

A STUDY OF SEVERAL COMMERCIAL LIQUID SCINTILLATION COCKTAILS FOR MEASUREMENT OF LOW LEVELS OF TRITIUM IN WATER

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ABSTRACT. We describe the methods used in a study of water-based commercial liquid scintillation cocktails to determine the performance of each for the measurement of low levels of tritium in water. The cocktails used were very close to their maximum load capacities and maximum vial volumes; counting was performed in the window corresponding to maximum figure of merit. For each cocktail, we measured the correlation between counting efficiency and quenching, and studied the background stability. We calculated for each cocktail the optimization function and detection limit, taking into account background instability. We also evaluated the accuracy of each cocktail for ^3H measurement.

INTRODUCTION

Electrolytic preconcentration is required for reliable measurement of low levels of tritium in water, but in some cases, application of the resources of liquid scintillation (LS) spectrometry may avoid this tedious and time-consuming procedure. For measurements of this kind, we must reach the lowest possible detection limits and attain the best accuracy. When using commercial LS water-based cocktails, the best conditions for reaching the lowest detection limits are related to the counting mixture (volume, water content) and to counting conditions (width and position of the counting window). Therefore, we had to optimize these three variables. In a previous study, Rauret *et al.* (1990) introduced an optimization function that takes these variables into account. This function relates to the detection limit; its minimum corresponds to the best conditions for using the cocktail and to the best counting window. It has the expression

$$y = (1/fM)B^{1/2}/E \quad (1)$$

where f = fraction of water in the counting mixture, M = mass of the counting mixture, E = counting efficiency and B = background.

The lower the minimum value of this function, the better the performance of a cocktail. Using the optimization function, Rajadel (1991) showed that, for two different water-based cocktails, the best conditions were maximum load capacity stated by the manufacturer and maximum volume of the counting mixture. We assume that these conditions are met by other commercial cocktails, and the composition of mixtures are similar. The optimization function is only a first step in assessing the performance of a cocktail, because it does not consider background stability (Florkowski 1981). The detection limit, calculated below, does take into account the background stability; we use this for evaluating the performance of the cocktails under optimum conditions.

To obtain the most accurate ^3H result, one must know precisely the counting efficiency corresponding to the counting window used for each of the counting mixtures. The efficiency depends on the quenching associated with each counting mixture, which depends on water content in the counting mixture, because water is a strong quenching agent, and on the intrinsic quenching effect of the vials. We have observed that different vials show distinct values of the quenching parameter with the same counting mixture.

The composition of counting mixtures can be known precisely, but the constancy of water content cannot be guaranteed, due to inherent imprecision in measuring small volumes. This, and the use of different vials, lead to variation in the counting efficiency of different mixtures. The best way to determine the counting efficiency of each counting mixture is to establish an experimental correlation curve between counting efficiency and a quenching parameter in the same conditions of counting, that is, using water as a quenching substance (Takiue, Fujii & Homma 1990). In this way, the effect of both aforementioned factors on counting efficiency are taken into account.

Once the optimum counting mixture and counting window have been established, and the relation between quenching and efficiency is known, the detection limit must be estimated by measuring several blanks in randomly selected vials. If the experimental variance of the series of count rates obtained is greater than the Poisson variance, we use experimental variance to calculate the detection limit. If experimental variance is smaller than the Poisson variance, we use this value to calculate the detection limit. Other workers have studied the best conditions for using commercial LS cocktails (François & Limandas 1971; Florkowski 1981; Swailem 1984; Schönhofer & Henrich 1987; Rozanski, Stichler & Schwarz 1991). Here, we apply the principles explained above to a study of several commercial LS cocktails in glass and polyethylene vials and describe routine measurements.

METHODS

We use a Packard Tri-Carb® 2000CA/LL counter with linear amplification, multichannel analyzer with 4096 channels (0–2000 keV range), three-dimensional Spectralyzer™ to discriminate background radiation from decay events, three independent regions with variable limits for counting, external standard source of ¹³³Ba, spectrum storage possibility and refrigeration. We set option LL to “on”. We use low-K borosilicate 20-ml glass vials and polyethylene 20-ml vials (Packard). Reagents were: 1) commercial LS cocktails Insta-Gel® II, Insta-Gel®, Pico-Fluor™ LLT and Pico-Aqua™ (Packard), and Optiphase HiSafe™ 3 (LKB); 2) distilled, ³H-free water; and 3) ³H standards (see preparation below).

