

CHAPTER 19

Modern Techniques for Quench Correction and dpm Determination in Windowless Liquid Scintillation Counting: A Critical Review

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ABSTRACT

With the advent of readily available computing power, it seems reasonable to describe the probability of the liquid scintillation process replacing quench curves. The pulse height spectrum and the counting efficiency can be expressed as functions of the scintillator photon yield as measured by the external standard Compton spectrum. The energy dependence of the photon yield can be accounted for by combining information from the sample spectrum and the Compton spectrum. A variety of numerical techniques can then be applied to describe the spectral response and to calculate dpm values of an unknown from appropriate reference spectra.

These methods for determining dpm values have recently been applied to liquid scintillation counters equipped with multichannel analyzers. Although these "windowless" dpm determinations are very convenient to the user, many inherent characteristics of the scintillation process may render results invalid under certain experimental conditions.

Indeed, the photon yield at a particular energy is significantly affected by the microscopic environment of the nuclide and the composition of the sample, expressed by the concept of ionization quenching. As a further complication, the prompt and delayed components of the fluorescence depend on these parameters as well. As a consequence, theoretical expressions proposed to account for ionization quenching must remain approximations; their validity needs to be verified for each cocktail-sample combination. Due to the unstructured nature of LSC pulse height spectra, it is difficult to accomplish this verification using spectral overlay and comparison techniques. Pulse height discrimination is often required after the fact to make results less dependent on varying experimental conditions.

Numerical methods applied to windowless dpm counting will be reviewed, and the results will be compared to methods based on quench compensated discrete window settings.

INTRODUCTION

In the field of optical spectroscopy, energy dispersion is obtained using filters or monochromators that can be calibrated independently of the sample using absolute physical methods. In liquid scintillation counting, this is not the case. Although the response of the PMT and its related pulse shaping and

aplication circuits can be determined independently of the sample, quench compensation is required to correlate the pulse height measured in the multi-channel analyzer with the electron energy of the nuclear event. Most commercial systems monitor the quench level using the mean sample pulse height (SIS) and the Compton edge from an external source of gamma radiation (tSIE or H#). Horrocks has presented the results of extensive studies determining the energy needed to produce a photoelectron in a liquid scintillation counter.¹ This energy depends both on electron energy and on quench level. These functions are not linear. Rundt et al., investigated theoretical expressions for the effect of ionization quenching and found them all dependent on adjustable parameters which vary with the solvent.² The theoretical functions are valid for chemically quenched homogeneous samples only.

The reference method of compensating for quench effects, the method of standard addition, is too labor intensive for routine use. Usually, "quench curves" are constructed using a series of standards at various quench levels. Ideally, the standards are prepared using the same cocktail and quench material present in the sample. A variety of mathematical methods is then used to interpolate counting efficiency values for the measured value of the quench indicating parameter.

In practice, commercially prepared sets of quench standards in a toluene based cocktail, yield satisfactory results for ^3H and ^{14}C . In no small part, this is due to the large body of experimental information available on the use of these two nuclides. Indeed, hardware, software, and cocktail formulations have been optimized to ensure reliable results for the broadest possible range of applications. Especially important are experiments using emulsifier cocktails to count aqueous samples.

The use of liquid scintillation counters equipped with multichannel analyzers and the computing power to automatically analyze the results offers considerable convenience for the user. Channel selection in the MCA has replaced adjustment of analog threshold values, and spectral storage features even allow for post run analysis. This has allowed the development of windowless protocols for dpm determinations that are very general and almost as easy to use as "absolute" instruments such as monochromator based spectrophotometers. Nevertheless, the physics of scintillation counting has not changed.

This presentation will focus on quench correction and dpm determination of dual labeled samples containing ^3H and ^{14}C because these are the two nuclides most commonly counted. The discussion can easily be generalized to other nuclides or to the triple label case.

Figure 1 is a schematic drawing of the beta spectra of ^3H and ^{14}C , as well as a composite of the two. The implicit assumption made in the drawing is that the spectra are from a sample at the same quench level. As is well known, the shape of a spectrum is distorted as quench changes. Consequently, accurate quench correction is a prerequisite for accurate dpm calculation, whether of single or multilabel samples.

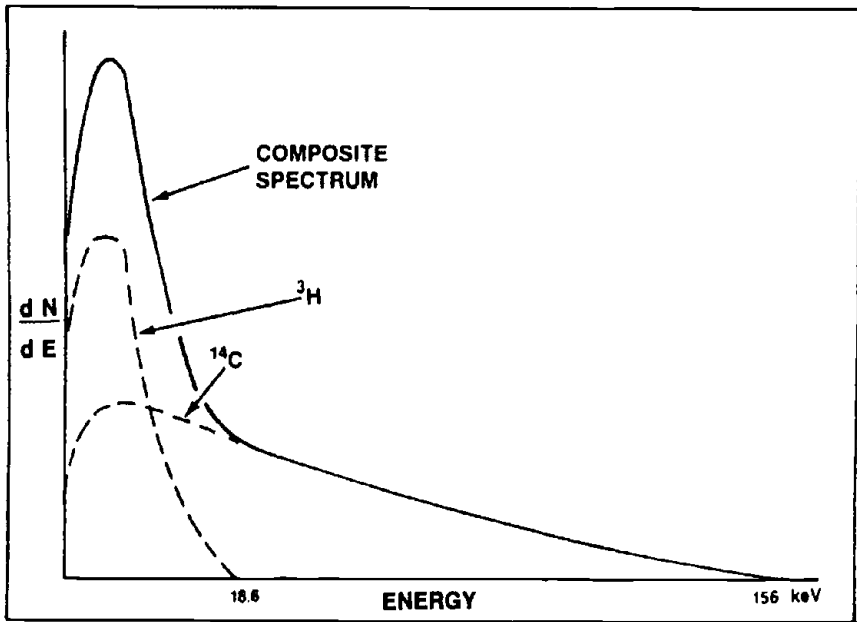


Figure 1. Schematic spectra for ³H, ¹⁴C, and dual label sample.

FIXED WINDOW SETTINGS

When using fixed window settings (see Figure 2), the multichannel analyzer is used in a quasianalog fashion. The energy scale is divided up into two regions, A and B, and the counts from these channels are summed up as cpm_A and cpm_B. According to the principle of radionuclide exclusion, the lower limit of region B is chosen above the endpoint energy of the low energy nuclide. This allows direct calculation of the high energy nuclide dpm_H without interference from the low energy nuclide. The efficiency for the high energy nuclide in channel B, E_{HB}, is interpolated from a quench curve.

$$dpm_H = \frac{cpm_B}{E_{HB}} \tag{1}$$

When calculating dpm_L of the low energy nuclide, the counts need a spill down correction due to the high energy nuclide in the low energy channel, E_{HA}. The efficiency for the low energy nuclide in the A channel, E_{LA}, is also needed.

$$dpm_L = \frac{cpm_A - dpm_H E_{HA}}{E_{LA}} \tag{2}$$

The relative precision for the low energy nuclide in the dpm value can be expressed as proportional to factor analogous to the figure of merit (E₂/B) where B is the spill down (= dpm_H E_{HA}).

