

THE RELATION BETWEEN PHOTOMULTIPLIER TUBE OUTPUT PULSE SHAPES AND ALPHA/BETA SEPARATION EFFICIENCY

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ABSTRACT. Alpha/beta separation relies on the principle of photomultiplier tube (PMT) anode pulse-shape/decay discrimination to distinguish between these two types of nuclear decay. The aim of this study is to assess the factors influencing pulse shape, and hence, the efficiency of separation. We have studied a range of commercially available cocktails and, on the basis of the results, formulated a number of others for this specific purpose. The addition of naphthalene, which is known to stretch PMT anode pulse widths, as expected, enhances the separation. In contrast, the addition of dimethylantracene (DMA), which acts in a similar manner to naphthalene, actually has an adverse effect on the separation. The solvent, di-isopropylnaphthalene (DIN), has a similar enhancing effect to naphthalene and has the added advantages of being relatively non-toxic and non-flammable. We have developed a cocktail based on this solvent specifically for α/β separation. α and β pulse shapes from a range of cocktails, including those with DMA, were collected from the analog circuitry using a storage oscilloscope. Those cocktails that brought about efficient separation have α and β pulse shapes that are quite different from one another, whereas those from DMA-containing cocktails are similar in shape. This type of measurement is a useful but non-quantitative indicator of separation efficiency.

INTRODUCTION

The ability to measure the activity of alpha-emitting radionuclides by liquid scintillation counting (LSC) has been recognized for many years, as has the fact that they produce a different response from beta emitters at the photomultiplier tube (PMT) anode and can be separated on this basis (Thorngate, McDowell & Christian 1974; McKlveen & Johnson 1975). The provision of α/β separation capabilities is a comparatively recent feature on commercially available, conventional LS spectrometers. The only exception to this is the development and marketing of the Photon/Electron-Rejecting Alpha Liquid Scintillation (PERALS®) spectrometer (McDowell & McDowell 1991, 1993), which is designed principally for the measurement of α emissions. The $4\text{-}\pi$ counting geometry of LS spectrometry results in *ca.* 100% counting efficiency for α -emitting radionuclides, which, together with the low-background count rates possible with pulse-shape or decay discrimination (PSD or PDD), makes the technique a very useful alternative to conventional α spectrometry using passivated implanted planar silicon (PIPS) and silicon surface barrier (SSB) detectors in certain instances. The much poorer resolution of LS spectrometry relative to semiconductor detectors is a major disadvantage, brought about by the relatively inefficient light production by α particles (~a factor of 10 less energy-to-light conversion than for β particles) and the relatively large amount of energy required to produce a photoelectron at the PMT photocathode. To improve resolution, research has focused on extractive scintillants (Abuzeida *et al.* 1987; McDowell & McDowell 1991, 1993; Yang, Zhu & Möbius 1991). However, little has been done with scintillation cocktails for aqueous media.

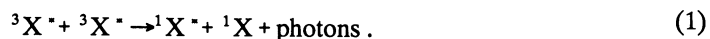
In some areas, extractive scintillators are ideal for α/β separation, particularly with a specific nuclide. In others, the very specificity of the extractants add to the complexity of the preparative chemistry. For example, direct addition of water to an aqueous holding cocktail can effectuate gross α screening of reactor primary coolant water. Although an aqueous cocktail for α/β separation is desirable, we did not know how different cocktail constituents variously affect PDD.

Liquid Scintillation Spectrometry 1992, edited by

J. E. Noakes, F. Schönhofer and H. A. Polach. RADIOCARBON 1993, pp. 225–232

To understand how cocktail composition affects the separation of α and β events, one must look at why PDD is possible from a molecular level. We can distinguish α from β events by examining the electronic pulses produced at the PMT anode of the detector. These pulses consist of two components, prompt and delayed (Horrocks 1974), which occur in different proportions, resulting in longer α pulses than β pulses.

