CHAPTER 44

Time-Resolved Liquid Scintillation Counting

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ABSTRACT

A comparison is made between standard, two-tube coincidence liquid scintillation counting and the newly developed technique of time resolved-LSC (TR-LSC). In conventional LSC, coincidence requirements are fulfilled only by the fluorescence from excited primary singlets. Any delayed component that results from triplet-triplet annihilation is ignored by the circuit. TR-LSC, however, makes use of slow decaying pulse components. Certain scintillators, such as calcium fluoride, and scintillating glasses have much longer fluorescence decay times. Others are characterized by a prompt scintillation pulse followed by after pulses. These different pulse characteristics are analyzed by TR-LSC and used as discrimination criteria to validate scintillation counts.

TR-LSC recognizes and discriminates background in low-level LS counting. It uses the long pulse duration due to the interaction of cosmic rays with the glass of the photomultiplier tubes, the scintillation vials,and any other material surrounding the sample. This results in a two to fourfold improvement of the figure of merit (E^2/B) as compared to conventional LSC. The issues of cocktail composition and quench correction are addressed.

TR-LSC can also be used in dedicated liquid scintillation counters. The long pulse duration is used as a criterion to accept counts while discriminating pulses from thermionic emission. This allows single photomultiplier detection with efficiencies and backgrounds comparable to two-tube coincidence counting. The effect of cocktail and sample composition on performance will be correlated with lifetime data.

INTRODUCTION

Two-tube coincidence counting has remained the state of the art in liquid scintillation counter design. Instruments and cocktails were optimized for this configuration because it gives the best overall counting performance. Cocktails using scintillators with short lifetimes allow for maximum tube noise reduction using coincidence circuits with short coincidence resolving times. High efficiency is maintained because short lifetime scintillators release all of their energy within a few nanoseconds and give the maximum possible pulse height at the photomultiplier anode. When cocktails containing long lifetime scintillators are used, the photons emitted during the tail end of the scintillation pulse arrive too late and are ignored by the coincidence counting circuit.

This leads to an appreciable loss in efficiency. In specialized applications, such as radioactivity flow monitors based on heterogeneous counting, solid scintillators (e.g., calcium fluoride) and doped glasses are used. These have much longer luminescence decay times than dissolved organic fluors. Consequently, coincidence resolving times in the microsecond range must be used to obtain an acceptable efficiency. This in turn increases the background due to tube noise significantly. Time resolved LSC[1] makes use of the fact that scintillators do not give off their light energy instantaneously.

TIME RESOLVED COUNTING

The scintillation pulse originating from a scintillator is a burst of photons lasting from a few nanoseconds to several hundred microseconds. In Figure 1 the photoluminescence decay curve of a typical cocktail is shown in schematic form. This is not the pulse shape of a single decay, rather it is a function describing the probability of a photon being emitted as a result of that decay. Immediately after the decay, we have the prompt pulse or fast component. In liquids this time lasts from 2 to 8 nsec and represents the fact that most scintillation energy is emitted as direct fluorescence from excited singlet states of the secondary scintillator. The delayed pulse or slow component is attributed to the delayed fluorescence emission from a process called triplet-triplet annihilation. In this process, two scintillator molecules in the electronically excited triplet state collide to form one excited singlet state from which fluorescence occurs.

In Figure 2, the average pulse shape due to a high energy decay is shown for a conventional scintillation cocktail and a solid scintillating particle. The relative amount of light originating from prompt singlet emission and the delayed

