

Determination of Tritium Content in Radioisotope Wastes by a Wet Oxidation Method

Heung Nae Lee, Seung Dae Yang, Kwang Yong Jee,^{*} and Se Chul Sohn^{*,*}

Advanced Radiation Technology Institute, Korea Atomic Energy Research Institute, Jeonbuk 580-185, Korea

[†]Nuclear Chemistry Research Division, Korea Atomic Energy Research Institute, Daejeon 305-353, Korea

^{*}E-mail: nscsohn@kaeri.re.kr

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Tritium is a naturally occurring radioisotope produced continuously in the atmosphere by the neutron interaction of cosmic ray with helium (${}^4\text{He}(n, np){}^3\text{H}$). It is also produced as a by-product or special product in nuclear reactor systems. Tritium produced in nuclear power reactors as a result of the fission of heavy nuclei and by neutron interaction with coolants, moderators, and some light elements (${}^7\text{Li}$, ${}^9\text{Be}$, and ${}^{10}\text{B}$).¹ Tritium labeled materials are extensively used as tracers, in density gauges, in teletherapy, and as the self-luminous light sources in industrial, medical, educational, and research organizations.² Tritium is a radioactive isotope of hydrogen and has a half-life of 12.3 years. It decays to ${}^3\text{He}$ by emitting low-energy beta radiation with an average energy of 5.7 keV and a maximum energy of 18.6 keV.^{3,4}

In general the amount of tritium present in a sample is measured by three methods: the sample oxidizer method,⁵ the bomb oxidation method,⁶ and the wet oxidation method.⁷ The sample oxidizer method has been used commercially for the separation of tritium by igniting the sample for a short period of time, i.e. for about 5 min. However in this method, less than 1 g of the sample can be ignited at a time. If the sample has a low density, there may be difficulty in measurement because this method cannot use large volumes. The bomb oxidation method, on the other hand, can handle a larger weight of sample (up to 20 g), but

it produces large quantities of water because of complete ignition of the sample. Hence, a longer time is required to reduce the volume of produced water produced. The wet oxidation method can treat an amount of about 5 g and can control the volume of the H_2O produced. However this method cannot handle non-combustible samples such as the glass bottle.

The Ministry of Education, Science and Technology (MEST) in Korea regulates radioisotope (RI) wastes through the Notice 2008-64 (100 Bq/g). Under this regulation the wastes need to be self-disposed by a nuclear enterprise. During this process of self-disposal, the volatile radionuclides (${}^3\text{H}$, ${}^{14}\text{C}$, ${}^{32}\text{P}$, ${}^{35}\text{S}$, ${}^{125}\text{I}$, ${}^{131}\text{I}$, etc.) present in the wastes are the difficult-to-measure (DTM) radionuclides. Since the wastes are composed of both scissile and unscissile samples, they need to be measured using an established method.

In this study, the wastes generated from various institutes or industries were classified as combustible and non-combustible materials. Some examples of the samples are vials, pipette tips, tubes, syringes, papers, bottles, etc. The radioisotope (RI) wastes containing tritium were chemically separated and analyzed by a wet oxidation method modified for open vessel equipment, which was capable of handling samples of large size and weight (Figure 1).

The background count rate and specific activity were evaluated from the detection limit (L_D , cpm)⁸ and the minimum detectable activity (MDA, Bq/g).^{5,10,11} respectively.

$$L_D(\text{cpm}) = 2.71 + 4.65\sqrt{C_b T_b} \quad (1)$$

$$\text{MDA}(\text{Bq/g}) = \frac{2.71 + 3.29\sqrt{C_b T_b(1 + T_s/T_b)}}{\epsilon_{\text{eff}} \times W \times T_s \times 60} \quad (2)$$

C_b : Background count rate (cpm), T_b : Background counting time (min), ϵ_{eff} : Counting efficiency, W : Weight of sample (g), and T_s : Sample counting time (min).

The MDA values of the solid samples for tritium counting were measured to be $\sim 1 \times 10^{-2}$ Bq/g. For the counting time of 30 min, the counting efficiency was 30%. And the mass was about 20 g. As shown in the equation 2, the counting efficiency (ϵ_{eff}) was influenced by the MDA value at the same counting time (30 min) and the same weight (20 g). If the count rate of the sample is below L_D , it means that the activity of the sample is not detectable (N.D.). Even if the count rate is over L_D , if the

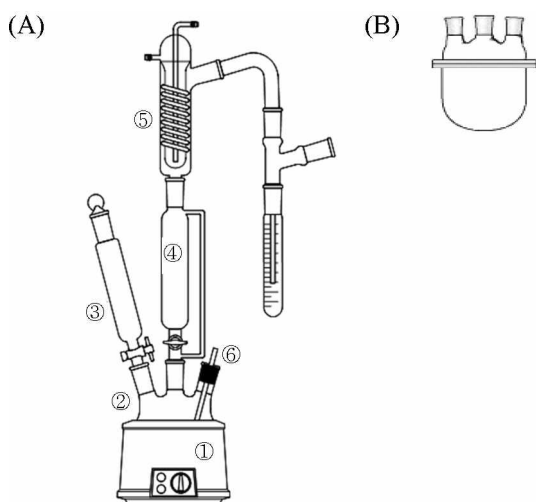


Figure 1. Wet oxidation equipment. (A) A full equipment set and (B) an enlarged round bottom flask. ① Heating mantle, ② Round bottom flask, ③ Dropping funnel, ④ HTO collector, ⑤ Reflux condenser, and ⑥ He gas inlet.

