

STUDY OF THE SIZES AND DISTRIBUTIONS OF  
COLLOIDAL WATER IN WATER-EMULSIFIER-TOLUENE SYSTEMS

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The number of applications of liquid scintillation counting to the measure of radionuclides in aqueous samples has increased at a very rapid rate over the last few years. In the majority of these applications, the aqueous samples are dispersed into liquid scintillation solutions by the use of emulsifiers. The aqueous phase is dispersed as tiny micelles of much less than a few microns in size. The sizes, numbers, and distributions of these micelles could effect the real and apparent efficiency of the liquid scintillation processes. For very low energy radiations, the ability to even detect the radiations may be greatly dependent upon these properties of the colloidal systems.

In this work several radionuclides with different modes of decay have been employed in an effort to gain insight into the nature of these emulsion systems. Two different emulsion systems were studied because each showed certain characteristics which were important in the understanding of their applications to the problems of liquid scintillation counting.

### Experimental

Two emulsifier systems were used in this study; Triton X-100 (Rohm and Haas) and BBS-3 (Beckman Instruments, Inc.). Triton X-100 is an alkylphenoxy-polyethoxyethanol and BBS-3 is a mixture of special purpose emulsifiers. As will be seen later, the properties of these two emulsifier systems showed quite different (not always understood) properties.

These emulsifier systems were studied using the radionuclides  $^3\text{H}$ ,  $^{109}\text{Cd}$ - $^{109\text{m}}\text{Ag}$  and  $^{233}\text{U}$ . The  $^3\text{H}$  studies supplied data for the excitations by low energy beta particles ( $E_{\text{max}} = 18.6$  keV). The  $^{109}\text{Cd}$ - $^{109\text{m}}\text{Ag}$  studies supplied data for excitations by low energy conversion electrons (88 and 69 keV) and Auger electrons (29 keV). Finally, the  $^{233}\text{U}$  studies supplied data for excitations by mono-energetic alpha particles (4.8 MeV).

All counting data was obtained using a Beckman LS-300 which was coupled with a Nuclear Data (Model 1100) multi-channel analyzer<sup>(1)</sup>. The pulse height spectra were obtained from the logarithmic output pulses of the LS-300 and all spectra show plots of the differential count rate (counts/unit time/unit pulse height) vs. the pulse height response (channel number - 0 to 256).

In every sample the total volume of aqueous and liquid scintillation solution was maintained at a constant volume (12 ml) to eliminate any effects that could be caused by difference in the geometry between the light source (liquid scintillation solution) and the detectors (the multiplier phototubes).

All counting was done in one of two liquid scintillation solutions:

Solution 1 - 84% by volume Toluene  
16% by volume BBS-3

with solutes: butyl-PBD 8g/l  
PBBO 0.5 g/l

Solution 2 - 67% by volume Toluene  
33% by volume Triton X-100

with solutes: PPO 5 g/l  
M<sub>2</sub>-POPOP 0.2 g/l

These two solutions were chosen because they are the recommended<sup>(2,3)</sup> compositions for counting tritiated water samples.

### Tritium Counting

Figure 1 shows the counting efficiencies for tritium in Solution 1 and Solution 2 as a function of the ml of H<sub>2</sub>O containing a constant known amount of tritiated-water. Solution 1 (BBS-3) showed constant counting efficiency up to a volume of 1.85 ml of H<sub>2</sub>O at which point further H<sub>2</sub>O additions caused a separation of two phases with marked decrease in counting efficiency. Solution 2 (Triton X-100) showed a gradual decreasing counting efficiency with increasing water content. The dotted line is necessary to indicate that for some part of the plot there was also a separation of the system into two phases. However, at high water content, the Triton X-100 system formed a gel which