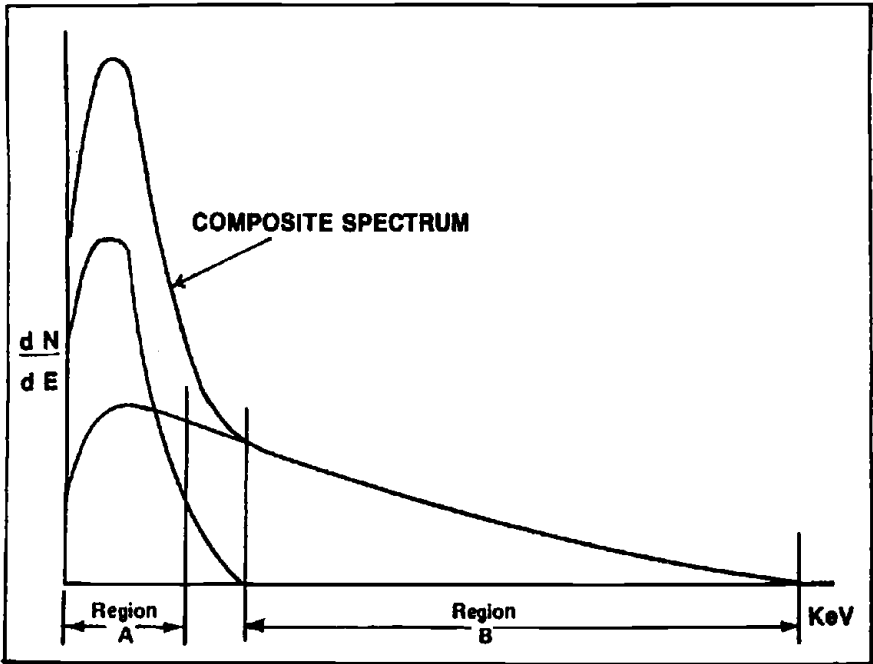


Figure 2. Fixed window region settings.

$$\% \text{ Precision} \approx \frac{E_{LA}^2}{dpm_H E_{HA}} \left(\approx \frac{E^2}{B} \right) \quad (3)$$

The relative precision is highly quench dependent because as quench increases, the ^3H efficiency decreases and the spill down from the ^{14}C increases. The dotted lines in Figure 3 represent quench curves obtained using the fixed window method, while the solid lines represent quench curves obtained by automatically adjusting the windows as a function of quench. In our case the quench level is determined by the quench indicating parameter of the external standard tSIE. This method is also called automatic efficiency control (AEC) because the efficiency of the high energy nuclide in the low energy channel is kept constant. As a result, the relative precision is independent of quench level.

The absolute precision of dpm_L , however, still depends on the relative activity of the high energy nuclide, $R = dpm_H/dpm_L$.

$$\text{Precision} \approx \frac{E_{LA}^2}{\frac{dpm_H}{dpm_L} E_{HA}} = \frac{E_{LA}^2}{R E_{HA}} \quad (4)$$

As R increases the precision decreases due to increasing spill down, which leads to an activity ratio dependency.

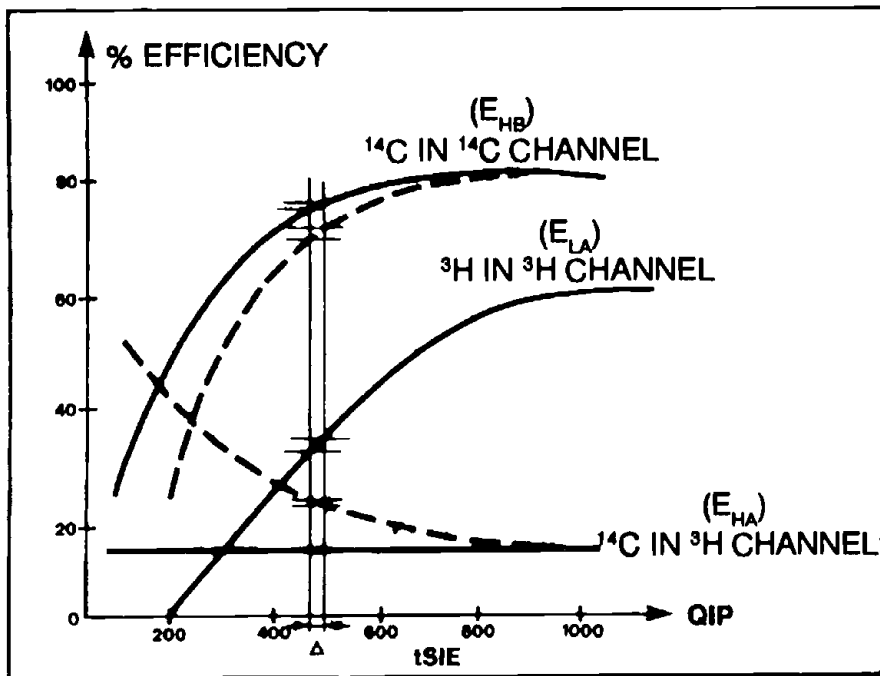


Figure 3. Quench curves: automatic window tracking (solid line), fixed window setting (dashed line).

FULL SPECTRUM DPM

One method of calculating dpm without windows and using the information in the full spectrum is to separate out the counts due the two nuclides with the spectral index of the sample (SIS) (see Figure 4). Since the spectral index of the composite, SIS_T , is a cpm weighted average of the spectral indices of the low energy nuclide, SIS_L , and the high energy nuclide, SIS_H , it is possible to assign the correct proportion of the total count rate, cpm_T , to the low and high energy nuclide, cpm_L and cpm_H .

$$cpm_L = \frac{SIS_H - SIS_T}{SIS_H - SIS_L} \quad cpm_T \tag{5a}$$

$$cpm_H = \frac{SIS_T - SIS_L}{SIS_H - SIS_L} \quad cpm_T \tag{5b}$$

While SIS_T is measured, the SIS_H and SIS_L values are interpolated from a quench curve (see Figure 5), as are the full spectrum efficiencies used to calculate dpm values.

