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Performance of nonylphenol-ethoxylates-free liquid scintillation cocktail for tritium determination in aqueous samples

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Abstract
The paper evaluates the performances of nonylphenol ethoxylates free cocktail (ProSafe LT+, Meridian Biotechnologies Ltd.) for tritium measurement using liquid scintillation counting and the laboratory's routine procedure. The optimum ratio of sample and liquid scintillation cocktail for 20 ml vial volume was investigated, choosing a ratio of 8:12 ml of sample: scintillation cocktail. Good results were obtained for linearity (investigated between 0.3 MBq l^{-1} and 6 Bq l^{-1}), repeatability, and trueness, and prove its applicability both for operation and environmental monitoring of tritium at nuclear facilities.

Keywords Nonylphenol ethoxylates · Scintillation cocktail · Tritium measurement

Introduction

Nonylphenol ethoxylates (NPE's) are important components of the majority of liquid scintillation cocktails available on the market. They are involved in forming homogeneous mixture of sample and liquid scintillation cocktail and, due to their aromatic nucleus, they are facilitating the transfer of the radioactive decay into the light. The European Commission announced the addition of NPE to Annex XIV, the list of chemicals subject to authorization under the EU **R**egistration, **E**valuation, **A**uthorization and Restriction of **Ch**emical substances (REACH) legislation [1]. NPE's are toxic to aquatic organisms producing reproductive and developmental effects. Upon degradation they become more environmentally persistent and even more toxic products including NonylPhenol (NP). NP has been detected in breast milk, blood and urine, producing harmful effects in development. Thus, users are required to obtain, by sunset date of 2021, special authorization for the production or use of these compounds, regardless of the purpose for which they are used. This has led and will lead to the cessation of NPE production by the manufacturers, and users will have to find alternatives by using other less harmful chemical compounds.

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The availability of liquid scintillation cocktails will be adversely affected by the change in EU regulations preventing the use of NPE's. Their price will be higher to include the necessary authorizations, but even so, the NPE's production will be limited due to lower market demand. A special case is tritium measurement in aqueous samples using the liquid scintillation method. It is a common method used by environmental radioactivity laboratories of nuclear power plants (NPP) in order to establish tritium level in the surrounding areas of nuclear reactors, tritium being one of the monitored radioisotopes regardless of the type of nuclear facility [2]. A wide range of tritium concentrations can be found in the NPP's environment, from environmental level, around 1–4 Bq l^{-1} [3] to accepted tritium level by release limits imposed by nuclear facility's license. The tritium samples are usually prepared in aqueous form, whether it is a gaseous form, liquid form, or assimilated in living organisms as tissue free water tritium and organically bound tritium [4]. The environmental tritium level is usually low, and due to this characteristic, some types of liquid scintillation spectrometers used are dedicated to low-level measurement and they are able to detect approximately 1 Bq l^{-1} of tritium in water without electrolytic enrichment [5].

The liquid scintillation cocktail plays a major role in obtaining a good limit of detection without implying other time-consuming procedures (electrolytic enrichment) especially for a monitoring program where sample numbers are high. They have to meet a few requirements for tritium measurement as follows: long term stability of sample cocktail

mixture due to long time measurement of low level radioactivity, sometimes more than 2000 min/sample [6]; low background of liquid scintillation cocktail; and good tritium efficiency counting. Traditionally, liquid scintillation cocktail providers have dedicated liquid scintillation cocktails for low level tritium measurements, but none of them offer an NPE free cocktail for tritium measurement, with one exception, Meridian Biotechnologies Ltd. The proposed liquid scintillation cocktail is ProSafe LT+. In order to investigate the compatibility of ProSafe LT+ to our routine procedure for tritium measurement in the environment, we adopted a verification plan that included linearity, repeatability, and trueness, after establishing an optimum ratio of sample: liquid scintillation cocktail. The results of these experiments are presented in this paper.

Methods, materials and equipment

Tritium activity concentration in aqueous sample is an ISO standardized method adopted at the national level [7]. Materials and procedures used in these experiments are following the recommendations of the mentioned standard. High density polyethylene vials of 20 ml (HDPE, PerkinElmer), and scintillation cocktail ProSafe LT+ (Meridian Biotechnologies LTD.) were employed. Tritium-free water (blank water) was deuterium depleted water with D/D+H value of around 15 ppm [8]. A calibrated solution of [H^3]HO provided by PerkinElmer (reference standard NIST SRM4927E) which had a certified tritium concentration of 2632100 (±3.208%) DPM g^{-1} (reference date June 2017) was diluted in order to prepare standard solution and samples with known activity. The calibrated balance (OHAUS Explorer Pro EP413CM) was used in the dilution procedure. The zero readings were checked and a test weighing was performed before and after each weighing process. The combined uncertainty of the weighing procedure was evaluated taking into account display uncertainty, maximum drift and balance precision. No buoyancy correction was applied.

