

Chapter 8

Quenching Corrections for Emulsion Systems

H. S. Wagstaff

Fisons Scientific Apparatus, Laboratory Chemicals, Bishop Meadow Road, Loughborough, England

and

A. R. Ware*

Chemistry Department, Loughborough University of Technology, Loughborough, England

INTRODUCTION

The counting of aqueous solutions of radiolabelled material using emulsifiers of the alkyl phenol ethoxylate type is now a routine operation in many laboratories. Depending on the water content, various types of 'emulsion' can be obtained and these appear to fall into four general types. At low water concentrations a clear solution is obtained, at high concentrations a gel and at water concentrations between 15–25% by volume an unstable and/or a true emulsion. The concentration boundaries of these regions are affected by both temperature and the presence of dissolved electrolytes. In all systems, the water added and any other compounds present in solution or suspension may act as a quencher resulting in a loss in the light emitted by the scintillators. The effect of quench can be measured in liquid scintillation counting by the use of an internal standard, an external standard or the channels ratio method. All three methods have been tried with emulsion systems. The most convenient method of quench correction is to use an external standard, but this has given rise to contradictory statements in the literature,¹⁻¹⁰ in particular with regard to the measurement of tritium activity.

The suggestion that quench curves should be obtained for each possible quenching compound is clearly not always a practical possibility as the exact composition is not always known and may vary between samples. A general external standard quench correction curve would therefore be invaluable in routine analysis to obtain absolute activities.

In this work quench curves were obtained by use of an external standard and by the channels ratio method and the extent to which general quench curves may be applied will be discussed.

* Current address: Central Radiochemical Laboratory, Central Electricity Generating Board, Chalk Lane, Cockfosters, Hertfordshire, England.

EXPERIMENTAL

The emulsifier used was an iso-octyl phenol polyethoxyethanol containing 10 moles of ethylene oxide (Triton X-100). Previous work by Fox^{10,11} has indicated that this emulsifier can be used with toluene to count aqueous solutions. A range of concentration ratios for emulsifier and toluene is possible. It was decided to use a concentration ratio of 1 part by volume emulsifier to 2 parts by volume toluene throughout the work. This value is one which is commonly used in practice and lies within the range suggested by Fox¹¹ to give a good merit stability quotient (MSQ).

All samples were prepared according to the method of Benson¹² which involves a warming and cooling cycle of the sample prior to counting. This method produced samples which gave reproducible counting rates for periods up to 10 days for a large range of water concentrations, thus allowing a series of samples to be counted several times on four different instruments for comparative purposes. The four instruments used were a Beckman LS100 operated at a controlled temperature of 12 °C and employing a ¹³⁷Cs external standard source, a Nuclear Chicago Unilux operated at a controlled temperature of 12 °C and employing a ¹³³Ba external standard source, a Packard 2420 operated at an ambient temperature of 23 °C and employing a ²²⁶Ra external standard source and a Beckman operated at an ambient temperature of 26 °C and employing a ¹³⁷Cs external standard source.

All samples were counted in the preset ³H channel of the instrument, the automatic external standard channels ratio (AESCR) as set on the instrument and a sample channels ratio (CR). The sample channels ratio was obtained by counting in the preset total ³H channel (A) and a channel (B) set such that it contained the lower 20% of the ³H count in A. The ratio CR was calculated after the counts had been corrected for background as follows:

$$CR = \frac{(\text{count in channel A}) - (\text{count in channel B})}{\text{count in channel B}}$$

A concentrated scintillant solution of 10.5 g l⁻¹ PPO and 0.15 g l⁻¹ POPOP in toluene was prepared. Six millilitres of this solution was present in all samples ensuring that the total weight of scintillants was the same in all cases. Tritiated water (0.5 ml) containing 50,000 disintegrations min⁻¹ was added to each sample; this enabled the sample channels ratio to be measured accurately. In practice the channels ratio is clearly not accurate for low active samples. Sufficient distilled water, toluene and Triton were then added to give a total volume of 15 ml and water concentrations ranging from 3.3–40% by volume.

The samples were then counted on the four counters described above. All samples were cycled and counted three times. The samples were counted long enough to give a 2σ error of 1.5% on all counts. Curves of percentage water concentration against counting efficiency are shown in Figs. 1 to 4. The AESCR and CR were also calculated and the curve of AESCR against counting efficiency is shown in Figs. 1 to 4. A similar smooth curve was obtained for CR against counting efficiency for water concentrations from 3.3–10% and from 26.7–40% by volume, but to avoid confusion it is not shown in the diagrams.