$^3\text{H}$  AS THO

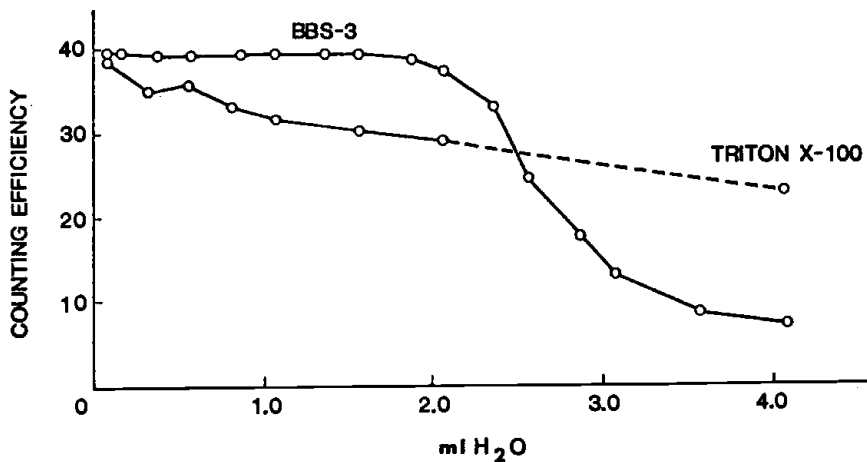


Figure 1. Tritium counting efficiency as function of volume of  $^3\text{H}$ -water in liquid scintillator solutions containing the detergent systems, BBS-3 (Solution 1) and Triton X-100 (Solution 2).

prevented the two phase from separating.

Figures 2 and 3 show spectra tritium in Solution 1 as a function of water content. Figure 2 shows the spectra for  $^3\text{H}$ -toluene. The increasing water content had no effect upon the spectra. This demonstrates that the water and scintillating phases of the total water-emulsifier-toluene system are separate and the water content does not interfere with the basic scintillation processes which are taking place in the organic phase of the system. Figure 3 shows the spectra for tritiated-water and  $^3\text{H}$ -toluene. The tritiated-water spectra show only a very slight shift to lower pulse heights with increasing water content. The tritiated water spectra are all shifted relative to the  $^3\text{H}$ -toluene spectrum. These data show the effect of decreased pulse height as a result of the beta particles having to travel at least for a fraction of their range in the non-scintillating media, water.

Figure 4 shows three methods of monitoring quench in liquid scintillator systems as applied to the Solution 1 as a function of water content. All three methods fail in the region of two phases.

#### $^{109}\text{Cd}$ - $^{109\text{m}}\text{Ag}$ Counting

Figure 5 shows the relative scintillation efficiency for the 88 keV conversion electrons of  $^{109}\text{Cd}$ - $^{109\text{m}}\text{Ag}$  aqueous sample in Solution 1 and Solution 2 as a function of water content. The similarity between these plots and Figure 1 are very evident. In both cases (tritium and  $^{109}\text{Cd}$ - $^{109\text{m}}\text{Ag}$ ), the excitations are produced by electrons.

Figures 6 and 7 show the pulse height spectra for  $^{109}\text{Cd}$ - $^{109\text{m}}\text{Ag}$ . Figure 6 gives the spectra obtained in Solution 1 (BBS-3) and the spectra (offset for clarity) all overlap indicating no measurable quench caused by increasing water content. Figure 7 shows the spectra obtained in Solution 2 (Triton X-100) and clearly increases in water content show dramatic shifts in the pulse height spectra similar to those which were obtained by adding a chemical quenching agent such as nitromethane. Table 1 lists data for  $^{109}\text{Cd}$ - $^{109\text{m}}\text{Ag}$  counted in Solution 2.

#### $^{233}\text{U}$ Counting

Figure 8 shows the relative scintillation efficiencies and energy resolution for  $^{233}\text{U}$  aqueous samples in Solution 1

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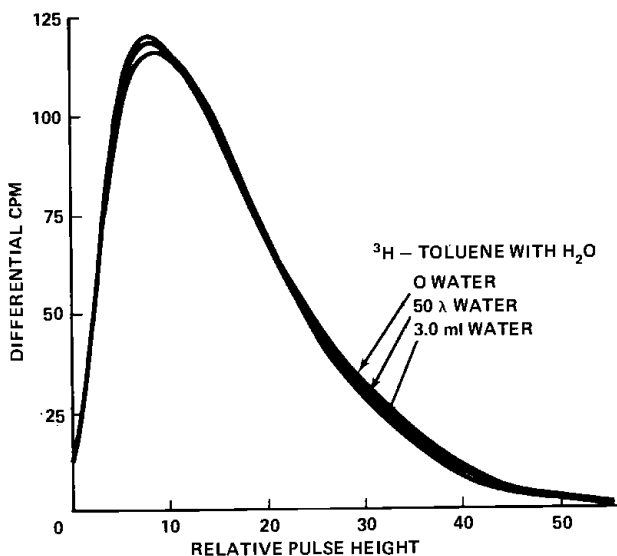


Figure 2. Pulse height spectra for  $^3\text{H}$ -toluene in Solution 1 as a function of  $\text{H}_2\text{O}$  volume.

