

Removal of Impurities from Environmental Water Samples for Tritium Measurement by means of Liquid Scintillation Counter

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SUMMARY

Liquid Scintillation counting is now the most popular method to measure the tritium concentration. It takes much time with a lot of doing to distill off the impurities in the sample water before mixing the sample with liquid scintillation cocktail. In the light of it we investigated the possibility of an alternative method with membrane filters for purification. As a result, the filtration was proved to be available to tritium measurement.

1. INTRODUCTION

In Japan, measurements of tritium concentrations in the terrestrial and subterranean water and rainwater are now carried out in many laboratories by means of the Tritium Analyzing Method, a Radioactivity Measurement Series Volume 9 published by the Ministry of Science and Technological Agency (1). According to the method, distillation is essential to avoid misestimation caused by quenching, chemical luminescence and other radioactive substances. However, because of the following four reasons, a possible alternative using the membrane filter was investigated.

[a]. The distillation method takes much time and labor to distill off and wash out the used utensils.

[b]. Such substances as those which have lower boiling points and not very higher ones than boiling point of water can hardly be removed because you need to heat enough to vaporize the water thoroughly.

[c]. Generally you have scarcely any quenchable substances in the environmental water samples.

[d]. Scintillation cocktail as known a non-quenching liquid has been on the market lately.

2. EXPERIMENTS AND RESULTS

The environmental water samples, some of them were added some quenchers previously, were distilled or were filtrated. The concentration of micro-compounds in the original water and in the processed samples was analyzed. The processed samples were mixed with scintillation cocktail and their tritium concentrations were measured using a low-background liquid scintillation analyzer. A small amount of tritium was added into each sample to observe the spectrum and the external standard channels ratio (ESCR) which was an index of the quenching, and we made a comparison of the different processes.

2.1. SAMPLE WATER PROCESSING

Environmental water is usually filtrated with filter with 0.45 μ m pore-size and distilled until fully vaporized. However, we tried other two filtration methods. One method was with only 0.45 μ m filter (rough filtration) and the other was with putting 0.45 μ m filter upon 0.1 μ m one (accurate filtration). The 0.45 μ m pore-size membrane filter was made of cellulose and 0.1 μ m pore-size polycarbonate. The double filters method was to prevent the choking by the accurate filtration. The filtrations were carried out by sucking, and took only one or two minutes to do double washing by the sample itself. On the contrary, the distillation method took from several hours to some days although it differs depending on the samples. Table 1 below shows the comparison of those three purification methods.

Table 1, Three removal methods

Rough filtration	Filtration by cellulose type membrane filter , pore size 0.45 μ m
Accurate filtration	Filtration by cellulose type membrane filter , pore size 0.45 μ m + polycarbonate type membrane filter , pore size 0.1 μ m
Distillation	Filtration by cellulose type membrane filter , pore size 0.45 μ m + Distillation until completely dry

2.2. CONDITION OF LIQUID SCINTILLATION MEASUREMENT

The laboratory apparatuses for measurement are an LB3 type low background liquid scintillation analyzer of Aloka Co. & Ltd., an Ultima Gold LLT, a liquid scintillation cocktail of Packard Japan Co. & Ltd.,

polyethylene vials 145 SLD made by Zinseer Analytic Co. & Ltd., the inside of the vial is coated with Teflon and the effective volume of the vial was $1.45 \times 10^{-4} \text{m}^3$ (145mL). This vial generates less statistic electricity and has larger capacity than the one made of Teflon which is ordinary used for tritium measurement. Therefore it is suitable for a low-level tritium measurement by the low background liquid scintillation analyzer (2). We put $6.5 \times 10^{-5} \text{m}^3$ (65mL) of liquid scintillation cocktail into $6.5 \times 10^{-5} \text{m}^3$ (65cc) of sample water contained in the polyethylene vial and mixed them well a week before the measurement. The measurement took 50 minutes except 400 minutes when quenching by calcium chloride, ammonium chloride and nitric acid. The energy range of the liquid scintillation analyzer was set having the maximum SN rate against the tritium standard sample mentioned above.

2.3. CHEMICAL LUMINESCENCE DUE TO IMPURITIES AND MISCALCULATION BY RADIOACTIVE NUCLEI

The accurate filtered samples and the distilled samples were measured with the liquid scintillation analyzer (Table 2). There was no distinct difference between the filtration and the distillation. We need to analyze more samples to confirm what material causes the chemical luminescence and how residual radioactive nuclei affect.