Three water concentrations were then chosen for further study of quench effects caused by chemical additives present in the system. The concentrations chosen were

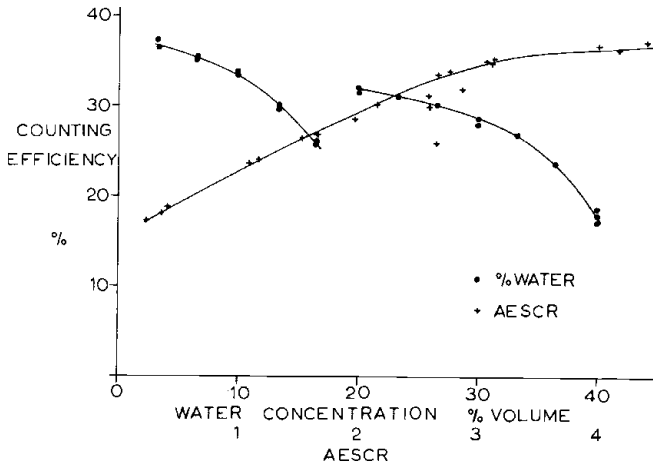


Fig. 1. The variation in counting efficiency with water concentration and AESCR for the Beckman LS100 controlled temperature counter (12 °C).

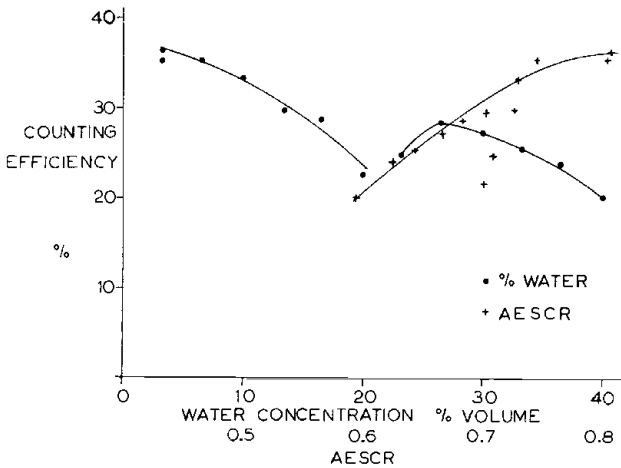


Fig. 2. The variation in counting efficiency with water concentration and AESCR for the Packard ambient temperature counter (23 °C).

10%, 26.7% and 40% water. Quenching agents investigated were carbon tetrachloride which should remain in the organic phase and the sodium salt of trichloroacetic acid which should remain in the aqueous phase. A series of samples were made up at each of three water concentrations for each quench agent. The quench effect was measured by determining both the AESCR and the CR for all samples. The results obtained on the controlled temperature Beckman are shown in Figs. 5 and 6 for water concentrations of 10% and 26.7%. For comparison the solid line indicates the curve of AESCR and CR against counting efficiency obtained for the samples of variable water concentration.

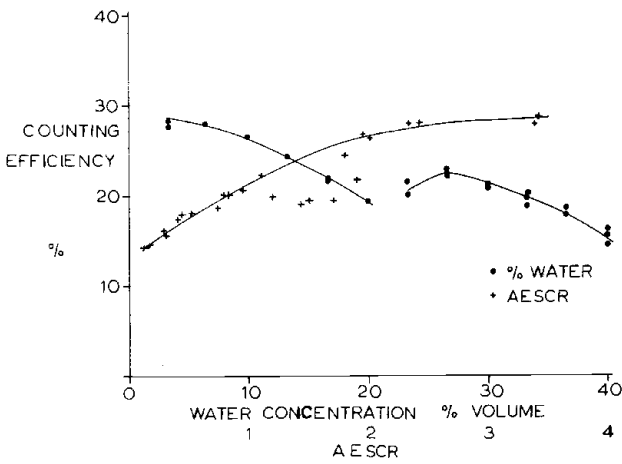


Fig. 3. The variation in counting efficiency with water concentration and AESCR for the LS100 ambient temperature counter (26 °C).

