

THE DEVELOPMENT OF AN ALPHA/BETA SEPARATION LIQUID SCINTILLATION COCKTAIL FOR AQUEOUS SAMPLES

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(Received September 14, 1992)

Scintillation cocktail components were studied with regard to their impact on pulse decay discrimination (PDD) and hence the separation of alpha from beta activity, using a Packard 2250 CA α/β . Di-isopropyl naphthalene (DIN) was found to be the most suitable solvent, both from safety considerations and also the fact that it acts in a very similar manner to naphthalene in stretching the pulses produced at the photomultiplier tube anode and hence enhancing the separation. Increasing the surfactant concentration and the use of dimethylanthracene (DMA) as secondary fluor degraded the cocktail's performance. PMT anode pulse shapes were found to be a useful indicator of PDD efficiency but could not give a quantitative guide.

The separation of alpha from beta activity using liquid scintillation spectrometry is a relatively new feature in commercial instruments although the technique was first demonstrated experimentally around 20 years ago.^{1,2} The separation of the activities is based on pulse shape discrimination (PSD), a technique which had previously been widely used in neutron spectroscopy.^{3,4} However, until recently, the PERALS instrument developed at Oak Ridge National Laboratory by McDowell and coworkers, has been the only commercial liquid scintillation spectrometer to employ PSD. PERALS is used to separate alpha events from a β/γ background, but is unable to make quantitative measurements of beta activity. The past 5 years have seen the introduction of dual purpose instruments (i.e., with the ability to carry out beta measurements or simultaneous alpha/beta separation and measurement) by all the major LSC manufacturers.

Pulse shape discrimination or pulse decay discrimination (PDD) exploits the fact that pulses produced at the PMT anode of a liquid scintillation spectrometer are made up of two components – the prompt and the delayed.⁵ By studying the scintillation process at an electronic level, it is possible to understand the source of the two components. As ionising radiation passes through matter (in this case the scintillation cocktail) it gives up its energy causing electrons to be excited into singlet or triplet states. Excited singlet states rapidly (i.e., in less than 80 ns) lose their energy via fluorescence, giving rise to

the prompt component of the pulse. The delayed component is derived from the decay of excited triplet states. The radiative process for triplet states (phosphorescence) is "forbidden", i.e. it has a very low probability of occurring. Therefore, for a triplet state to release its energy as a photon it must first collide with another triplet state in a process called triplet annihilation [Eq. (1)].⁶ As this process is bimolecular, the



lifetime of a triplet state is much longer (>300 ns)⁶ than for an excited singlet. The higher specific ionisation of alpha particles causes a greater proportion of triplet states to be formed than for beta particles,⁷ hence, alpha particles give rise to a more delayed release of photons and thus longer duration pulses. This difference in pulse length forms the basis for PPD.

The 4 π geometry of liquid scintillation spectrometry (LSS) results in approximately 100% counting efficiencies for alpha emitting radionuclides. This, combined with the low backgrounds obtainable with PDD, makes LSS a useful tool in the assay of alpha-activity. However, it has the distinct disadvantage of having much poorer resolution than conventional alpha-spectrometry using silicon surface barrier (SSB) or passivated implanted planar silicon (PIPS) detectors. This is due to the relatively inefficient light production of alpha-emitters² (approximately a factor of 10 less energy to light production than with beta-emitters) and the relatively large amount of energy required to produce a photo-electron in the PMT. In an attempt to overcome this, many workers in this field have concentrated their efforts on extractive scintillators.⁸⁻¹⁰ These systems extract the radionuclide of interest into the organic phase, minimising the problems associated with quenching, i.e., energy resolution is improved as the quenching is reduced while the associated problem of peak identification with variable quenching is eliminated. Also, extractive scintillators can make the preparative chemistry faster and simpler when a single radionuclide or isotopes of a single element are to be studied.

However, in many situations where LSS is applicable, the use of extractive scintillators is not appropriate. For example, gross alpha screening of air filters or surface wipes may simply require the separation of alpha from beta activity and a gross alpha count rate, with no differentiation between the nuclides present. Therefore, the selectivity of extractive scintillators makes them unsuitable for this purpose. Another example is that of alpha screening of reactor coolant water. In this case not only are extractive scintillators too selective, but their use complicates the preparative chemistry.

The development of a cocktail for aqueous media is particularly pertinent at this time since the recommendation for improving alpha/beta separation has, until now, largely

been to simply add a high percentage of naphthalene. However, since naphthalene has a relatively high toxicity (TLV = 10 ppm), its use and disposal do present problems. In addition, the introduction of "environmentally safe" cocktails¹¹ based on the naphthalene derivative—di-isopropylnaphthalene (DIN) as the solvent represents an interesting prospect, particularly in view of the fact that work carried out in this laboratory using the Packard 2000 CA/LL with the low level option enabled and Ultima Gold XR (a DIN based cocktail) gave less than 1% counting efficiency for alpha emitting radionuclides. The low level option also utilises pulse shape analysis, but in this mode, longer duration events are classified as constituting the unquenchable component of the background (cosmically derived) and are rejected.¹² Furthermore, the recent development of the MicroScint (Packard Instrument Company) range of cocktails which employ DIN as the solvent and dimethylantracene (DMA) as the secondary fluor represents yet another interesting prospect. This cocktail range was designed specifically for single PMT counting to produce long decay constants in order that true events could be distinguished from shorter duration PMT noise pulses.