Photons incident on the PMT cathode originate from the radiative decay of excited singlet and triplet states of the fluor molecules in the cocktail. The prompt component arises from the fast, exponential decay of excited singlet states ($\tau < 80$ nsec). Triplet states can produce photons only upon collision with another molecule in the triplet state (Eq. 1), resulting in a longer lifetime ($\tau > 300$ nsec), and hence, the delayed component of the pulse (Brooks 1979). The higher specific ionization of α particles causes a greater proportion of excited molecules to be in triplet states than those excited by β particles, and thus, the longer pulse.



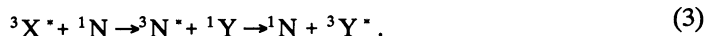
Traditionally, cocktails for standard β counting techniques with the addition of 20% naphthalene have been employed for α/β separation LS spectrometry (e.g. Oikari *et al.* 1987). These largely satisfy separation requirements. However, a cocktail that can enhance separation to the same degree, or better, and, at the same time, is safer to handle, is obviously of great advantage to both manufacturer and user. The manufacturer has fewer distribution problems and will conceivably sell more of the safer product, whereas the user is not restricted to working in a fume-hood-type environment, and is likely to have fewer disposal problems.

The development of an "environmentally safe" cocktail for α/β separation in aqueous media is timely, given 1) the recent introduction of the naphthalene derivative, di-isopropylnaphthalene (DIN) as a solvent for cocktails used in conventional β counting (Thomson 1991) (see Table 1) and 2) the introduction of the MicroScint™ (Packard Instrument Co.) range of cocktails that use DIN as their solvent but also contain dimethylantracene (DMA) as the secondary fluor. This range of cocktails was designed specifically for single PMT counting to produce long decay constants that would enable differentiation of true events from shorter duration PMT noise by PSD.

TABLE 1. Safety Data for Naphthalene and Di-isopropylnaphthalene

	Flash point	TLV	Biodegradable
Naphthalene	80°C	10 ppm	No
DIN	152°C	--	Yes

Naphthalene, N, improves α/β separation by acting as an intermediate in the energy transfer process between the solvent, X, and fluor, Y (Brooks 1979; McDowell 1986) (Eqs. 2, 3). This more energetically favorable route increases the production efficiency of excited fluor molecules. The production rate of fluor triplet states is especially enhanced, as energy transfer to triplet states relies on physical approach, and so is affected by the concentration of both the fluors and the intermediate, N, in the cocktail. As more triplet states become occupied, the delayed component of the PMT anode pulses increases, with the effect of stretching the α pulses relative to the β pulses.



The ability of N to act as an intermediate results from the extensive delocalization of its π electrons. Thus, one can assume that, where aromaticity is maintained, N derivatives, such as DIN, will have the same effect on PDD as N itself. DMA, with three conjugated benzene rings, stretches PMT anode pulses even more than does N, and could further enhance the separation of events.

We present results here on the development of cocktails specifically for α/β separation in aqueous media. We discuss the major factors influencing separation and the advantages of these “new” cocktails. We also present PMT anode pulses to demonstrate changes in pulse shapes in relation to separation.

METHODS

We studied α/β separation efficiencies of a series of commercially available cocktails (Packard Instrument Co.), and re-evaluated them after adding 20% N to the cocktail. We then formulated and tested a range of experimental cocktails. We determined the separation efficiency by taking a pure α emitter (${}^{238}\text{Pu}$) and a pure β emitter (${}^{90}\text{Sr}/{}^{90}\text{Y}$), placing them in separate vials and determining the distribution of events between the α and β MCAs of a Packard Tri-Carb® 2250 CA α/β over a range of PDD settings. The percent misclassification was then plotted against PDD setting, in order to determine the crossover point (Fig. 1).