ProSafe LT+ has a Di–IsopropylNaphtalene (DIN) base, increasing the counting efficiency compared to a PhenylXylylEthane (PXE) base. The measurement of radionuclides in aqueous phase assumes formation of a stable microemulsion, the compounds in the scintillation cocktails responsible for this being the surfactants: alkyl phenol ethoxylates (included on the list of REACH SVHC control substances) or alcohol ethoxylates [9]. ProSafe cocktails are based on alcohol ethoxylates and as such do not contain NPE's either as a base component or as a derivate component. This type of liquid scintillation cocktail is suitable for drain disposal, and biodegradable. In order to evaluate its characteristics for tritium measurement, it will be compared with Gold Star LT2, a liquid scintillation cocktail from the same provider, dedicated to low level tritium measurement.

The low level liquid scintillation spectrometer, Quantulus 1220™ (Wallac), was used in the experiments. The Peltier cooling unit ensures 14 °C inside Quantulus 1220 and its measurement chamber. The laboratory routine procedure of tritium measurement involves internal standard method for evaluation of counting efficiency. A typical batch contains a tritium standard (known activity around 230,000 DPM/sample), blank sample (tritium-free water, in our case deuterium depleted water) and unknown samples (at least 18 samples) prepared according ISO standard method. In order to check the quench level of the batch [10], the External Spectral Quench Parameter [SQP(E)] obtained with ^{152}Eu external source is recorded, accepted variation being less than 1% (due to statistically nature of disintegration process and source positioning changes inside the counting chamber). In this way, one can assure the same level of quench of the samples batch. Total counting time of a sample is 500 min (50 min/sample, 10 cycles). The combined uncertainty of tritium measurement was calculated according ISO 9698:2010, paragraph 8.2, with a confidence level of k = 1.96.

In order to verify the ProSafe LT+ performances before being introduced into routine use, the first step was to establish the optimum ratio of sample to liquid scintillation cocktail [11]. The known tritium activity of 32,515 ± 3.211% DPM g^{-1} (T1) was prepared by dilution from the certified Tritiated water (aprox. 1 g of certified Tritiated water to 80 g of blank water). Here and after, the uncertainty of the spike samples combines the uncertainty of the certified Tritiated water, and the uncertainty due to their dilutions. Various amount of diluted T1 was used for each of eleven samples prepared using the total available vial volume of 20 ml, and various ratios of sample:liquid scintillation cocktail starting to 1:19 ml to 18:2 ml. The blank samples were prepared respecting the same ratios of sample:liquid scintillation cocktail. Measurement conditions are described above. Different amount of diluted T1 used in this experiment acts as a quenching agent, number of counts decreasing with increasing amount of sample, and the spectra are shifted in tritium window of 10-250 channels, Fig. 1.

The calculated detection limit according ISO standard (paragraph 8.4, k = 1.96), Fig. 2, indicated lower detection limits for different ratios starting to 7:13 ml to of 10:10 ml. The background in tritium window varied from 1.425 CPM (Count per Minute) to 1.041 CPM, with lower value for 8:12 ml ratio. The counting efficiency drops from 34.4% (±0.1%) for 1:19 ml ratio to 1% (±0.1%) for 18:2 ml ratio, with phase separation for ratios higher than 10:10 ml. The figure of merit (ratio of square counting efficiency and background count rate) is used in low level radioactivity measurement of the weak beta emitters as tritium. It defines a region of the spectrum where the loss in counting efficiency