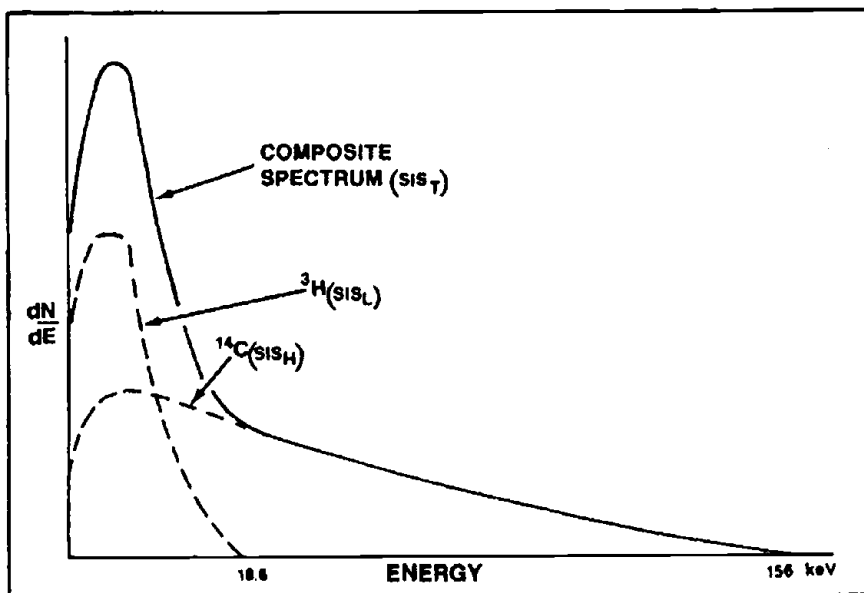


Figure 4. Full spectrum dpm.

$$\text{dpm}_L = \frac{\text{SIS}_H - \text{SIS}_T}{\text{SIS}_H - \text{SIS}_L} \frac{\text{cpm}_T}{E_L} \quad (6a)$$

$$\text{dpm}_H = \frac{\text{SIS}_T - \text{SIS}_L}{\text{SIS}_H - \text{SIS}_L} \frac{\text{cpm}_T}{E_H} \quad (6b)$$

We see from the curve that both the efficiency and the SIS interpolations depend on the accuracy of the external standard quench indicating parameter since the curves have a slope. Furthermore, the leveraging effect in Equation 6 on the difference between SIS_T and SIS_H (and to a lesser extent SIS_L) magnifies the effect of any inaccuracies on calculating dpm_L . The dpm calculation is now quite sensitive to experimental conditions affecting the QIP_{ES} differently from SIS.

Figure 6 contains the results of SIS measurements of tritium standards made up in a variety of cocktails. We see that the relationship between the quench indicating parameters of the external standard and the internal standard is similar for all cocktails, but not identical. Using the tSIE (see Figure 7) brings some improvement, but a discrepancy remains.

Since the early work on homogeneous solutions as presented in Birks's³ monograph reviewed at the International Symposium on Organic Scintillators at Argonne,⁴ the photochemical literature has expanded into the area of colloid solutions such as those used in emulsifier based cocktails. Interest in laser dyes, which include some common scintillators, has led to a better understanding of the prompt and delayed components of scintillator emissions. It turns

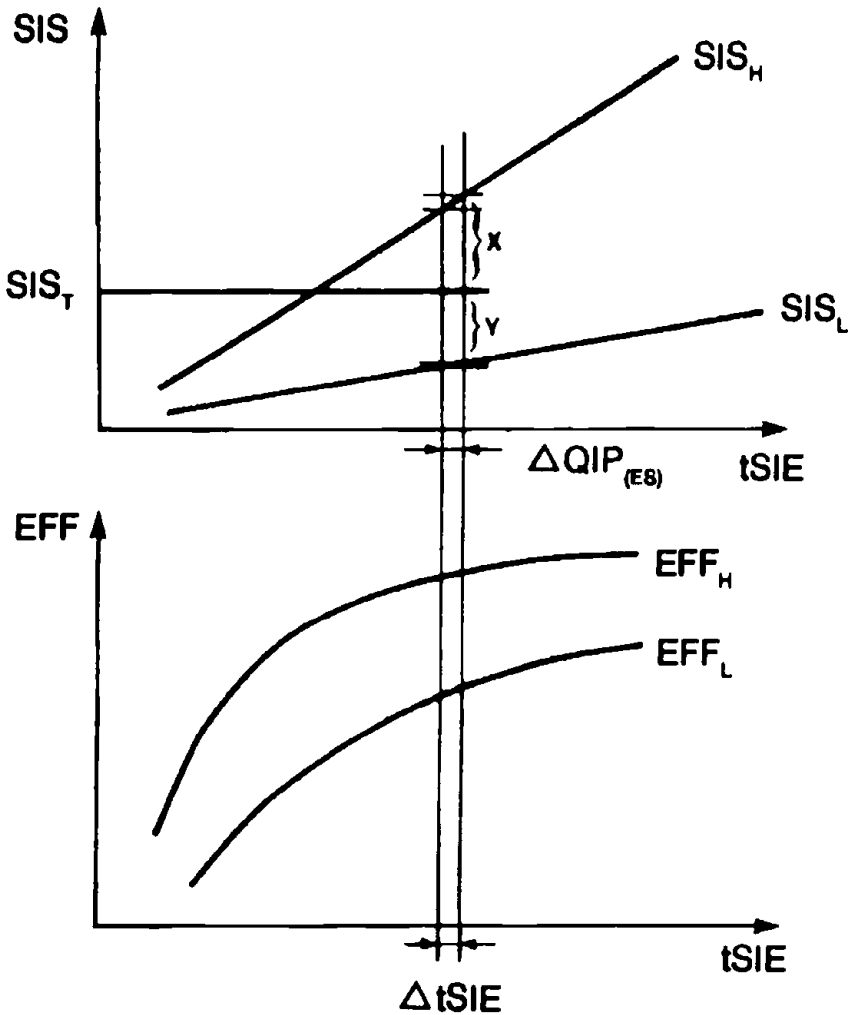


Figure 5. Full spectrum dpm quench curves.

out that the microscopic environment of the nuclide in the sample varies with sample load and sample composition. Furthermore, this effect is different for the prompt and delayed component of the scintillation pulse. Tracks from high energy electrons pass through the different phase regions of emulsifier cocktails so that their effect tends to be averaged out. Low energy electrons, such as those emitted by tritium, do not. This makes it difficult to correlate scintillation efficiencies of high energy electrons with the scintillation efficiency of low energy electrons. Unfortunately, it is precisely this correlation that is at the heart of all spectral interpolation schemes, whether they use the sample spectrum alone or a combination of sample and external standard spectra. This

