

IMPROVED RESULTS USING HIGHER RATIOS OF SCINTILLATOR SOLUTION TO BENZENE IN LIQUID SCINTILLATION SPECTROMETRY

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ABSTRACT. Practical effects of the volumetric or weight ratio of scintillator solution to sample benzene in liquid scintillation spectrometry were examined here for radiocarbon dating. It is concluded, using a LKB-Wallac Quantulus™ 1220 and Teflon™-copper 3 mL vials with scintillator of toluene-based PPO and POPOP, that solutions containing the same concentrations of the same ratio, 1.3 or more, of scintillator solution to sample benzene show the same cpm/g and the same channel value of external standard spectrum, irrespective of different gross volumes of solutions. The addition of scintillator solution reduces background in 0.5 mL or so of benzene, and results in an appreciably enlarged figure of merit.

INTRODUCTION

The most efficient scintillators for radiocarbon counting are believed to be butyl-PBD (Polach et al. 1983) or a combination of butyl-PBD and secondary fluor (e.g. Hiller et al. 1994). They are usually dissolved directly in sample benzene. Polach et al. (1983) stated that “dry butyl-PBD increased efficiency based on signal to background ratio by 25% for any vial”. The most commonly used scintillation cocktail was PPO + POPOP previously dissolved in toluene (Polach et al. 1983). Using this toluene-based scintillator, which is thought to be negative, this paper shows how to hurdle the volume dependence in scintillation spectrometry and provides an alternative method to the benzene-dilution process for various small sample benzene.

METHOD

I do not know of any papers that discuss in detail the practical effect of the volumetric or weight ratio of scintillator solution to sample benzene in liquid scintillation spectrometry, although some papers specify it without comment. Based on the concept that the desirable ratio should bring low background, high count efficiency, small variance of counts, and high reproducibility, I examined the practical effect, and furthermore, obtained the relation between the ratios and the efficiencies of ^{14}C -scintillation counting.

The liquid scintillation counter used is a Quantulus™ 1220 by LKB-Wallac. All measurements were done under the ready-made setting for counting of ^{14}C . The used value of counts per minute (cpm) of a window ranging from channels 50 to 650 of multichannel analyzer (MCA) No. 1-half-1 means beta type events plus background (Wallac Oy 1995).

The Teflon™-copper 3 mL vials used are recommended for LKB Quantulus™ 1220 by LKB-Wallac and in many papers (e.g. Rauret et al. 1989). If not tightened, the caps tend to become loose when carried by an automatic sample changer. The 3 mL vials may accept at most 2.8 mL of solution, as more than that will be partly overflowed by compression of inside air. The background of 21 vials showed an average with 1σ , $0.232 \text{ cpm} \pm 0.068$ (Poisson standard deviation, 50 min \times 10 cycles, inactive benzene 1 mL, scintillator solution 0.5 mL). The variations among them are low enough for this study.

The ^{14}C standard used is ^{14}C -toluene, 5×10^5 dpm/g supplied by Packard. It was diluted by inactive benzene produced by Wako Pure Chemical Industries, Japan. A mixture of PPO (2,5-Diphenyloxazole) 4 g and POPOP 0.1 g in 1 L of toluene described by Kashida and Iwakura (1965) was used as a scintillator solution (all supplied by Dojindo Laboratories, Japan).

Relation between Gross Volumes and Volumetric Ratios of Scintillator Solution to Standard Benzene

Solutions with gross volumes of 1.0, 1.5, 2.0, and 2.5 mL contained scintillator solutions and standard benzene at the ratios of 1/5, 1/4, 1/3, 1/2, and 1/1, respectively. The ratios less than 1.0 have been adopted by many researchers (e.g. Tamers 1965; Polach et al. 1983; Rauret et al. 1989). The latter two studies used PPO + POPOP in toluene with some other scintillators to compare efficiencies. Ambers et al. (1986) used 9.5 mL of PPO in toluene to 5.5 mL benzene to check inter-vial variation in background of 20 mL glass vials.

Twenty vials were twice measured at a counting time of 15 min per vial, and the sequential counting cycles of 30, respectively. The "cpm" divided by weight (g) of standard benzene of ^{14}C makes "cpm/g" in Figure 1. The concentration of ^{14}C of standard benzene used here was 581.6 dpm/g, and the background was much less than 1.0 cpm/g. Therefore, "cpm/g" in Figure 1 might be compared to count efficiency. Series of solid squares from solutions of 1.0, 1.5, 2.0, and 2.5 mL are each linked by solid lines. These solid squares belonging to the same ratios of scintillator solution to standard benzene were again classified by trending broken lines.