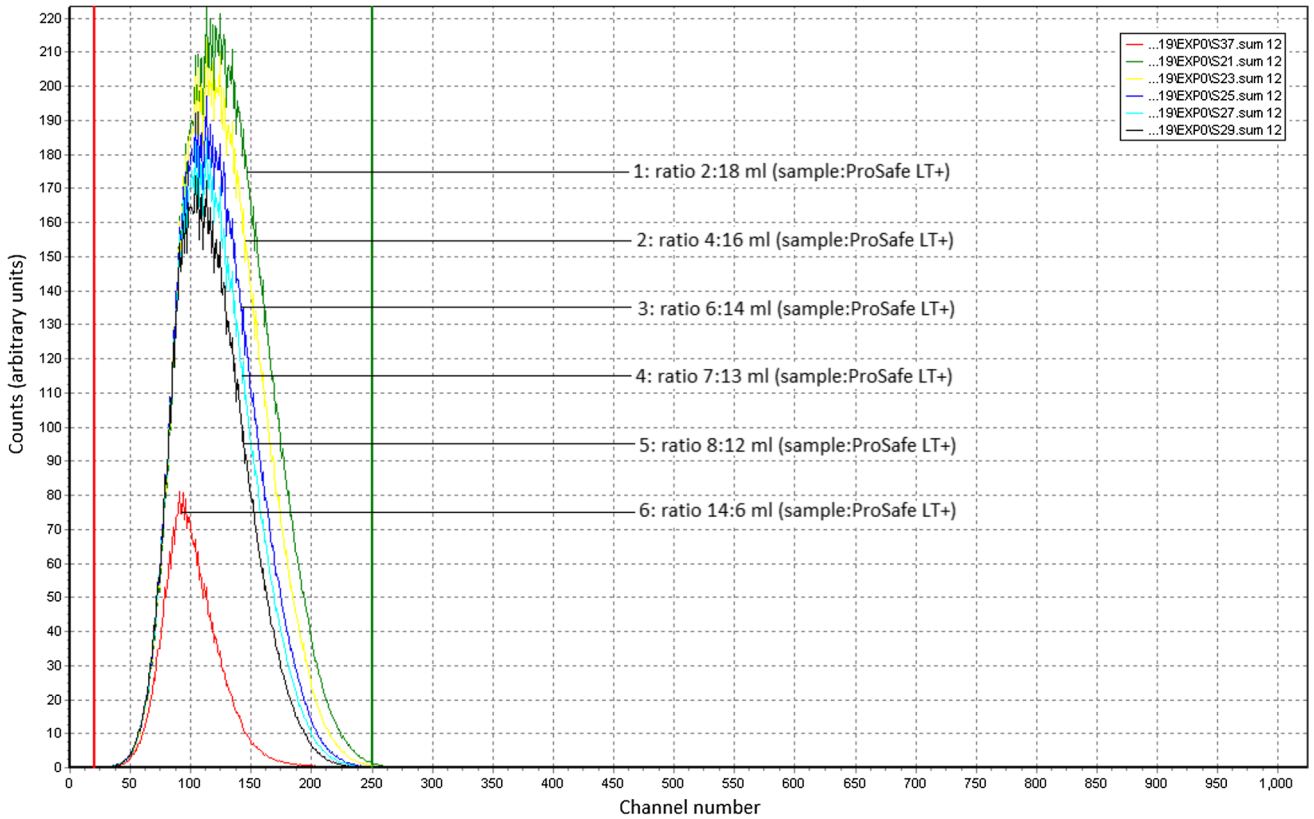

Fig. 1 Tritium spectra of different ratios of sample: ProSafe LT+ (20 ml volume)

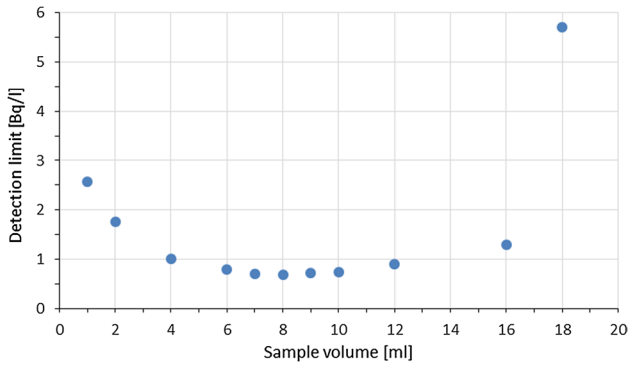

Fig. 2 Detection limit for tritium as a function of sample volume (total volume constant at 20 ml)

is minimum and the background is lower than for the whole spectrum. The optimized windows at the best figure of merit was obtained for two ratios, 7:13 ml and 8:12 ml. We chose 8:12 ml ratio due to a decrease of more than 30% of background counting rate (from 1.041 CPM to 0.675 CPM) and small changes in counting efficiency of less than 2% (from 20.8% to 20.4%) recorded for this optimized window.

This ratio of 8:12 ml is used in the actual verification procedure that followed the Eurachem suggestions [12]. The linearity has been explored between 307 kBq kg^{-1} and 6 Bq kg^{-1} water, values that can be found during operation and environmental monitoring program of a nuclear facility source of tritium. The repeatability tests were performed on standard activity vials used with each batch prepared for tritium analysis. Trueness was evaluated by measurements of spiked samples and reference samples of inter-laboratory exercises.

Results and discussion

Linearity

Linearity analysis is essential in the measuring procedure, especially in the environmental monitoring program where the tritium activity concentration of the same type of sample varies from high to low level depending on the increasing distance from tritium source. In order to check linearity in a wide range of tritium activity concentration we divided the experiment in two stage; one for high tritium activity concentration and the other for low level tritium activity concentration. Five sources were prepared adding the chosen amount of T1 source to obtain equally spaced intervals, Table 1. Measuring times were chosen to obtain roughly the

Table 1 Dilution procedure for samples with high tritium activity concentrations. Uncertainty values are reported at k = 1

Sample/step	1	2	3	4	5
Weight of T1 (g)	5.002 ± 0.001	4.000 ± 0.001	3.001 ± 0.001	2.001 ± 0.001	1.002 ± 0.001
Weight of blank water (g)	3.001 ± 0.001	4.004 ± 0.001	5.006 ± 0.001	5.999 ± 0.001	7.002 ± 0.001
Dilution factor (%)	0.6 ± 0.14	1 ± 0.14	1.67 ± 0.14	2.99 ± 0.14	7 ± 0.14
Total tritium activity in sample corrected at the day of measurement (Bq)	2463.3 ± 79.2	1970.5 ± 63.3	1478.2 ± 47.5	985.7 ± 31.7	493.5 ± 15.9
Tritium activity concentration corrected at the day of measurement (Bq g^{-1})	307.8 ± 9.9	246.2 ± 7.9	184.6 ± 5.9	132.2 ± 4	61.7 ± 2

same relative uncertainty on net counting ratio (homoscedasticity condition, [13]).