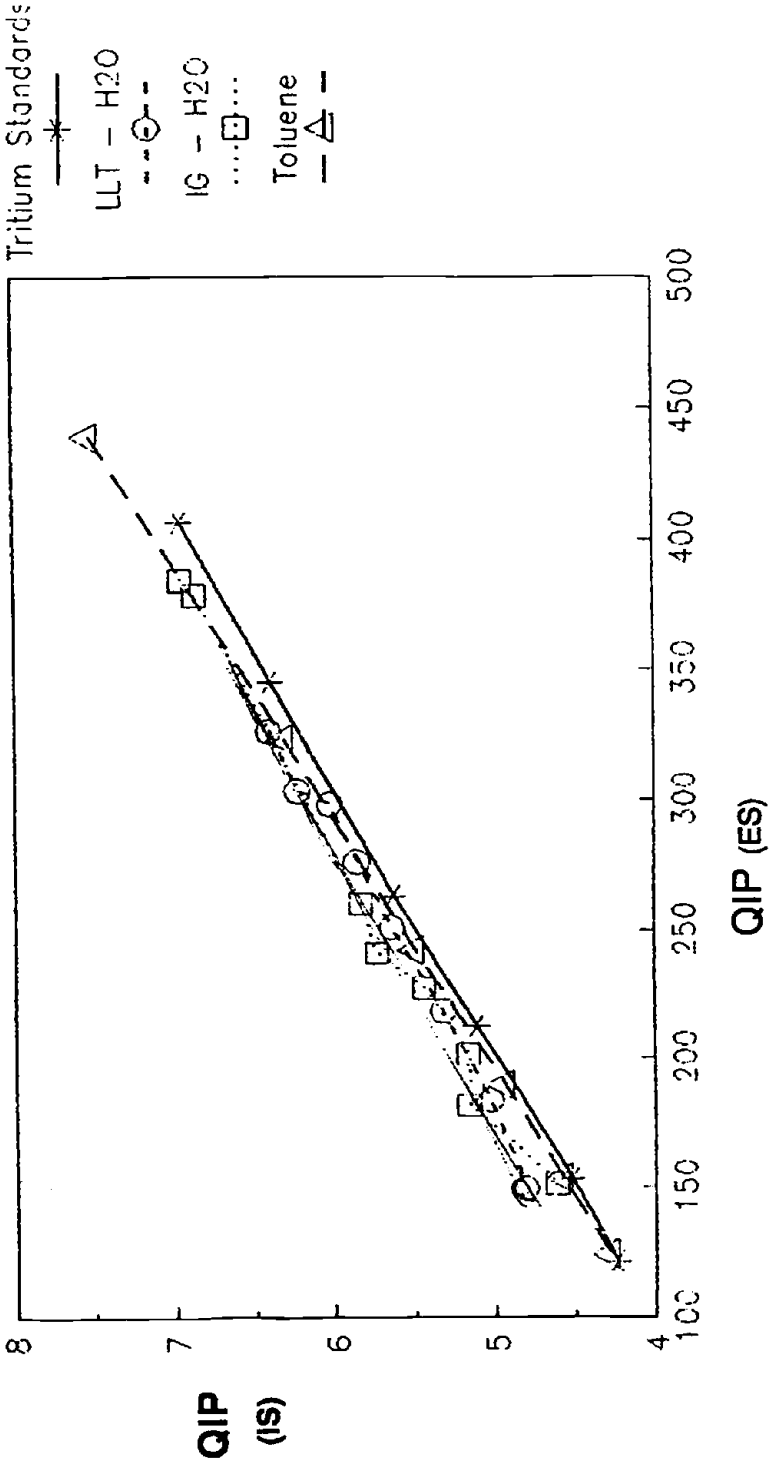


Figure 6. Effect of various cocktails on the relationship $QIP_{(IS)} = f(QIP_{ES})$.

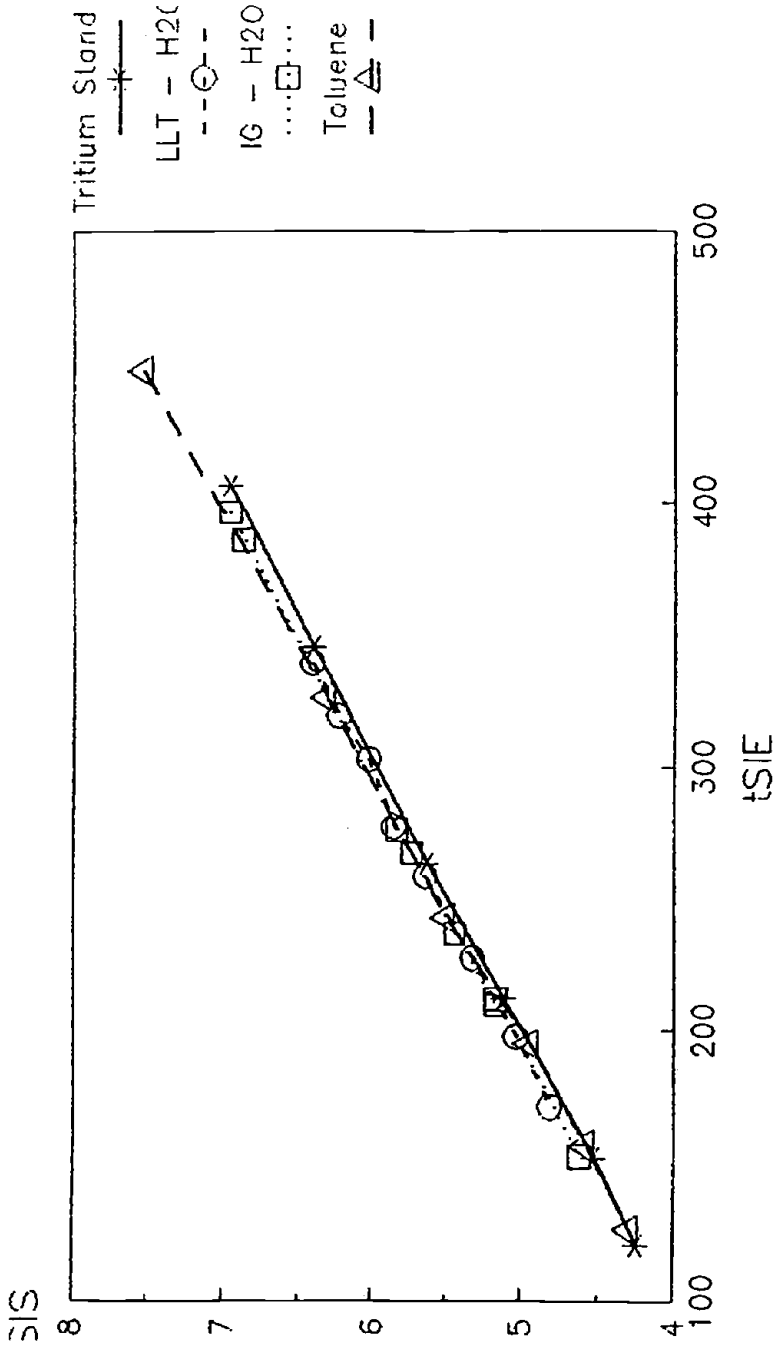


Figure 7. Effect of various cocktails on the relationship $SIS = f(tSIE)$.

problem becomes even more critical when quench standard and sample are counted in different cocktails. As a consequence, theoretical expressions accounting for ionization quenching break down in the critical low energy region. They are approximations whose validity needs to be verified for each cocktail/sample combination.

SPECTRUM OVERLAY TECHNIQUES

An alternative method of windowless counting that does not reduce the spectrum to a single parameter is the spectral overlay technique (see Figure 8). In this technique, the QIP of the external standard is measured and used to interpolate the spectra of quench standards channel by channel to the quench level of the sample. The spectra are normalized to separate the shape function from the counting efficiency.