Figure 1 shows some of the following data. The more the ratio of scintillator solution to standard benzene increases, the more the values of cpm/g increase. The four broken lines, except a broken top line, show that the more gross volumes, the more the values of cpm/g. The maximal ratio 1.0 of scintillator solution to standard benzene gives the almost identical values of cpm/g, irrespective of weight difference. The ratio used, e.g. by Tamers (1965), Polach et al. (1983), and Rauret et al. (1989), is 1/4, which shows relatively low efficiency in Figure 1.

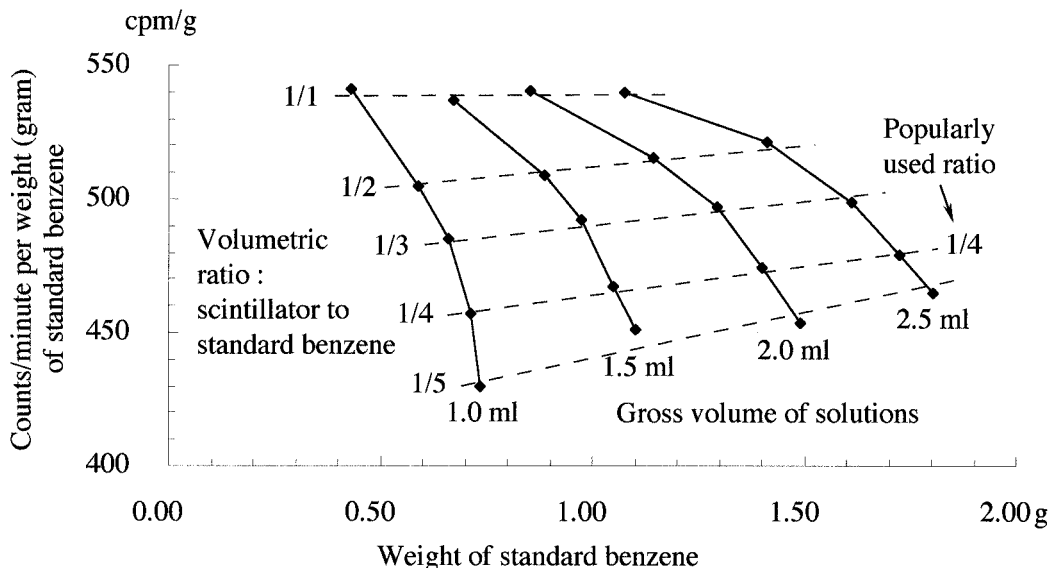


Figure 1 Relation between gross volumes (connected by a solid line) and volumetric ratios of scintillator solution to standard benzene (grouped by a trending broken line). The concentration of standard benzene used was 581.6 dpm/g.

Relation between Ratios of Scintillator Solution to Standard Benzene, and cpm/g or SQP(E)

Solutions with gross volumes of 2.7, 2.4, and 2.1 mL contained scintillator solution and standard benzene at the ratios irregularly ranging from 0.03 to 3.25. Twenty-one vials were measured at the counting time of 15 min per vial and the sequential counting cycles of 20, respectively. The SQP(E) (spectral quench parameter of the external standard) was measured for 1 min every measurement. In the Quantulus, the external standard of 1 μCi ^{152}Eu is moved close to the base of the vial, external standard spectrum is measured and SQP(E) (i.e. the channel above which 1% of the observed counts from the Compton continuum is obtained) is calculated and measured (Wallac Oy 1995).

The top and bottom sections of Figure 2 show the relation between the ratios of scintillator solution to standard benzene and cpm/g, and the one between the ratios and SQP(E), respectively. Two curves here were obtained with extremely high values of decision coefficient, 0.9881 and 0.9782, by the iteration least-squares method. Two expressions here are of saturation curves, $y = K - a \cdot b^x \rightarrow y = K - a \cdot b^x$ ($K > a > 0$, $0 < b < 1$). Incidentally, any other possible curves were applied, but this type of curve showed the best fit. The concentration of ^{14}C standard benzene used was 581.6 dpm/g. The first constant term, K (cpm/g), on the right side of the above expression means the saturation level, which is 548.69 here. Therefore, 548.69 cpm/g by 581.6 dpm/g equals 94.3%, which means a count efficiency. The above and below curves approach to a saturation level at $x \approx 0.9$ and 1.3, respectively. The higher the value of SQP(E), the higher count efficiency. Therefore, the solutions of a 1.3 or higher ratio produce relatively stable values on the y-axis.

