

LSC

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Available Quench Parameters in TriCarb LSC's

counters to determine the activity of different types of samples. In some cases the users might have problems to decide which of the different methods are best suited to determine the activity in a given sample. This application note will give a short introduction into all the available methods for quench correction and will discuss advantages and disadvantages of the individual processes.

The following methods are available on TriCarb liquid scintillation counters:

1. Internal standardization.
2. Determination of quench using the sample spectrum.
3. Determination of quench via an external γ -standard.
4. Other methods.

Please also read application note *Use and Preparation of Quench Curves in Liquid Scintillation Counting*. This explains in very detail the preparation of quench curves with a TriCarb liquid scintillation counter. One other method for DPM determination is the Direct DPM Method² which allows DPM calculations without the use of quench curves. Please read the corresponding application note for further details. A further application note is available for the Full Spectrum DPM Method³ (FS-DPM). For interested users of further methods the specialized literature is available with information about methods such as the CIEMAT-NIST method or the TDCR-method (Triple to double coincidence ratio).

Introduction

A range of methods is available in modern liquid scintillation

Internal Standardization

Using this method you first measure the unknown sample in a simple CPM protocol ($\text{cpm}_{(S)}$). After this first measurement you add a known amount of activity of a standard ($\text{dpm}_{(ST)}$) and count the sample again ($\text{cpm}_{(S+ST)}$). On the understanding that the counting efficiency for sample and standard is identical which means that the addition of the standard does not change the counting efficiency, the following equations can be used to determine the activity of the unknown sample:

$$\text{cpm}_{(S+ST)} = \text{cpm}_{(S)} + \text{cpm}_{(ST)} \quad (1)$$

$$\text{cpm}_{(ST)} = \text{dpm}_{(ST)} \cdot \text{counting efficiency} \quad (2)$$

Inserting equation (2) in (1) results in:

$$\text{cpm}_{(S+ST)} = \text{cpm}_{(S)} + \text{dpm}_{(ST)} \cdot \text{counting efficiency}$$

Transformation of the equation to get the efficiency results in:

$$\text{Efficiency} = \frac{\text{cpm}_{(S+ST)} - \text{cpm}_{(S)}}{\text{dpm}_{(ST)}}$$

With the known efficiency we can now calculate the activity of the sample:

$$\text{dpm}_{(S)} = \frac{\text{cpm}_{(S)}}{\text{Efficiency}}$$

This method results in very accurate measurements. However, this method has some practical disadvantages which explain why this method is rarely used. The method is time and labor consuming because each sample has to be measured twice. In addition, calibrated radioactive standards are expensive and the use of these standards for routine analysis in large sample series is not possible in most cases. In some cases, especially for low level customers who have small sample numbers in many cases, this method is preferred due to the accuracy. The main error is usually a small pipetting error.

Quench Correction Using the Sample Spectrum

In early scintillation counters neither multi channel analyzers nor spectral distributions of the sample were available. The LSC's (Liquid Scintillation Counter) could only use discriminators with two or three channels. Good window settings allowed the use of energy ranges with different influence of quench. This very first

method for quench correction using the sample spectrum was called channel ratio method.

Channel Ratio Method

This method is based on the fact that quench does not only reduce the counting efficiency but also results in a shift of the sample spectrum to lower energies. This means that the amount of shift to lower energies can be used to measure the quench level and the counting efficiency. The oldest and simplest method is the channel ratio method. This method is illustrated in Figure 1. Several standards with the same activity but different quench level are necessary (Table 1). For a precise quench curve you should better use more than just four standards. All standards will be measured in two channels, one open window (channel A) which includes the total energy range and one channel which only contains the upper energy range of the spectrum. As you can see in Figure 1 there is a significant shift of the spectrum towards lower energy with increasing quench in a way that the counting efficiency in channel B is much more influenced. As a result, the ratio of counts measured in channel B and A will decrease with increasing quench. Thus the channel ratio is a value to describe the amount of quench. Because we know the activity of the standards we can determine the counting efficiency for each standard in channel A from the cpm-value of the measurement. In a graph (quench curve) we can now display the counting efficiency as a function of the channel ratio. From this quench curve in Figure 1 we can now determine the efficiency of unknown samples using a measurement in two different windows to determine the channel ratio. The activity of the sample can now be calculated from the efficiency obtained from the quench curve and the CPM-value from the measurement in channel A.

Table 1. Measurement of standards for the channel ratio method.

