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Comparative Study of Tritium Analysis Method with High-Volume Counting Vial

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ABSTRACT

Background: Tritium (^3H) analysis in groundwater was difficult because of its low activity. Therefore, the electrolytic enrichment method was used. To improve the detection limit and for performing simple analysis, a high-volume counting vial with the available liquid scintillation counter (LSC) was investigated. Further, it was compared with a conventional 20-mL counting vial.

Materials and Methods: The LSC with the electrolytic enrichment method was used ^3H analysis in groundwater. A high-volume 145-mL counting vial was compared with a conventional 20-mL counting vial to determine the counting characteristics of different LSCs.

Results and Discussion: When a Quantulus LSC was used, the counting window between channels 35 and 250 was used. The background count was approximately 1.86 cpm, and the counting efficiency increased from 8% to 40% depending on the mixing ratio of the volume of sample and cocktail solution. For LSC-LB7, the optimum counting window was between 1 and 4.9 keV, which was selected by the factory (Hitachi Aloka Medical Ltd., Japan) by considering quenching using a standard external gamma source. The background count of LSC-LB7 was approximately 3.60 ± 0.29 cpm when the 145-mL vial was used and 2.22 ± 0.17 cpm when the 20-mL vial was used. The minimum detectable activity (MDA) of the 20-mL vial was greater for LSC-LB7 than for Quantulus. The MDA with the 145-mL vial was improved to 0.3 Bq/L when compared with the value of 1.6 Bq/L for the 20-mL vial.

Conclusion: The counting efficiency when using the 145-mL vial was 27%, whereas it was 18% when using the 20-mL vial. This difference can be attributed to the vial volume. The figure of merit (FOM) of the 145-mL vial was four times greater than that of the 20-mL vial because the volume of the former vial is approximately seven times greater than that of the latter. Further, the MDA for ^3H decreased from 1.6 to 0.3 Bq/L. The counting efficiency and FOM of LSC-LB7 was slightly less than those of Quantulus when the 20-mL vial was used. The background counting rate of the Quantulus was lower than that of the LSC-LB7.

Keywords: LSC-LB7, High Volume Vial, Tritium

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Introduction

Tritium (^3H) is the radioactive hydrogen isotope with pure beta emitter (E_{max} = 18.6 keV) and have a half-life of 4,500 ± 8 days [1]. This radionuclide is naturally produced in the environment by cosmic-ray bombardment of nitrogen and deuterium in the upper atmosphere and also some of them is produced artificially by nuclear power plants. Produced tritium is reacted very quickly with hydrogen and oxygen and changed to water molecules. Tritium is generally encountered in various components of the hydrosphere including atmosphere, rivers, marine waters, underground waters, interstitial water in soils and sediments. Therefore, it is widely used in the field of hydrogeology for its tracing properties enabling to estimate water origin, residence time, dynamic, mixing, storage volumes of groundwater and their zone of discharge in surface waters [2–5].

Tritium concentration in water (HTO form) is often reported in tritium unit (TU) and 1 TU represents one HTO molecule in 10^{18} H_2O molecules and this means 0.1190 ± 0.0002 Bq/kg of water. Tritium activity measurement in environment is very difficult due to its very low concentration. Theoretical tritium production rate in atmosphere is about 0.5 atoms · cm^{-2} · s^{-1} and the total amount of ^{3}H in the earth is about 3.6 kg [6]. The ^{3}H amount is 10–20 TU at the northern hemisphere and below 10 TU at the southern hemisphere [7, 8]. Therefore this low activity are difficult to analyze directly. To overcome this difficulty, most of the water samples were enriched using electrolytic enrichment method [9, 10]. Liquid scintillation counter (LSC) is mostly used instrument for ^{3}H analysis and most of the LSC used 20 mL vial.

In this study, we used 145 mL vial available LSC for analyzing natural level tritium and electrolytic enrichment method was also applied for extremely low activity tritium measurement. And ^{3}H analysis was compared with two kinds of LSC and counting vials.