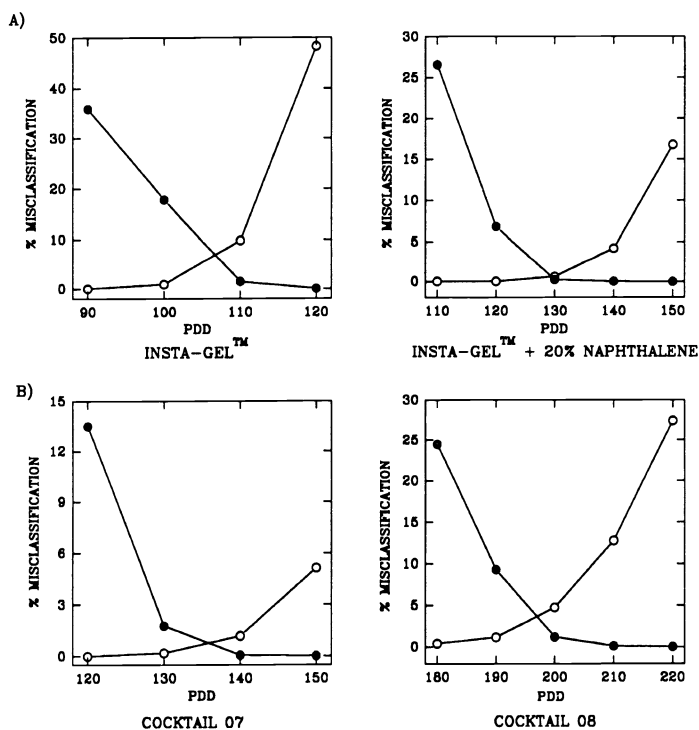


Fig. 1. Some typical crossover plots showing the effect of A) the addition of 20% N and B) changing the secondary fluor from bis-MSB to DMA. \circ = α event in β MCA; \bullet = β event in α MCA.

We studied the effect of quenching on misclassification of α and β events by using vials containing either ^{241}Am or ^{36}Cl in Cocktail 07B to obtain a crossover plot on the Tri-Carb® 2550TR/AB. We then progressively decreased the transformed spectral index of the external standard (tSIE) (*i.e.* increased quenching) by adding 50- μl volumes of 0.1 M HCl, and redetermined the misclassification using the same PDD setting. The tSIE was plotted against percent misclassification (Fig. 2).

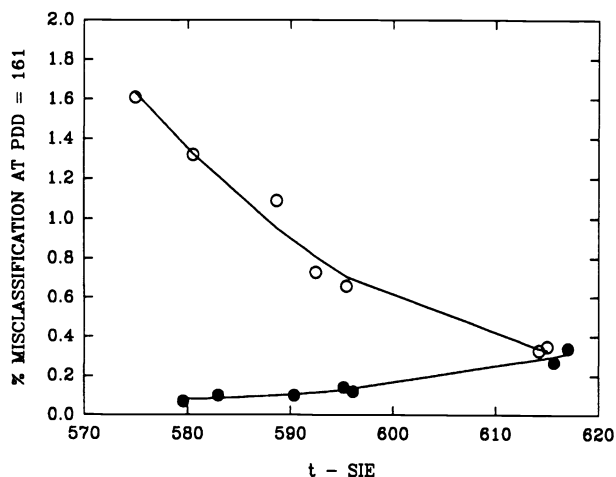


Fig. 2. The effect of tSIE on misclassification of α and β events for Cocktail 07B. \circ = α event in β MCA; \bullet = β event in α MCA.

Finally, we counted vials containing either ^{241}Am or ^{36}Cl in a Packard Tri-Carb® 2550TR/AB with a Hewlett Packard digitizing oscilloscope connected to the PMT anode. This enabled the shapes of the pulses received at the PMT anode to be recorded and comparisons made, both between α and β events and between cocktail types.

RESULTS AND DISCUSSION

Table 2 summarizes our results and gives the compositions of the various cocktails. The solvent, the surfactant concentration and the presence of pulse-stretching additives are the three main areas of interest with regard to their impact on α/β separation.