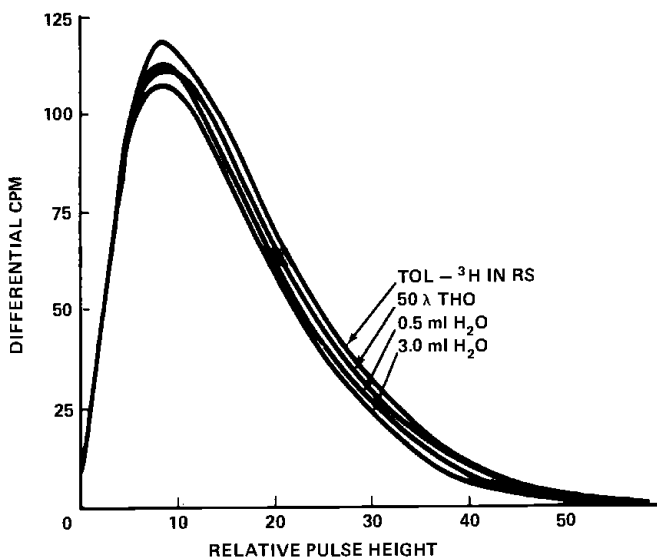


Figure 3. Pulse height spectra for  $^3\text{H}$ -toluene and  $^3\text{H}$ -water in Solution 1 as a function of  $\text{H}_2\text{O}$  volume.

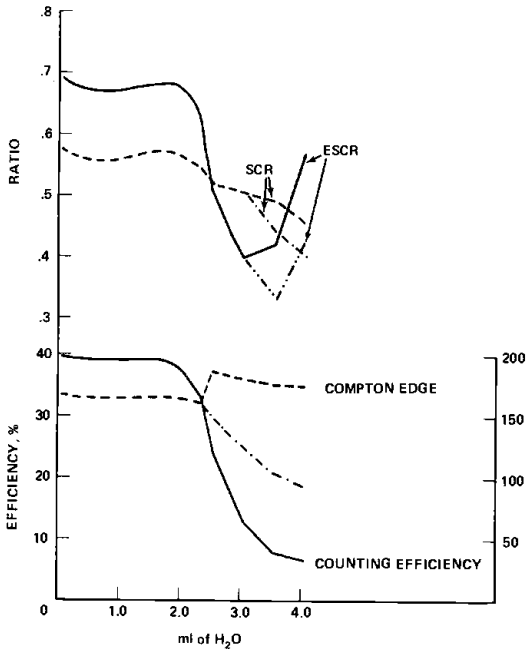


Figure 4. External Standard Channels Ratio (ESCR), Sample Channels Ratio (SCR) and Compton Edge pulse height values as a function of the volume of water in Solution 1. Also showing the <sup>3</sup>H counting efficiency as a function of H<sub>2</sub>O volume.

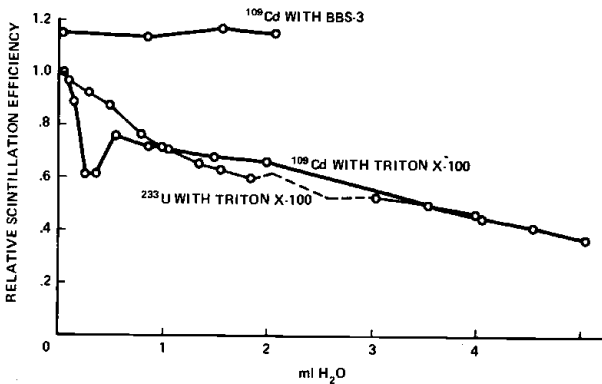


Figure 5. Relative scintillation efficiency as a function of volume of water in liquid scintillation solutions containing BBS-3 (Solution 1) and Triton X-100 (Solution 2) for excitation with <sup>109</sup>Cd-<sup>109m</sup>Ag and <sup>233</sup>U.