To a previously tared hermetic glass bottle, 75 ml of distilled ³H-free water were added and weighed. The contents of a vial of a certified 4.69×10^6 dpm g⁻¹ (1 March 1988) of ³H-labeled water (Amersham International plc) were then poured into the bottle and weighed again (standard T1). In another previously tared glass bottle, 85 ml of the same water were added and weighed and then 1.5 ml of T1 were also added and weighed (standard T2). In this way, an activity standard, T2, of 4315.3 dpm g⁻¹ of ³H in water was obtained. Activity standards for the accuracy check were prepared in the same way, by gravimetric dilution of a suitable volume of T2, according to the final specific activity desired.

Nominal composition of a counting mixture is the composition (ratio of water to cocktail) to be attained when preparing blank and sample counting mixtures. Due to imprecision of volumetric measurement, the actual compositions of those counting mixtures fluctuate around the nominal composition. The nominal composition used for the different LS cocktails studied is close to, but slightly lower than the maximum capacity of the cocktail. We establish the nominal composition for each cocktail experimentally, so that phase separation does not occur in the standards with the greatest amount of water, when preparing the series of standards used for calibration of the efficiency as a function of quenching.

The standard with the nominal composition (see preparation below) is counted for 4 h at 1-h intervals. A blank with the same composition is also prepared and counted for 48 h at 12-h intervals. The spectra (accumulated counts in each channel) of the standard and the blank are

stored. The 4 ^3H spectra and 4 background spectra are summed and divided by their respective total times by computer calculation. In this way, spectra per unit time (cpm spectra) are obtained. By subtracting these spectra, the net ^3H spectrum per unit time is calculated. We obtained the efficiency spectrum for ^3H by dividing this by the activity of the standard solution. Finally, the energy range furnishing the minimum value of $B^{1/2}/E$ (equivalent to maximum figure of merit) is found, by iterative calculation, from the ^3H efficiency spectrum and from the background spectrum per unit time. We adopt this window as counting window.

To establish the calibration curve of efficiency as a function of quenching parameter, we use 11 randomly selected vials for preparing activity standards with variable amounts of water and total volume of 20 ml. One standard contains the nominal total amount of water, 5 contain less water and 5 contain more. The total amount of water in the standards varies at increments of 0.1 ml and the amount of scintillation cocktail varies at the same increments, to keep the total volume constant at 20 ml. To each vial, suitable amounts of scintillation cocktail and distilled ^3H -free water are added to a total volume of 18.5 ml. The vials are then weighed and, finally, 1.5 ml of T2 is added to each vial, which is stoppered, shaken and weighed again. In this way, the activity of each standard is precisely calculated as the product of the weight of T2 and its specific activity. The standards are counted for 180 min. For each 15-min interval, the count rate and the measured quenching parameter are printed out. The counting efficiency of each standard is calculated and correlated with the mean value of the quenching parameters, by means of a 3rd-degree polynomial regression. We use t-SIE as a quenching parameter, obtained with the external source. For preparing samples, the nominal amount of scintillation cocktail is added to the vial and weighed. The nominal amount of distilled sample water is added and weighed again. One sample is prepared with the standard for an accuracy check. For background measurement, blanks are prepared in the same way in randomly selected vials, but with distilled, ^3H -free water.

We count samples and blanks alternately for 24 h at 96-min intervals, and the count rate and the t-SIE values are printed out for each interval. To assess any deviation or dispersion in counting results other than those expected from natural radioactive decay, we calculate the ratio between the Poisson standard deviation and the experimental standard deviation. Referred to here as counting quality parameter (see calculations, below), this ratio must be close to 1, if counting is normal; if its value is too low (<0.6), we reject the counting. We take the mean value of the count rates of all the blanks as background. Similarly, the ratio between the Poisson standard deviation of the background and the experimental standard deviation of the blank count rates, referred to here as background stability parameter (see calculations, below), is an expression of the background stability. It must be close to 1, if background is stable; small values indicate background instability.