The nine more sources, with lower tritium activity concentration, were prepared in the domain of an environmental monitoring program of a nuclear facility source of tritium. 100 mg of Tritiated daughter water T_1 was added to 100 g of blank water obtaining 498.5 ± 3.217% Bq kg^{-1} Tritiated water, T_2. Various amount of T_2 was used to obtain tritium activity concentration between 250 and 6 Bq kg^{-1}, typical values of a monitoring program, Table 2. In this case it was not possible to obtain the same counting uncertainty of the prepared sample due to Poisson contribution.

In order to respect the homoscedasticity condition, samples were measured in two batches: one with five samples of high tritium activity concentrations, and the other with nine samples of low tritium activity. The counting times were different: 100 min/sample for high tritium activity, and 500 min/sample for low tritium activity. The background counting time was the same of 500 min. Results are shown in the Table 3. The uncertainty of the spike samples combines the uncertainty of the certified Tritiated water and the dilutions uncertainty.

The background during the measurements of the two sets of spike samples varied between 0.638 and 0.667 CPM, and the efficiency at the best figure of merit was around 20%, equating to a detection limit around 1 Bq kg^{-1} water, far from the tritium activity concentration of the spike samples. Variation coefficient of standard deviation of SQP(E) was below 1%, proving that this parameter can be used in verifying the quench level of the batch, considering that the same type of water was used for all 14 samples.

The correlation coefficient of the five samples of high tritium activity data set was close to 1 ($R^2 = 0.99997$), Fig. 3. Investigating in details the low level domain, Fig. 4, the plot

Table 2 Dilution procedure for samples with low tritium activity concentrations. Uncertainty values are reported at k=1

Sample/step	6	7	8	9	10	11	12	13	14
Weight of T2 (g)	4 ± 0.001	3.001 ± 0.001	2.002 ± 0.001	1.004 ± 0.001	0.501 ± 0.001	0.404 ± 0.001	0.302 ± 0.001	0.202 ± 0.001	0.104 ± 0.001
Weight of blank water (g)	4.001 ± 0.001	5.001 ± 0.001	6.002 ± 0.001	6.997 ± 0.001	7.501 ± 0.001	7.589 ± 0.001	7.698 ± 0.001	7.799 ± 0.001	7.896 ± 0.001
Dilution factor	1 ± 0.14%	1.666 ± 0.14%	2.998 ± 0.14%	6.969 ± 0.14%	14.972 ± 0.14%	18.785 ± 0.14%	25.490 ± 0.14%	38.609 ± 0.14%	75.923 ± 0.14%
Total tritium activity in sample corrected at the day of measurement (Bq)	1.99 ± 0.06	1.50 ± 0.05	1 ± 0.03	0.5 ± 0.02	0.25 ± 0.01	0.20 ± 0.01	0.15 ± 0.01	0.101 ± 0.003	0.052 ± 0.003
Tritium activity concentration corrected at the day of measurement (Bq g^{-1})	0.249 ± 0.008	0.188 ± 0.006	0.125 ± 0.004	0.063 ± 0.003	0.031 ± 0.001	0.025 ± 0.001	0.019 ± 0.001	0.0125 ± 0.0004	0.0063 ± 0.0004

Table 3 Linearity verification of ProSafe LT+ in the application domain, between 6.3 and 307.8 kBq kg^{-1} water

Sample	Tritium activity/sample (Bq)	Tritium activity concentration (Bq kg^{-1})	Relative uncertainty of Tritium activity concentration (%)	Net counting ratio (CPM)	Relative uncertainty of net counting ratio (%)	Spectral quench parameter SQP(E) (channels)	Relative uncertainty of SQP(E) (%)
1	2463.3	307,800	3.211	29876.30	0.21	678.28	0.45
2	1970.5	246,200	3.211	23885.34	0.22	679.39	0.5
3	1478.2	184,600	3.211	17824.65	0.24	669.72	0.36
4	985.7	132,200	3.211	11932.67	0.21	677.22	0.22
5	493.5	61,700	3.211	5968.24	0.21	675.31	0.67
6	1.99	249	3.217	25.76	2.69	672.77	0.34
7	1.5	188	3.217	18.71	3.24	678.27	0.36
8	1	125	3.217	12.58	3.91	674.58	0.33
9	0.5	63	3.217	6.27	5.39	672.14	0.24
10	0.25	31	3.217	3.37	6.93	673.79	0.24
11	0.2	25	3.217	2.69	7.25	677.34	0.45
12	0.15	19	3.217	2.01	8.70	670.76	0.35
13	0.1	12.5	3.217	1.44	9.71	671.74	0.5
14	0.052	6.3	3.217	0.71	11.62	672.32	0.3
Average						674.55	
σ (%)						0.46	

