METHODS FOR DETERMINING ^{3}H FROM RADIOACTIVE WASTE GENERATED BY TRIGA REACTOR

LILIANA BUJOREANU

Institute for Nuclear Research (RATEN ICN) Pitești, Romania
e-mail: liliana.bujoreanu@nuclear.ro

Abstract

In this paper, three methods for the determination of tritium (^{3}H) in the radioactive waste generated from the TRIGA reactor operation, namely distillation, combustion and acid stripper were studied. Because the waste from the TRIGA reactor operation contains a wide range of gamma radionuclides which, in addition to the gamma rays, also emit beta particles that may interfere with the measurements performed to determine the ^{3}H activity, a chemical separation step must be performed. The distillation technique was applied to separate ^{3}H isotope from other β-γ emitters for its subsequent measurement by liquid scintillation spectrometry (LSC) using the proper liquid scintillator. Combustion is the second method used to separate ^{3}H from other radionuclides present in the radioactive waste generated by the TRIGA reactor operation. During the combustion process, all hydrogen isotopes, including tritium, are oxidized to water which due to the high combustion temperatures is in the form of steam. The steam is condensed in an air-cooled condenser and the tritiated water is collected in the tritium counting vial together with the liquid scintillation cocktail MONOPHASE. The analytical method used for inorganic and organic ^{3}H measurement in radioactive waste is based on the acid dissolution and wet oxidation processes. In order to measure ^{3}H activity by LSC, homogeneous samples were obtained. As tritium is stable in acid conditions and remains in the reaction vessel during acid stripping/wet oxidation, this method can be applied for matrix dissolution in solid radioactive waste. For tritium measurement, the solution from the reactor vessel is distilled to separate ^{3}H for LCS measurement. For liquid radioactive waste distillation is recommended to be applied for tritium separation in view of its measurement by LSC.

Keywords: *Liquid scintillation counting, Combustion, Activity, Acid stripper, Radioactive waste*

Introduction

Tritium (^{3}H), a radioactive isotope of hydrogen, is naturally produced in very small quantities in the atmosphere and is one of the radionuclides generated by nuclear reactor operation, both by ternary fission and by activation. Tritium has a half-life of 12.3 years and decays to ^{3}He with the emission of a beta particle and no gamma ray [1].

Liquid Scintillation Counting (LSC) is a very sensitive and widely used technique for the detection and quantification of radioactivity. To be measured by LCS, the sample must be prepared so that liquid scintillation analyzer quantifies a homogeneous mixture of sample and scintillation solution. The scintillation solution (the cocktail) consists of a mixture of a solvent and a solute (scintillator). The counting efficiency is calculated using the following relation [2]:

$$Efficiency\ (\%) = \frac{Counts\ Per\ Minute}{Disitegration\ Per\ Minute} \qquad (1)$$

Most of the radioactive waste generated by TRIGA reactor operation follows in the category of low and intermediate level waste (LIL) which may be treated and conditioned to meet the waste acceptance criteria for their disposal in National Repository Baita Bihor.

The liquid wastes are collected and stored in eight tanks, according to the generation sources, and after a proper control these are transferred to the Radioactive Waste Treatment Department (STDR) for treatment and conditioning in view of their disposal.

Solid low level waste (LLW) is produced from various operations performed daily in the reactor and are sorted and collected as compactable (paper, textile, plastic, rubbers) and non-compactable radioactive waste (tools, metallic parts, glass) and transferred to STDR for their processing in view of disposal [3].

The radioactive waste from TRIGA reactor contains a wide range of radionuclides, therefore to measure the concentration activity of ^{3}H in any category of waste it has to be transferred in liquid phase and separated from other interfering radionuclides (i.e. mainly gamma radionuclides that emit by their disintegration not only γ rays but also β particles).

Methods and Experimental set-up

Gamma ray Spectrometry

The gamma ray spectrometry is a non-destructive technique that does not require a laborious sample preparation.

Because the gamma ray energies are well defined and high resolution γ-ray spectrometers are now available, the gamma-ray spectrometry allows identification and quantification of a wide range of radioisotopes [4].

To obtain accurate and reliable results, the first step in gamma spectrometry analysis is the energy and efficiency calibration of gamma spectrometer. It is important that these calibrations are correctly performed since the calibration results will affect all the subsequent analyses. The gamma ray spectrometry [5] was applied in quantification and identification of gamma ray emitters present in liquid and solid radioactive waste.