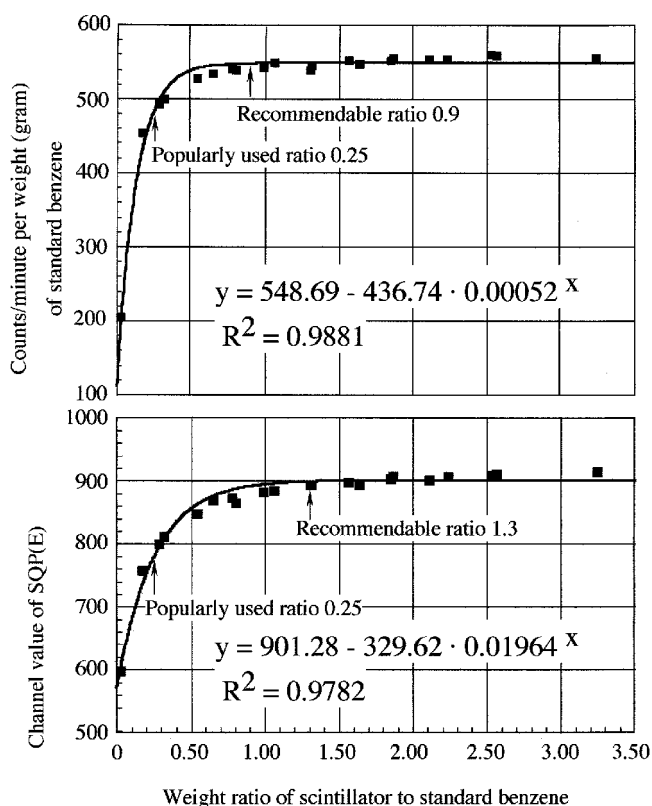


Figure 2 Top graph: relation between the ratios of scintillator to standard benzene (x-axis) and cpm/g (y-axis); bottom graph: relation between the ratios (x-axis) and SQP(E) (y-axis).

Although the values of cpm/g for ^{14}C benzene with scintillator solutions have been thought to depend on gross volumes of solutions by many researchers, they saturate when the ratio of scintillator solution to standard benzene is more than 1.3, as stated above. In other words, irrespective of gross volumes of solutions, values of cpm per weight of standard benzene or of SQP(E) are almost identical at such ratios of scintillator solution to standard benzene.

Incidentally, measurements of cpm, and of SQP(E) were 20 in number for every vial sample, and their averages and Gaussian standard-deviations were calculated. Figure 3 shows the relation between the ratios of scintillator solution to benzene and the values of standard-deviation of cpm and of SQP(E). The regression lines, whose low decision coefficients are insignificant, show decreasing tendencies. Many researchers have been using solutions with scintillator solutions which are less than sample benzene, but solutions with higher ratios roughly show lower variations.

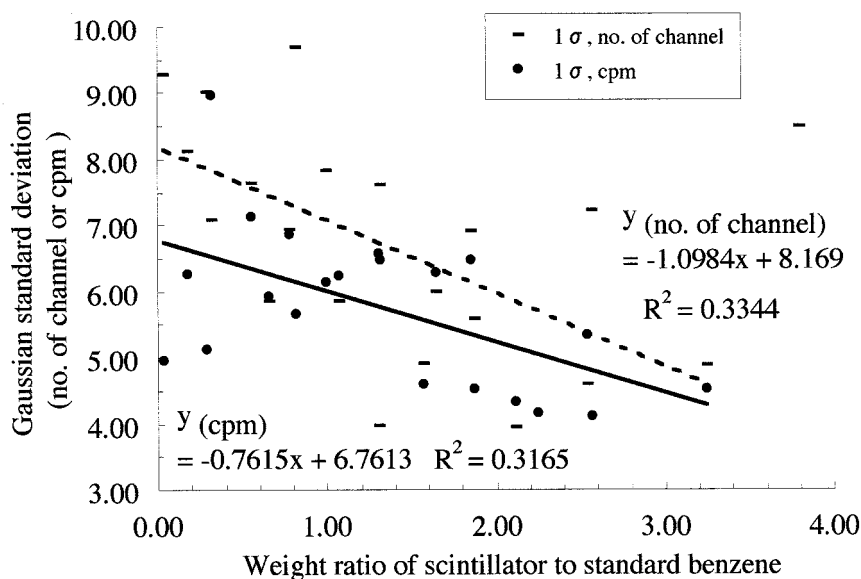


Figure 3 Relation between the ratios of scintillator solution to benzene and the values of standard-deviation of cpm and of SQP(E)