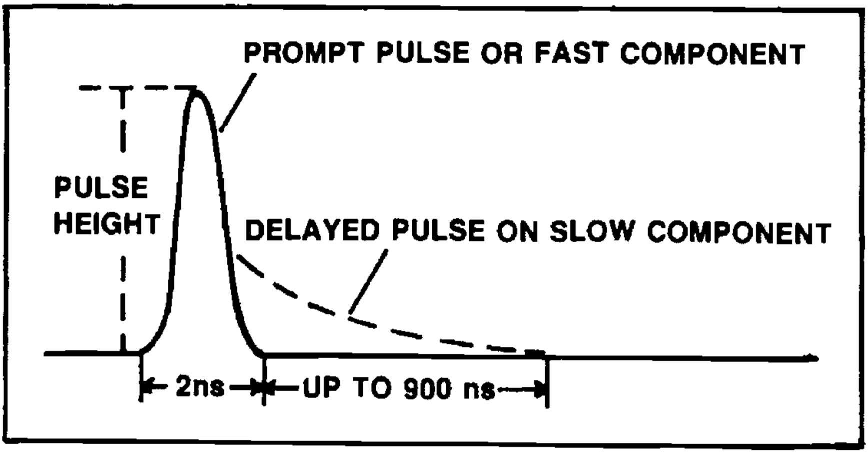

Figure 1. Typical cocktail photoluminescence decay curve.

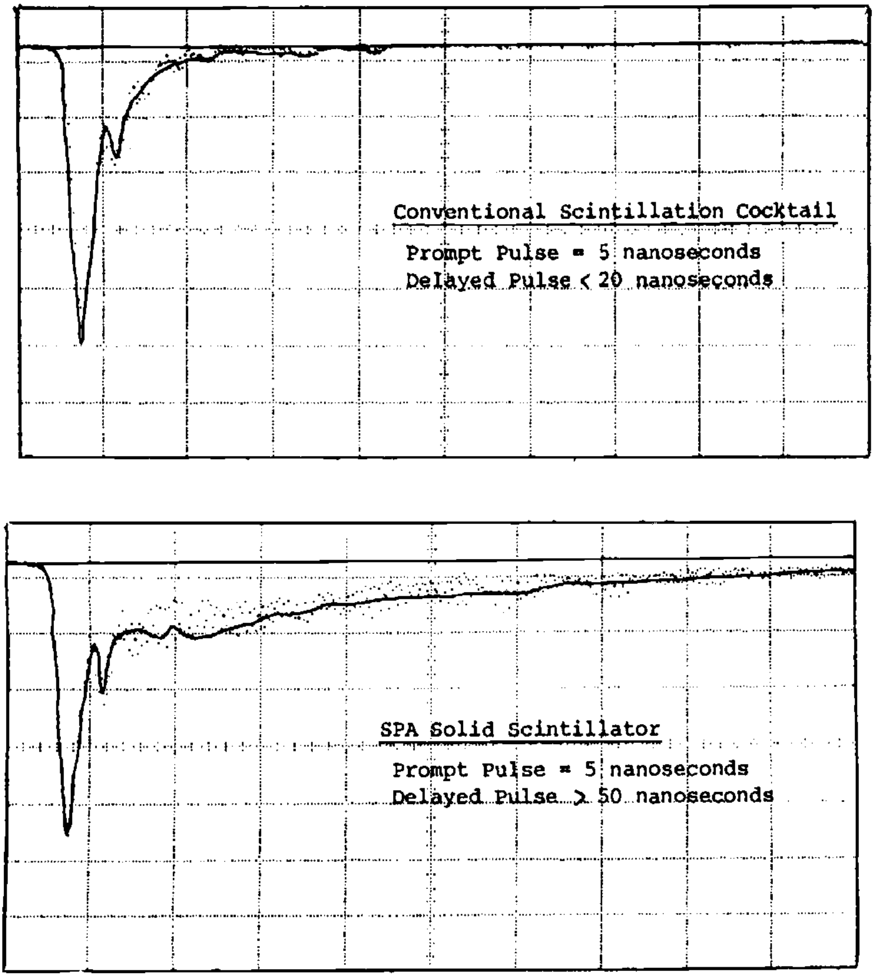

Figure 2. Averaged pulse shape due to high energy decay: conventional cocktail (top), solid scintillator.

component depends on the specific ionization of the sample. Since beta particles, cosmic rays, and Compton electrons have lower specific ionization than alpha particles, the concentration of triplets formed in the track is lower. As a result, triplet-triplet annihilation is less likely to occur and the delayed component is diminished. This is the basis for alpha particle discrimination using pulse height analysis.