Analyses of radioactive solid waste (paper and resin) using gamma ray spectrometry

Following the measurements performed by the gamma spectrometry, the presence of the beta-gamma emitting radionuclide ^{137}Cs was observed having an activity of 2.75Bq/g in the solid waste paper-type and the radionuclide ^{60}Co was observed having an activity of 4.25x10^{3}Bq/g in the resin waste.

Analyses of liquid radioactive waste using gamma ray spectrometry

Liquid waste samples from four waste collection lines of TRIGA reactor and water sampled from the reactor pool were analyzed by gamma spectrometry and the data obtained are presented in the Tables 1 and 2, respectively.

Table 1. Radionuclide activity in liquid waste

Radionuclide	***Activity [Bq/ml]***
Mn-54	0.696
Co-57	0.0376
Co-58	1.77
Co-60	10.5
Sb-124	0.29
Cs-137	0.05

Table 2. Radionuclide activity in pool water

Radionuclide	***Activity [Bq/ml]***	***Activity MDA [Bq/ml]***
Co-58	<MDA	0.019
Co-60	<MDA	0.020
Cs-137	<MDA	0.0235

Combustion of solid radioactive waste

To measure the tritium content in solid radioactive waste, tritium has to be extracted from the waste matrix in a solution and, as it is a low beta emitter, absence of other beta-gamma emitters in the samples to be analyzed by liquid scintillation counting (LCS) is a prerequisite. The PerkinElmer Sample Oxidizer, Model 307 (Figs. 1 and 2) provides an automatic method for preparing a sample for measuring tritium by liquid scintillation counting. In accordance with PerkinElmer Sample Oxidizer Operation Manual, the performance of the equipment [6] is obtained using: fresh chemicals (MONOPHASE® S), typical parameters of combustion time and reagents volumes that must be determinate based on sample size [7].

According to the Operational Manual, before the solid waste combustion, preliminary tests to evaluate the tritium recovery were performed using a verification procedure.



Fig. 1. Model 307 PerkinElmer Sample Oxidizer

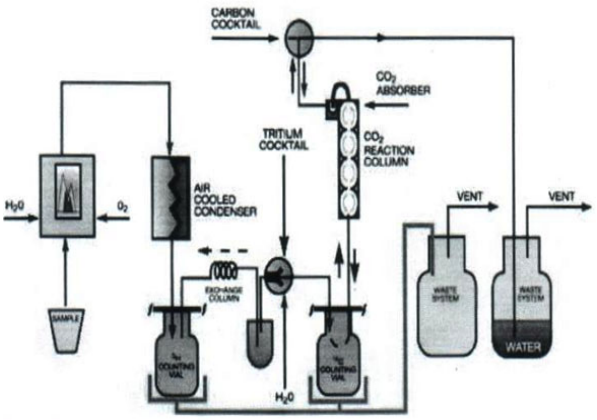


Fig. 2. Flow diagram of sample preparation with the 307 Sample Oxidizer

This test consists in the following sequence of operations:
- 0.2ml non-radioactive SPEC-CHEC solution was pipetted into a combusto-cone that was then inserted into the ignition basket and the sample was burned. When the program was completed, the ^{3}H collection vial was removed and marked as *1BKG;*
- the combustion procedure was repeated three more times and in each of the resulted vials (marked as *2STD, 3STD* and *4STD*) it was added 0.2ml of ^{3}H SPEC-CHEC standard solution with activity of 1.4x10^{6}DPM/ml;
- 0.2ml of ^{3}H SPEC-CHEC standard solution was pipetted into a combusto-cone and immediately the sample was combusted. The ^{3}H collection vial was marked with *5REC*; this step was repeated two more times and the resulted vials were marked as *7REC* and *9REC*.

After stabilization, the seven vials were counted by LSC method using TriCarb3110TR.

^{3}H recovery percentage was computed using the relation:

$$\%\ recovery = \frac{[RECsample\ dpm]}{[AvgSTD\ dpm]} \text{x}100 \qquad (2).$$

^{3}H recovery yield was in the range of 87.83-90.8% (see Table 3) with an average of 89.32%, this value was used to correct the experimental results obtained on radioactive waste paper-type and resin.