High Linearity of Calibration Curves

Gross volumes in this experiment were composed of 2.80 and 1.40 mL. The 21 vials were measured for 20 cycles (1 cycle = 30 min) each. The ratio of scintillator solution to benzene for 2.80 and 1.40 mL solutions was higher, 2.5, in either case than usual. The contents of standard benzene for 2.80 mL solutions are 0.00 to 0.80 mL in measures of 0.08 mL, and for 1.40 mL 0.00 to 0.36 mL in measures of 0.04 mL. The concentration of ^{14}C standard benzene used was 4874.7 dpm/g. Graphs A and B of Figure 4 show regression lines with decision coefficients 0.9998 and 1.000, respectively, where the x-axis is weight (g) of standard benzene, and the y-axis is cpm-difference of standard benzene and background. Graph C includes 19 data shown in Graphs A and B, but 4 marks are overlapped. Its decision coefficient is 0.9999. In other words, all the values of cpm/g are almost the same, an average 4474 cpm/g with one Gaussian sigma 29. The values of cpm to dpm, count efficiencies (E), are 91.7% on average and 0.5% on standard deviation.

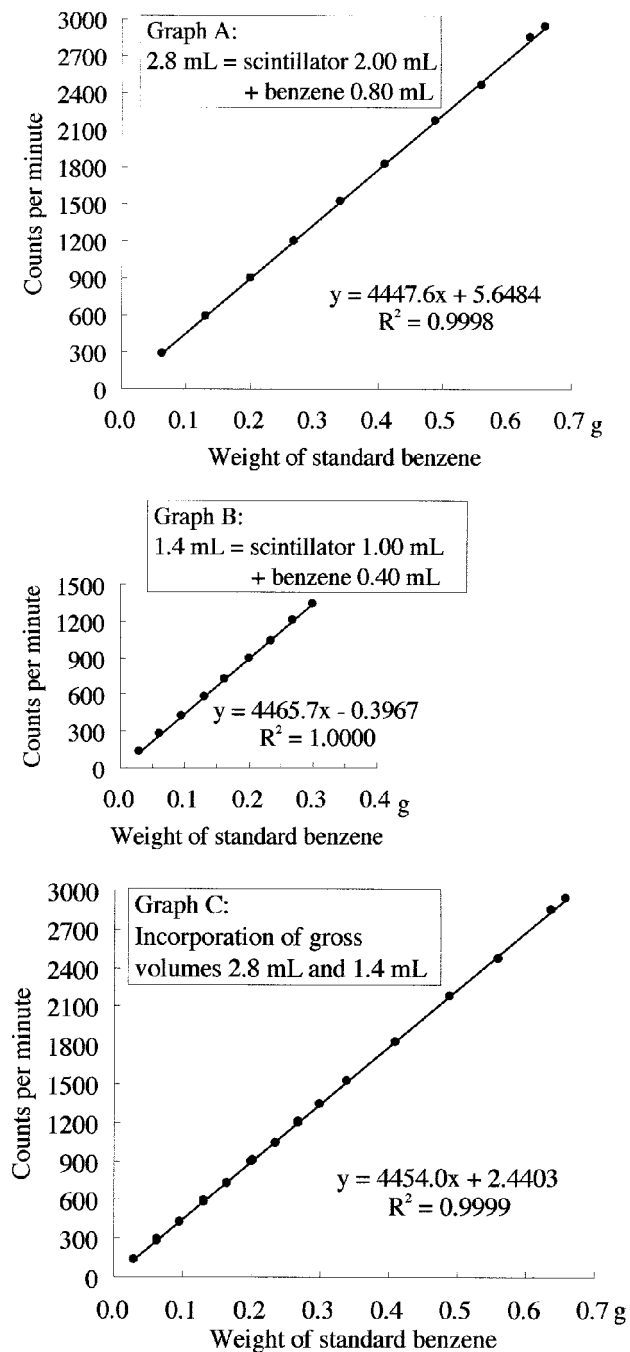


Figure 4 Calibration curves (regression lines with decision coefficients) of ^{14}C showing high linearity. Graphs A, B, and C, respectively show calibration curves of gross volumes 2.8 mL and 1.4 mL, and of incorporation of Graphs A and B.