It is in this context that it was decided to study commercially available cocktails capable of holding aqueous samples, with respect to their α/β separation capabilities and on the basis of the results to attempt the development of an improved cocktail, specifically for alpha/beta separations. The focus of this work has been to look in detail at the effect of the various cocktail components on the efficiency of PDD and to use this information to produce a range of experimental formulations.

Experimental

In order to accurately quantify the efficiency of PDD, an alpha emitter (^{238}Pu) and a beta emitter ($^{90}\text{Sr}/^{90}\text{Y}$) (both approximately 2000 dpm per vial) were placed in separate vials and counted over a range of PDD (pulse decay discriminator or time discriminator) settings, using a Packard 2250 CA α/β . This instrument uses separate multichannel analyzers (MCA's) for the alpha and beta activities when in the α/β mode. By plotting PDD against percent misclassification of events, i.e., assignment to the wrong MCA, it is possible to find the optimum PDD setting for α/β separation and the minimum level of misclassification, i.e., the crossover point (see Fig. 1).

A comparison of the crossover characteristics of a range of cocktails was made. The cocktails were chosen and formulated on the basis that they varied in one component only, thus enabling the influence of each to be assessed. Hence, an ideal α/β separation cocktail could be developed.

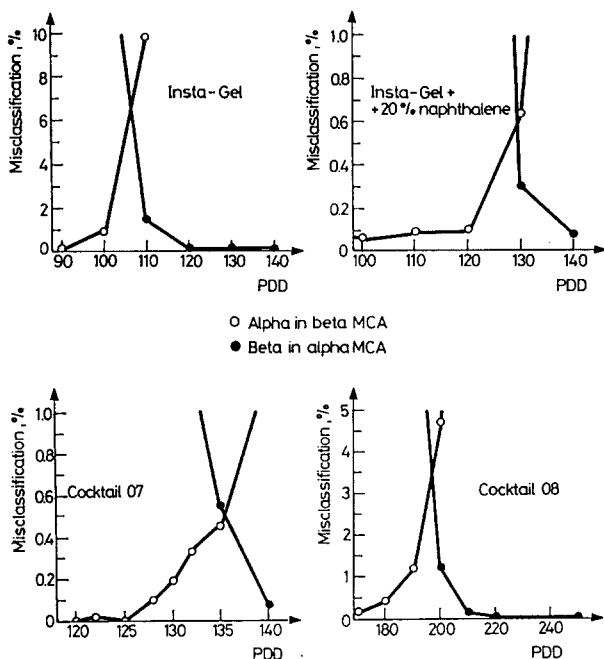


Fig. 1. Crossover plots for four of the cocktails studied

In addition, pulse shapes were collected at the PMT anode of a Packard 2550 TR α/β with a Hewlett Packard digitizing oscilloscope. A qualitative comparison was made between these data and the crossover characteristics of various cocktails.

Results and discussion

The results of the cocktail comparison are summarised in Table 1.

Naphthalene has traditionally been added to liquid scintillation cocktails as an aid to PDD. It improves the efficiency of energy transfer to the fluors and increases peak resolution.¹³ Work done by YANG et al.⁹ on the addition of naphthalene in extractive scintillation cocktails was confirmed in this study for aqueous accepting cocktails. Insta-Gel yielded 6.8% misclassification while the addition of 20% naphthalene reduced this to 0.5%. Insta-Gel XF which differs only in the solvent (pseudocumene rather than xylene) also gave 0.5% misclassification in the presence of 20% naphthalene. A similar result (0.7% misclassification) was also obtained for experimental Cocktail 09 which

Table 1
Crossover characteristics and composition of a selection of the cocktails studied:

| Cocktail | Cross-over, % | Solvent | Primary fluor | Secondary fluor | Surfactant, % |
|----------------------------------|---------------|------------------------------|---------------|-----------------|---------------|
| Insta-Gel | 6.8 | 60–69% xylene | PPO | bis-MSB | 30–40 |
| Insta-Gel + 20% naphthalene | 0.5 | 48–55% xylene | PPO | bis-MSB | 25–32 |
| Insta-Gel XF + 20% naphthalene | 0.5 | 48–55% pseudocumene | PPO | bis-MSB | 25–32 |
| Pico Fluor 40 + 20% naphthalene | 1.4 | 45–55% pseudocumene | PPO | bis-MSB | 25–35 |
| Pico Fluor LLT + 20% naphthalene | 0.9 | 56–60% pseudocumene | PPO | bis-MSB | 20–24 |
| Pico Fluor 15 + 20% naphthalene | 0.15 | 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 | 35–45 |
| 01M | 1.07 | 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 | 0.33 | 66–75% DIN | PPO | bis-MSB | 25–34 |
| 07B | 0.38 | 78–83% DIN | PPO | bis-MSB | 17–22 |
| 07D | 0.16 | 90% DIN | PPO | bis-MSB | 10 |
| 09 | 0.7 | 44–52% PXE + 20% naphthalene | PPO | bis-MSB | 28–36 |
| 10 | 0.35 | 44–52% PXE + 20% DIN | PPO | bis-MSB | 28–36 |

employs phenylxylylethane (PXE) as the solvent. It differs slightly in having a marginally higher surfactant content than the Insta-Gels.