Measurement of Standards for the Channel Ratio Method				
Sample	cpm(A)	cpm(B)	Channel Ratio	Efficiency in Channel A
Standard 1	51680	35200	0.675	0.76
Standard 2	43520	22848	0.525	0.64
Standard 3	23800	5950	0.250	0.35
Standard 4	13600	1360	0.100	0.20

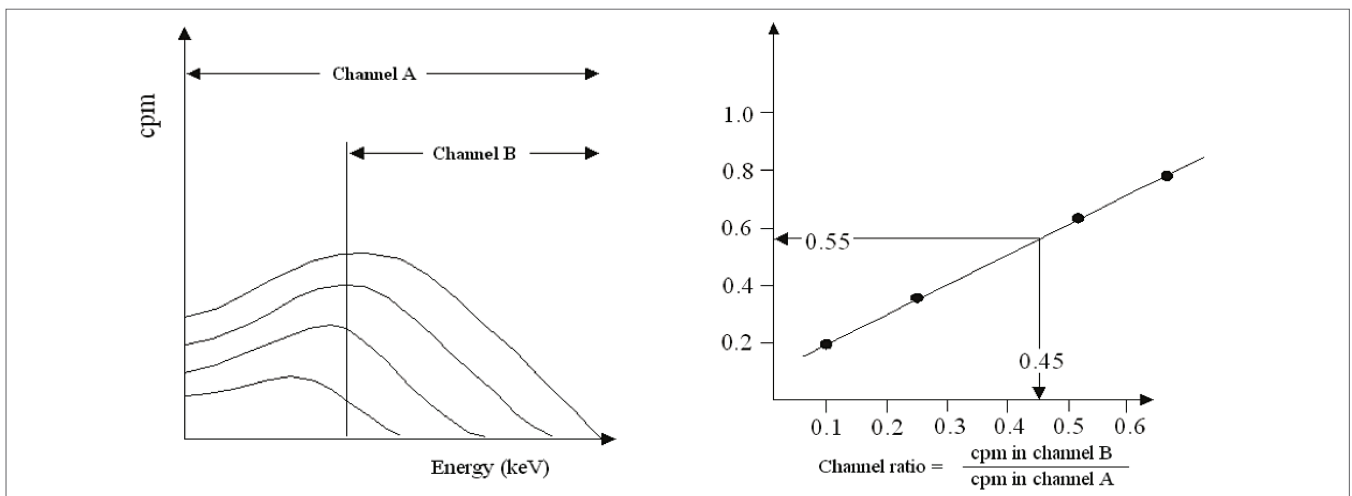


Figure 1. Principle of the channel ratio method.

In contrast to the external standard method each sample has to be measured only once with the channel ratio method and a quench curve that has been established can be used for a lot of samples. On the other hand the disadvantage of the channel ratio method is that samples with strong quench will only have a few counts in channel B which results in long counting times for results with good counting statistics. Another challenge is the optimization of the discriminator settings. In case you use a very low limit for the lower discriminator setting of channel B changes in the quench will only result in very small changes of the channel ratio. On the other hand if you use a very high energy discriminator setting for the lower limit of window B heavily quenched samples cannot be measured because the spectral endpoint might be before the lower limit of channel B. This means the method can only use a limited dynamic range.

In early LSC counters there was no way to avoid these disadvantages. Modern PC based systems now make full use of the total sample spectrum which offers additional possibilities for quench correction.

SIS (Spectral Index of the Sample)

With the introduction of the multi channel analyzer in liquid scintillation counters additional information about the radioactive sample was available. It was now possible to acquire and visualize the full spectral distribution of the sample for better quench evaluation. As a result of quench the spectrum will be shifted to lower energies. Would it be possible to present this energy shift in a single number it would be possible to use this value as a quench parameter.

One idea is to use the average kinetic energy to describe the quench level. The SIS-value represents the average kinetic energy of all measured β -particles.

$$SIS = K \frac{\sum_{x=0}^U x \cdot n(x)}{\sum_{x=0}^U n(x)}$$

The formula is the sum of all channels divided by the number of channels resulting in the average kinetic energy. The normalization factor K is chosen in a way that the SIS value will result in the endpoint energy of the corresponding energy distribution.

