OPTIMIZATION OF LIQUID SCINTILLATION COUNTING FOR ^{14}C DATING*

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ABSTRACT. The effects of different measurement conditions and sample preparation in liquid scintillation counting of benzene for ^{14}C dating were tested. The goal of this work was to find the highest figure of merit through the variation of scintillation cocktail to benzene ratio, and measurement windows. Measurements were performed on 5ml of benzene plus increasing quantities of scintillation cocktail (7g of PPO and 0.5g of Me$_2$POPOP in 1L of scintillation-grade toluene). Spectra of both background and standard were obtained and the counting windows selected for the highest figure of merit (Q). The best condition was 5ml of benzene plus 0.75ml of scintillation cocktail. This spectrum is compared with that of 1) pure toluene-^{14}C plus cocktail, and 2) pure benzene-^{14}C in which the equivalent amount of PPO and Me$_2$PO-POP present in 0.75ml of cocktail was dissolved. A correlation between the increase of the amount of cocktail and the broadening of the spectrum was observed. The effect of wrapping the upper part of the counting vial with aluminum foil to reduce background was also tested. A drastic background increment was observed in the low energy range, for unwrapped vials; the standard spectrum showed a broadening and a lower counting efficiency which reduced the figure of merit.

INTRODUCTION

The new facilities and equipment of the INGEIS ^{14}C laboratory led us to re-evaluate the old Packard Tri-Carb 3255 LSC system. Measurements were performed on 5ml synthesized benzene plus 1.25ml of scintillation cocktail (7g of PPO and 0.5g of Me$_2$POPOP in 1L of scintillation-grade toluene) in commercial glass vials. The ratio of 1ml cocktail: 4ml benzene was recommended by Florkowski *et al* (1977). The upper part of the vial was wrapped in aluminum foil, just above the liquid level in order to reduce the background, avoiding cross-talk between photomultipliers. Ca 500 dates were measured in this way.

In January 1984, a new Packard 300 LSC (Model 4530) became operational. The possibility of spectra editing by means of its built-in multichannel analyzer led us to assess the quality of the measuring conditions. Several spectra with different amounts of cocktail, with and without aluminum foil were obtained and compared with the toluene ^{14}C Packard standard to obtain the best figure of merit (Q). The results led us to change the cocktail to benzene ratio to 3:20 and to define the best window setting for the ^{14}C dating samples.

APPARATUS AND REAGENTS

—Packard Tri-Carb 300 Model 4530 Liquid Scintillation Spectrometer[1]
—Packard glass vials, ca 22ml volume
—PPO, Me$_2$POPOP and Toluene Puresolv Packard
—Benzene p a grade May & Baker (used as background sample)
—NBS oxalic acid SRM 4990 (standard benzene sample)

597

EXPERIMENTAL

1) *Choice of the optimum amount of cocktail to be added to 5ml of benzene.* Spectra of both standard and background with 0.25, 0.50, 0.75, 1.00, and 1.25ml of scintillation cocktail were recorded for aluminum-foil wrapped glass vials. Lower and upper levels for the best figure of merit were determined. Results are shown in Table 1. Spectra are shown in Figure 1.

The background spectra are basically the same for the five graphs (Fig 1). Their shape resembles the Compton-electron distribution spectrum of the Radium-226 external standard source obtained in previous experiments, suggesting that an additional shielding of this source would improve the performance. Unfortunately, the external standard source cannot be removed in this model because it is necessary for the photomultipliers normalization routine.

The standard spectra become broader with the increment of cocktail, but in any case, they are substantially narrower than that of the toluene standard (Fig 2). The integral standard activity reaches its maximum for 0.50ml cocktail, remaining almost constant with further additions.

This supposed "quenching" of the benzene samples with respect to toluene cannot be due to impurities; liquid gas chromatography plus mass spectrometry analysis revealed a purity of 99.995%.

2) *Influence of dissolved oxygen in benzene samples.* Two spectra of standard benzene were recorded; a first one, equilibrated with air at room temperature and a second one, after 15 minutes of high purity argon bubbling. Spectra are shown in Figure 2. It is well known that oxygen quenching is important but the end-tail energy of both spectra are still considerably lower than in the toluene spectrum.

3) *Influence of toluene added to the cocktail.* A set of standard and background spectra were recorded but with the amount of solid scintillator present in 0.75ml of cocktail, both without toluene (Fig 3). It can be shown that they are equivalent to those of 0.75ml cocktail addition (Fig 1). As a consequence, the toluene added to the cocktail has no effect on broadening of the spectra, but the amount of scintillator does.