Figure 3 is a schematic which emphasizes the fact that a typical afterpulse pattern consists of individual photoelectrons. The prompt pulse is usually much larger than the afterpulses since it contains a large number of photons emitted in a time too short for the dynode circuit of the photomultiplier to resolve. The photons causing afterpulses, due to the slow component, are

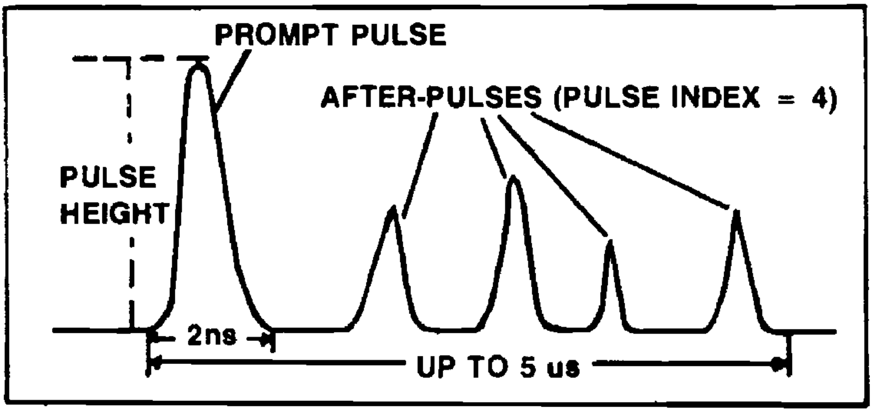

Figure 3. Typical pulse pattern due to beta decay.

fewer in number and spread out over time so as to be distinguishable as single photoelectrons.

The triplet concentration in the track does not depend solely on the specific ionization; however, it also depends on the composition of the cocktail. The concentration of oxygen in a cocktail exposed to air, for instance, is high enough to scavenge most triplets and practically eliminate afterpulses due to the delayed component. In deoxygenated solutions, triplets survive to recombine and cause afterpulsing.

Solid scintillators, such as glass, exhibit significant afterpulsing for a different reason. Oxygen quenching and other diffusional mechanisms do not occur in solids so the triplet states formed from the nuclear decay are not quenched, but they can emit light with their characteristically long lifetime. This results in afterpulsing due to an "unquenchable" delayed component.

LOW-LEVEL COUNTING

Time resolved techniques can be used in low-level counting to recognize background pulses from the natural radioactivity of the glass vial and the envelope of the PMT. The most likely number of afterpulses for a given energy is greater for glass than for liquid scintillation cocktails; thus, when a cosmic particle passes through the system, it can be discriminated against by counting the number of afterpulses—the burst counting technique. In this technique, each coincidence opens a burst counting window which counts the number of afterpulses occurring to about five microseconds after the event. The total number of afterpulses is defined as the pulse index.

Using the pulse index it is possible to create a 3-D spectral plot containing time resolved information on the delayed component (see Figure 4). We see that a background sample gives of an appreciable number of afterpulses at the low energy end of the spectrum. An unquenched ^{3}H sample (see Figure 5) gives

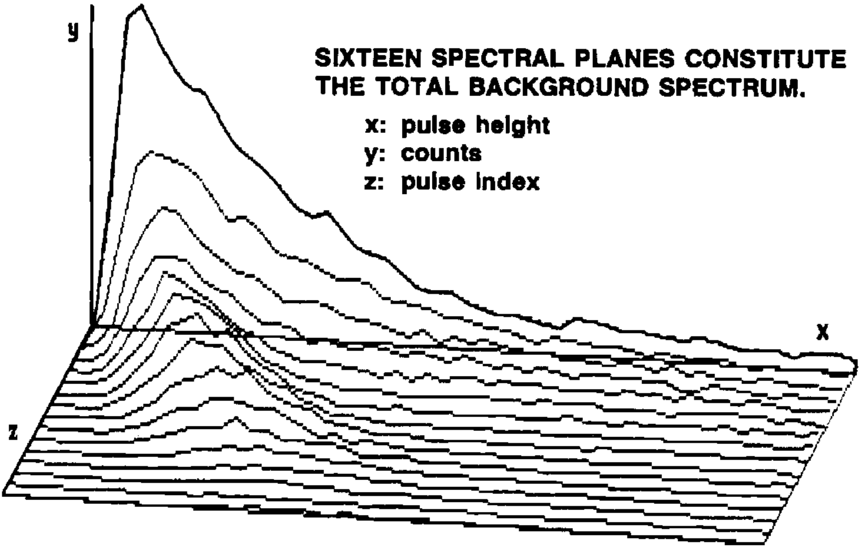

Figure 4. Three-dimensional plot of pulse height spectrum of background sample. The pulse index is the third dimension.

off few afterpulses and only at the high energy end of the spectrum. An air quenched ^3H sample (see Figure 6) gives off almost no afterpulses.