This is very helpful and gives a value that can be verified visually with the help of standard samples with known quench level. All measured pulses will be used to calculate the SIS-value in only one counting window. This eliminates one disadvantage of the channel ratio method. The difficult decision about the position and size of the two counting windows is not necessary anymore. However, the basic principle is still the same. Increasing quench will result in a shift of the spectrum to lower energies and thus to lower SIS-values. Counting standards of known activity will result in their SIS values which can be displayed with the corresponding efficiencies to get the quench curve in Figure 2:

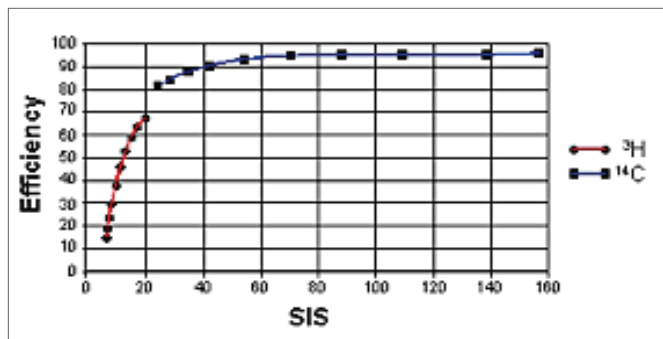


Figure 2. ^3H - and ^{14}C -quench curve with SIS quench parameter.

Once the SIS-value of the unknown sample has been determined from the sample spectrum, the efficiency can be obtained from the above quench curve which now allows the calculation of the activity in dpm-values.

The SIS-value was a significant improvement over the channel ratio method for the determination of the quench level because the setting of energy windows was much easier now. However, the SIS method is still based on the sample spectrum. All methods for quench correction which are based on the sample spectrum are of limited use for low activity samples. The reason is the bad counting statistics for such samples resulting in large errors. In addition the measurement and quantification of dual labeled samples with this method is not possible.

Quench Determination Using an External γ -Source

As already mentioned above, the external standardization is based on the use and analysis of a Compton spectrum resulting from a γ -emitter (^{137}Cs , ^{226}Ra , ^{152}Eu or ^{133}Ba). As soon as this γ -emitter comes into close proximity with the scintillation vial, interactions with vial and cocktail will produce Compton electrons. Compton electrons and the resulting Compton spectrum are in the same way influenced by quench phenomena as β -particles. This means that the energy shift of the Compton spectrum obtained from the external standard can be used to determine the quench in a sample.

Usually you need a series of standards with increasing quench. The standard series will then be measured with and without the external standard in close proximity to the sample. By subtraction of the pure sample spectrum from the spectrum measured with close proximity of the external standard we can obtain the pure Compton spectrum. The energy shift to lower energy will again be combined with a corresponding quench parameter. A graph of this quench parameter versus counting efficiency which can be obtained from the known activity of the standards, will result in a quench curve. A quench parameter determined for an unknown sample will give the efficiency of this sample and the corresponding activity using the graph just created.

Both the standard series as well as the external standard source have high activities resulting in good counting statistics which allow the accurate determination of quench levels even in samples with low activities. For the determination of activities in low level or dual label samples this is the method of choice.

Channel Ratio Method

The calculation of quench parameters based on the shift of the Compton spectrum can be analyzed with the channel ratio method in the simplest case. However, in this case we again have the same problem that we already discussed above. Especially the determination of the optimum channel settings can be laborious. In addition further problems can influence the channel ratio method. In case you use plastic vials the so called "Plastic Vial Effect" reduces the accuracy of DPM measurements. Diffusion of scintillation cocktail into the wall of the scintillation vial results in a plastic scintillator which can also emit Compton electrons. This results in a change of the Compton spectrum and in a change of the quench parameter. The degree of change depends on the time the scintillator has to diffuse into the plastic. In addition you can also observe a dependency of the channel ratio method on the volume of the sample in the LSC vial (volume effect).

Later other methods have been developed to reduce the influence of volume or plastic vial effect. One of the first attempts was the H-Number from Beckman.

H-Number (Horrocks Method)

The H-number uses the inflection point of the Compton edge of the logarithmic ^{137}Cs spectrum to determine a quench parameter. The aim of the H-value was to eliminate a problem present in all counters at that time namely the plastic vial effect. Figure 3 illustrates changes in the spectrum caused by the plastic vial effect. This was especially problematic for low level measurements with long counting times.

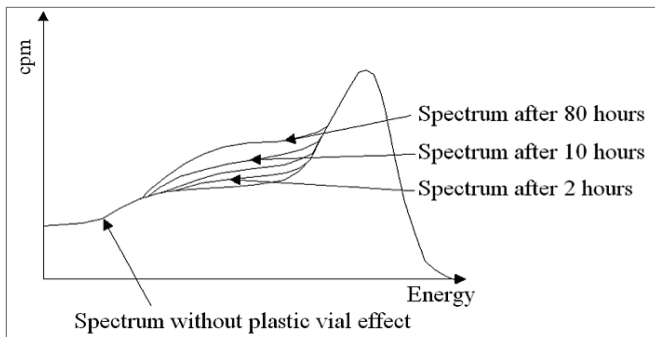


Figure 3. Plastic Vial Effect in case of logarithmic ^{137}Cs spectrum.