Table 3. Values of DPM for ^{3}H

Sample	DPM	Rec. (%)
1BKG	80	
2STD	156370	
3STD	166929	
4STD	157903	
5REC	140881	87.83
6MEM	187	
7REC	145650	90.8
8MEM	176	
9REC	143315	89.34
10MEM	340	

The first step for all solid waste samples preparation for ^{3}H measurement is to obtain a stable homogeneous solution suitable for LSC analysis. A waste sample of 0.2g was used to evaluate ^{3}H activity applying the combustion process.

During this process, tritium is retained together with the MONOPHASE reagent in a 20 ml vial and the process gases are passed through three bubble flasks connected in series, containing the following solutions:

- bubble flask I: 50ml HCl 1N to retain any potential ^{137}Cs released in gaseous forms from the solid waste sample during the combustion;
- bubble flask II and III: each 50 ml NaOH 1M to retain the carbon dioxide.

^{3}H concentration in the samples obtained by combustion was measured by liquid scintillation spectrometry, using *Normal Activity Count Mode (*typical count rate more than 500CPM and 60 minutes count time) and the experimental results are reported in Table 4.

To determine the ^{137}Cs content in the combustion gases discharged through the off-gas system, 10ml of solution were taken from the bubbler flask I for measurement by gamma spectrometry. Following the measurements, the ^{137}Cs activity was 2.35Bq/g which is very close to the value of this radionuclide activity measured by gamma spectrometry (2.75Bq/g).

The experimental results obtained for ^{3}H measurement by LSC after the combustion of resin waste are reported in Table 5. At the end of the combustion process, ^{3}H is retained together with scintillation liquid in a 20ml vial, while ^{60}Co, whose melting temperature ($1495^{0}C$) is well above the combustion temperature, will remain in the ash resulting from the combustion.

Table 4. Experimental data on ^{3}H measurement in paper type solid waste

Sample ID	^{3}H Measured activity [DPM]	^{3}H Measured activity* [DPM]	^{3}H Measured activity ** [Bq/sample]	^{3}H Measured activity [Bq/g]
H1-H	39	-	-	-
H2-H	39	-	-	-
H3-H	39	-	-	-
H4-H	42	3	0.044	0.22
H5-H	40	1	0.014	0.07
H6-H	37	-	-	-
H7-H	42	3	0.044	0.22
H8-H	39	-	-	-
H9-H	42	3	0.044	0.22
H10-H	41	2	0.029	0.14
Blank	**39[DPM]**			
***Average Activity*=0.176Bq/g**				

Act.=Measured Activity-Blank Activity; Act.**=measured activity corrected for combustion recovery(89.3%)*

Table 5. Experimental data on ^{3}H measurement in resin waste

Sample ID	^{3}H Measured activity [DPM]	^{3}H Measured activity* [DPM]	^{3}H Measured activity ** [Bq/sample]	^{3}H Measured activity [Bq/g]
H1-H	41	2	0.029	0.145
H2-H	40	1	0.014	0.07
H3-H	40	1	0.014	0.07
H4-H	39	-	-	-
H5-H	39	-	-	-
H6-H	40	1	0.014	0.07
H7-H	41	2	0.029	0.145
H8-H	41	2	0.029	0.145
H9-H	41	2	0.029	0.145
H10-H	40	1	0.014	0.07
Blank	**39[DPM]**			
***Average Activity*=0.107Bq/g**				

Act.=Measured Activity-Blank Activity; Act.**=measured activity corrected for combustion recovery (89.3%)*

Distillation technique

Alternative to the combustion, distillation was applied to separate tritium by other beta-gamma emitters present in liquid radioactive waste generated from TRIGA reactor operation. After its extraction by distillation, tritium concentration was measured by LSC.

The experimental set-up used for distillation of liquid waste samples (see Fig. 3) consists of a heat resistant flask, a refrigerant and the collection vessel of the distillate. Vapour condensation is done using a refrigerant tightly attached to the exhaust pipe [8].