By accepting only counts with a low pulse index, a spectrum free from glass

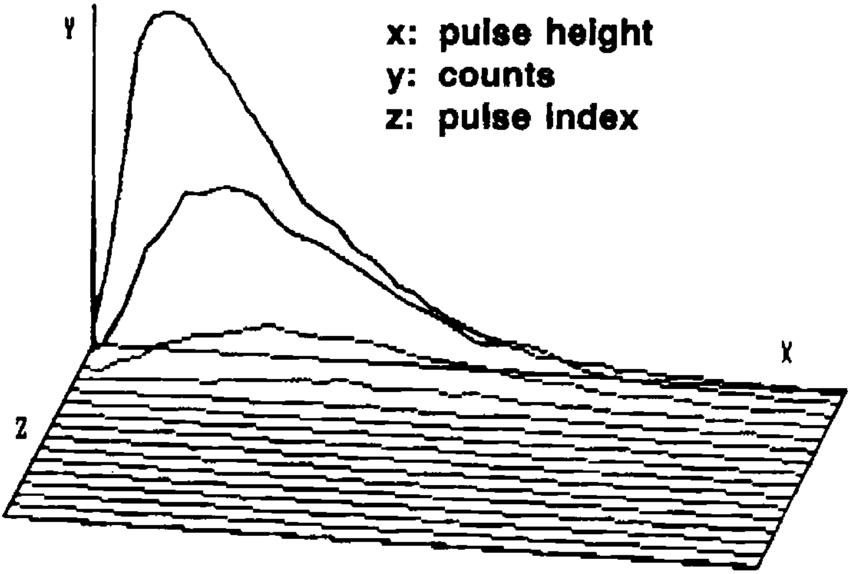

Figure 5. Three-dimensional spectrum of an unquenched ^3H sample.

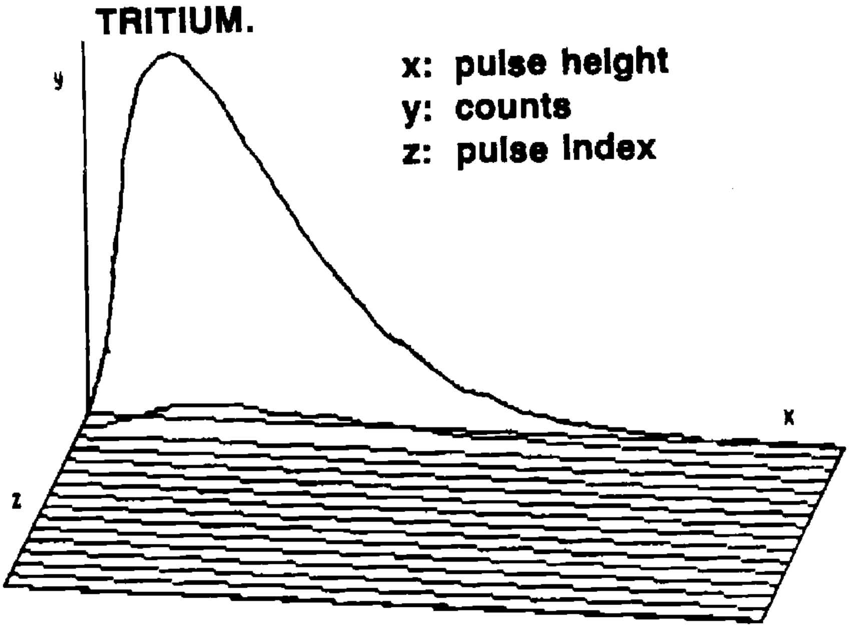

Figure 6. Three-dimensional spectrum of an air quenched ^{3}H sample.

scintillation counts is obtained. This background reduction comes at the price of a reduction in efficiency, since there is a significant probability that sample events will also result in a pulse index, leading to rejection of the count. This is especially true for deoxygenated samples and long lifetime scintillators which have a significant delayed component. Nevertheless, the effect of using the pulse index on low-level performance can be dramatic (see Table 1) because a large part of the background is due to glass scintillations. When air quenched samples are analyzed, the figure of merit (E^2/B) can be improved significantly, because the reduction of efficiency due to the time resolved circuit is overshadowed by the background reduction.