The three Pico Fluor cocktails (with 20% naphthalene) show a continuous decrease in misclassification, from 1.4% to 0.15% as the concentration of surfactant decreases. This indicates the importance of the surfactant concentration and demonstrates that aqueous cocktail development will be a compromise between water holding capacity (and hence surfactant concentration) and the acceptable degree of misclassification. This improvement trend in separation performance is also seen with Ultima Gold and Ultima Gold XR, and the experimental 07–07D series, all of which are DIN based.

As DIN is used in the manufacture of carbonless copy paper, its toxicological properties have been extensively studied.¹¹ It has not been identified as hazardous by the U.S. Environmental Protection Agency while its high flash point (152 °C) makes it

non dangerous in accordance with national and international traffic regulations and generally, because it has been demonstrated to be biodegradable, sewer disposal is permissible. In addition, the majority of the results presented here demonstrate superior separation performance than were obtained with naphthalene. A comparison of Cocktails 09 and 10 shows that the addition of 20% DIN to PXE produced 0.35% misclassification as opposed to 20% naphthalene with PXE which produces 0.7% misclassification of events.

The misclassification results for Cocktail 07 and for Ultima Gold are not significantly different, however, the former has a much greater mineral acid and water holding capacity.

YANG et al.⁹ looked at the effect of various primary fluors on the efficiency of separation. They concluded that PPO was the best choice after economic considerations

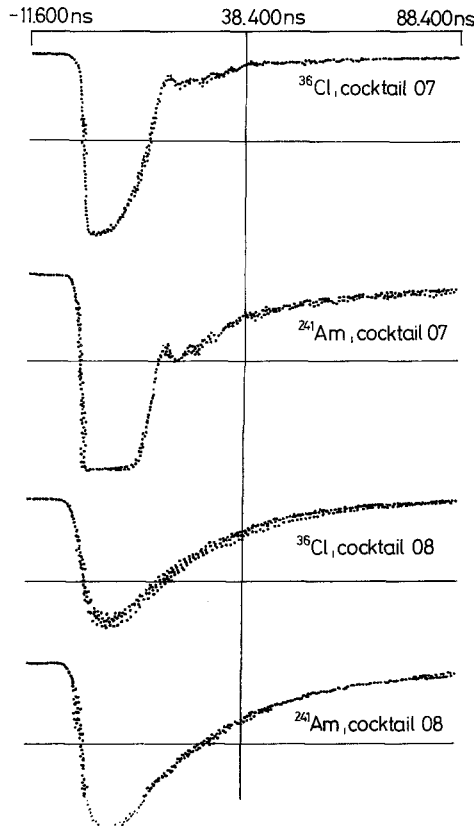


Fig. 2. PMT anode pulse shapes for Cocktails 07 and 08

had been taken into account. In this work, only the secondary fluor was varied – either bis-MSB or DMA was used. DMA was considered because of its long fluorescence life-time which it was thought might further improve the separation. By comparing Ultima Gold XR with Microscint 40, Cocktail 01M with 02M, and Cocktail 07 with 08 where the only difference in the pairs of formulations is the secondary fluor, it can be seen that DMA containing cocktails produced a much higher rate of misclassification.

An examination of the pulse shapes produced at the PMT anode shows why DMA has a detrimental effect on PDD. For PDD to work efficiently, the alpha and beta pulse shapes should be very different. A cocktail such as Cocktail 07 (Fig. 2) gives a sharp beta pulse, with a broader alpha pulse which has significant afterpulsing. Cocktails containing DMA, such as Cocktail 08, give rise to broad alpha pulses, but the beta pulses are also substantially broadened, hence, they are subject to greater misclassification.

It was demonstrated that looking directly at the pulses as they were produced at the PMT anode was a useful, quick check on experimental cocktails. Within seconds it was possible to determine whether a cocktail has potential for α/β separation. This gave an indication of whether it was worth proceeding with the more time consuming determination of crossover characteristics. This method could not however give a quantitative measure of the cocktail's effectiveness.

Conclusions

The results presented here demonstrate that DIN based cocktails were comparable with and indeed often superior to the more traditional cocktails in combination with naphthalene. In addition to its excellent alpha/beta separation capability, Cocktail 07 has extremely good water and mineral acid holding capacities (Table 2) as well as having many safety features not found in the traditional cocktails. This formulation should

Table 2
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 |

prove useful for researchers requiring to use relatively large samples. Cocktail 07D has much more limited holding capacities, however, its improved separation performance may prove useful in some instances.

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J. M. P. thanks the U.K. Natural Environment Research Council and Packard Instrument Company for studentship support. The authors also thank the engineering section of Packard for help with pulse shape measurements.

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