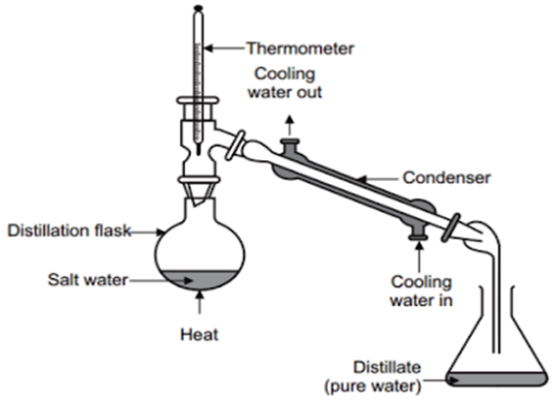


Fig. 3. Experimental set-up for distillation of ^{3}H

The mixture of liquids to be distilled is introduced into the flask up to a maximum of two thirds of its volume, and the flask is heated so that the distillation proceeds slowly and does not create overpressure, therefore the thermometer indicates the actual temperature of the boiling substance.

Ten samples of liquid radioactive waste (labelled D1-D10) of 250ml each were distilled for tritium separation and, to measure ^{3}H concentration by LSC, 1ml of distillate was mixed with 10ml of Ultima Gold XR liquid scintillation cocktail. The experimental results are reported in Table 6.

Table 6. Experimental data on ^{3}H measurement in liquid waste

Sample ID	**^{3}H Measured activity [DPM]**	**^{3}H Measured activity* [DPM]**	**^{3}H Measured activity [kBq/l]**
D1	1850	1825	30.41
D2	1830	1805	30.08
D3	1830	1805	30.08
D4	1845	1820	30.3
D5	1841	1816	30.26
D6	1845	1820	30.33
D7	1847	1822	30.36
D8	1838	1813	30.21
D9	1842	1817	30.28
D10	1840	1815	30.25
Blank	**25[DPM]**		
	***Average Activity*=30.25 kBq/l**		

Act.=Measured Activity-Blank Activity*

A volume of 10ml of distillate was sampled and measured by gamma spectrometry to determine the possible presence of β-γ radionuclides. The results are shown in Table 7.

Table 7. Gamma emitters activity

Radionuclide	**Activity [Bq/ml]**	**MDA activity [Bq/ml]**
Mn-54	<MDA	0.024
Co-57	<MDA	0.009
Co-58	<MDA	0.0019
Co-60	<MDA	0.02
Sb-124	<MDA	0.017
Cs-137	<MDA	0.024

MDA = Minimal Detectable Activity

To measure ^{3}H content in the water pool, ten samples (labelled P1-P8) of 250ml water sampled from the TRIGA reactor pool were distilled. 1ml from distillate was mixed with 10ml Ultima Gold XR liquid scintillation cocktail and measured by LSC. The results are reported in Table 8.

Table 8. Experimental data on ^{3}H measurement in liquid waste from reactor pool

Sample ID	**^{3}H Measured activity [DPM]**	**^{3}H Measured activity* [DPM]**	**^{3}H Measured activity [kBq/l]**
D1	3738	3713	61.88
D2	3827	3802	63.36
D3	3707	3682	61.36
D4	3556	3531	58.85
D5	3686	3661	61.01
D6	3711	3686	61.43
D7	3663	3638	60.63
D8	3725	3700	61.66
D9	3738	3713	61.88
D10	3827	3802	63.36
Blank	**25 [DPM]**		
	***Average Activity* = 61.27 kBq/l**		

Act.=Measured Activity-Blank Activity*

A volume of 10ml of distillate was measured by gamma spectrometry to determine the possible presence of β-γ radionuclides. The results are presented in Table 9.

Table 9. Radionuclide activity

Radionuclide	**Activity [Bq/ml]**	**MDA activity [Bq/ml]**
Co-58	<MDA	0.0159
Co-60	<MDA	0.0182
Cs-137	<MDA	0.0199

MDA = Minimal Detectable Activity

Acid dissolution and wet oxidation

In different solid radioactive waste, tritium may be present both in inorganic form (tritiated water), but also as organic species. Acid dissolution and wet oxidation method developed for inorganic and organic C-14 measurement was tested for inorganic and organic ^{3}H measurements in radioactive waste. The experimental-up (Fig. 4) consists of a reaction vessel, a dropping funnel, a nitrogen supply and a vacuum pump, two gas washing lines with a catalytic furnace between.