TABLE 1

Obtained values of background and standard activities
for different measuring conditions

| Ml of cocktail | Al foil | Settings for the best Q | | Standard activity (cpm) | Bkg activity (cpm) | Q | Integral standard activity (0–100)kev (cpm) |
		Lower level (keV)	Upper level (keV)				
0.25	Yes	5	37	42.26 ± 0.21	10.37 ± 0.10	172 ± 3	48.08 ± 0.22
0.50	Yes	9	46	36.71 ± 0.20	6.56 ± 0.08	205 ± 3	50.22 ± 0.23
0.75	Yes	11	53	35.05 ± 0.19	5.92 ± 0.08	208 ± 4	50.28 ± 0.23
1.00	Yes	11	59	35.39 ± 0.19	6.14 ± 0.08	204 ± 4	49.83 ± 0.22
1.25	Yes	11	62	35.44 ± 0.19	6.57 ± 0.08	191 ± 3	48.98 ± 0.22
1.25	Yes	11	63	34.87 ± 0.19	5.99 ± 0.09	203 ± 4	47.23 ± 0.23
1.25	No	15	79	34.22 ± 0.21	6.35 ± 0.08	184 ± 4	46.01 ± 0.25

1.A

1.B

1.C

1.D

1.E

Fig 1. Spectra of standard and background on 5ml benzene with:
1.A 0.25ml
1.B 0.50ml
1.C 0.75ml
1.D 1.00ml
1.E 1.25ml cocktail addition
—— standard spectra
--- background spectra
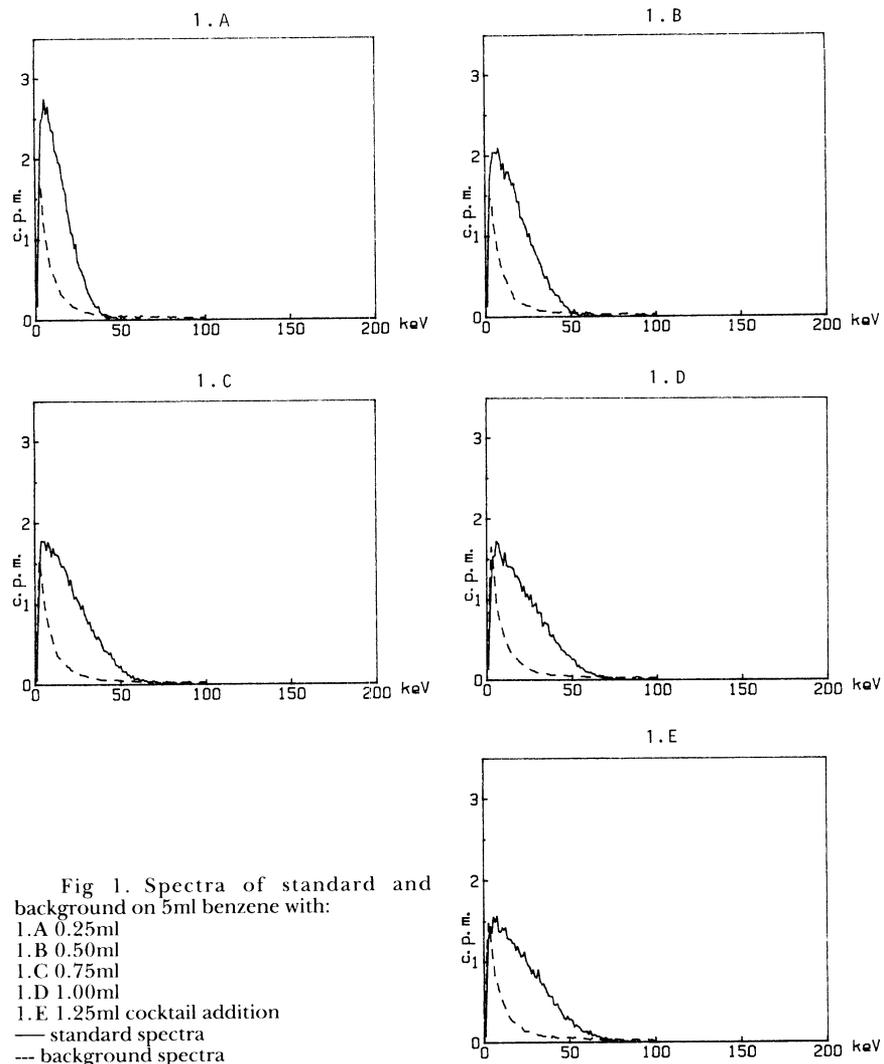
4) *Influence of aluminum foil wrapping.* Another set of standard and background spectra for the 1.25:5 cocktail to benzene ratio were recorded with and without aluminum foil (Fig 4). The background is highly increased, (especially in the low energy region) and standard spectrum becomes broader when aluminum foil is removed; integral standard activity decreases, yielding a lower Q (Table 1).