The cpm values of the nuclides are adjusted by a method of fitting the least square of the standard spectra to the composite spectrum of the sample. When the best fit is obtained, the cpm values for the nuclides are known, and the dpm values can be calculated directly using the efficiencies.

$$\text{dpm}_L = \frac{\text{cpm}_L}{E_L} \quad (7a)$$

$$\text{dpm}_H = \frac{\text{cpm}_H}{E_H} \quad (7b)$$

This numerical method is derived from fields such as optical spectroscopy, which allow for absolute energy calibration. The error in the energy value is at least constant if not negligible. This allows for curve fitting routines to evaluate the goodness of fit based only on the variability of the photon count rate. The energy is assumed to be known exactly. In LSC count spectra, this assumption is not valid. As a result, these algorithms tend to give spurious results when challenged by errors in the energy value.

One way to overcome this problem is to allow the fitting procedure to "adjust" the quench level at which the standard spectra are calculated. Now the quench level is no longer a measured value; it becomes the third parameter in a least square fit of the interpolated spectra to the measured composite spectrum. The added parameter improves the fit. However, the algorithm assumes that the physics of the sample is identical to that of the standards. That is, the effect of sample preparation is not accounted for.

Figure 9 illustrates the consequences of adjusting QIP_{ES} . Two single label tritium standards are shown in toluene and a gel phase cocktail (Insta-Gel). The Insta-Gel spectrum is slightly deformed due to beta self-absorption in the gel phase. In order to improve the least square fit, an overlay technique will raise the external standard QIP to broaden, and thus deform, the whole spectrum.

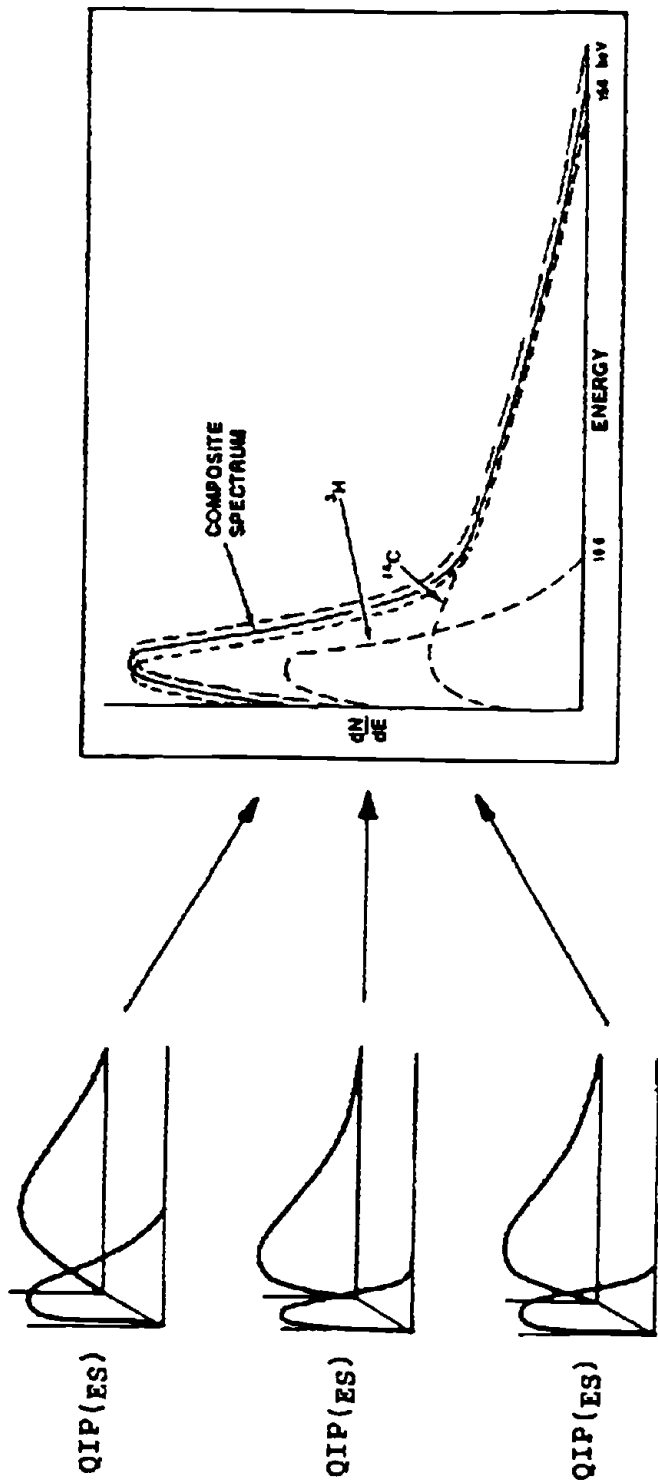


Figure 8. Spectrum overlay technique.