Table 1. The measurement of tritium (12.17 Bq) counting for simulated solid wastes

Sample	Weight (g)	Exp. (Bq)	Yield (%)	RSD (%)
Vial	19.5	11.68	96.0	1.25
Tube	20.3	11.75	96.6	2.05
Vinyl	10.1	11.67	95.9	1.56

Table 2. Specific activity for tritium content in RI wastes of the representative combustible materials.

Sample	Type	Activity (Bq/g)
C01	Vial, Tip	1.226 ± 0.454
C02	Paper, Vinyl	2.086 ± 0.935
C03	Tube, Tip	2.597 ± 0.099
C04	Vial	6.524 ± 0.538
C05	Vial	17.24 ± 3.85
C06	Vial	18.29 ± 3.64
C07	Cotton, Paper	20.42 ± 4.21
C08	Paper, Vinyl	21.58 ± 0.75
C09	Vial	30.07 ± 8.76
C10	Vial	51.48 ± 11.93
C11	Vial	619.6 ± 75.1

Table 3. Specific activity for tritium content in RI wastes of the representative non-combustible materials.

Sample	Type	Activity (Bq/g)
NC01	Vial	3.76 ± 1.19
NC02	Tube	5.95 ± 2.11
NC03	Reagent bottle	13.70 ± 1.92
NC04	Tube	388.7 ± 8.7
NC05	Vial	1254 ± 234
NC06	Vial	1598 ± 170

specific activity of the sample is below the MDA value, this activity would be regarded as N.D.

The recovery efficiency for tritium of the simulated samples was measured using an open vessel device. The percentage of the counting for tritium was found to be about 96% with an error tolerance of (1~2)% RSD (Table 1). The count rate was monitored in cpm (counts per minute). The cpm was converted to dpm (dis-integrations per minute), which is adjusted with the counting efficiency (25~30%). Generally, the counting efficiency for tritium is about 35% if 14 mL of the cocktail and 5 mL of water are used as the LSC samples.⁵ In this case, the low efficiency was caused by a quencher such as NO_x generated from the sample.

The radioisotope (RI) wastes generated from the various organizations were classified into combustible and non-combustible materials. Combustible wastes, of which there were 47 RI samples, were composed of PE vials, PE tubes, papers, syringes, plastics, reagent bottles, etc. Non-combustible wastes, of which there were 12 RI samples, were typically made up of glass objects such as vials, reagent bottles, tubes, etc. The experimental should treat a large weight or volume of the samples to minimize the matrix effect since most of the samples were large in their

size, and furthermore the samples were heterogeneous. The specific activities of the combustible and non-combustible wastes generated from the various organizations were measured with ($1.23 \times 10^0 \sim 6.23 \times 10^3$) and ($3.76 \times 10^0 \sim 6.38 \times 10^4$) Bq/g, respectively. The representative results are shown in Tables 2 and 3. The RSD was less than 30% except for C01 (37%), C02 (45%), and NC02 (35%) samples. The relatively low RSD was due to the low specific activity and heterogeneous sample type (tube, paper, vinyl, etc). The RI wastes with higher activity than that allowed in the regulation as per the Notice (100 Bq/g) were monitored within 15% for combustible samples and 50% for non-combustible samples.

In summary, RI wastes with low density and low homogeneity generated from industrial, medical, educational, and research organizations were treated by a wet oxidation method using modified open vessel equipment to measure the activities of tritium. The recovery efficiency of tritium for the simulated experiment was around 96% with (1~3)% RSD. The counting efficiency was measured to be (25~30)% and the MDA was found to be 1×10^{-2} Bq/g. The specific activities for the combustible and non-combustible materials were measured to be ($1.23 \times 10^0 \sim 6.23 \times 10^3$) and ($3.76 \times 10^0 \sim 6.38 \times 10^4$) Bq/g, respectively. The RSD of the specific activity was typically less than 30%. Hence, it can be concluded that a wet oxidation method using open vessel equipment can be used both for the treating the samples of low density such as the paper and vinyl and the heavy weight samples such as metal and reagent bottles.

Experimental Section

Reagent. Tritium in the HTO form purchased from Amerisham Co. was used after the activity was diluted to 117 Bq/mL. The RI wastes used were those generated from the industrial, medical, educational, and research organizations since 1995.

Equipment. Open vessel equipment was manufactured for treating a large weight and/or size in an acidic condition. The tritium contents were determined by a liquid scintillation counter, LSC 2500 TR/AB (Model Chill Pack 1419, Perkin-Elmer). The measured cpm was converted to dpm by adjusting the counting efficiency.

The simulation of the solid wastes: 5 g of K₂S₂O₈ and 0.5 g of AgNO₃ were added to 50 mL of 1.5 M H₂SO₄ solution. 20 g of the solid wastes (vials, pipette tips, tubes, syringes, paper, glass) and 0.1 mL the standard tritium (HTO; 117 Bq/mL) were then added to the solution. After refluxing for 3 h, the collection of tritium (HTO) was distilled to the collector (Figure 1). 5 mL of distilled water in HTO form as LSC samples was mixed with 14 mL of Ultima-Gold XR. The samples and the background were counted by LSC for 30 min and the count was adjusted by the quenching correction curve.

The distillation of the RI wastes: The same procedure as the simulation experiment was repeated except that in this case (10~30) g of the RI wastes brought from the various organizations was used. The activities of tritium (HTO) produced from the distillation were counted by LSC. This was adjusted by the quenching correction curve and the background count rate for 30 min.

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