Materials and Methods

Tritium was analyzed with two kinds of LSC, one is Quantulus 1220 (PerkinElmer Inc., Waltham, MA, USA) and the other is AccuFLEX LSC-LB7 (Hitachi, Tokyo, Japan), and counting performance was compared with 20 mL and 145 mL Teflon lined polypropylene vial. These two instrument used guard counter for reducing the effects of external radiation, anti-coincidence signal detection and massive layer of lead but LSC-LB7 has been realized by the unique detector structure for counting with the vial up to 145 mL as well as 20 mL [11–13].

For ^{3}H analysis, about 1 L groundwater samples are distilled and electrolytic enrichment process was performed as previous work [10]. For the comparison of different counting vials, 500 mL groundwater was used for 20 mL counting vial and 1 L sample was used for 145 mL counting vial.

For comparison of detection efficiency and figure of merit (FOM), 1 mL of diluted ^{3}H standard solution (^{3}H activity, 60 Bq/g; SRM 4926E) was added to the each 20 mL and 145 mL counting vial and distilled water, which was old groundwater, was mixed with liquid scintillation cocktail solution (Ultima Gold LLT; PerkinElmer Inc.) with different volume ratio. All prepared samples were counted after 1 day for eliminating luminescence effect. FOM of each vials were compared with water and cocktail mixing ratio and MDA (minimum detectable activity) was also calculated by counting old groundwater.

Tritium counting efficiency was estimated using the National Institute of Standards and Technology (NIST) standard water sample (SRM 4926E, water). After counting condition was compared, some groundwater samples were analyzed with two kinds of LSC and vials and compared analytical result.

Results and Discussion

Direct environment ^{3}H counting is impossible by LSC counting. Because current environmental ^{3}H concentration is below 20 TU. Most available direct ^{3}H content by LSC was more than 40 TU, therefore electrolytic enrichment method was used. For the detection of low content of ^{3}H, 145 mL counting vial available LSC was used and compared with conventional 20 mL counting vial. The counting efficiency and FOM with water and cocktail mixing ratio was shown in Fig. 1. FOM was calculated as following Equation (1). This value was varied from 1,300 to 14,000 depends on water and cocktail mixing ratio in case of 20 mL vial. But this value of 145 mL vial when counted by LSC-LB7 was ranged from 27,000 to 450,000.

$$\mathrm{FOM} = \frac{(E \cdot V)^2}{B} \tag{1}$$

where, E is counting efficiency (%), V is sample volume (mL), and B is background (cpm). When Quantulus LSC was used, counting window was used between 35 to 250 channels. The background count was about 1.86 cpm and counting efficiency was changed from 8% to 40% with mixing ratio. In case of LSC-LB7, optimum counting window was set between 1 and 4.9 keV, which window was selected by factory considering quenching by using standard external gamma source. The background of LSC-LB7 was about 3.60 ± 0.29 cpm and 2.22 ± 0.17 cpm when 145 mL and 20 mL vial was used. Counting efficiency was changed from 10% to 32% with different water cocktail mixing ratios. Optimum counting condition was acquired from FOM data, and 10 mL:10 mL water