A series of 2.80 mL presents lower variations of cpm of ^{14}C beta ray than of 1.40 mL, using the ratio of standard deviation to average. The former presents higher channel values, 921.0 ± 6.0 of SQP(E) than the latter, 903.2 ± 7.2 . A series of 2.80 mL shows higher reproducibility than of 1.40 mL.

Quenching Correction and Performance

The standards were made as follows: 0.1 mL of ^{14}C solution of 3834.3 dpm/g, 2.0 mL of PPO + POPOP in toluene, variable volumes of CCl_4 benzene solution and inactive benzene up to a total volume of 2.8 mL were added to each 3 mL Teflon-copper vials. Twelve activity standard solutions with increasing CCl_4 concentrations from 0 to 0.75% (v/v) were obtained. The solution in a vial among them was composed only of scintillator solution and inactive benzene. They were all measured at 20 min by 20 cycles with 1-min-long measurements of SQP(E) every cycle under the ready made setting for counting of ^{14}C , except for changing channel ranges from 70–500 to 1–1024 in windows 2 and 5.

The values of measurements (cpm) are converted to relative efficiencies (%) using ^{14}C concentrations of NISTII, and the quench correction curves are plotted in Figure 5. These two kinds of plots and regression curves, of which the expressions and determination coefficients are shown here, are almost overlapped. The purities of benzene synthesized from NISTII and palaeozoic marble are more than 99.6%, analyzed by gas chromatography. The figure of merit (FM), E^2/B , was 18214 calculated using an efficiency (E) of NISTII ($(15.583 \text{ cpm/gC}) / (18.305 \text{ dpm}_{1999}/\text{gC}) \times 100 = 85.1\%$) and a background (B) cpm value of marble (0.3976). Each counting time was 1250 min. It is included among FMs reported by Polach et al. (1988), Kalin (1989), Hogg and Noakes (1992), and Pawlyta et al. (1998) using the Quantulus with butyl-PBD fluor.

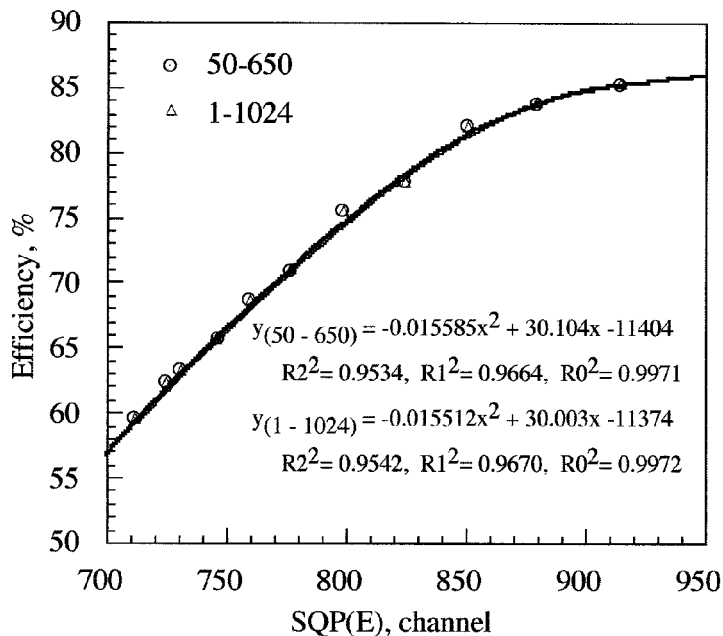


Figure 5 Quench correction curves of measurements for channels 50-650 and 1-1024

Alternative Measurement Method of Small Sample Benzene

Eighteen samples dropped in 3 mL Teflon-copper vials were measured for 15 min for 10 cycles each. Their constituents are described at the bottom of Figure 6. The ratios between scintillator solutions and benzene are identical with each other positionally in the solutions containing 0.5, 1.0, and 1.5 mL of benzene. Efficiencies, irrespective of different solution volumes, are unchanged. Background increases with benzene volume, not scintillator solutions. Therefore, FM decreases when benzene volume increases. Such trends were pointed out by Rauret et al. (1988) and others. The maximum determinable age increases with FM based on the equation by Gupta and Polach (1985: 97). Consequently, smaller solutions can give more maximum ages. The lower graph in Figure 6 shows that the ratios of Poisson standard deviation to dpm decrease when benzene volume increases. The absolute values of error in age increase with the Poisson standard deviations by the net counts of sample and oxalic acid standard, based on the equations by Gupta and Polach (1985: 111–3). Therefore, larger volumes of benzene can produce more precise ages. Figure 6 also shows that the addition of scintillator solution hardly raises the background and error of measurements. This scintillator solution peculiarity might modify the established knowledge that the background contribution to the count rate increases as the total volume in the vial increases.