The data in Table 1 contains the results of a ^{14}C benzene sample prepared with a benzene synthesizer. A small glass vial was used to analyze 3.5 mL sample volume. On optimization, the counting region for this sample was

Table 1. Effect of Pulse Index Discrimination on Background, Efficiency, and E^2/B for ^{14}C-Benzene

Degree of Pulse Index Discrimination	^{14}C Efficieny (%)	Background (CPM)	E^2/B (Figure of Merit)
None	83.45	9.67	720.15
Normal	81.87	7.07	948.05
High sensitivity	78.50	4.74	1300.05
Low level	70.70	1.38	3560.00

Note: 3.5 mL Benzene with 4 g/L in small glass vial, O_2 quenched, 10 to 100 keV.

Table 2. Effect of Pulse Index Discrimination on Background, Efficiency and E^2/B for ^3H

Degree of Pulse Index Discrimination	^3H Efficieny (%)	Background (CPM)	E^2/B (Figure of Merit)
None	26.50	18.45	38.06
Normal	26.24	12.75	54.08
High sensitivity	24.68	9.25	65.85
Low level	22.59	3.33	153.25

Note: 10 mL InstaGel and 10 mL H_2O in large glass vial, 0.5 to 5.0 keV, O_2 quenched.

found to be 10 to 102 keV. As pulse discrimination is applied, the efficiency drops from 84% to 70%, but the background drops from 9.67 to 1.38 counts. This results in an almost fivefold increase in figure of merit.

Similar results were obtained on a tritiated water sample (see Table 2). The sample consisted of 10 mL tritiated water mixed with 10 mL of Insta-Gel in a large glass vial. The optimal counting region was determined to be 0.5 to 5 keV. While the efficiency is reduced only 15%, the background is reduced to 18% of its original value. This results in a fourfold increase in the figure of merit.

ANTI-COINCIDENCE GUARD SHIELDING[2]

The time resolved technique can be used to implement anticoincidence guard shielding in a low-level counter. For this application the normal reflector is replaced by a guard shield that has a scintillating plastic with a long lifetime. For small volume samples in small glass vials, a special adapter fitting into large vial cassettes can fulfill the same function. When cosmic or environmental radiation excite the slow fluor in the plastic, they produce afterpulses that lead to a high pulse index and a rejection of the count.

In Table 3, data showing the effect of using various degrees of pulse rejection are displayed for a ^{14}C benzene sample in a small vial. The scintillator used was 6 g/L PPO and 0.2 g/L POPOP. We see that the time resolved counting coupled with the slow fluor coincidence shielding raises the figure of merit from 1167 to 9520. The data for tritium (see Table 4) also shows an improvement, from 272 to 1745. Here, however, the combination of vial holder with guard shield does not give a significant advantage over either used alone.

Table 3. ^{14}C Benzene in PPO (6 g/L) and POPOP (0.2 g/L)

Degree of Pulse Index Discrimination	Sample	^3C Efficiency (%)	Background (CPM)	E^2/B (Figure of Merit)
None	Sample only	64.99	3.62	1167
Maximum	Sample only	54.05	0.76	3844
Maximum	+ vial holder	60.99	0.63	5904
Maximum	+ guard elevator	66.20	0.51	8593
Maximum	+ vial holder & guard detector	63.98	0.43	9520

Table 4. ^3H Benzene in PPO (6 g/L) and POPOP (0.2 g/L)

Degree of Pulse Index Discrimination	Sample	^3H Efficiency (%)	Background (CPM)	E^2/B (Figure of Merit)
None	Sample only	54.71	10.99	272
Maximum	Sample only	50.94	3.05	851
Maximum	+ vial holder	49.38	1.37	1778
Maximum	+ guard holder	38.44	0.86	1718
Maximum	+ vial holder & guard detector	37.13	0.79	1745

Table 5 contains results from a study of large volume tritiated water samples in Insta-Gel. The use of the guard detector significantly improves the figure of merit for counting environmental water samples.