The impact of increasing surfactant concentration can be seen with three sets of cocktails, the Ultima Gold™, experimental 07 group (both DIN-based) and the Pico-Fluor™ (pseudocumene-based with 20% N) cocktails. In all groups, the degree of misclassification at the crossover point decreases with decreasing surfactant concentration. The cocktails that give the most efficient separation (*ca.* 0.2% crossover) are those with the smallest surfactant concentration (*i.e.*, Pico-Fluor™ 15 + 20% N and Cocktail 07D). A plot of crossover point against tSIE (Fig. 3) shows a relation between misclassification and quench. As the tSIE decreases, the separation of α and β pulses is degraded. More specifically, as quench increases, misclassification of α events greatly increases. The small improvement in the number of β events correctly classified is not sufficient to compensate for the misclassified α events (Fig. 2). The quenching can be due to both surfactants or to the sample, itself. This implies that, to obtain an extremely high degree of α/β separation, one must use a cocktail with low sample-holding capacity (<0.5 ml water), which would then minimize the quench on both counts. However, in many situations, it is not possible to use such a small sample, so a compromise must be made between sample size and separation efficiency. At the same time, by altering the surfactant type, sample-holding capacity may be improved without increasing misclassification. Cocktail 07 and Ultima Gold™ both perform well in α/β separation, but the former has a larger capacity for aqueous solutions (Table 3). Also, the tSIEs of samples

TABLE 2. Crossover Characteristics and Composition of a Selection of the Cocktails Studied

Cocktail	Crossover (%)	Solvent	Primary fluor	Secondary fluor	Surfactant
Insta-Gel®	6.8	60–69% xylene	PPO	bis-MSB	30–40%
Insta-Gel® + 20% N	0.5	48–55% xylene	PPO	bis-MSB	25–32%
Insta-Gel® XF + 20% N	0.5	48–55% pseudocumene	PPO	bis-MSB	25–32%
Pico-Fluor™ 40 + 20% N	1.4	45–55% pseudocumene	PPO	bis-MSB	25–35%
Pico-Fluor™ LLT + 20% N	0.9	56–60% pseudocumene	PPO	bis-MSB	20–24%
Pico-Fluor™ 15 + 20% N	0.2	64–69% pseudocumene	PPO	bis-MSB	11–16%
Ultima Gold™	0.6	65–70% DIN	PPO	bis-MSB	30–35%
Ultima Gold™ XR	2.2	55–60% DIN	PPO	bis-MSB	40–45%
MicroScint™ 40	4.6	55–60% DIN	PPO	DMA	40–45%
01M	1.1	55–65% DIN	PPO	bis-MSB	35–45%
02M	3.6	55–65% DIN	PPO	DMA	35–45%
08	3.7	60–70% DIN	PPO	DMA	30–40%
07	0.5	60–70% DIN	PPO	bis-MSB	30–40%
07A	0.3	66–75% DIN	PPO	bis-MSB	25–34%
07B	0.4	78–83% DIN	PPO	bis-MSB	17–22%
07D	0.2	90% DIN	PPO	bis-MSB	10%
09	0.7	44–52% PXE + 20% N	PPO	bis-MSB	28–36%
10	0.4	44–52% PXE + 20% DIN	PPO	bis-MSB	28–36%