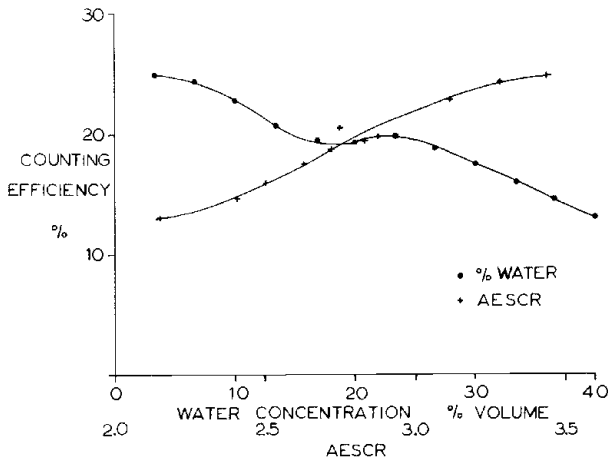


Fig. 4. The variation in counting efficiency with water concentration and AESCR for the Nuclear Chicago Unilux controlled temperature counter (12 °C).

Urine-quenched samples were also prepared and counted. The urine was decolourised to minimise colour quench effects. The results are also indicated in Figs. 5 and 6. No results were obtained for the 40% water samples as the quench had taken the spectrum below the range of the channels as set.

The results for the Packard instrument for all three water concentrations are shown in the same manner in Figs. 7 to 9.

The results for the Beckman LS100 operated at 26 °C are shown in Figs. 10 and 11. The results for the 26.7% water samples were very unreliable. This series of counts was

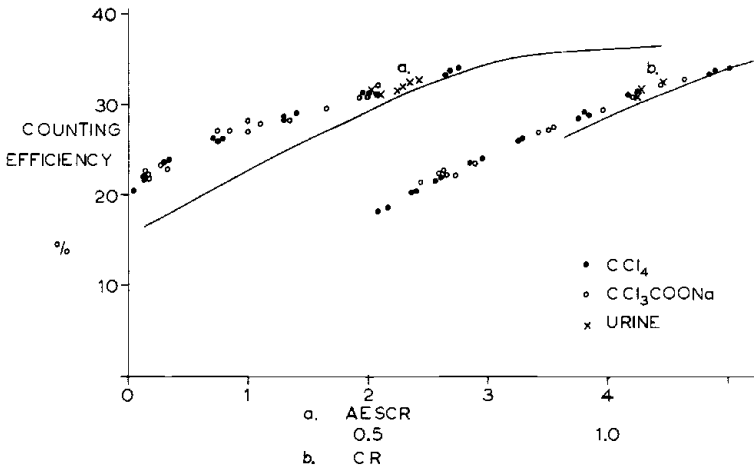


Fig. 5. Quench curves for 10% water samples showing AESCR and CR variations for the Beckman LS100 controlled temperature counter (12 °C).

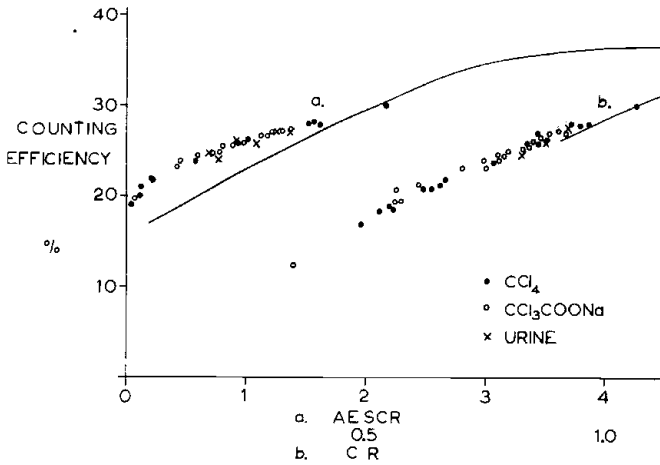


Fig. 6. Quench curves for 26.7% water samples showing AESCR and CR variations for the Beckman LS100 controlled temperature counter (12 °C).

performed at the highest temperature and as indicated by Tarkkanen¹³ the unstable two-phase region for emulsions moves to higher water concentrations as the temperature is increased. The value of 26.7% water comes on the edge of the unstable region according to the AESCR against counting efficiency curve of Fig. 3 and a 1-2 °C rise in temperature would make the 26.7% water concentration samples become two-phase. This was in fact observed and the samples reverted to a single phase on cooling.

The quench correction curves obtained for the Nuclear Chicago Unilux are shown in Figs. 12 to 14.