Table 2, Differences of tritium counts between "Filtration" and "Distillation"

Sampling point	Sampling date	Net counts (counts/50min)		Counting efficiency(%)		Sample activity concentration(Bq/L)	
		Filtration	Distillation	Filtration	Distillation	Filtration	Distillation
River Water(A)	2/8/94	29.8	21.6	16.5	15.8	0.93	0.70
River Water(B)	5/11/93	22.4	26.9	16.3	15.8	0.71	0.87
River Water(B)	11/4/93	14.3	21.6	15.8	14.9	0.47	0.74
Tap water	10/3/91	14.2	26.4	15.0	14.8	0.49	0.91
Tap water	1/31/91	12.7	20.2	13.2	14.9	0.49	0.70
Cooling water pool	5/8/95	52.2	62.3	13.8	15.2	1.94	2.10

2.4. MEASUREMENT OF IMPURITIES

We applied three methods for removal of impurities from river water, tap water and cooling water pool samples and then estimated residual impurities such as organic compounds, anions and metallic elements (Table 3). Even by rough filtration most of the organic compounds remained nearly the detectable limit. Anions were almost fully removed by the distillation, whereas they were not sufficiently removed by the filtrations. Iron was a conspicuous element and its concentration was 387ppb after the rough filtration and 55ppb after the accurate filtration in the cooling water pool. The reduction of iron by the accurate filtration would owe to the colloid conditioned element. Concentrations of residual copper were 5.1ppb after the rough filtration and 4.3ppb after the accurate one at a maximum concentration. Other metallic elements were not estimated under that experiment.

Table 3, Residual impurities of environmental water samples applied three removal methods

No. Matter		Cooling water pool			Tap water			River water			Detection limit	Unit
		Filtration		Distil-lation	Filtration		Distil-lation	Filtration		Distil-lation		
		Rough	Accu-rate		Rough	Accu-rate		Rough	Accu-rate			
1	1,1-Dichloroethylene	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	0.5	ppb
2	Dichloromethane	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	0.5	ppb
3	t-1,2-Dichloroethylene	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	0.5	ppb
4	c-1,2-Dichloroethylene	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	0.5	ppb
5	Chloroform	1.1	0.9	1.0	0.9	1.3	1.2	1.6	1.1	1.1	0.5	ppb
6	1,1,1-Trichloroethane	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	0.5	ppb
7	Carbon Tetrachloride	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	0.5	ppb
8	1,2-Dichloroethane	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	0.5	ppb
9	Benzene	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	0.5	ppb
10	Trichloroethylene	0.6	0.6	0.6	0.6	0.5	0.6	N.D.	0.6	N.D.	0.5	ppb
11	1,2-Dichloropropane	0.7	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	0.5	ppb
12	Bromodichloromethane	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	0.5	ppb
13	c-1,3-Dichloropropene	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	0.5	ppb
14	Toluene	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	0.5	ppb
15	t-1,3-Dichloropropene	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	0.7	N.D.	N.D.	0.5	ppb
16	1,1,2-Trichloroethane	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	0.5	ppb
17	Tetrachloroethylene	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	0.5	ppb
18	Dibromochloromethane	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	0.6	N.D.	0.5	ppb
19	m,p-Xylene	N.D.	N.D.	N.D.	N.D.	N.D.	0.6	N.D.	N.D.	N.D.	0.5	ppb
20	o-Xylene	N.D.	N.D.	N.D.	N.D.	N.D.	0.7	N.D.	N.D.	N.D.	0.5	ppb
21	Bromoform	0.7	0.7	0.7	0.7	0.7	0.9	0.7	0.7	0.8	0.5	ppb
22	1,4-Dichlorobenzen	N.D.	N.D.	N.D.	N.D.	N.D.	0.7	N.D.	N.D.	0.6	0.5	ppb
23	4-Bromofluorobenzen	I.S.	I.S.	I.S.	I.S.	I.S.	I.S.	I.S.	I.S.	I.S.	0.5	ppb
24	Chlorine ion	18.01	17.99	N.D.	3.84	3.88	N.D.	8.91	8.94	N.D.	0.20	ppm
25	Nitric acid ion	N.D.	N.D.	N.D.	0.39	0.40	N.D.	1.40	1.46	N.D.	0.20	ppm
26	Sulphuric acid ion	20.02	19.99	N.D.	9.88	9.89	0.21	30.60	30.66	N.D.	0.25	ppm
27	Fe	378.0	55.0	N.D.	22.0	N.D.	N.D.	N.D.	N.D.	N.D.	2.5	ppb
28	Cu	5.0	2.9	1.2	5.1	4.3	1.5	1.7	2.6	1.3	1.0	ppb