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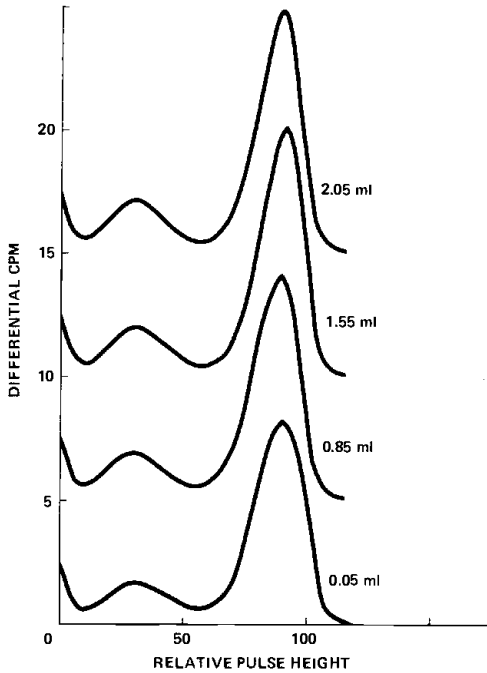


Figure 6. Pulse height spectra (displaced on Y axis for clarity) for  $^{109}\text{Cd}-^{109\text{m}}\text{Ag}$  source in Solution 1 for different volumes of work.

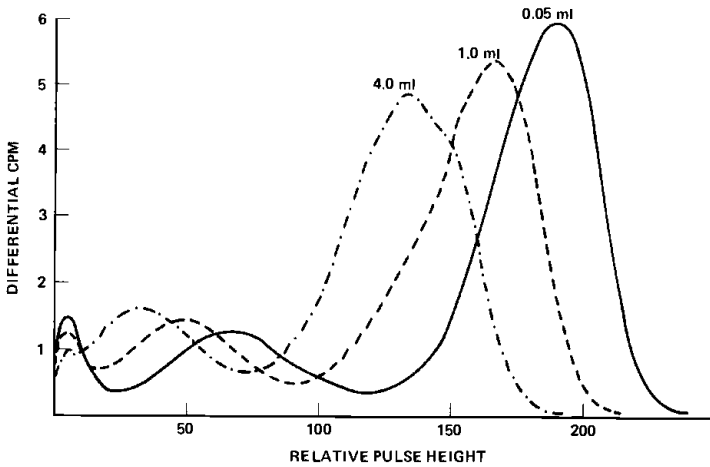


Figure 7. Pulse height spectra for  $^{109}\text{Cd}-^{109\text{m}}\text{Ag}$  source in Solution 2 for different volumes of water.

TABLE 1

<u>Water Content ml</u>	<u>Relative Scintillation Efficiency</u>	<u>Counts in <math>^{88}_{55}\text{Sr}</math> 69 keV Peak x 10<sup>5</sup></u>
0.05	1.000	2.98 (a)
0.15	.974	2.97
0.35	.923	2.80
0.55	.875	2.88
0.85	.765	2.81
1.05	.715	2.87
1.55	.678	2.89
2.05	.660	2.90
4.05	.466	2.80

(a) Small variations most likely due to pipetting errors.

TABLE 2

Vol. of H <sub>2</sub> O ml	CPM		Total	Relative Peak CPM, %	Peak Pulse Height	Relative Scintillation Eff, %	Energy Resolution %
	In Peak	In Tail					
0.15	39,336	4,454	43,790	89.8	82.5	100.0	47.5
0.25	39,734	4,725	44,459	90.7	81.5	94.9	50.1
0.35	39,880	4,552	44,432	91.0	81.5	94.9	51.8
0.55	39,842	4,554	44,396	90.9	81.0	92.3	49.9
0.85	39,659	4,750	44,409	90.5	80.5	89.9	48.1
1.05	41,138	5,438	46,576	93.9	80.5	89.9	48.1
1.35	42,723	4,453	47,176	97.5	80.0	87.5	43.2
1.55	43,079	4,436	47,515	98.3	80.5	89.9	42.1
1.85	43,429	4,082	47,511	99.1	81.5	94.9	39.5
2.05	43,746	3,609	47,355	99.8	79.5	85.2	44.4
2.35	43,269	4,161	47,430	98.7	80.0	87.5	46.6
2.55	43,821	3,895	47,716	100.0	79.0	83.3	43.2

(BBS-3) and Solution 2 (Triton X-100) as a function of the water content. Table 2 lists the actual data for the  $^{233}\text{U}$  samples in Solution 1. Figure 9 shows typical pulse height spectra for  $^{233}\text{U}$  in Solution 1 at two different water content values; 1.8 ml and 2.0 ml.

