

RADIOASSAY OF LOW SPECIFIC ACTIVITY TRITIATED WATER BY IMPROVED LIQUID SCINTILLATION TECHNIQUES

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THE liquid scintillation technique has achieved considerable popularity as a radioassay method for tritiated water because it combines ease of sample preparation with adequate counting efficiency. However, for low specific activity samples, i.e. samples producing a count approaching that of background, counting times become long and the advantages of the technique become marginal. The purpose of this paper is to describe a method of scintillator-sample preparation that increases scintillator performance resulting in a substantial decrease in counting time for low specific activity samples. This is accomplished in two ways: (a) making the water sample-scintillating solution ratio optimum, and (b) deoxygenating the scintillating solution. In general, the techniques described here can be applied in the radioassay of water soluble radioisotopes other than tritium.

MAKING THE WATER SAMPLE-SCINTILLATOR RATIO OPTIMUM

Since the best scintillating solutions employ toluene, or xylene, as a solvent it is necessary to use a mutual solvent such as ethanol to incorporate tritiated water into the solution. (Solutions employing dioxane and naphthalene as well as ethanol and toluene have been reported.⁵ The general method outlined here for determining optimum ratios of the various solution components can also be applied to such solutions.) The introduction of a tritiated water sample and the mutual solvent ethanol into a toluene scintillating solution causes a reduction in pulse height and, therefore, in counting efficiency. This 'quenching' is primarily due to the poor energy transfer properties of water and ethanol. It is important, therefore, to use the *minimum* amount of ethanol required to make a given amount of tritiated water soluble in the toluene scintillating solution. Figure 1 gives an experimentally determined curve of the ethanol-water ratio necessary for amounts of water from 0.1 to 10.0 ml in total scintillating solution (total scintillating solution refers to 100 ml of a ternary solution of water-ethanol-toluene). The ethanol-water ratio is the minimum recommended value required to maintain solubility at -25°C (in practice most solutions are measured at low temperatures to minimize

phototube noise). Data were obtained using ACS grade toluene and absolute ethanol. As a primary scintillating solute 2,5-diphenyloxazole (PPO) at a concentration of 4.0 g/l. of toluene was used with 0.1 g/l. of toluene of 1,4-di-[2-(5-phenyloxazole)]-benzene (POPOP) as a wavelength shifter.^{2,3} These concentrations in toluene were used in all the scintillating solutions described hereafter.

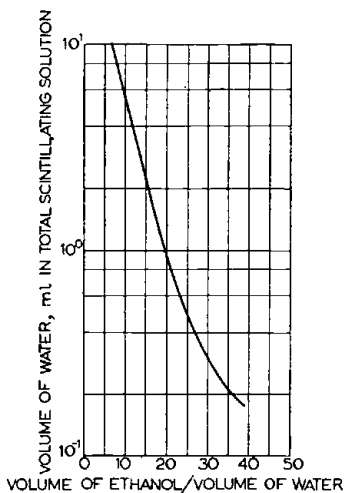


Fig. 1. Minimum recommended ethanol-water ratio for solubility in toluene to -25°C (the toluene containing 2, 5-diphenyloxazole, 4 g/l. toluene and 1, 4-di-2-(5-phenyloxazole)-benzene, 0.1 g/l.). All volumes specified at 22°C . Total scintillating solution refers to a 100 ml ternary solution of water-ethanol-toluene.

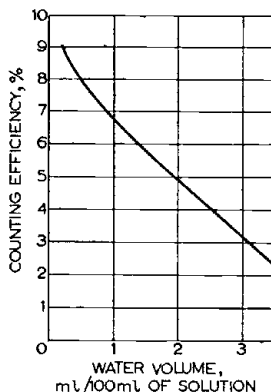


Fig. 2. Percentage counting efficiency of air saturated 2,5-diphenyloxazole; 1,4-di-2-(5-phenyloxazole)-benzene in toluene ethanol scintillating solutions as a function of tritiated water content (water-ethanol ratios of Fig. 1 used).

A number of samples using various volumes of tritiated water and the appropriate amounts of ethanol in a 2,5-diphenyloxazole; 1,4-di-[2-(5-phenyloxazole)]-benzene toluene scintillating solution were prepared and counted using a Tracerlab liquid scintillation counter, CE-1.¹⁰ The results of these measurements are seen in Fig. 2, where the counting efficiency is plotted as a function of the water content in ml/100 ml of total scintillating solution. It can be seen that as the volume of the water sample is increased the counting efficiency decreases. Samples were counted at efficiencies up to 12%. The highest counting efficiency, however, is not too meaningful since solutions which provide the highest counting efficiency are far from optimum solutions.

An optimum solution may be defined as the solution which will provide a specified statistical accuracy in the shortest counting time. A small volume of water sample provides high counting efficiency but a small number of radioactive events; a large volume of water provides low counting efficiency with a large number of events. Thus, the product of water volume, W and counting efficiency, E approaches zero as the water volume approaches either very small or very large values. Therefore, if the product, EW of water

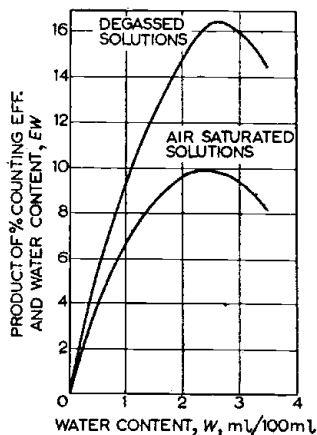


Fig. 3. Curves indicating optimum values of water content for degassed and air-saturated 2,5-diphenyloxazole; 1,4-di-2-(5-phenyloxazole)-benzene in solutions (water-ethanol ratios of Fig. 1 used).

volume and counting efficiency is plotted against the water volume, the peak of the resulting curve will indicate the optimum volume of water. The parameter values for this optimum solution will depend on the type of scintillating solutes and solvents used, the radioisotope counted and the efficiency of the counting system used in making the measurements. Thus, the optimum ratio need only be determined once for a given solute-solvent combination, a given

radioisotope and a given counting system. In a specified counting system the efficiency depends only on the water volume and not on the specific activity of the solution; thus, the position of the peak of the EW vs. W curve will not be dependent on specific activity.