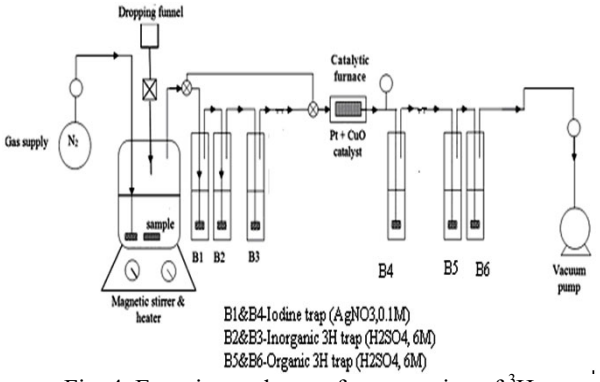


Fig. 4. Experimental setup for separation of ^{3}H

An Erlenmeyer flask (300 ml) with a three-hole rubber stopper (two for gas and separator funnel inlets and one for gas outlet) was used as reaction vessel and a tap-water cooling loop, made of copper tubing, that fit the outer side of the Erlenmeyer flask ensured the vapor condensation.

The reaction vessel was placed on a heater with magnetic stirring. To ensure that no gases escaped from the system, all dissolution and wet oxidation experiments were carried out under vacuum (0.2bar below atmospheric pressure) and the carrier gas (N2) was introduced into the system with a flow rate of 60 to 80 ml/min (controlled by a flow meter) [9].

The acid stripping/wet oxidation method was applied for a solid sample (paper) of 2.06g. For acid stripping stage, 100ml of H_2SO_4 were used. For wet oxidation, a mixture of 30ml $K_2S_2O_8$, 12ml $AgNO_3$ and 5ml distillation water was used. To measure ^{3}H released in gas phase during acid stripping/wet oxidation, two samples from B2 inorganic ^{3}H trap and B5 organic ^{3}H trap were prepared using 1ml solution resulted from the acid stripping stage with 10ml of adequate liquid scintillation cocktail (UltimaGold AB). The results obtained by LCS are presented in Table 10.

Table 10. Experimental data ^{3}H measurement in solid waste

Mass sample [g]	^{3}H	Activity [Bq/g]
2.06	^{3}H anorganic	0.07
	^{3}H organic	0.16
	^{3}H total	0.23

Following the measurements carried out by gamma spectrometry of the solution sampled from the reaction vessel, ^{137}Cs with an activity of 2.25Bq/g was found, very close to the value iniatialy measured by gamma spectrometry in this waste type (2.75Bq/g). This indicates that the ^{137}Cs was completely retained in the reaction vessel, not influencing the measurements performed by LSC. To obtain real results regarding tritium activity in liquid radioactive waste, the acid stripping and wet oxidation steps must be followed by a distillation step of the resulting sample in the reaction vessel.

The acid stripping/wet oxidation was also applied to spent ion exchange resin, for a sample of 9.915g and using as stripping acid 5ml of H_2SO_4 6M (resin sample was introduced in reaction vessel together with 20ml NaOH 2M).

During acid stripping, the radionuclides released in gaseous phase and carried by the nitrogen gas are washed using the first gas washing line, line that is isolated from the system by means of a three-way valve placed before the first scrubbing bottle and the fourth one. Two wet oxidation steps were performed by adding 5ml $K_2S_2O_8$, $AgNO_3$, and 3ml distillation water.

For ^{3}H measurement, two samples from B2 inorganic ^{3}H trap and B5 organic ^{3}H trap were prepared using 1ml solution sampled from these traps and 10ml of adequate liquid scintillation cocktail (Ultima Gold AB). The results obtained by LSC measurement are presented in Table 11.

Table 11. Experimental data ^{3}H measurement in resin waste

Mass sample [g]	^{3}H	Activity [Bq/g]
9.915	^{3}H anorganic	0.03
	^{3}H organic	0.66
	^{3}H total	0.7

The ^{60}Co radionuclide presence in resin samples can influence the results of ^{3}H measurements by LSC as this radionuclide emits by its disintegration both γ and β. For this reason, the first gas washing bottle of the experimental set-up is an acid trap aiming to absorb any γ emitting radionuclides such as Cs, Co, Fe, Mn etc., which may be released as gases during acid stripping/wet oxidation processes.

Analyzing by gamma spectrometry an aliquot of 10 ml from the solution of the reaction vessel, ^{60}Co was identified in this solution in activity close to the one initially measured on the resin sample by gamma spectrometry ($3x10^3$Bq/g).