Again, Figure 8 shows a close correlation with the scintillation efficiency plots of Figure 5 and the counting efficiency plots of Figure 1. The energy resolutions are approximately the same in either Solution 1 or Solution 2. Furthermore, the very high specific ionization of alpha particles (from  $^{233}\text{U}$ ) would lead to considerable energy loss of the alpha particles leaving the water micelles if the size of the water micelles were increased even a small amount. This would be reflected in a marked increase in the energy resolution. It can be seen, especially with Solution 2, that even though the scintillation efficiency decreased, the energy resolution stayed fairly constant. This seems to indicate that the micelle sizes do not change with increased water content. Rather the number of fairly uniform size micelles has been increased.

#### Low Water Content Second Phase

The dip in the plot for Solution 2 in Figure 8 at low water content, 0.1 to 0.3 ml, is due to a separation of the water into a second phase. Figure 10 shows spectra for  $^{233}\text{U}$  in Solution 2. Plot (a) is the spectra for a sample containing 0.2 ml aqueous that has separated completely. Plot (b) is the same sample which has been shaken to disperse the aqueous phase. Even shaking the sample does not seem to completely disperse the aqueous phase as evident by the high count rate in the tail (below the peak) and the very wide peak. Addition of an extra 1.0 ml of water to the sample narrowed the peak of the spectrum, eliminated most pulses from the tail and increased the number of counts in the peak. Further, the added water stabilized the emulsion and prevented subsequent phase separation.

#### High Water Content Second Phase

At water contents greater than 2.0 ml in Solution 1, the counting system separates into two phases, see Figure 1. Figure 11 shows spectra for a tritiated water sample of 3 ml in 9 ml of Solution 1. Curve (a) is the spectrum obtained when the two phases are together in a single counting vial. The top and bottom phases were each 6 ml in volume. The two

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$^{233}\text{U}$  IN  $\text{H}_2\text{O}$

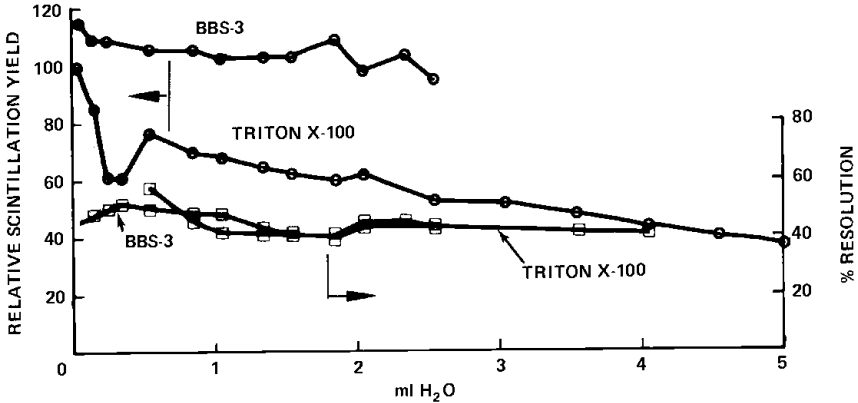


Figure 8. Relative scintillation efficiency and % resolution as a function of volume of water in liquid scintillator solutions containing BBS-3 (Solution 1) and Triton X-100 (Solution 2) for excitations with alpha particles from  $^{233}\text{U}$ .