DISCUSSION

There is a strong shift to lower energies of the end tail which appears in standard benzene spectra, which cannot be explained by impurity quenching.
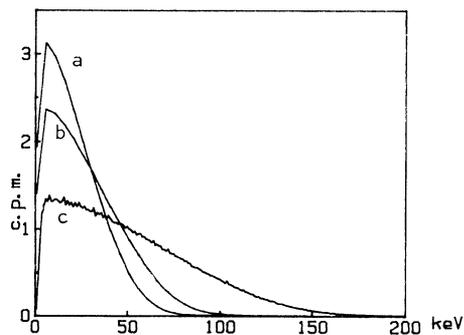
Fig 2.
a. Air-equilibrated benzene standard spectrum
b. Argon-purged benzene standard spectrum
c. Toluene Packard standard spectrum

Fig 3. Standard (– –) and background (- - -) spectra of 5ml benzene plus the equivalent amount of PPO and Me_2PO-POP present in 0.75ml cocktail in solid form

4.A

4.B
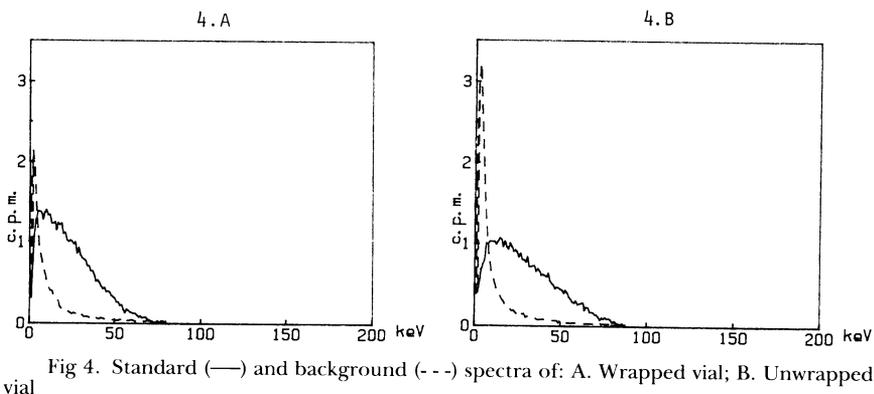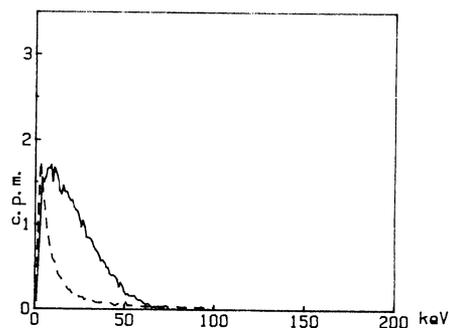
Fig 4. Standard (——) and background (- - -) spectra of: A. Wrapped vial; B. Unwrapped vial

Comparison with half-value quencher concentrations $[Q]_{0.5}$, (*ie,* the concentration of quencher that reduces the fluorescence quantum efficiency to one half) reported by Birks (1977) indicates that the amount of impurity necessary to produce such quenching is much higher than the measured impurity content of the synthesized benzene (ca 50ppm).

The possibility of a dissolved oxygen quenching was assayed by recording spectra prior and after 15 minutes argon bubbling in the sample (Fig 2), concluding that this is a real source of quenching. However, after the oxygen removal, the end-tail energy of the benzene spectrum is still lower than that of the toluene.

Increasing cocktail amount reduces this quenching, as a consequence of the solvent excitation lifetime reduction, making it less susceptible to quenching (Birks, 1977), considering that dissolved oxygen acts as a diffusion-controlled quencher (Wehry, 1967) obeying the Stern-Volmer equation (Parker, 1968).

Birks (1977) also reported lower relative pulse heights for benzene than for toluene with different scintillators and in the absence or presence of a quencher. These facts evidently can be explained by the much lower fluorescence quantum efficiency of benzene than for toluene (Parker, 1968).

A final comparison must be made between spectra obtained with and without wrapped vials (Fig 4). The reflectant aluminum surface avoids the crosstalk of the photomultipliers reducing background and increasing the counting efficiency due to the multiple reflections on the foil (Table 1). The shift of the end-tail energy in the standard spectra by the wrapping of the vials cannot as yet be explained.

CONCLUSIONS AND REMARKS

A LSC such as the Packard 300 is useful in studying the liquid scintillation process in more detail and in defining new operating conditions, which are 3:20 cocktail to benzene ratio and 11-53 keV window setting, yielding a figure of merit Q=208 ± 4, for 5ml benzene.

In the course of this study, unexpected questions and answers about the scintillation process arose. The most important reason for quenching (in absence of chemical impurities) is dissolved oxygen, the influence of which is partially overcome with increment of the cocktail concentration. Nevertheless, ^{14}C benzene spectra show lower end-tail energies than that of toluene, concluding that the lower fluorescence quantum efficiency of the first is the ultimate reason for this phenomenon. The effectiveness of the aluminum foil wrapping of the vials was established, increasing counting efficiency and decreasing background, thus yielding a higher Q.

It must be pointed out that the optimum measuring conditions for benzene ^{14}C dating are quite different from the window setting suggested by the manufacturers for ^{14}C measurements.

We recommend that experimental conditions be studied carefully, such as concentration of scintillator and solvent, wrapping, and instrument specifications, in order to avoid errors in measurements which could result in poorer values of Q.

Future research in optimization will be to test different primary scintillators to obtain the best matching between emission spectrum and wavelength response of the photomultipliers, avoiding if possible the use of a secondary scintillator.

ACKNOWLEDGMENTS

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