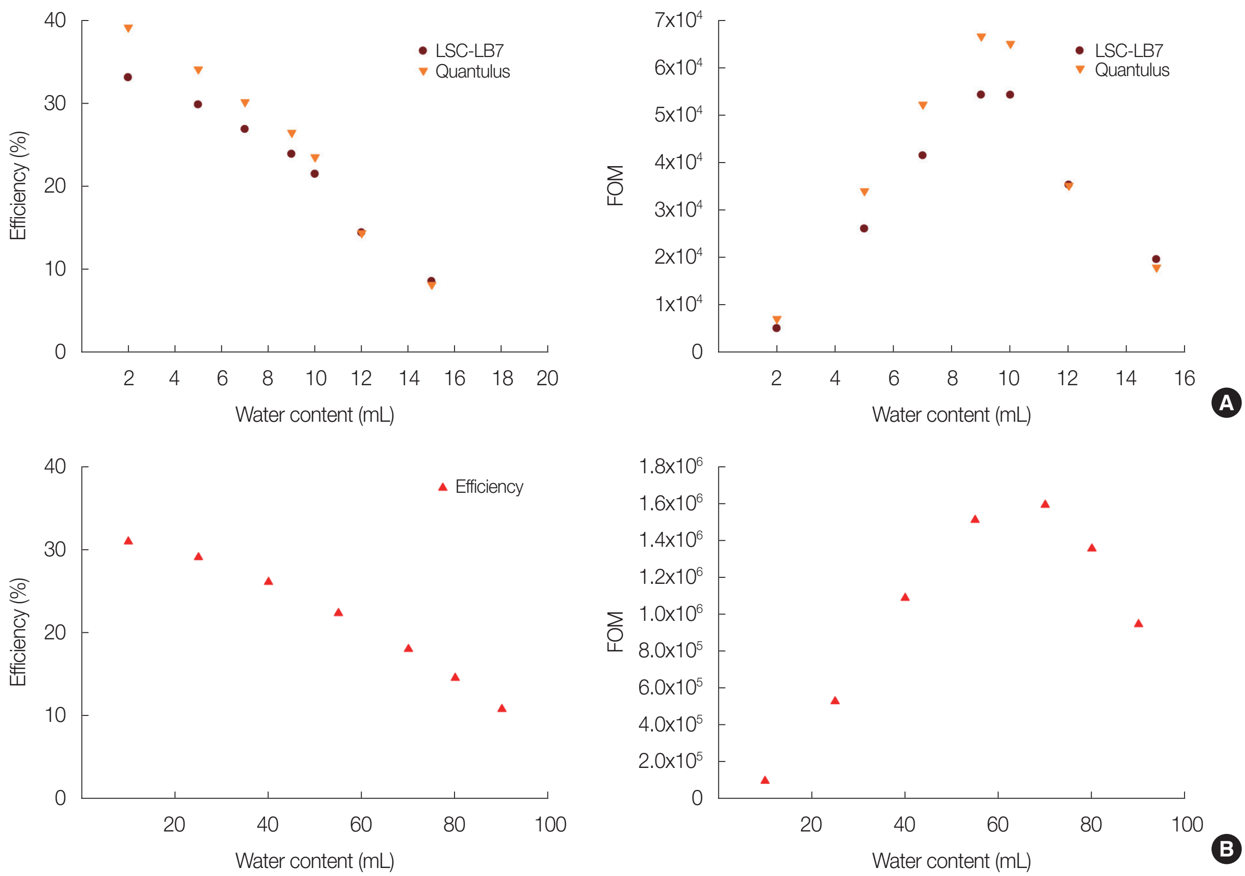

Fig. 1. Counting efficiency and figure of merit (FOM) comparison with different counting vials: (A) 20 mL vial and (B) 145 mL vial.

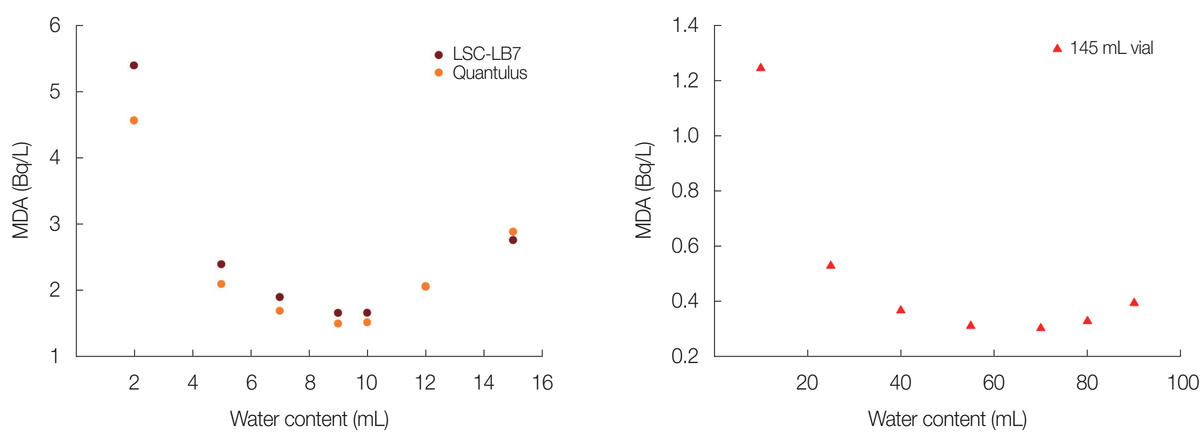

Fig. 2. Detection limit comparison with different counting vials (right) and liquid scintillation counter (left). MDA, minimum detectable activity.