$^{233}\text{U}$  IN RS-VI

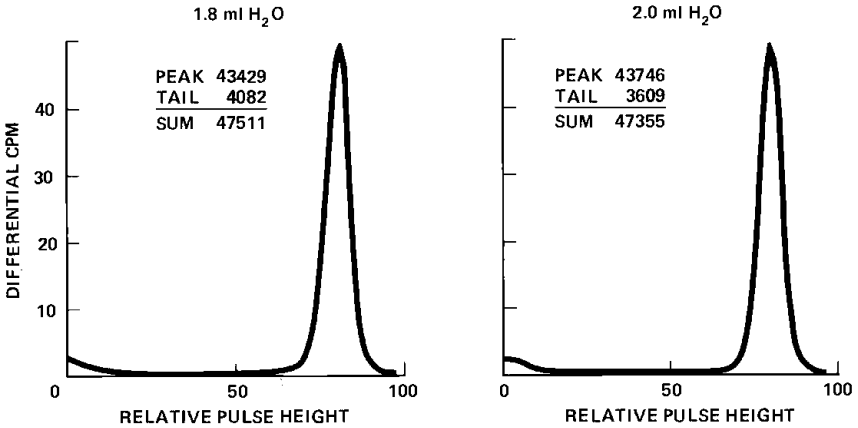


Figure 9. Typical pulse height spectra for  $^{233}\text{U}$  alpha particles in Solution 1 at different volumes of water. "Peak" denotes the counts which are present in the peak of the distribution. "Tail" denotes the counts which are present at pulse heights below the peak of the distribution. "Sum" denotes the sum of counts in the peak and tail.

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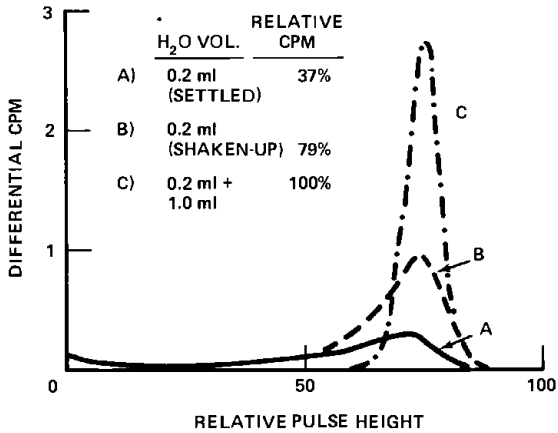


Figure 10. Pulse height spectra for sample of  $^{233}\text{U}$  in Solution 2 showing the stabilizing effect of added water.

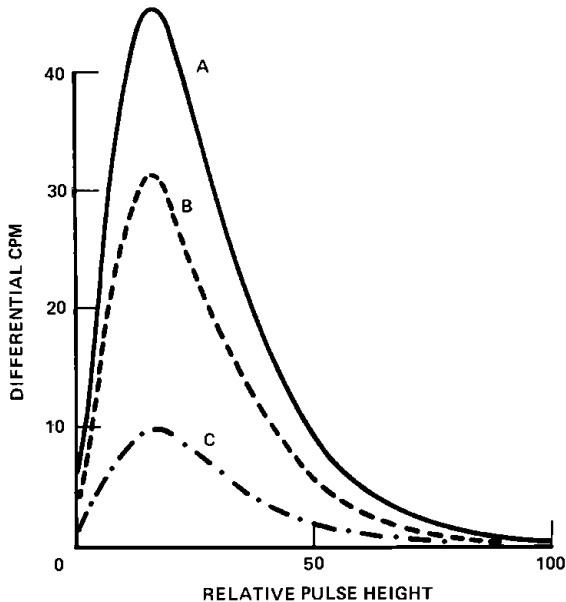


Figure 11. Pulse height spectra for  $^3\text{H}$ -water in a sample made of 3.0 ml of water and 9.0 ml of Solution 1. Curve A is spectrum obtained for two phases together in same vial. Curve B is spectrum of bottom phase alone in a separate vial. Curve C is spectra of top phase alone in a separate vial.

TABLE 3

	<u>Composition</u>		<u><math>^3\text{H}</math> Counting</u>	<u>Phase</u>	<u>Volume</u>	<u>Compton Edge</u>	<u><math>\% \text{H}_2</math> (a)</u>
	<u><math>\text{H}_2\text{O}</math></u>	<u>(THO)</u>	<u>Eff., %</u>			<u>Pulse Height</u>	
Combined Phases	3.0 ml			Top	6.0 ml	177	12.2
	9.0 ml	Solution 1	13.7	Bottom	6.0 ml	123	37.8
Separated	<u>Composition</u>		<u>Compton Edge</u>	<u>CPM</u>	<u><math>^3\text{H}</math> Counting</u>	<u>% of Initial</u>	<u>Volume</u>
Diluted	Phase		<u>Pulse Height</u>		<u>Eff., %</u>	<u><math>\text{H}_2</math></u>	<u>of <math>\text{H}_2\text{O}</math></u>
	Top + Solution 1		169.0	16,076	40.0	24.4	0.73 ml
	Bottom + Solution 1		160.5	39,950	32.0	75.6	2.27 ml

(a) Based on initial volume of phase and volume of  $\text{H}_2\text{O}$  in that phase.