The lower curve in Fig. 3 is an EW vs. W curve obtained using a 2,5-diphenyloxazole; 1,4-di-[2-(5-phenyloxazole)]-benzene in toluene solution and tritiated water counted on a Tracerlab CE-1 liquid scintillation counter. It can be seen that this instrument will always count tritium with a specified statistical accuracy in the shortest time if a sample volume of 2.3 ml/100 ml of this scintillating solution (not degassed) is used.

The use of optimum solutions presupposes the existence of adequate sample volumes. If, however, only a small volume of sample were available (less than the optimum value), then the largest available sample should be used. The existence of an optimum does not imply that a sample less than optimum should be diluted up to the optimum amount.

DEOXYGENATION OF THE SCINTILLATING SOLUTION

It is well known that the removal of dissolved oxygen from scintillating solutions greatly enhances the light output.^{4,8} This improvement has not yet been utilized in the liquid scintillation radioassay of tritium where any enhancement of light output would be of great advantage. The fact that the tritiated water must remain in solution during the deoxygenation procedure means that degassing must occur with negligible solution loss. Furthermore, in order to be suitable for routine use the degassing method must be simple and convenient. Standard degassing techniques such as vacuum distillation, or bubbling with an inert gas are unsatisfactory since both methods result in considerable loss of tritium through evaporation and solution carry-over.

An ultrasonic degassing method for liquid scintillators, previously reported,¹ has been satisfactorily applied to the radioassay of tritiated water.

In order to determine the degree of improvement in light output resulting from the ultrasonic degassing of water-ethanol-toluene scintillating solutions, a number of samples of 2,5-diphenyloxazole; 1,4-di-[2-(5-phenyloxazole)]-benzene in toluene scintillating solution containing various volumes of ordinary distilled water and ethanol were made oxygen free. The light produced in these solutions by an *external* strontium-90 source was determined by measuring the anode current produced in a 6292 DuMont multiplier phototube. The light outputs of these solutions were compared under identical experimental conditions with light outputs of similar solutions which had not been degassed. The percentage increase in light output of degassed relative to undegassed solutions is given in Fig. 4 as a function of the water content. In preparing all solutions the ethanol-water ratios of Fig. 1 were used. In Fig. 4 it is seen that the improvement in light output decreases with increasing

water content. This qualitatively corresponds to the fact that oxygen is less soluble in water and ethanol than in toluene.

It is possible for ultrasonic irradiation applied to liquids in the presence of air to cause oxidation reactions to occur in the liquid.^{6,7} Peroxides such as H_2O_2 which would be likely to form in aqueous and alcoholic solutions

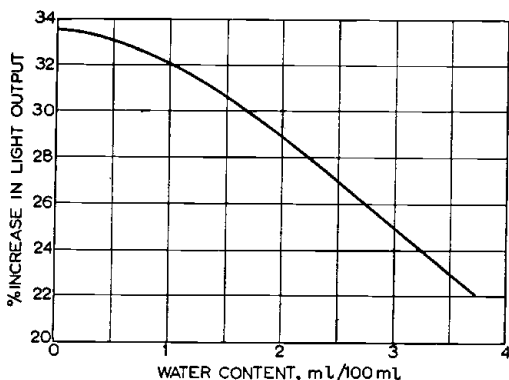


Fig. 4. Relative increase in light output due to degassing for 2,5-diphenyloxazole; 1,4-di-(5-phenyloxazole)-benzene in toluene-ethanol-water scintillating solutions (water-ethanol ratios of Fig. 1 used).

(used in scintillation work) are strong light quenching agents. In order to determine if quenchers were being generated, scintillating solutions of varying ethanol-water content were subjected to ultrasonic irradiation times much longer than the time required for degassing. These solutions were then allowed to equilibrate in air so that the dissolved oxygen content was the same as before irradiation. Measured values of the light outputs of these solutions before and after the treatment were the same indicating that no quenching agents had been generated.

Degassed solutions of varying tritiated water content were prepared and counted. The EW vs. W curve for these degassed solutions appears as the top curve in Fig. 3. It is seen that due to the improved performance of the deoxygenated solution the position of the peak has shifted to the right so that the new optimum water content is larger. In practice, by deoxygenation, the counting time to obtain a specified statistical accuracy is reduced by a factor which is the ratio of the EW values at the optimums for degassed and the not degassed solutions, i.e. $16.3/9.9=1.65$. This factor holds for source count rates large in comparison to background. For source rates not large compared to background (low specific activity samples) the factor is proportional to the square of the ratios,⁹ i.e. 2.7.

The solution loss due to the ultrasonic degassing treatment was determined by weighing and was found to average 0.75%. This small loss can be neglected

in many applications and for precise work the appropriate weight correction can be easily made.

CONCLUSION

The performance of the liquid scintillation method for the radioassay of low specific activity tritiated water can be considerably improved by techniques described here. Once the preliminary work of ascertaining the optimum solution ratios has been accomplished the only additional sample preparation time required is that of the degassing procedure (about 6 min per sample¹). In addition to the improvement obtained in scintillator performance by making the solution ratios optimum, an almost threefold reduction in counting time for low specific activity samples can be obtained by deoxygenation.

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