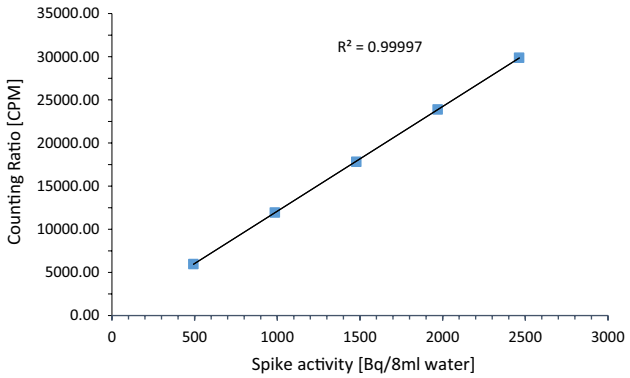

Fig. 3 Correlation between spike activity and net counting ratio in the application range, between 61.7 and 307.8 kBq kg^{-1} water

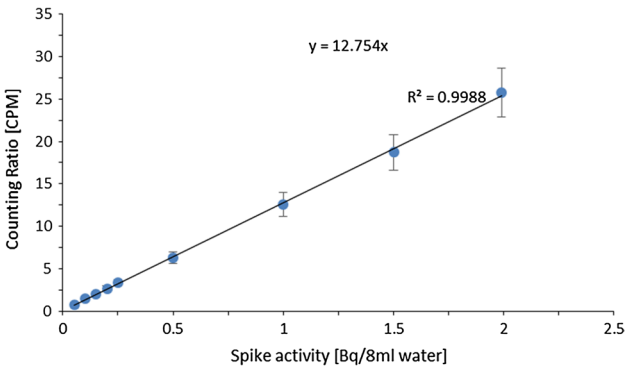

Fig. 4 Correlation between low level spike activity and net counting ratio

exhibits the same linear relationship, with a correlation coefficient of 0.9988.

The intercept of the regression line describing this correlation was $y = 12.754\times$. One can choose to use the intercept of the regression line in order to avoid questionable approximations below the limit of detection, where measurement uncertainty is higher than 50%, and sample counting rate can be lower than background counting rate. In fact, sometimes, especially in the case of drinking water (old groundwater), negative values can be recorded. The significance of the negatives values is that the measured sample has lower tritium activity than the blank water, and the recorded counting rate is lower than the measured background. Residues calculated as difference between measured counting rate (y) and calculated (y') using the regression line of the low level tritium spikes, are presented in Table 4.

Relative residues (residues on experimental counting ratio) exhibits a random distribution around zero, Fig. 5, thus demonstrating a linear response of the liquid scintillation cocktail to different level of tritium activity concentration [13].

Repeatability

The standard sample with known tritium activity concentration is a key element for establishing counting efficiency by the internal standard method used in our laboratory procedure. It is essential to have a good signal recorded by the liquid scintillation spectrometer, but it is also important to have a stable signal for the long period of time of

Table 4 Linear fit residue of the 14 spike samples

Sample	Net count rate experimental (CPM)	Calculated counting rate (CPM)	Residues (CPM)	Relative residues
1	29876.3	31416.99	−1540.69	−0.05
2	23885.34	25131.76	−1246.42	−0.05
3	17824.65	18852.96	−1028.31	−0.06
4	11932.67	12571.62	−638.95	−0.05
5	5968.24	6294.10	−325.86	−0.06
6	25.76	25.38	0.38	0.02
7	18.71	19.13	−0.42	−0.02
8	12.58	12.75	−0.18	−0.01
9	6.27	6.38	−0.10	−0.02
10	3.37	3.19	0.18	0.05
11	2.69	2.55	0.14	0.05
12	2.01	1.91	0.10	0.05
13	1.44	1.28	0.17	0.12
14	0.71	0.66	0.04	0.06

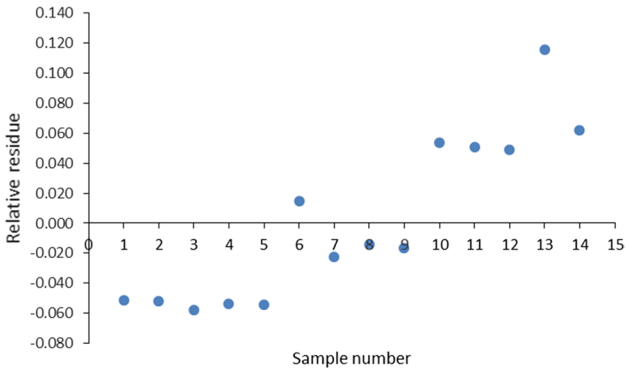

Fig. 5 Relative residues of the 14 spike samples

the measurement. A batch of 18 samples, one background and a standard is measured in around 1 week (50 min/cycle, 10 cycles). The standard sample does not need a 500 min counting time to have good measurement statistics, and a time of 100 min (10 min/cycle, 10 cycles) is settled in the laboratory routine procedure. Starting from diluted certified Tritiated water T1, we prepare 10 standard samples which were measured 100 min (10 min/cycles, 10 cycle). Results of the known tritium activity concentration of 32,515 ± 3.211% DPM g^{-1} are presented together with Chi square of each measurement and weight of each sample, Table 5. The background counting rate of 0.7 CPM had a small influence on the gross counting rate of the standard samples.