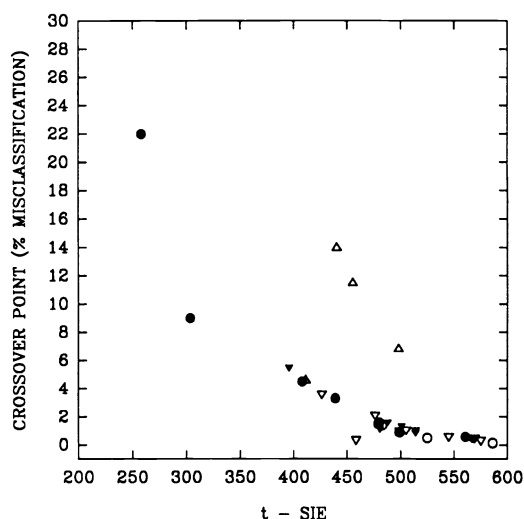


Fig. 3. Crossover point vs. tSIE for a selection of the cocktails and acid loadings. ● = Insta-Gel® + 20% N; ▼ = Ultima Gold™; ○ = cocktails containing 20% N; ▽ = DIN-based cocktails; △ = others (including those containing DMA).

TABLE 3. Water and Mineral Acid Holding Capacities of the DIN-Based Cocktails (ml Uptake Per 10 ml Cocktail)

Cocktail	H ₂ O	1M HCl	2M HCl	1M HNO ₃	2M HNO ₃	1M H ₂ SO ₄	2M H ₂ SO ₄
Ultima Gold™	3.5	0.25	0.10	0.70	0.30	0.10	Nil
Ultima Gold™ XR	10.0	2.00	0.90	3.00	1.75	0.40	0.10
07	10.0	5.50	2.25	3.25	2.25	6.50	4.00
07A	10.0	2.00	1.25	1.75	1.50	2.50	1.50
07B	2.25	1.25	1.00	1.25	1.00	1.50	1.00
07D	0.50	0.40	0.30	0.40	0.30	0.40	0.30

must be kept at a consistent level if they are to have the same crossover as the standards. However, the relation between tSIE and misclassification may be such that a “quench” curve could be used to correct for unavoidable differences in tSIE.

A comparison of cocktails both with and without 20% N confirms the results of Yang, Zhu and Möbius (1991). For example, Insta-Gel® alone gives a crossover point of 6.8% misclassification, but the addition of N improves this to 0.5%. This holds for several solvent systems, including xylene (Insta-Gel®), pseudocumene and phenylxylylene (PXE). The improvement observed in the presence of N is also seen with DIN-based cocktails, as expected. Comparing Cocktail 09 and Cocktail 10 shows that the addition of 20% DIN to PXE gives a 0.4% crossover, as opposed to 0.7% with 20% N. DIN alone as the primary solvent also gives comparable results to other solvents with the addition of N. For example, Cocktail 07A (DIN-based) and Pico-Fluor™ 40 + 20% N (pseudocumene-based) have similar surfactant concentrations, allowing the solvents to be more-or-less directly compared. 07A gives a 0.3% crossover, as opposed to the 1.4% of the Pico-Fluor™. Added to this is the greater safety of DIN, which is non-toxic, non-flammable and biodegradable, and thus is preferable in cocktail manufacture to N (Thomson 1991).

From research on the impact of primary fluors on α/β separation, Yang, Zhu and Möbius (1991) concluded that PPO is the most viable, once the cost has been considered. We used PPO in all the cocktails and compared two secondary fluors: bis-MSB and DMA. We anticipated that DMA might give even better separation of events than N, due to its greater pulse-stretching effect. However,

the opposite was true. Table 2 shows three pairs of cocktails identical in composition except for the secondary fluor. In every case, the DMA-containing cocktail shows a marked degradation in performance (e.g., Cocktail 01M (bis-MSB) gives 1.1% misclassification, whereas Cocktail 02M (DMA) gives 3.6% misclassification).