Definition of Symbols

- C_j = count rate measured in the j th counting interval
- C = count rate corresponding to total counting time
- t = duration of a counting interval
- n = number of intervals in total counting time
- B_k = count rate corresponding to k th blank
- B = background
- m = number of blanks counted
- var_t = Poisson variance referred to the total counting time
- var_i = Poisson variance referred to the counting interval
- var_e = experimental variance
- var = unspecified variance

- r = counting quality parameter
 R_B = background stability parameter
 x_j = value of the quenching parameter obtained in the j th interval
 E_j = value of the efficiency, expressed as a fraction, corresponding to x_j through the experimental correlation curve $E = f(x)$ between efficiency and quenching parameter
 E = value of the efficiency, expressed as a fraction, associated with a counting mixture
 R = net count rate
 a = weight of sample
 A = specific activity of the sample
 R_C = critical level expressed in cpm
 R_D = detection limit expressed in cpm
 A_D = detection limit expressed in dpm g^{-1} of water.

Count Rate Calculations

$$\begin{aligned}
 C &= (1/n) \sum C_j \\
 \text{var}_t(C) &= C/nt \\
 \text{var}_r(C) &= C/t \\
 \text{var}_e(C) &= [1/(n-1)] \sum (C - C_j)^2 \\
 r &= [\text{var}_t(C)/\text{var}_e(C)]^{1/2}.
 \end{aligned}$$

Efficiency Calculations

$$\begin{aligned}
 E_j &= f(x_j) \\
 E &= (1/n) \sum E_j \\
 \text{var}_e(E) &= [1/(n-1)] \sum (E - E_j)^2.
 \end{aligned}$$

Background Calculations

$$\begin{aligned}
 B &= (1/m) \sum B_k \\
 \text{var}_e(B) &= [1/(m-1)] \sum (B - B_k)^2 \\
 \text{var}_t(B) &= B/nt \\
 r_B &= [\text{var}_t(B)/\text{var}_e(B)]^{1/2}.
 \end{aligned}$$

Net Count Rate Calculations

$$\begin{aligned}
 R &= C - B \\
 \text{var}(R) &= \text{var}_t(C) + \text{var}(B).
 \end{aligned}$$

The greatest value between $\text{var}_e(B)$ or $\text{var}_t(B)$ is used as a value for $\text{var}(B)$.

Calculation of the Specific Activity of the Sample

$$\begin{aligned}
 A &= R/Ea \\
 \text{var}(A) &= A[\text{var}(R)/R^2 + \text{var}_e(E)/E^2].
 \end{aligned}$$

Calculation of the Detection Limit

Detection limits are calculated according to Currie (1968) but using experimental variance of the background if its value is greater than the Poisson variance.

Critical Level

$$R_C = k[\text{var}_i(B) + \text{var}_e(B)]^{1/2}, \text{ or}$$

$$R_C = k[2\text{var}_i(B)]^{1/2}$$

if the Poisson variance is less than the experimental variance.

Detection Limit

$$R_D = 2R_C + k^2/nt$$

$$A_D = R_D/Ea.$$

The factor, k, is the abscissa for the standardized normal distribution corresponding to a given confidence level. The same confidence level is used for the critical level and for the detection limit.

RESULTS AND DISCUSSION

Table 1 shows the results obtained in the study of the performance of Insta-Gel® II, Insta-Gel®, Pico-Fluor™ LLT and Pico-Aqua™ in glass vials, and Optiphase HiSafe™ 3 in both glass and polyethylene vials. We studied Insta-Gel® from two different batches (bought in 1989 and 1992), with slightly different results. We used polyethylene vials only with Optiphase HiSafe™ 3, because, according to its manufacturer, it does not diffuse through polyethylene vials. The second column shows the nominal composition used for each cocktail studied; the fourth column shows the corresponding optimum windows. Column OF presents the values of the optimization function; columns R_C and R_D show, respectively, the critical level and the detection limit, both calculated with a 5% risk level (k = 1.645). To take into account the amount of water measured, column A_D shows the detection limit expressed in dpm ³H per gram of water. The best values of the optimization function correspond to Insta-Gel® (first batch), due to its low background and high efficiency, to Pico-Fluor™ LLT, due to its high water holding capacity, and to Insta-Gel® II, due to