SINGLE TUBE COUNTING[3]

Time resolved LSC can also be applied to single tube counting of high activity samples. In this case, the pulse index alone is used as a time resolved coincidence criterion. Only those pulses followed by one or more afterpulses are accepted. The physical basis for the operation of the circuit is shown in Figure 7. We see that the typical pulse due to PMT noise has a short width, determined exclusively by the characteristics of the dynode string. The Ultima Gold pulse, on the other hand, has a more complex shape even with a distinguishable afterpulse.

A burst count circuit was modified to test this concept. In two pulse-mode, the circuit counts those events which result in two distinguishable pulses within the coincidence resolving time. In three-pulse mode, a triple coincidence is required.

The data in Figure 8 was obtained with this modified burst count circuit. The fact that efficiency varies with the cocktail used can be attributed to variations in the proportion of the delayed component. The lower efficiency in the three-pulse mode is due to the fact that the emission has decayed by the time the circuit has recovered from the first and second pulse. The samples were also counted in a regular 2000CA to show the performance of the cocktails. Because the geometry of the breadboard is different from the production

Table 5. ^3H Water Analysis in Large Glass Vial (8 mL sample, 12 mL Pico-Fluor LLT)

Degree of Pulse Index Discrimination	Sample	^3H Efficiency (%)	Background (CPM)	E^2/B (Figure of Merit)
None	Sample only	22.85	6.12	5460
Minimum	Sample only	25.39	6.63	6223
Maximum	Sample only	25.63	3.87	10863
Maximum	+ guard holder	23.77	2.29	15791

Note: 8 mL sample, 12 mL Pico-Fluor LLT.

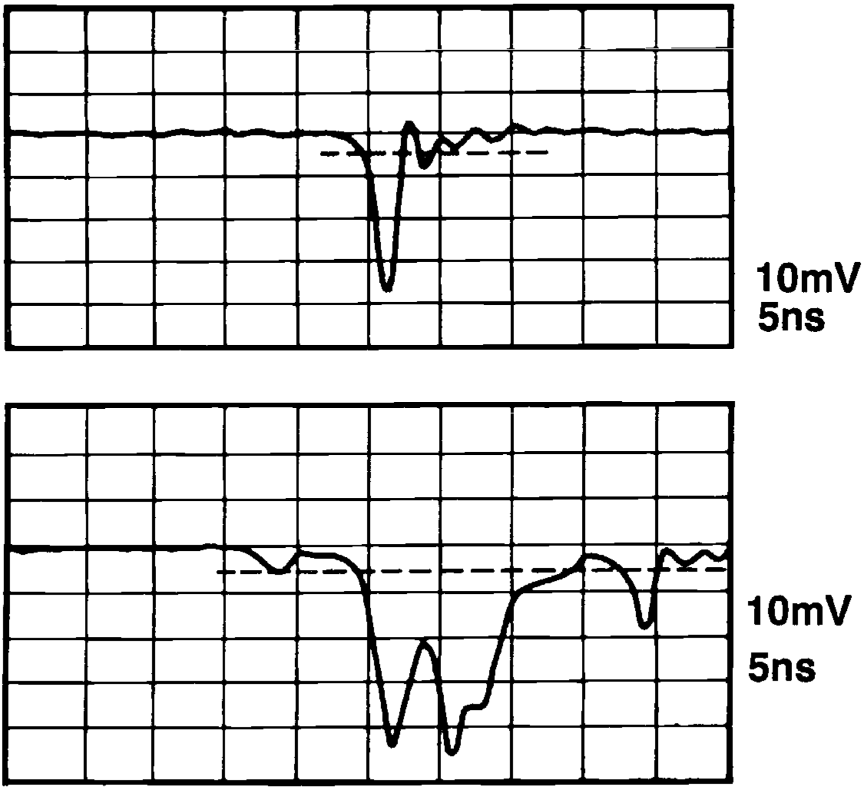

Figure 7. Oscilloscope traces of typical pulses: top) PMT dark noise, bottom) ^3H in Ultima Gold.

counter, it is difficult to assess the reason for the lower efficiency of the single tube circuit.