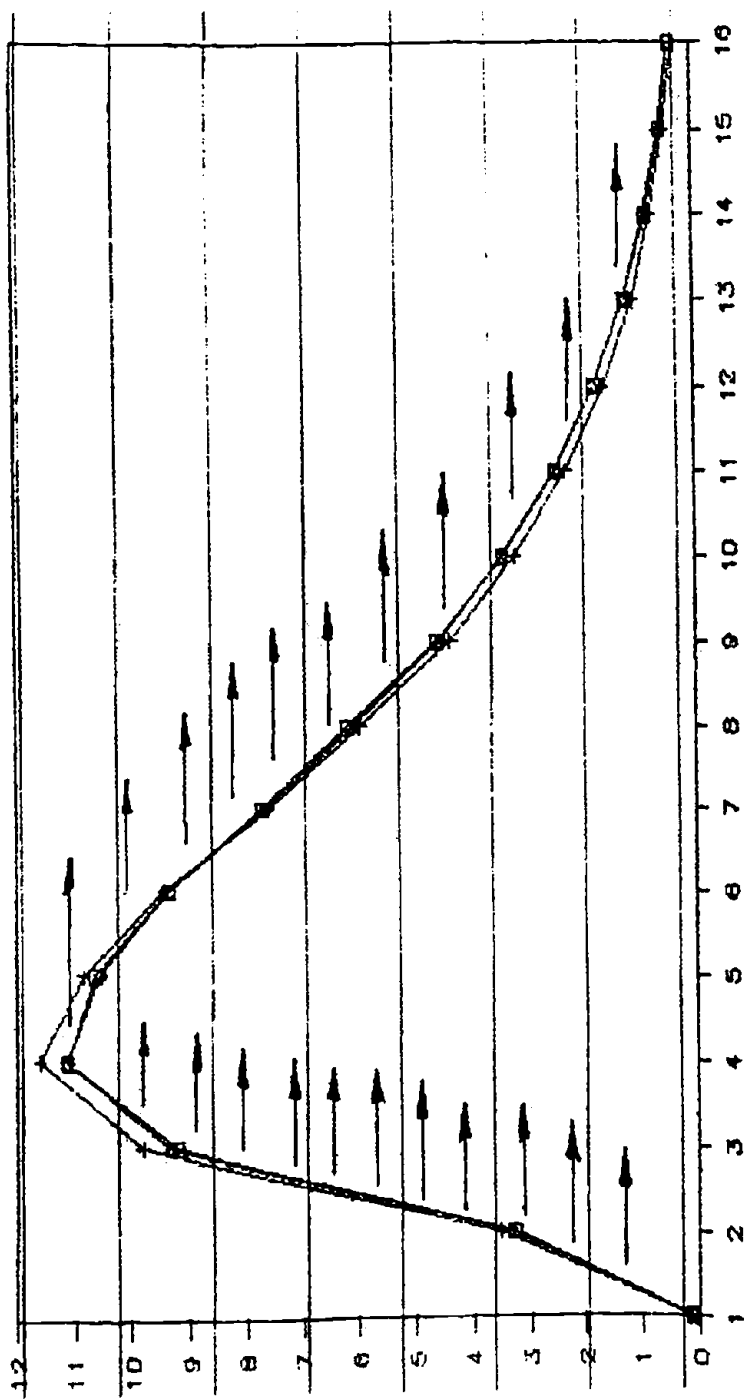


Figure 9. Consequences of adjusting QIPs on spectrum overlay technique.

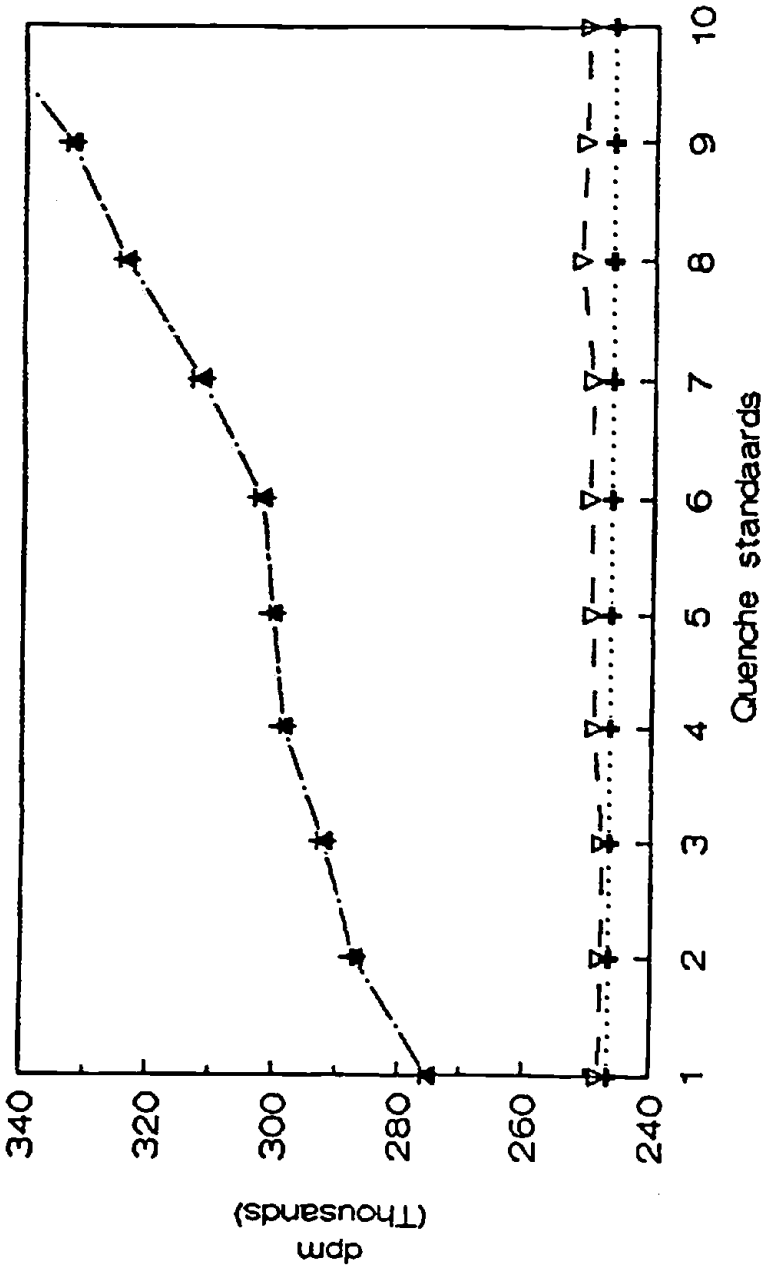
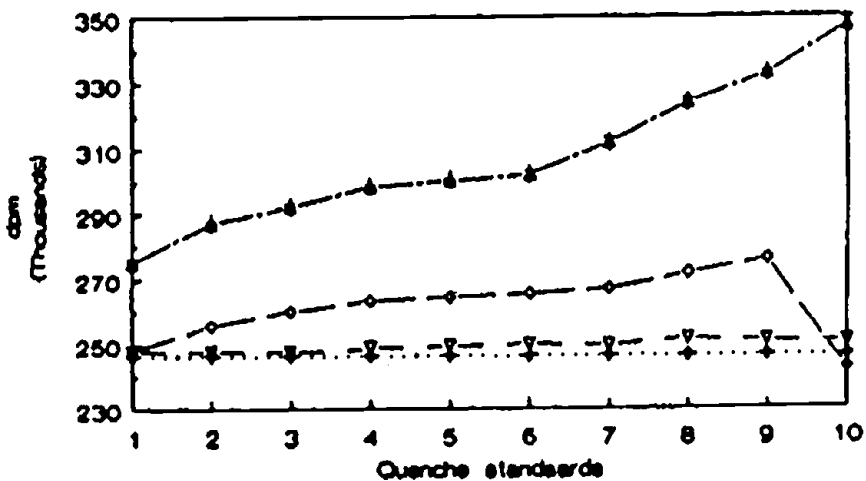


Figure 10. dpm Recovery of toluene samples using OptiFluor standards. + added dpm, ▲ DOT-dpm with OptiFluor library, ▽ AEC.