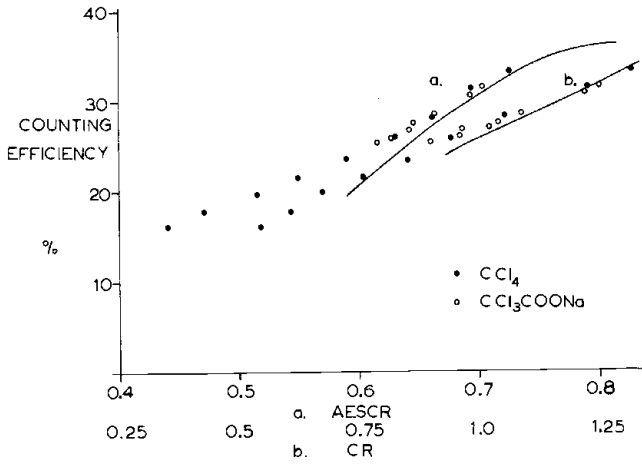


Fig. 7.

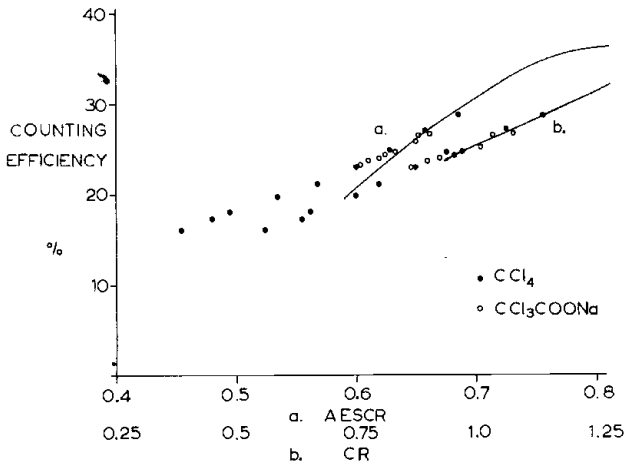


Fig. 8.

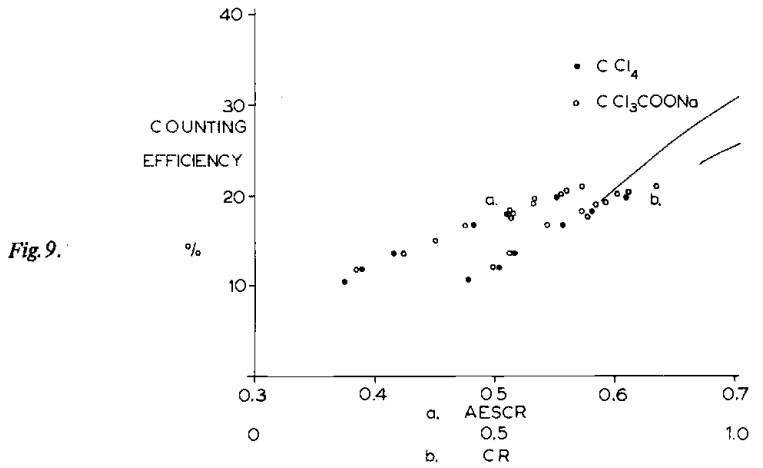


Fig. 9.

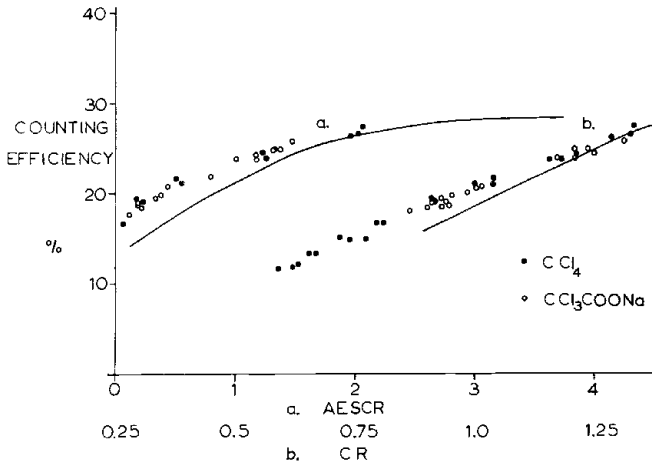


Fig. 10.

