}_2\text{O}_8$ and 2×5 ml of 4% AgNO_3 in two steps during subsequent heating (80–100°C) for 1 hours. The two ^{14}C -fractions

(organic and inorganic) were collected separately in gas washing bottles containing 2M NaOH.

2.5 Analysis

The purpose of the present work was to analyze the CO₂ concentration in liquid samples using two representative methods. First, the BaCO₃ precipitate was formed in the 250ml of NaOH solution added of 10g of NaHCO₃ and BaCl₂. The CO₂ extracted from the BaCO₃ precipitate was mixed with a CO₂ absorbent, CARBO-SORB E, and then trapped into the counting vial for LSC. The standard solution, NIST 4990C oxalic acid, was used in this method. Second, the 17 ml of Optiphase Hisafe3 reagent was directly mixed into 3 ml of NaOH solution. The amount of CO₂ concentration in this solution was measured using LSC.

Table 1. The Results of pre-tests for RCS analysis with NIST 4990C Oxalic Acid (Permafluor + Carbosorb)

ITEM	Only Inorganic (Na ₂ CO ₃)		Only Organic (CH ₃ COONa)		Organic + Inorganic	
	Inorg.	Org.	Inorg.	Org.	Inorg.	Org.
Net Counts	3355.7	139.6	14.4	860.3	3308.0	867.2
Collected CO ₂	2.539	1.935	2.399	2.299	2.424	2.388
Total BaCO ₃	24.07	24.61	24.04	24.20	24.80	24.06
Total CO ₂	5.37	5.39	5.36	5.40	5.53	5.37
Total counts	7638	394	36	2024	7554	1952
dpm	10772	555	51	2854	10652	2753
dps	179	9.26	0.85	47.6	177.5	45.9
Yield(%)	97.04	1.7	1.84	102.85	95.9	99.21
Wanted Yield	100	0	0	100	100	100
Known Bq	185	0	0	46.25	185	46.25

Samples below the detection limit were precipitated as BaCO₃ and the precipitate measured by LSC giving an improved detection limit of ~0.4Bq/kg. During the sample processing, the efficiency of the degassing of the water samples prior to water processing was tested to be 100% (n=1). The efficiency of the wet oxidation was also 100% (within statistical limits; n=8), i.e. no significant difference in the absorbed ¹⁴C activity in the wash bottles was seen between the two additions of wet oxidation chemicals. The degree of oxidation by means of the strong oxidant (i.e. the ability of converting the ¹⁴C-species to CO₂) was found to be nearly 100%, which means that the use of the catalyst oven had no significance during this part of the treatment.

2.6 Chemical speciation of Standard Solution

According to above results, small amount of organic form was founded in the process of inorganic solution experiment. That means these samples contaminated during the pretreatment process. And also, It shows the contamination of 1.7% inorganic form during the testing

of recovery efficiency by using standard organic solution. That means it require great skill for analyzing of ¹⁴C. But the process of mixed solution(Organic+Inorganic) shows the good results. Small hydrocarbons left in the water phase after degassing would have been found after the catalyst during the 1hr of acid stripping. If formic and acetic acid is present in the process water, only a small fraction would escape from the sample during the acid treatment, but effectively oxidized during the wet oxidation.

3. Result and Discussion

In order to analyze the C-14 concentration in liquid samples, pretreatment and CO₂ adsorption system was developed. The C-14 concentration in a various liquid solution was measured using C-14 standard solution. Organic, inorganic and mixture sample solutions were prepared. The recovery rates for C-14 in the sample solution were shown in Table 1. Total 6 sample solutions were prepared with organic, inorganic, and mixture respectively as a treatment method. The efficiency of inorganic sample solution was measured up to 98% but organic compounds are detected of 1.7% also. The recovery rate of organic sample solution was measured of 102.9%. Therefore, the measurement of C-14 concentration in organic and inorganic solutions was taken carefully. However, the rate of organic and inorganic mixture was good. The recovery efficiency for the mixture was consistent in addition of organic and inorganic solutions.

4. Conclusion

Two preparation methods for C-14 measurement in the liquid solution have been developed. The recovery test for C-14 concentration in the liquid solution was contented with up to 96% using C-14 standard solution. For the reliable analysis results of this method, additional studies were required with a various conditions. The results of observations with these methods were carried out in analysis of C-14 concentration dissolved in the reactor coolant and the spent fuel storage solution.

References

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