(N.D. ; Not detectable)

2.5. QUENCHING

As long as analyzing the tritium energy spectra of samples, the impurities did not significantly quench any water samples containing a small amount of tritium (Fig.1). Also calcium chloride, ammonium chloride and nitric acid reagent solutions (10-100ppm) containing from 1.75 to 17.53 Bq of tritium were estimated (Fig.2, Table 4) as to the energy spectra. No quenching was emerged from any solutions.

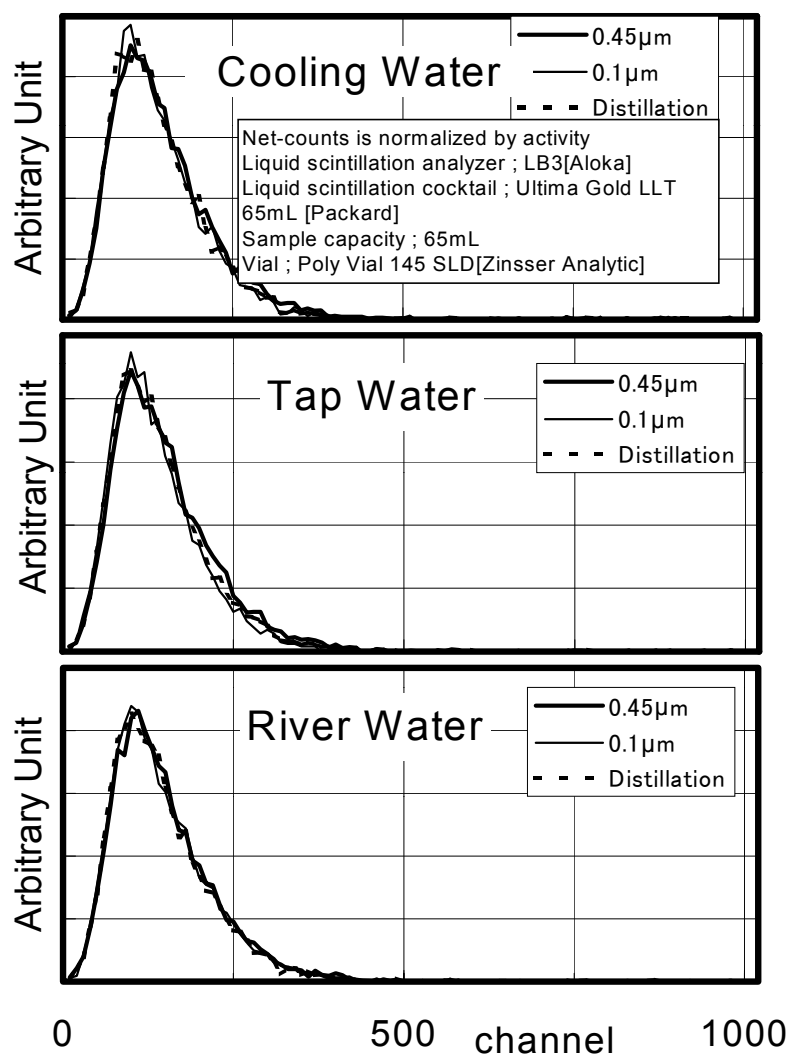


Fig 1, Tritium energy spectrum of environmental water applied three removal methods

Table 4, Tritium counting efficiency and ESCR (Reagent solution)

Reagent	Reagent concentration (ppm)	Tritium activity (Bq)	21-180ch Net counts (cpm)	Counting efficiency (%)	ESCR
CaCl ₂	99.97	16.87	147.0	14.5%	24.70
	30.76	5.19	43.2	13.9%	24.52
	10.00	1.69	15.1	14.9%	24.68
NH ₄ Cl	99.98	17.41	136.5	13.1%	24.60
	30.76	5.36	41.9	13.0%	24.54
	10.00	1.74	13.3	12.7%	24.58
HNO ₃	99.90	17.53	140.6	13.4%	24.52
	30.74	5.39	42.9	13.3%	24.52
	9.99	1.75	14.4	13.6%	24.56