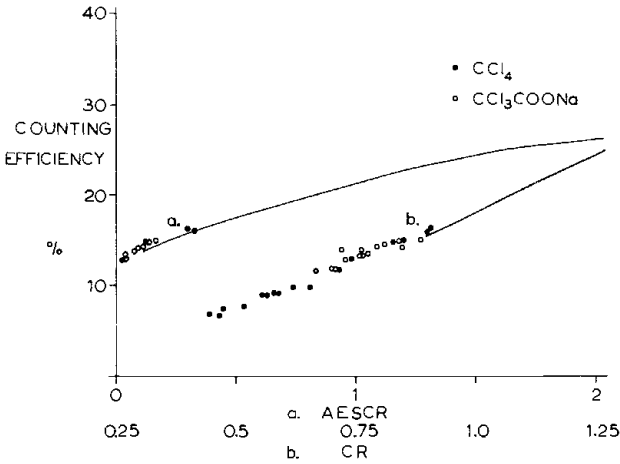


Fig. 11.

Fig. 7. Quench curves for 10% water samples showing AESCR and CR variations for the Packard ambient temperature counter (23 °C).

Fig. 8. Quench curves for 26.7% water samples showing AESCR and CR variations for the Packard ambient temperature counter (23 °C).

Fig. 9. Quench curves for 40% water samples showing AESCR and CR variations for the Packard ambient temperature counter (23 °C).

Fig. 10. Quench curves for 10% water samples showing AESCR and CR variations for the Beckman ambient temperature counter (26 °C).

Fig. 11. Quench curves for 40% water samples showing AESCR and CR variations for the Beckman ambient temperature counter (26 °C).

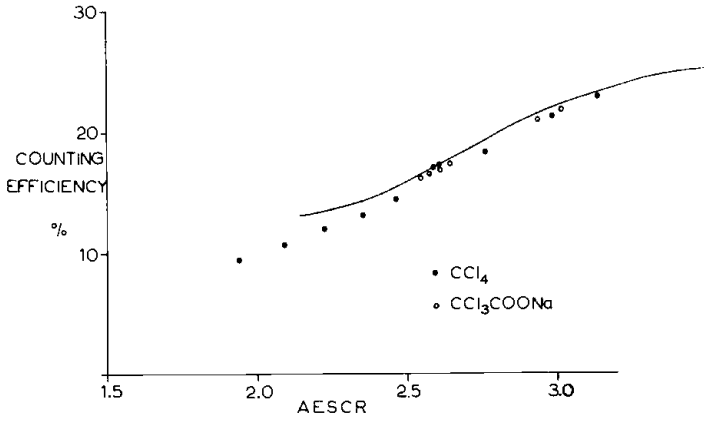


Fig. 12. Quench curves for 10% water samples showing AESCR variations for the Nuclear Chicago controlled temperature counter (12 °C).

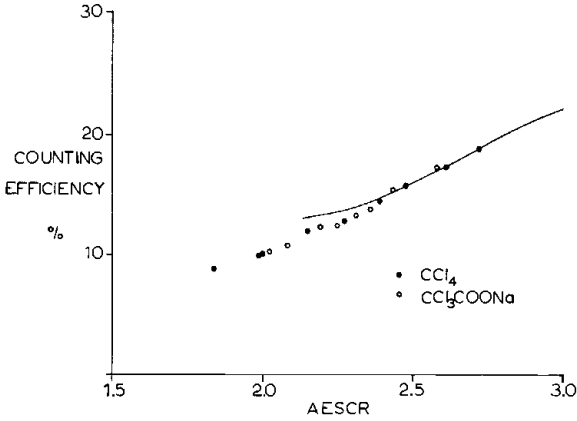


Fig. 13. Quench curves for 26.7% water samples showing AESCR variations for the Nuclear Chicago controlled temperature counter (12 °C).

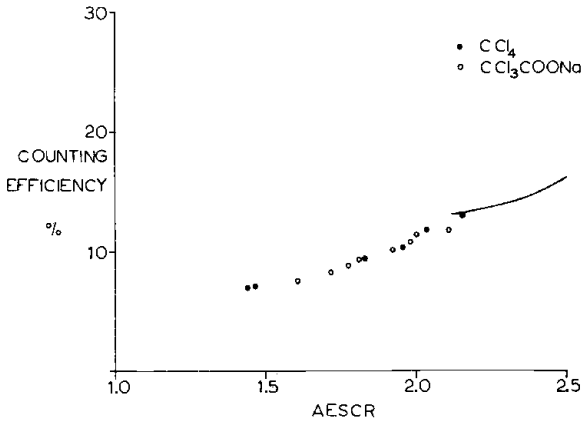


Fig. 14. Quench curves for 40% water samples showing AESCR variations for the Nuclear Chicago controlled temperature counter (12 °C).