TABLE 4

	<u>Composition</u>		<u><math>^3\text{H}</math> Counting Eff., %</u>	<u>Phase</u>	<u>Volume</u>	<u>Compton Edge Pulse Height</u>	<u>% <math>\text{H}_2</math> (a)</u>
	<u><math>\text{H}_2\text{O}</math></u>	<u>(THO)</u>					
Combined Phases	3.5 ml		8.2	Top	7.0 ml	177	16.9
	8.5 ml			Bottom	5.0 ml	110	46.3
Separated	<u>Composition</u>		<u>Compton Edge Pulse Height</u>	<u>CPM</u>	<u><math>^3\text{H}</math> Counting Eff., %</u>	<u>% of Initial <math>\text{H}_2\text{O}</math></u>	<u>Volume of <math>\text{H}_2\text{O}</math></u>
Diluted	Phase						
	Top + Solution 1	7.0 ml	169.0	22,325	40.0	33.8	1.18 ml
Diluted	Phase						
	Bottom + Solution 1	5.0 ml	160.5	35,360	32.0	66.2	2.32 ml

(a) Based on initial volume of phase and volume of  $\text{H}_2\text{O}$  in that phase.

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phases were separated (as efficiently as possible) by drawing off the top phase which is then transferred to a second counting vial leaving the bottom phase (with a little of the top phase) in the original counting vial. Curve (b) is the spectrum of the separated bottom phase and Curve (c) is the spectrum of the separated top phase. Figure 12 shows the Compton spectra for  $^{137}\text{Cs}$ - $^{137m}\text{Ba}$  gamma ray source; Curve (a) both phases together, Curve (b) the bottom phase alone and Curve (c) the top phase alone. The two distinct Compton edges indicate that each phase scintillates with its own efficiency.

Each separated phase was diluted with extra Solution 1 to reduce the quenching level to a measurable amount. Figure 13 shows the spectra for the Compton edge and the tritiated water for the 6 ml of the bottom phase with an additional 6 ml of Solution 1. The Compton edge showed only a single value which indicates the whole sample is counting with one efficiency. The value of Compton edge pulse height indicates the diluted solution has a 32% tritium counting efficiency. Figure 14 shows similar spectra for the 6 ml top phase with an additional 6 ml of Solution 1. Again, the Compton edge showed a single efficiency which corresponded to 40% for tritium. Tables 3 and 4 list the counting data for the combined and separated-diluted phase and the percentage of each phase which is  $\text{H}_2\text{O}$ .

### Conclusions

These data seem to lead to several conclusions. The decrease in counting efficiency and scintillation efficiency with increasing  $\text{H}_2\text{O}$  content, especially with Triton X-100, is not due to an increase in the size of the aqueous micelles. It is probably due to the water releasing some quencher, which was initially bound to the Triton X-100, into the organic phase. When the emulsion phase breaks down into two distinct phases, each phase has scintillation character and the radionuclides in each phase contribute to the total measured response. Solution 2 showed two regions of phase separation; at very low water content (0.8 - 3.3% by volume) and at moderate water content (15 - 25% by volume) in the 12 ml total volume samples. In cases of low water content in Solution 2, addition of extra water to increase content to approximately 15% by volume produced a more stable scintillation counting system without changing the scintillation efficiency.