and cocktail ratio was optimum when 20 mL vial was used. And also, 70 mL:70 mL water and cocktail ratio was optimum when 145 mL vial was used. But some overflow was occurred when 145 mL vial was used, therefore, 66 mL cocktail was used for sample analysis. Counting efficiency of 20 mL vial was little bit low in case of LSC-LB7. This LSC have three phototubes, so distance between sample and phototube was longer than two phototube LSC. Therefore, counting efficiency was low due to geometrically long distance. And also low efficiency was acquired in case of 145 mL vial. This result was occurred because all emitting light was not detected due to big size of vial rather than phototube.

Detection limit of two different LSC and vials was compared and the results were shown in Fig. 2. When the count-

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Table 1. Comparison Data of LB7 and Quantulus

	LB7	Quantulus
Efficiency (%)	18.2±0.2	28.7±0.3
Background (cpm)	3.60±0.29	1.86±0.23
MDA (Bq/L)	0.3	1.6
FOM	450,000	44,000
Enrichment time[a] (day)	8	10

Values are presented as mean±standard deviation.
MDA, minimum detectable activity; FOM, figure of merit.
[a]Sample volume was 600 mL.

ing time was 10 hours and 1 L sample was used, MDA value was calculated by Currie method [14]. MDA of 20 mL vial was high in case of LSC-LB7 rather than Quantulus due to high background count rate. But MDA was improved from 1.6 to 0.3 Bq/L when 145 mL vial rather than 20 mL vial was used. Above comparison data of LB7 and Quantulus was presented in Table 1. Despite of the advantage of the performance of the LB7, some disadvantage was exist. One of them is high amount of the cocktail consumption and the other is low counting efficiency due to use high volume counting vial.

Some groundwater samples were simultaneously analyzed using 145 mL and 20 mL vial and the results were shown in Table 2. Groundwater samples were 10 times concentrated by electrolytic enrichment method and counted with two kinds of LSC. Some samples could be detected when 145 mL vial was used, whereas 20 mL vial was below detection limit. Therefore, detection limit is improved when 145 mL vial was used and it is more efficient using 145 mL vial when analyze low activity tritium.

Table 2. Tritium Analytical Results Comparison with Different LSC

Sample	^{3}H (TU)		
	LSC-LB7	Quantulus	LB7/Quantulus
HS1-2	8.16±0.55	7.48±0.65	1.09
HS2-2	3.90±0.28	3.92±0.29	1.00
HS15-1	0.67±0.03	<0.5	-
HS15-2	<0.3	<0.5	-
MS-72	3.87±0.17	3.43±0.27	0.99
MS-84	<0.3	<0.5	-
MS-104	2.43±0.10	1.99±0.14	1.22
MS-106	1.67±0.07	1.74±0.16	0.96

Values are presented as mean±standard deviation.
LSC, liquid scintillation counter; TU, tritium unit.

Conclusion

For the analysis environmental ^{3}H, high volume vial available liquid scintillation counter was used. And ^{3}H analysis was compared with conventional 20 mL counting vial. Counting efficiency of 145 mL vial was decreased from 27% in case of 20 mL vial to 18% due to big size vial but FOM was four times increased than 20 mL vial. And MDA of ^{3}H was improved from 1.6 to 0.3 Bq/L due to seven times high sample volume. And also electrolytic enrichment time was decrease due to use high volume sample. FOM of LSC-LB7 was little bit low than Quantulus when 20 mL vial was used. Because LB7 had a high background and low counting efficiency rather than Quantulus, which was long distance between sample vial and detector due to high volume vial counting space.

Conflict of Interest

No potential conflict of interest relevant to this article was reported.

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Author Contribution

Formal analysis: Yoon YY. Funding acquisition: Kim Y. Methodology: Yoon YY. Project administration: Kim Y. Writing - review & editing: Yoon YY. Supervision: Kim Y.

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