Test Tellers

[3H]quenche strds: 246.5 \pm 3 1e3 dpm

gem kb peckard LKB
1 cal



Test Tellers

[3H]quenche strds: 246.5 \pm 3 1e3 dpm

kb gem peckard LKB
2 cal 1 cal

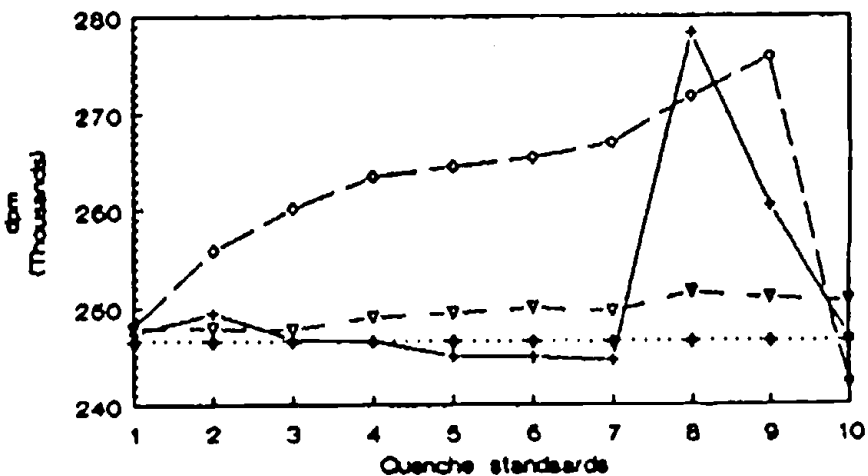


Figure 11. Effect of "fine tuning" the spectrum library on dpm recovery using the spectrum overlay technique: with one quenche standard (top), with two quenche standards.

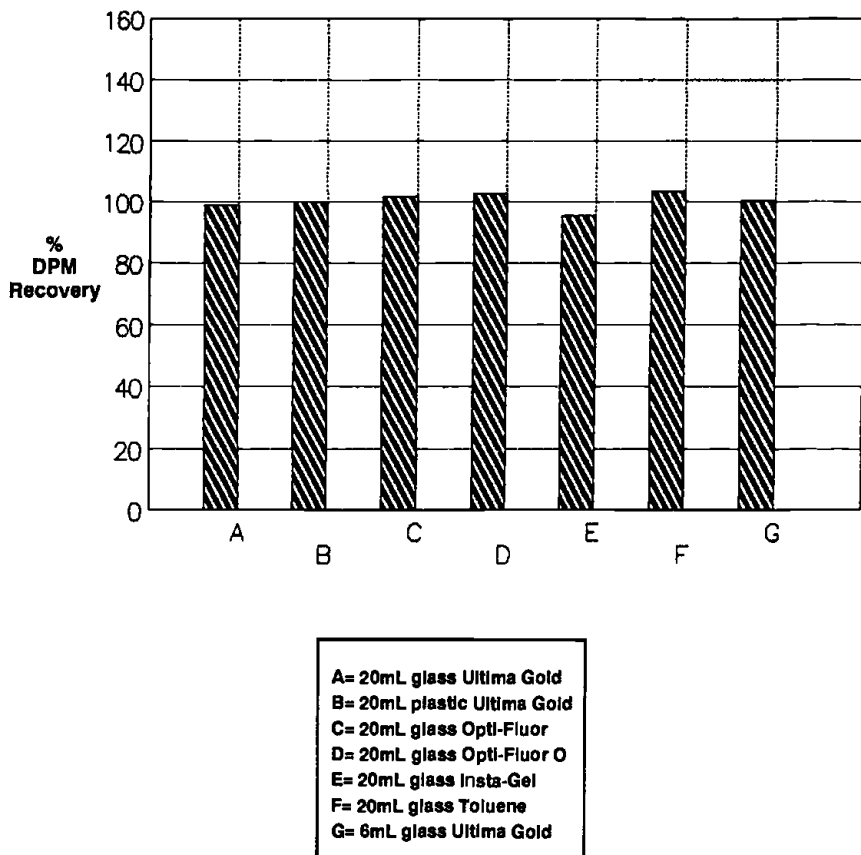


Figure 12. Effect of sample preparation on % dpm recovery of single label ^3H samples using AEC.

Figure 10 contains the test results of toluene single label samples using an Optifluor standard. While the automatic window racking method (AEC) results in values close to the dpm added, the spectral overlay technique leads to spuriously high dpm values. Clearly this technique is not reliable because of its sensitive to sample composition.

One way to improve the performance of the technique is to "fine tune" it by adding a standard prepared in the same cocktail as the sample. This ameliorates the problem (see Figure 11a), but even using a second quench standard (see Figure 11b) does not eliminate it. These results show that most reliable results are still obtained using several standards on a quench curve.

Figure 12 contains the data from a test of tritium samples prepared using different vial types and cocktail compositions. We see that the dpm recovery of Insta-Gel is under 100% due to self-absorption. The values from all other samples are quite close to 100%. In Figure 13, we see the performance of the

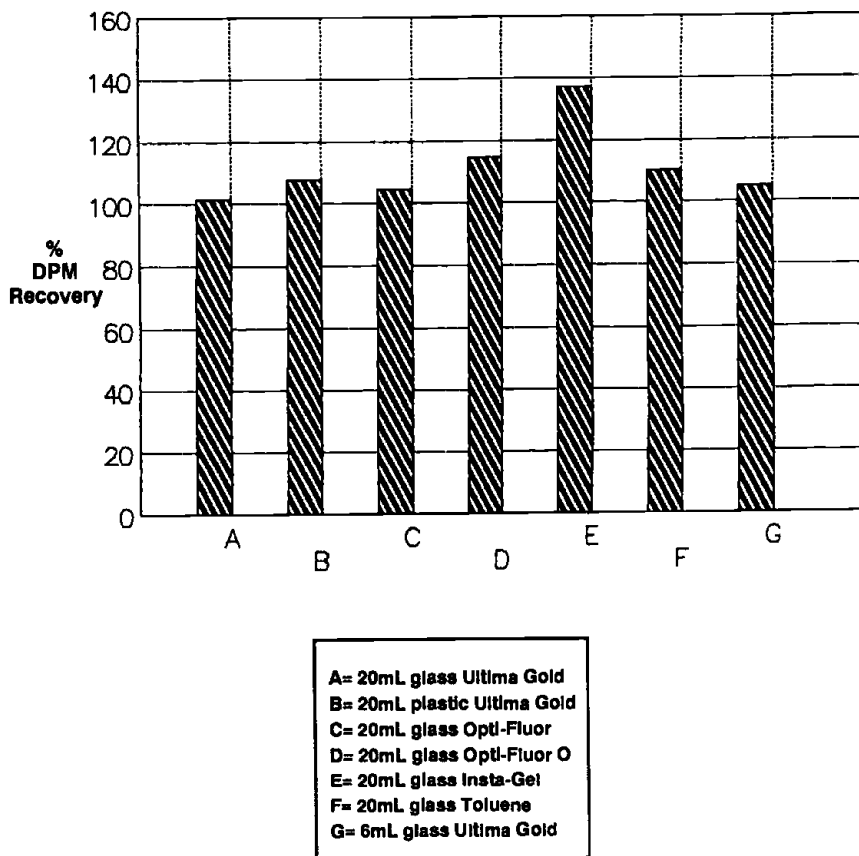


Figure 13. Effect of sample preparation on % dpm recovery of single label ^{14}C samples using spectrum overlay technique.

spectrum overlay technique. The error in the Insta-Gel sample is particularly large due to the effect of self-absorption, but by almost any standard of comparison, the overlay technique does not perform as well as automatic window tracking.