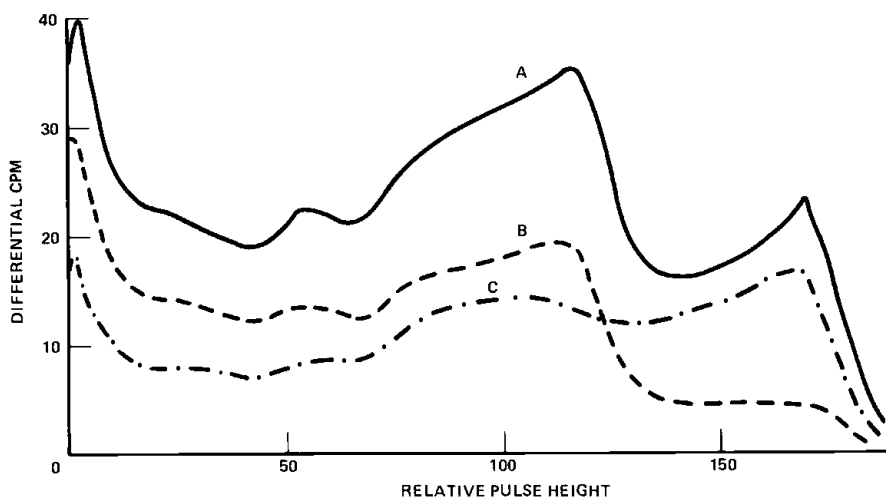


Figure 12. Pulse height spectra for  $^{137}\text{Cs}$ - $^{137}\text{Ba}$  produced Compton electrons and H-water for same samples as shown in Figure 11.

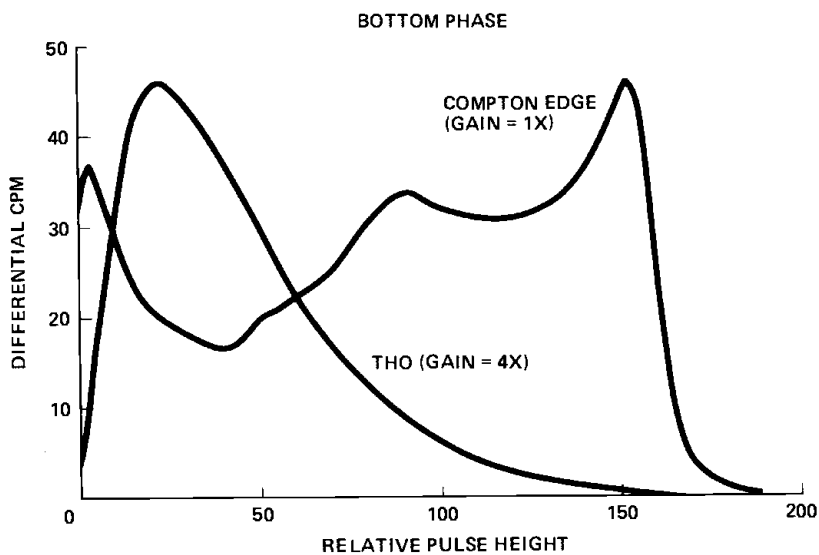


Figure 13. Pulse height spectra for  $^{137}\text{Cs}$ - $^{137}\text{Ba}$  produced Compton electrons and H-water for bottom phase after dilution with added Solution 1.

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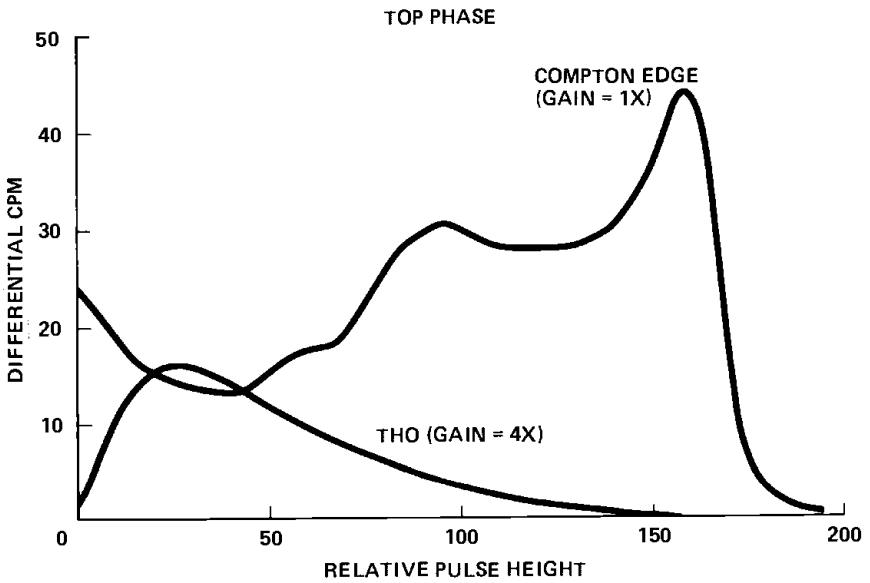


Figure 14. Pulse height spectra for  $^{137}\text{Cs}$ - $^{137\text{m}}\text{Ba}$  produced Compton electrons and  $^3\text{H}$ -water for top phase after dilution with added Solution 1.

References

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