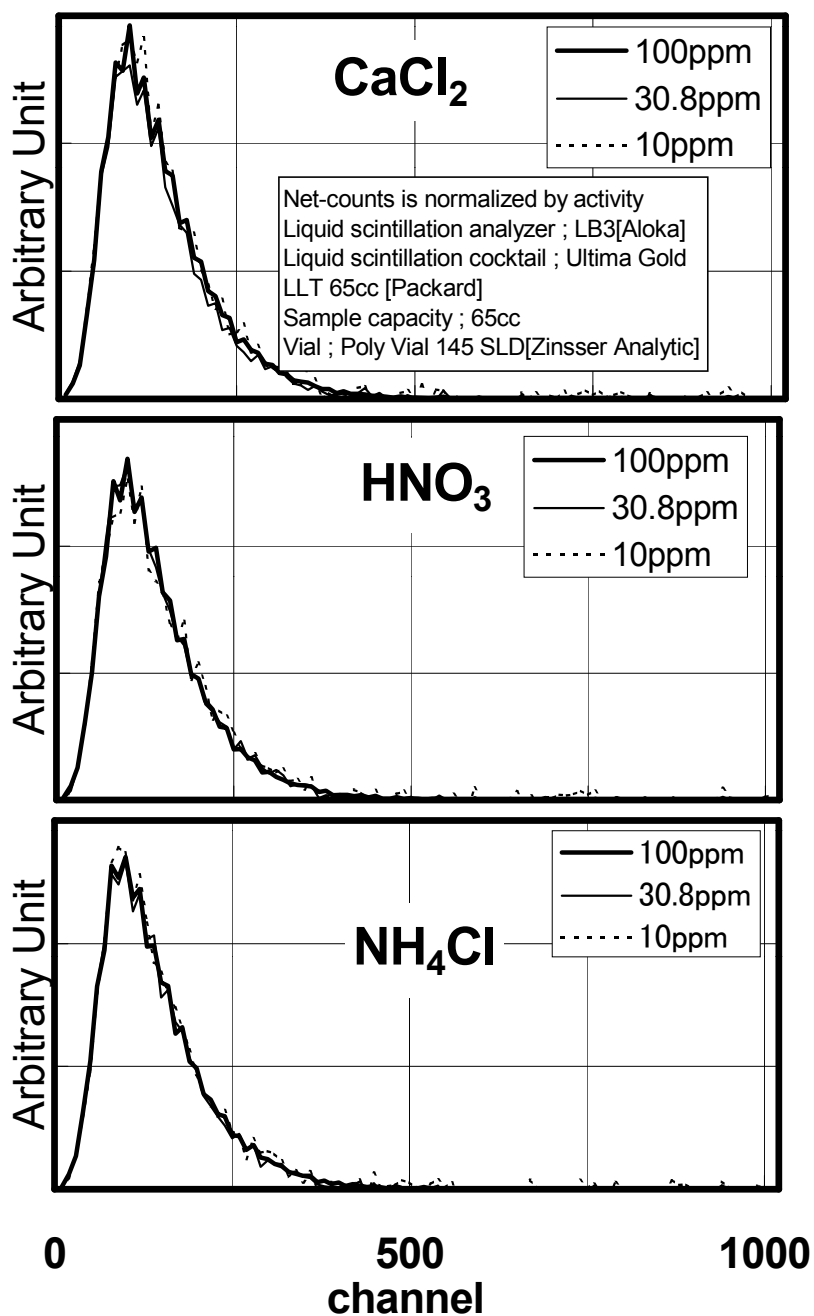


Fig 2, Tritium energy spectrum of three reagent solution

3. CONSIDERATION

Any significant quenching was not caused from the three impurity removal methods. As the view point of quenching, the filtrations for a removal method were able to be applied for the sample water collected, which barely contained effective quenchers. Indeed some of the environmental water samples possibly contain exceptional concentration of impurities, such samples would indicate unusual ESCR or degraded spectra. The misestimation will be avoided with distillation such samples.

4. CONCLUSION

For tritium measurement in the environmental water with the liquid scintillation analyzer, the membrane filtration is an available alternative to the previous distillation process.

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