Table 5 Repeatability test of T1 known tritium activity concentration

Sample	Weight sample and liquid scintillation cocktail (g)	Gross counts rate (CPM)	Relative uncertainty of counting ratio (%)	Chi square (of 10 cycles)	Spectral quench parameter SQP(E) (channels)	Relative uncertainty of SQP(E) (%)
Rep1	19.475	49069.1	0.14	9.491	672.4	0.5
Rep2	19.478	48855.5	0.14	11.229	679.55	0.41
Rep3	19.481	49148.7	0.14	8.745	679.98	0.62
Rep4	19.508	48703.3	0.14	6.611	675.78	0.63
Rep5	19.490	49050.4	0.14	12.841	673.96	0.51
Rep6	19.497	49197.2	0.14	14.138	667.73	0.39
Rep7	19.480	49314.8	0.14	14.971	676.19	0.45
Rep8	19.474	49245.2	0.14	12.184	675.18	0.5
Rep9	19.459	49156.6	0.14	8.751	673.81	0.39
Rep10	19.483	49492.0	0.14	11.202	676.54	0.39
Mean	19.483	49123.3			675.11	
σ	0.013	223.9			3.53	
σ%	0.06	0.5			0.52	

The mass of standard samples has an average of 19.483 g with a standard deviation below 0.1%. The gross counting rate of the standard samples exhibits a mean of 49123.3 CPM with a relative standard deviation of 0.5%. Repeatability is observed as the standard deviation of the counting rate, which must be below or comparable with other uncertainty sources. The combined uncertainty evaluated according to ISO 9698:2010 is between 3% for high activity and below 15% for low activity. All ten standard samples proved very good repeatability of the scintillation cocktail signal sent to the measurement equipment.

The Chi square test compares the observed variation of the counting rate with the expected statistical variation of the Poisson distribution. The Chi square of the 10 cycles was between 6.611 and 14.971, accepted variation of ten determinations being between 3.325 (95% probability) and 16.919 (5% probability). Each of the ten samples had an accepted Chi square proving good stability of the counting rate.

The SPQ(E) parameter exhibits a mean of 675.11 value with a relative standard deviation of 0.52%. This value is near that established for linearity samples of $674.55 \pm 0.46\%$ showing a constant level of quench for the experiments samples with 8:12 ml ratio of sample:scintillation cocktail. Its variation in the accepted range of 1% proves its utility as a qualitative indication of quench level among the prepared batch.

The same batch was measured after 1 week, Table 6, using the same liquid scintillation spectrometer, Quantulus 1220. The sample weights were the same, they did not lose components of liquid scintillation cocktail through the vial wall. The same good repeatability was observed with less than 1% of standard deviation for the counting rate.

Using sample 13 of 12.5 ± 0.4 Bq kg^{-1} (Table 2), we prepare another batch of 10 samples. The chosen activity is around 10 times lower than 100 Bq/l recommended by European Commission in drinking water [14]. Counting time was 500 min (50 min/sample, 10 cycles) for each sample including background. The background counting rate of 0.645 CPM was corrected from the gross counting rate of the sample, Table 7.

The relative standard deviation of the mixture weight was below 0.1%, spectral quench parameter has a relative standard deviation below 1%, and Chi square certified a good stability of the equipment and liquid scintillation mixture. The mean of the net counting rate was 1.472 CPM, with a relative standard deviation of 10.7%. The same batch was measured after 1 week from the preparation date, using the same Quantulus, Table 8. The batch was kept inside the Quantulus tray at 14°C. The recorded background was 0.723 CPM, with 12% higher than the first measurement of the batch. Despite the background variation, the mean count rate of the replicate samples was 1.332 CPM, in one standard deviation near previous measurement. The repeatability test of the low tritium activity, has a standard deviation around 10% from the net count rate, lower than the combined uncertainty calculated according ISO standard of 15%. The Chi square variation between 6.516 and 13.807 presents a good stability of the equipment and liquid scintillation cocktail.

The liquid scintillation cocktail ProSafe LT+ can be used for low level tritium activity with its necessary long period of the measurement.

Trueness

The trueness has been evaluated by measuring five samples received from different proficiency tests and samples

Table 6 Repeatability test of T1 after 1 week of the preparation

Sample	Weight sample and liquid scintillation cocktail (g)	Gross count rate (CPM)	Uncertainty of counting ratio (%)	Chi square (of 10 cycles)	Spectral quench parameter SQP(E) (channels)	Uncertainty of SQP(E) (%)
Rep1	19.474	48690.8	0.14	9.322	668.01	0.82
Rep2	19.477	48509.1	0.14	11.384	671.67	0.55
Rep3	19.480	48725.2	0.14	10.040	673.74	0.63
Rep4	19.508	49070.8	0.14	13.260	673.36	0.49
Rep5	19.490	49108.5	0.14	6.363	667.5	0.33
Rep6	19.496	49466.3	0.14	13.177	667.99	0.57
Rep7	19.481	49170.3	0.14	7.665	669.04	0.41
Rep8	19.473	49380.7	0.14	11.807	672.22	0.63
Rep9	19.459	48884.0	0.14	12.453	670.68	0.44
Rep10	19.483	49415.2	0.14	10.374	669.13	0.83
Mean	19.482	49042.1			670.33	
σ	0.013	331.4			2.316	
σ%	0.07	0.7			0.3	