We now point to pulse shapes recorded at the PMT anode (Fig. 4). Cocktail 07 gives α and β pulses that are distinctly different from each other. The α pulse is much broader than the β pulse, with a significant degree of after-pulsing. However, the two types of pulses produced by Cocktail 08 are both much broader, and are less distinct from one another. This suggests why DMA does not enhance separation in the same way as N. Whereas N has the effect of stretching the α pulses,

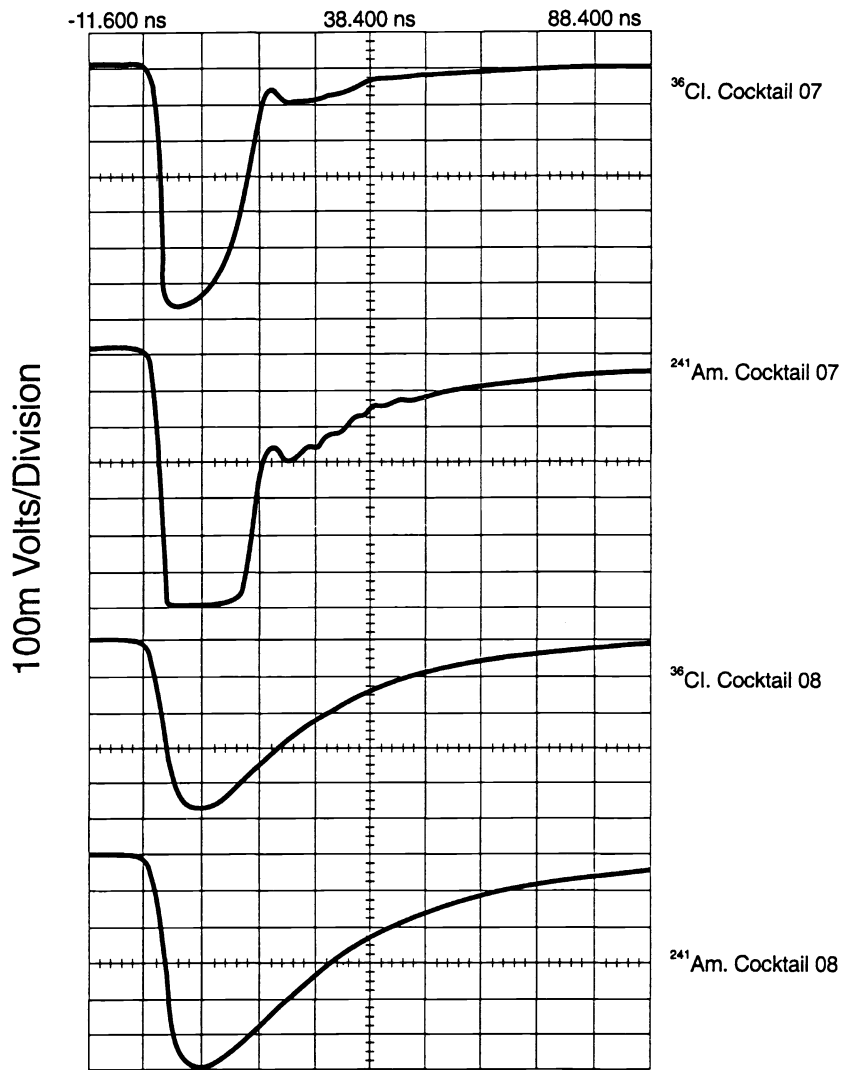


Fig. 4. α and β PMT anode pulse shapes for Cocktails 07 and 08

with little effect on the β pulses, DMA stretches both types of pulse to the point where they start to become less distinguishable from each other.

The PMT anode pulse shapes indicate the suitability of a cocktail for α/β separation, and whether it is worthwhile to proceed with the more lengthy determination of the precise crossover. However, they show no quantitative difference between two "good" α/β cocktails.

CONCLUSIONS

For general purposes, a cocktail similar in composition to Cocktail 07 or 07A would be suitable for α/β separation. When more complete separation is required, Cocktail 07D could be used. All three cocktails are DIN-based and give smaller misclassifications than other solvents with 20% naphthalene; they also have several safety advantages. Quenching plays an important role in efficient PDD, and hence, must be kept to a minimum and consistent between samples.

ACKNOWLEDGMENTS

J. M. Pates would like to thank the U. K. Natural Environment Research Council and Packard Instrument Co. for student support.

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