The third waste category of interest for ^{3}H measurement is the liquid waste generated by TRIGA reactor. For this waste category, the acid stripping/wet oxidation was applied in an attempt to separate tritium contained. The experimental tests were performed on 100ml sample, in two wet oxidation steps, using as stripping acid 5ml H_2SO_4 6M and, as oxidation reagent, a mixture of 5ml $K_2S_2O_8$+4ml $AgNO_3$+3ml distillation water.

For the determination of ^{3}H, two samples from bottles B2, B3, B5 and B6 were prepared using 1ml solution sampled from these bottles and 10ml of adequate liquid scintillation cocktail (UltimaGold AB). The result obtained by LSC measurements are presented in Table 12.

Table 12. Experimental data ^{3}H measurement in liquid waste

Volume sample [ml]	^{3}H	Activity [Bq/ml]
100	^{3}H anorganic	0.0032
	^{3}H organic	-
	^{3}H total	0.0032

As the liquid waste usually contains gamma radionuclides, a sample was taken from the reaction vessel and measured by gamma spectrometry.

The results obtained showed that, following the experimental tests performed, the activities of gamma radionuclides (^{54}Mn, ^{57}Co, ^{58}Co, ^{60}Co, ^{124}Sb, ^{137}Cs) remain in the reaction vessel without influencing the results obtained from the measurements performed by LSC.

For the pool water, the acid stripping wet oxidation method was applied on a sample of 100ml sample using as stripping acid and wet oxidation reagent the same solutions as in previous tests.

For the determination of ^{3}H, two paralele samples from bottles B2, B3, B5 and B6 were prepared using 1ml solution sampled from these bottles and 10ml of adequate liquid scintillation cocktail (UltimaGold AB) and the results obtained by LCS are presented in Table 13.

Table 13. Experimental data ^{3}H measurement in pool water

Volume sample [ml]	^{3}H	Activity [Bq/ml]
100	^{3}H anorganic	0.008
	^{3}H organic	-
	^{3}H total	0.008

Following the acid stripping and wet oxidation process, the results obtained regarding the activity of ^{3}H in liquid waste are different from the those obtained on the same type of samples by using the distillation technique.

For this reason, experimental tests were performed on samples of tritiated water with known activity (^{3}H = 25.28 Bq/ml), the acid stripping procedure being the same as in previous cases.

The results obtained from the measurement of samples by liquid scintillation spectrometry indicated that the values regarding the tritium activity are very close to the background values.

The results regarding the tritium activity in the sample taken from the reaction vessel indicate an activity very close to the initial one, namely 20.95 Bq/ml. This results confirm that during acid stripping/wet oxidation the tritium contained in the analysed samples remain in the reaction vessel and it is not released in gas phase to be captured in the dedicated gas washing bottle.

Conclusions

The main gamma emitters present in the paper-type solid radioactive waste and spent ion exchange resin are ^{137}Cs and respectively ^{60}Co. The main gamma emitters present in liquid radioactive waste sampled from the four waste collection lines of TRIGA reactor are ^{54}Mn, ^{57}Co, ^{58}Co, ^{60}Co, ^{124}Sb and ^{137}Cs. The main gamma emitters present in the pool water are ^{58}Co, ^{60}Co and ^{137}Cs.

Combustion, distillation technique, and acid dissolution and wet oxidation were applied to separate tritium from the waste of interest and liquid scintillation spectrometry was used to measure tritium concentration in the waste from TRIGA reactor.

The value of tritium activity obtained from the combustion method is around 0.176 Bq/g for paper-type solid waste, and 0.107 Bq/g for spent ion exchange resin, values very close to those obtained by acid dissolution and wet oxidation (0.23 Bq/g and 0.1 Bq/g) close to background level.

The value of tritium activity obtained from distillation method is 61.27 kBq/l for water sampled from the reactor pool, while in the liquid radioactive waste sampled from the collection lines of TRIGA reactor tritium content is 30.25 kBq/l.

As tritium is stable in acid conditions and remains in the reaction vessel during acid stripping/wet oxidation, this method can be applied to solid radioactive waste for matrix dissolution. For ^{3}H measurement by LSC, the solution from the reaction vessel is distilled to separate tritium.

For liquid radioactive waste, distillation is recommended to be applied for tritium separation in view of its measurement by LSC.

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