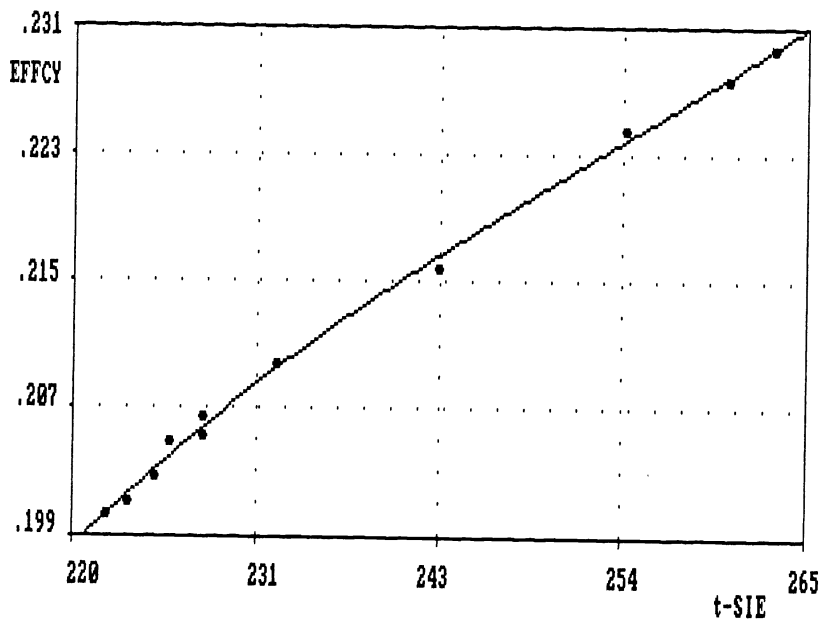


Fig. 1. Variation of the efficiency as a function of quenching with Insta-Gel®

TABLE 1. Performance of Several Liquid Scintillation Cocktails

Scintillation cocktail	Nominal composition water/cocktail (ml)	Vial type	Counting window (keV)	E (%)	B (cpm)	m	I_B	OF*	R_C (cpm)	R_D (cpm)	A_D (dpm g ⁻¹)
Insta-Gel® II	9.7/10.3	Glass	0.5/3.5	20.8	2.024	12	0.55	0.705	0.128	0.259	0.131
Insta-Gel® (1)**	9.7/10.3	Glass	0.5/4.0	22.8	2.184	10	0.74	0.668	0.107	0.217	0.098
Insta-Gel® (2)**	9.8/10.2	Glass	0.5/4.0	20.6	2.363	5	1.23	0.761	0.094	0.190	0.094
Pico-Fluor™ LLT	10.7/9.3	Glass	0.5/4.0	20.5	2.332	12	0.79	0.696	0.107	0.216	0.099
Pico-Aqua™	9.8/10.2	Glass	0.5/3.5	20.4	2.398	10	1.20	0.774	0.095	0.192	0.096
Optiphase HiSafe™ 3	9.8/10.2	Glass	0.5/4.0	19.1	2.032	8	1.65	0.762	0.087	0.177	0.094
Optiphase HiSafe™ 3	9.8/10.2	Polyethylene	0.5/3.5	16.2	1.352	10	0.55	0.732	0.104	0.211	0.133

*Optimization function

**Insta-Gel® from 1st and 2nd batch, respectively

TABLE 2. Accuracy of Several Liquid Scintillation Cocktails

Scintillation cocktail	Vial type	Observed specific activity A (dpm g ⁻¹)	A ± s(A)	True specific activity (dpm g ⁻¹)	Relative error (%)
Insta-Gel® II	Glass	30.42 ± 0.14		29.77	2.17
Insta-Gel®(1)	Glass	9.90 ± 0.077		9.87	0.37
Insta-Gel®(2)	Glass	11.51 ± 0.14		11.52	0.0
Pico-Fluor™ LLT	Glass	1.06 ± 0.15		1.08	-2.4
Pico-Aqua™	Glass	9.23 ± 0.069		9.42	-2.0
Optiphase HiSafe™ 3	Glass	9.18 ± 0.13		9.21	-0.36
Optiphase HiSafe™ 3	Polyethylene	11.64 ± 0.089		11.65	-0.13

its low background. However, these cocktails do not afford the best detection limits because of their background instability ($r_B < 1$). The best detection limits correspond to cocktails with good background stability, in particular, to Insta-Gel® (second batch), due to its high efficiency, and to Optiphase HiSafe™ 3 with glass vial, due to low background.

Figure 1 shows the experimental correlation between efficiency and quenching obtained with Insta-Gel®. Table 2 shows the values of the specific activity found in the standards for the accuracy check using the different scintillation cocktails, compared with their true values and the corresponding relative errors. In general, accuracy is good; only Insta-Gel® II and Pico-Aqua™ present a relative error greater than the relative uncertainty (referred to one standard deviation) due to the counting.

ACKNOWLEDGMENTS

We thank Silvia Soriano for laboratory assistance and Jordi Llumà for his useful computer program to determine the optimum counting window.

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