Table 7 Repeatability test of sample 13

Sample	Weight sample and liquid scintillation cocktail (g)	Net count rate (CPM)	Uncertainty of counting ratio (%)	Chi square (of 10 cycles)	Spectral quench parameter SQP(E) (channels)	Uncertainty of SQP(E) (%)
Rep1	19.494	1.467	9.71	5.741	678.36	0.56
Rep2	19.465	1.205	10.15	7.185	678.31	0.54
Rep3	19.482	1.545	9.25	3.584	674.82	0.79
Rep4	19.479	1.482	9.62	9.690	674.67	0.73
Rep5	19.476	1.607	9.53	6.058	677.71	0.63
Rep6	19.505	1.503	9.17	11.504	676.57	0.73
Rep7	19.498	1.544	9.33	11.443	673.88	0.59
Rep8	19.472	1.341	9.02	11.007	672.37	0.73
Rep9	19.506	1.738	9.62	8.403	670.18	0.74
Rep10	19.498	1.285	9.02	9.169	669.67	0.83
Mean	19.488	1.472			674.65	
σ	0.015	0.158			3.18	
σ%	0.08	10.7			0.5	

Table 8 Repeatability test of sample 13 after 1 week from the preparation

Sample	Weight sample and liquid scintillation cocktail (g)	Net count rate (CPM)	Uncertainty of counting ratio (%)	Chi square (of 10 cycles)	Spectral quench parameter SQP(E) (channels)	Uncertainty of SQP(E) (%)
Rep1	19.493	1.142	8.64	12.953	673.27	0.62
Rep2	19.464	1.222	9.17	6.156	670.97	0.66
Rep3	19.482	1.465	9.25	7.159	672.34	0.27
Rep4	19.477	1.264	9.33	11.285	673.36	0.49
Rep5	19.475	1.272	8.91	9.031	671.91	0.53
Rep6	19.503	1.425	9.53	13.177	674.31	0.57
Rep7	19.495	1.122	9.21	7.522	671.18	0.44
Rep8	19.470	1.487	9.67	13.527	675.11	0.63
Rep9	19.505	1.434	10.31	7.090	673.27	0.74
Rep10	19.496	1.485	9.17	13.807	671.29	0.91
Mean	19.486	1.332			672.701	
σ	0.014	0.143			1.396	
σ%	0.07	10.8			0.2	

spiked with Tritiated certified water at different tritium activity concentrations. These were used spiked samples from linearity experiments. The evaluation criterion was based on zeta scores (ζ) as defined by ISO 13528:2015 [15] and acceptability criterion was its values lower than ± 2.

The samples containing high tritium activity concentration were measured 100 min (10 min/cycle, 10 cycles), with a counting efficiency of 20.07% and a background counting rate of 0.667 CPM, at the best figure of merit. The calculated activity and their uncertainties were presented in Table 1, and they were obtained by dilution of the certified Tritiated water. The zeta score varied between − 0.95 and 0.11, Table 9, and all the measurements fulfill the acceptability criterion.

The low level tritium concentration samples were measured 500 min (50 min/cycle, 10 cycle), with a counting efficiency of 20.34% and a background of 0.638 CPM, at the best figure of merit. The calculated activity and their uncertainties are present in detail in Table 2. The zeta score varied between − 0.68 and 1.32, Table 10, being lower than ± 2.

The Hydrology Department of the International Atomic Energy Agency (IAEA) organizes every 4 years a proficiency test (PT) for measurement of low level tritium in water sample, in 2018 being organized the Tenth Intercomparison exercise, TRIC2018. Tritium activity concentration in these samples is very low, below 1 Bq l^{-1} requiring tritium enrichment, but the organizers send one to three samples with special request of direct measurement. The reference tritium activity concentrations are in Tritium Units

(TU), and in order to report in Bq l^{-1}, one can use 1 Bq l^{-1} corresponds to 8.390 ± 0.015 TU [16]. Two other samples are from PT organized in 2017 and 2018 by LGC Standards Proficiency Testing. All the five samples were prepared using 8:12 ml ratio of sample: liquid scintillation cocktail, and measured using the laboratory routine procedure. The mean count rate of the background was 0.665 ± 11% CPM, and the counting efficiency of 20.54% at the best figure of merit. The detection limit (according ISO 9698:2010) was 0.7 Bq l^{-1}. The SQP(E) parameter varied between 673.53 and 678.57, its relative standard deviation of the batch being below 1%. The measured tritium activity concentration was corrected to the day of the measurement. The zeta scores obtained for the proficiency tests samples fulfill the acceptability criterion, Table 11, its variation being between − 1.14 and 0.48.