CONCLUSION

The results presented above demonstrate that the addition of digital time resolved techniques to liquid scintillation counting has already resulted in technical innovations that advance the state of the art. Further research into this area, combined with a better understanding of the mechanisms involved in creating the delayed component of the scintillation pulse in solid and liquid phase detectors, promises to widen the field of applications for soft beta counting.

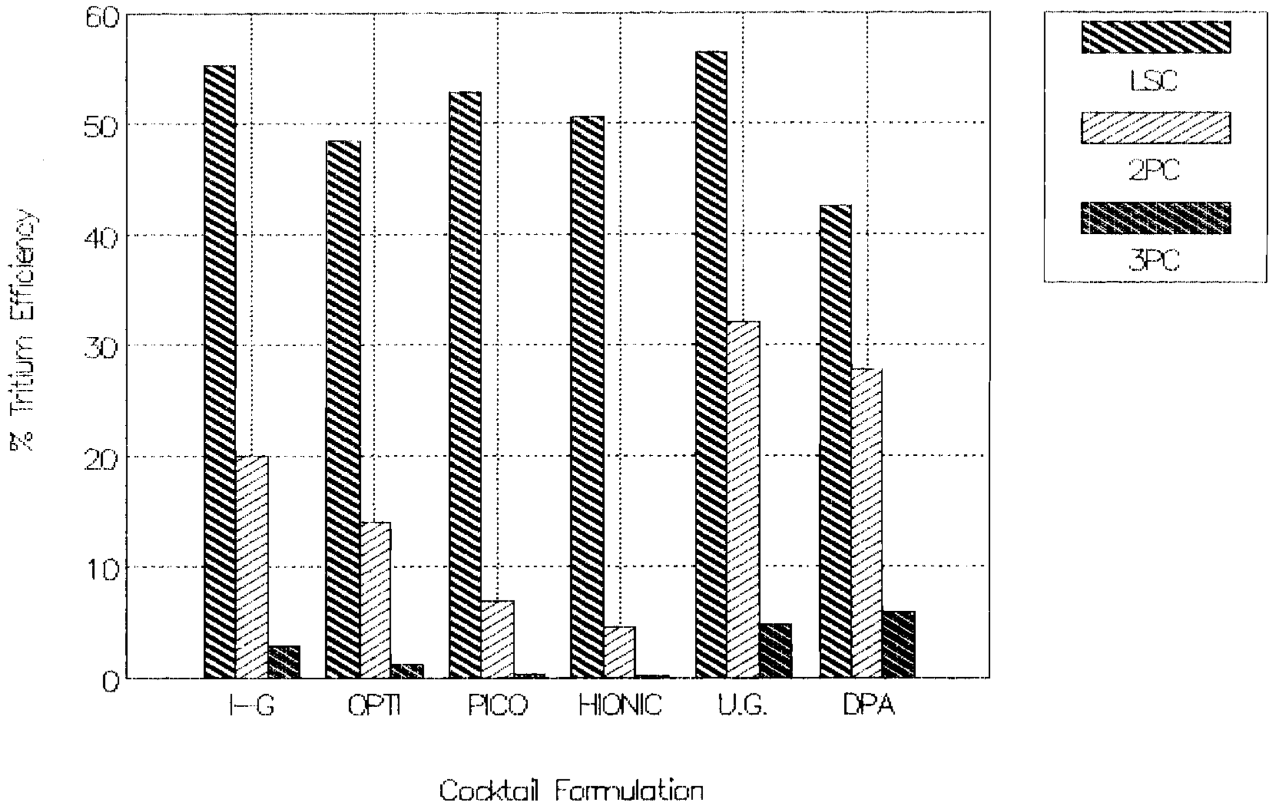

Figure 8. Tritium efficiency for different cocktail formulations. LSC: liquid scintillation counter, 2PC: single tube counter with time resolved double coincidence, 3PC: single tube counter with time resolved triple coincidence.

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