Tritium quantification in metallic samples

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1. Introduction

ITER radwastes are generated from various facilities, which are Tokamak, hot cell building, RWB, and tritium plant building during operation and maintenance of ITER. The treatment systems of the radwastes are for long half lives intermediate radawstes (Type B radwastes generated in Tokamak), the radwastes including pure tritium (from tritium plant and fuel), and low level solid and liquid radwastes (Type A radwastes). The radwastes are required to be analyzed for radionuclide inventory before the radwastes will be stored at ITER hot cell facilities for 20 year according to the ITER policy. Especially, tritium shall be analyzed becaussue of its concentration in the waste potentially higher than the Type B tritium criterion.

There are several destructive or non-destructive methods for assay of tritium in metallic samples. A non-destructive method generally adopts high-sensitive photo film along with β - particle detection technique. Other non-destructive ones are the Radiography (RG) technique in which it applies the magnetic microscope and radioluminography (RLG) based on the photo stimulated luminescence (PSL). In destructive analysis methods, electrochemical layer-by-layer etching (ELLE) and chemical acid dissolution or chemical acid leaching method (CAD of CAL) have known as mostly common techniques. The CAD or CAL technique as a destructive method has a merit of accurate analytical result and convenient test method compared to above non-destructive methods. Accordingly, it is considered that CAL method is the most suitable for tritium quantification.

CAL method has already been developed in Nuclear Chemistry Research Division (NCRD). However, some metallic samples need to be analyzed for improvement of analytical reliability of CAL method. Considering tritium concentration in ITER radwastes, radwastes of CANDU type NPP was selected as a proper sample, since ITER sample has 10^{-9} Bq/g of radioactivity. Compared to samples in PWR and BWR NPP, tritium concentration in the coolant of Korean CANDU NPP has been reported to have a concentration of 0.1 MBq/m^3 during 2000 ~ 2006, whereas the case of Korean PWR NPP was about 0.003 MBq/m^3 in the same time frame.

The samples aimed at this project for tritium measurement are pressure tubes irradiated by nuclear fuels of CANDU type Korean NPP, which had been used for supporting nuclear fuel bundles. Although the CANDU samples are difficult to be directly compared to ITER metallic radwastes, they were prepared for evaluation of application of CAL method.

2. Methods and Results

2.1 Quench Calibration for Tritium measurement

To obtain the counting efficiency form quench levels in tritium counting, 73,059 Bq of a tritium standard (spec-check, Packard) was put into each 10 scintillation vials. And 14 ㎖ of Ultima Gold LLT cocktail was added on each vial. Finally, nitromethane used as a quenching agent was also added in the range of 0 ~ 100 ㎕ to each vial. A quench indicator in which we use the gamma activity of ^{133}Ba as the external quench standard monitoring prior application was adjusted to tSIE/AEC (transformed spectral index of external standard) mode, and a quenching correction curve was prepared.

2.2 Chemical separation of tritium in metallic samples

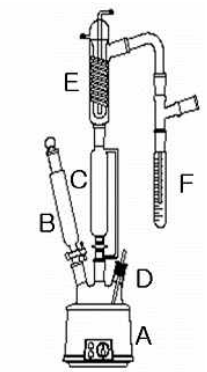

Figure 1. Apparatus for tritium analysis by CAL
A: Reactor(200 mL flask), B: 3N H_2SO_4,
C: Tritium receiver, D: He Bubbler,
E : Cooler, F: Pt-catalyst

The CALM device for tritium quantification was estabilished through some basic literatures and installed for tritium quantification in the radioactive substance as shown in Figure 1. In Figure 1, the reactor of the apparatus consists of 200 mL flask (A), oxidant inlets (B),

and O_2 gas bubbler (D). Most of the gaseous tritium is converted to the liquid form of tritium (HTO) by oxidation reaction in the reactor. However, the non-reacted gaseous tritium with the oxidant is converted to liquid form by Pt catalyst in the collector (F). Moreover, liquefied tritium is distillated and collected in the funnel pressure equalizer (C) after oxidation reaction.

Tritium separation system for CALM is required for closed environment, distillation and collection device of tritiated water, which was particularly manufactured in order to develop the tritium quantification. The chemical method for the tritium quantification is that radwaste samples and potassium persulfate ($K_2S_2O_8$) are put into a reactor for chemical oxidization, and sulfuric acid (H_2SO_4) drops slowly into the reactor for converting chemical gas form of tritium to liquid form through oxidation reaction. At that time, non-reacted gaseous tritium with chemical oxidants is oxidized on the surface of Pt catalyst and converted into tritiated water.

2.3 Minimum Detectable Activity (MDA)

The minimum detection activity (MDA) or minimum detectable limit is the term generally used in the radioactivity measurement field as the minimum radioactive concentration level in which it can be actually detected. A Lower Limit of Detection (LLD), which is also used for the reliability evaluation of analyzed results in the field of analytical chemistry, is the statistically calculated value considering counting value of the back ground and counting efficiency. Compared to LLD, MDA includes not only many factors affecting sample size, measurement time, self absorption, chemical yield, and radioactive concentration but also the characteristics (blank and counting efficiency) of the detector. Accordingly, the measurement results can be easily changed by the factors mentioned in the upper part. MDA has to be calculated in case of any change. Moreover, even in case of the revised analytical method and replaced measurement equipment, MDA has to be re-calculated.

Calculation of MDA of tritium using LSC is as follows

$$MDA = \frac{2.71 + 4.65\sqrt{C_b T_b}}{E_{ff} \times V_S \times T_S \times 60} \qquad (1)$$

MDA (Bq/g)	:	Minimum Detectable Activity
$E_{ff.}$	:	Counting Efficiency
V_S (g)	:	Weight of Sample
T_S (min)	:	Sample Counting Time
T_b (min)	:	Background Counting Time
C_b (cpm)	:	Background Counting Rate

Table 1. LSC parameter for the calculation of MDA

radionuclide	$E_{ff.}$	C_b (cpm)	T_b (min)	T_S (min)
Tritium	0.35	6	30	30

Table 2. Minimum detectable activity for tritium quantification

Sample	Weight (g)	MDA (Bq/g)
Metallic Radwaste	5	4.5E-2
	10	2.2E-2
	20	1.1E-2

When measuring the radioactivity of tritium using LSC, counting efficiency, the substrate mass, measure-ment time, blank measurement time, blank counting rate, and etc could affect the measurement value of tritium. Each measurement variables are shown in table 1.

2.4 Tritium measurement

Through CAL method, tritium concentration in the sample was analyzed to be 4.9E+2 Bq/g. Aslo, to confirm the complete leaching of tritium from the sample, CAL method tried to apply over again for the leached sample with acids. As a result of 2nd acid leaching, tritium concentration was measured as 4.2 Bq/g, which tritium detection amount reaches about 0.8% level comparing to the result of 1st acid leaching. It was confirmed that 99% of tritium in the sample was detected through 1st acid leaching.

3. Conclusion

In order to improve the analytical reliability for tritium quantification in metallic radwastes, spent pressure tube generated from CANDU type NPP, which was substituted for ITER metallic radwastes, was considered to test tritium analysis method (CAL). Through CAL method, tritium was analyzed. In was confirmed that about above 99% of tritium was completely extracted from the sample.

REFERENCES

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