In order to compare ProsafeLT+, the same proficiency test samples were prepared with GoldStar LT2, classic liquid scintillation cocktail provided by Meridian Biotechnologies Ltd. for tritium determination. The ratio of 8:12 ml of sample: liquid scintillation cocktail was used, and the batch of standard, background and the five samples were measured 500 min. (50 min/samples, 10 cycles). The mean count rate of the background was 0.731 ± 8.5% CPM, the counting efficiency of 23.53% at the best figure of merit, and a detection limit of 0.6 Bq l^{-1} (according ISO 9698:2010). The SQP(E) parameter varied between 690.13 and 699.56, its relative standard deviation of the batch being below 1%. The measured tritium activity concentration was corrected to the day of the measurement. The zeta scores obtained for the proficiency tests samples, Table 12, varied between − 0.52 and 1.02, lower than accepted values of ± 2.

Despite lower counting efficiency of ProSafe LT+, expected behavior due to NPE's lack, the detection limit and uncertainty are comparable with the traditional liquid scintillation cocktail of the same provider.

Table 9 Trueness evaluation by measurement of high spiked tritium samples

Samples	Calculated tritium activity (Bq kg^{-1})	Uncertainty (Bq kg^{-1})	Measured tritium activity (Bq kg^{-1})	Uncertainty (Bq kg^{-1})	ζ
1	61,700	2000	61956.8	3879.8	0.06
2	132,200	4000	123874.0	7754.0	− 0.95
3	184,600	5900	185039.1	11581.1	0.03
4	246,200	7900	247955.7	15517.8	0.10
5	307,800	9900	310148.4	19409.2	0.11

Table 10 Trueness evaluation by measurement of low level spiked tritium samples

Samples	Calculated tritium activity (Bq kg^{-1})	Uncertainty (Bq kg^{-1})	Measured tritium activity (Bq kg^{-1})	Uncertainty (Bq kg^{-1})	ζ
1	249	8	264.3	16.60	0.83
2	188	6	187.8	12.08	− 0.01
3	125	4	129.0	8.14	0.45
4	63	3	64.4	4.10	0.27
5	31	1	30.6	2.25	− 0.16
6	25	1	23.6	1.82	− 0.68
7	19	1	20.6	1.39	0.96
8	12.5	0.4	11.9	1.04	− 0.54
9	6.3	0.4	7.3	0.61	1.32

Table 11 Trueness evaluation by measurement of proficiency tests samples using ProSafe LT+ liquid scintillation cocktail

Sample	Organizers	Reference tritium activity concentration (Bq kg^{-1})	Reference uncertainty (Bq kg^{-1})	Measured tritium activity (Bq kg^{-1})	Uncertainty (Bq kg^{-1})	ζ
T32	IAEA TRIC2018	4.82	0.02	4.62	0.49	− 0.40
T33	IAEA TRIC2018	14.31	0.06	14.81	1.05	0.48
T34	IAEA TRIC2018	59.76	0.22	57.35	2.11	− 1.14
AQ548	LGC-2018	35.16	0.58	34.34	1.74	− 0.45
AQ528	LGC-2017	72.07	1.18	70.99	2.61	− 0.38

Table 12 Trueness evaluation by measurement of proficiency tests samples using GoldStar LT2 liquid scintillation cocktail

Sample	Organizers	Reference tritium activity concentration (Bq kg^{-1})	Reference uncertainty (Bq kg^{-1})	Measured tritium activity (Bq kg^{-1})	Uncertainty (Bq kg^{-1})	ζ
T32	IAEA TRIC2018	4.82	0.02	4.58	0.44	−0.52
T33	IAEA TRIC2018	14.31	0.06	14.4	0.95	0.09
T34	IAEA TRIC2018	59.76	0.22	57.72	1.91	−0.52
AQ548	LGC-2018	35.16	0.58	37.72	1.54	1.02
AQ528	LGC-2017	72.07	1.18	71.64	2.44	−0.11

Conclusions

Tritium measurement using the liquid scintillation counting method is one of the most popular methods applied in the operation and environmental monitoring programs of nuclear facilities. Changes in EU regulations will adversely affect the liquid scintillation cocktail providers, and by consequence tritium measurements using the liquid scintillation method.

The ProSafe LT+ (Meridian Biotechnologies Ltd.) is a liquid scintillation cocktail dedicated to tritium measurements and adapted to EU regulation. Its sample holding capacity of 8 ml in 20 ml volume vial, is the same as that used for other liquid scintillation cocktails in our routine procedure. The counting efficiency of around 20% is lower than the counting efficiency of around 24% established for Gold Star LT2 (same provider), but its lower background (below 0.7 CPM) enabled a good limit of detection, below 1 Bq l^{-1}. It is necessary to mention that the Quantulus 1220 has been in operation since 1998, and counting efficiency is certainly higher than that obtained in these experiments, the photomultipliers aging phenomenon being observed during its exploitation [17].

The ProSafe LT+ has a very good linearity of the signal on a very wide range of tritium activity concentration, from 0.3 MBq l^{-1} to 6 Bq l^{-1}, being suitable both for operation and environmental monitoring of nuclear facilities. Its repetability and its trueness fulfilled acceptability criteria proving that this liquid scintillation cocktail can be used in the laboratory routine procedure. The ProSafe LT+ behavior for tritium standard calibration curve [18] remains to be investigated.

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