DISCUSSION AND CONCLUSIONS

All the instruments gave the now familiar curve for water concentration against counting efficiency showing the region of two-phase separation leading to a discontinuity in the curve. Fox¹¹ has indicated that the two-phase region, although being physically unstable, can give consistently stable but low counting efficiency and this was confirmed. The AESCR against counting efficiency curves showed a smooth curve for water concentrations from 3.3% to 10% and 26.7% to 40%, but the results in the two-phase region did not fit the curve and recycled counts were not reproducible. As the counts had been shown to be stable this suggests that the AESCR was changing with time. This was found for both AESCR and CR measurements. This suggests that the use of any channels ratio technique in this two-phase region is unreliable. Quench curves for variable water concentration could be set up outside this region provided no other quenching agent was present.

The samples quenched with CCl_4 and CCl_3COONa at a fixed water concentration appear to give the same quench curve for any of the four counters even though the curves were not necessarily the same between counters. All are apparently reliable and useful. The urine samples counted on the Beckman counter also fitted the quench curves. Within the errors of the method it would appear that the same quench curve may be obtained for many different quenching agents.

The effect appears to be similar no matter whether the agent is soluble in aqueous or organic solution. Further, the quench effect can be satisfactorily measured by the AESCR or the CR values. This is not to say that the methods can be universally applied to all counters and samples. As can be seen in all the diagrams, Figs. 5 to 14, the quench curve obtained for the variable water concentration samples is different from that obtained for the samples quenched with CCl_4 , CCl_3COONa and urine. The quench mechanism would appear to be different for the two cases and quench curves are only reliable if either the water concentration or additives is kept constant. The four instruments employed three isotopes of widely differing γ -energies.

From the results, each of the isotopes gave suitable quench correction curves and consequently are all equally applicable. It was noticed that the manufacturers preset channels were not necessarily the optimum and more suitable channels might yield improved curves.

Provided samples are not counted in the two-phase region, which will vary with temperature, and that samples are made at a given water concentration, quench correction curves would appear to be a practical possibility for ^3H -labelled compounds. It is recommended that samples are put through a warming and cooling cycle during preparation and that the counter is operated at a controlled temperature.

ACKNOWLEDGEMENT

The authors wish to thank the School of Agriculture, Nottingham University, Sutton Bonnington, and Fisons Pharmaceuticals for loan of the Nuclear Chicago and Packard counters.

REFERENCES

1. L. A. Baillie, *Intern. J. Appl. Radn. Isotopes* 8, 1 (1960).
2. V. Tarkkanen, in *Liquid Scintillation Counting*, Vol.2 (eds. M. A. Crook, P. Johnson and B. Scales), Heyden, London, 1972, p. 177.

3. J. Van der Laarse, *Intern. J. Appl. Radn. Isotopes* 18, 485 (1967).
4. J. C. Turner, *Intern. J. Appl. Radn. Isotopes* 20, 499 (1969).
5. J. C. Turner, *Intern. J. Appl. Radn. Isotopes* 19, 557 (1968).
6. P. Rauschenback and H. Simon, *Fresenius Z. Anal. Chem.* 256, 119 (1971).
7. M. A. Friedman, A. McEvoy, G. Miller and S. Epstein, *Anal. Chem.* 43, 780 (1971).
8. L. E. Anderson and W. O. McClure, *Anal. Biochem.* 51, 173 (1973).
9. E. Rapkin, *Gel and Emulsion Counting of Aqueous Solutions*, Intertechnique Review.
10. B. W. Fox, in *Liquid Scintillation Counting*, Vol. 2 (eds. M. A. Crook, P. Johnson and B. Scales), Heyden, London, 1972, p. 189.
11. B. W. Fox, in *Liquid Scintillation Counting*, Vol. 3 (eds. M. A. Crook and P. Johnson), Heyden, London, 1973, p. 202.
12. R. H. Benson, *Anal. Chem.* 38, 1353 (1966).
13. V. Tarkkanen, in *Liquid Scintillation Counting*, Vol. 3 (eds. M. A. Crook and P. Johnson), Heyden, London, 1973, p. 177.