POST COUNT dpm WITH AUTOMATIC WINDOW TRACKING

In order to obtain the most reliable performance and maximum precision it is possible to combine automatic window tracking with automatic region adjustment. In this method, the full spectra of all quench standards are stored in the computer. This allows the software to create quench curves with any region settings, saving the user from having to recount the samples. When the sample is counted, the energy limits of region A are adjusted to obtain the best precision for the activity ratio of that particular sample (see Figure 14a). Once

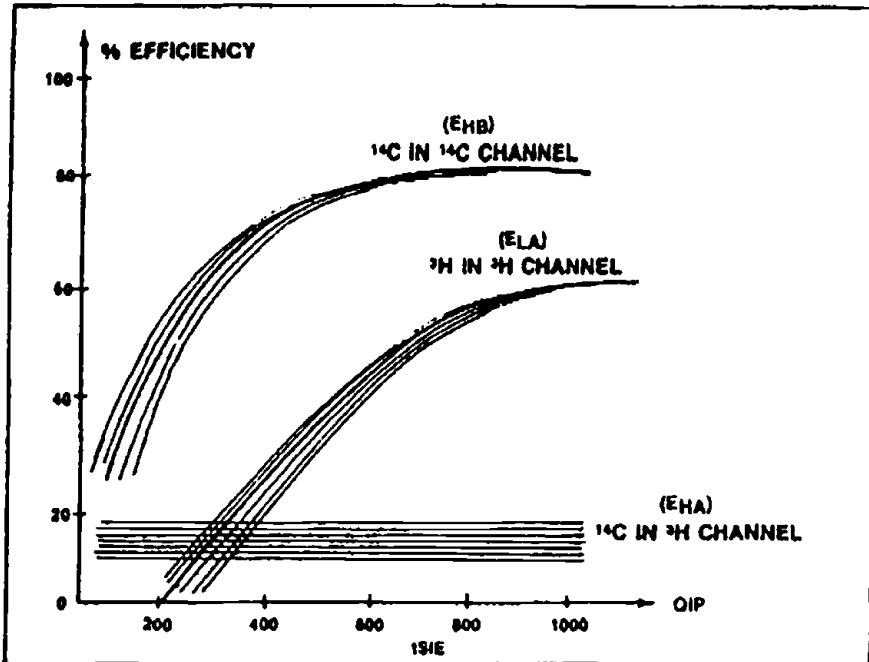
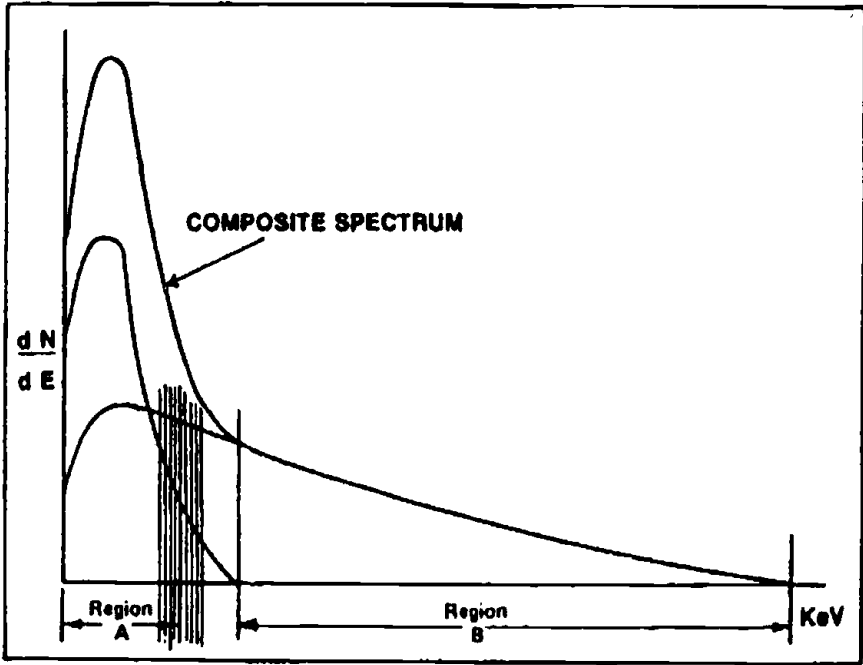


Figure 14. Automatic optimization of region settings for quench and activity ratio using Uniquench-dpm.

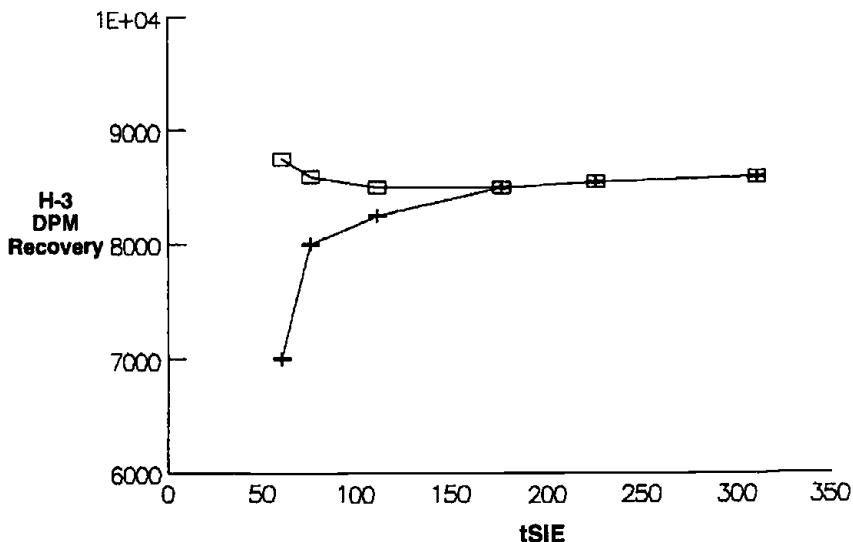


Figure 15. dpm recovery of AEC and Uniquench-dpm for $^3\text{H}:^{14}\text{C}$ (1:15) sample.

the region is determined, the stored quench spectra are used to create a full quench curve under the optimum conditions for that sample (see Figure 14b).

The improved performance obtained by adjusting the region settings is shown in Figure 15. We see that the regions set for the unquenched standards no longer give good results at higher quench levels (lower tSIE). Adjustment of the regions extends the range of good performance considerably.

CONCLUSION

In this review of quench correction methods, we see that addition of computing power to a state of the art liquid scintillation counter will result in improved performance and more convenience for the user. However, the physical problems connected with the relationship between external standard and sample spectra still remain. Software techniques based on a probabilistic analysis of instrument performance and sample composition now allow us to extract the maximum possible amount of information from the sample spectrum. However, for general purpose instruments, they are no substitute for an appropriately chosen set of quench standards and algorithms that respect the limitations on precision set by counting statistics and our limited knowledge of nuclear track photochemistry.

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