When the amount of carbon in the sample for dating is insufficient to yield a full dating component, CO₂ or benzene is added to it (Gupta and Polach 1985). Gupta and Polach cautioned against diluting sample benzene with inactive benzene, because of possible sample benzene contamination by quenching impurities in commercially available analytical grade benzene. But, using the Quantulus

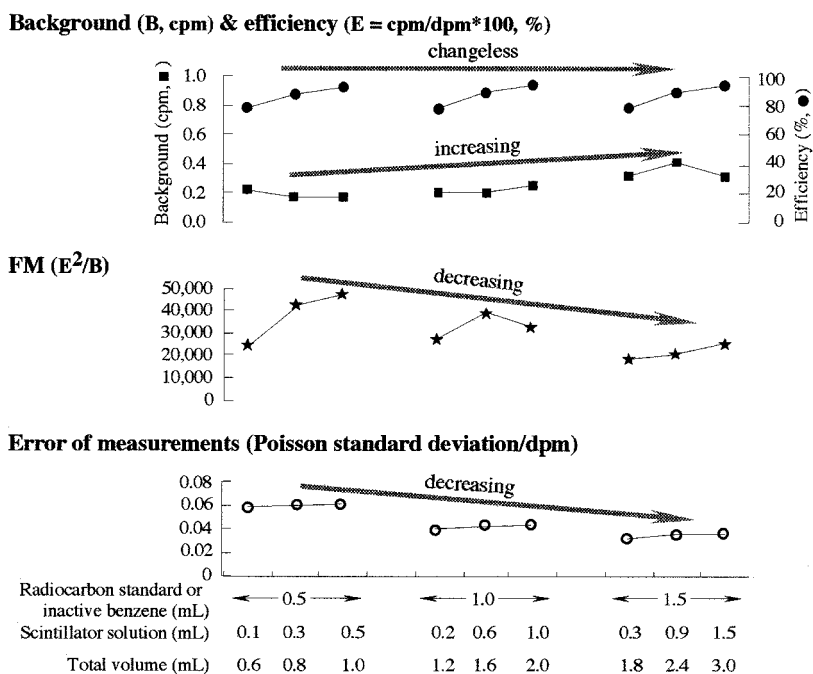


Figure 6 Background of inactive benzene and scintillator solutions, and efficiencies and figures of merit (FM) of ¹⁴C standard benzene (581.6 dpm/g) and scintillator solutions (PPO + POPOP in toluene) in 3 mL Teflon-copper vials.

and 3.0/0.3 mL Teflon-copper vials, Polach et al. (1988) obtained relatively precise results for small sample ^{14}C radiometry by diluting sample benzene. This maximum dilution ran up to 100 times, i.e. 0.03 mL to 3.0 mL.

As shown in Figure 6, although adding benzene raises background, adding scintillator solutions does not raise it within each solutions of 0.5, 1.0, and 1.5 mL of benzene. If anything, adding scintillator solutions reduces background in the solutions containing 0.5 mL of benzene. Their values of FM are considerably enlarged as scintillator solutions are added. I recommend adding scintillator solutions, especially in small sample benzene, instead of inactive benzene. A series of small benzene samples synthesized are usually variable in volume, and all the samples should be measured sequentially. The forementioned identical ratio method of scintillator-solution/sample-benzene makes sequential measurements of small samples possible, provided that all variable volumes of inactive benzene and scintillator solution are prepared for background estimation.

CONCLUSION

For liquid scintillation spectrometry, solutions containing the same concentrations, with the same ratios of 1.3 or more, of scintillator solution to sample benzene show the same cpm/g and the same channel value of external standard spectrum, irrespective of different gross volumes of solutions. When volumes of a series of sample benzene synthesized are relatively small and varied, all the volumes made can be measured at the same run. What is better, only one volume of oxalic acid solution can also represent any other volumes of oxalic acid solution. In contrast to previous studies, adding scintillator solutions reduces background in small samples (0.5 mL or so) of benzene, and as a result, FM can be considerably enlarged. This method could take the place of the benzene dilution method that is usually used for small samples. The results here could be extended to other radio nuclides, scintillators, vials, and counters.

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