This effect is based on the diffusion of cocktail into the wall of the plastic vial. This results in the formation of a plastic scintillator and a change of the resulting spectrum. As long as the channel ratio method was the only available method this effect resulted in incorrect channel ratios in plastic vials and therefore in inaccurate DPM-values. To avoid this plastic vial effect in Beckman counters only one point at the end of the spectrum (Compton edge) was used to determine the quench parameter as illustrated in Figure 4. The plastic vial effect has almost no influence on this range of the spectrum and therefore the quench parameter is also independent from this effect.

This was a significant improvement over the channel ratio method; however it is difficult to exactly determine the position of the Compton edge.

Figure 4 explains the determination of the H-number. The logarithmic scaling of the higher energy range has much lower resolution and as a result it is necessary to determine the Compton edge very carefully. Consequently Beckman used 32000 channels in the H-plus number because a smaller number of channels resulted in large errors in the determination of the Compton edge and of the corresponding quench correction.

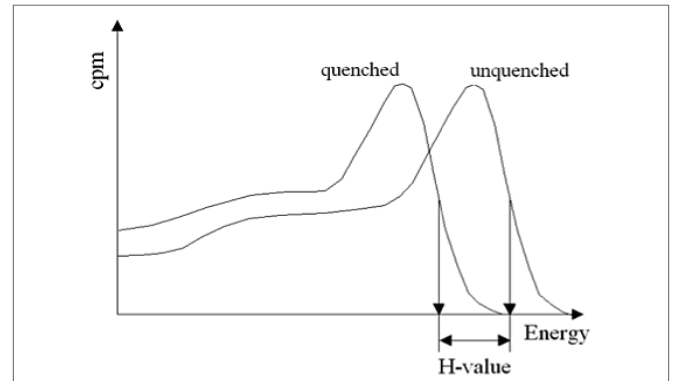


Figure 4. Determination of the H-number.

The difference in the position of the unquenched and quenched Compton edge reflected on the energy scale is called H-number. Therefore the H-number increases with increasing quench. Due to the high number of channels used for this method the number of counts in each channel is smaller compared to other methods and as a result it is necessary to use longer counting times to obtain acceptable statistical accuracy. Also the determination of the Compton edge is not very precise. Already very small deviations on the logarithmic scaling can cause significant errors in the determination of the quench level especially in cases of strong quench. In these cases the Compton edge is not only shifted to lower energy but also flattened which makes it more difficult to determine the inflection point.

SQP (E)-value (Spectral Quench Parameter of the External Standard)

Also counters from the company Wallac (today PerkinElmer) had the same problems with the plastic vial effect. In the first counters from Wallac ^{226}Ra was used as the external standard. In modern counters the SQP(E) parameter was used to decrease the plastic vial effect. This method uses the endpoint of the acquired ^{226}Ra spectrum (^{152}Eu in newer instruments) in a logarithmic scale to determine the quench. The endpoint is defined as the point of the spectrum that includes 99.5% of all counts as illustrated in Figure 5.

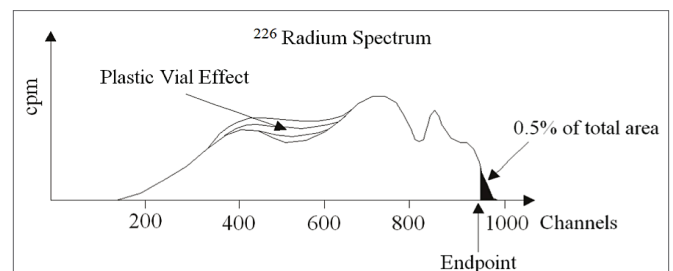


Figure 5. Determination of quench with the SQP (E).

However, the endpoint is not independent on the plastic vial effect. The point where we have accumulated 99.5% of all counts in the spectrum is dependent on the total spectrum which also includes the part with the spectral distortion due to the plastic vial effect. A stronger plastic vial effect will result in a stronger energy shift to lower energies of the SQP(E) value.

In order to further reduce the plastic vial- and volume effect the first 400 channels of the 1024 channel analyzer were excluded from the calculation of the activity. But this is only a reduction of the effect because part of the effect is also visible in higher channels.

In addition the exclusion of the first 400 channels reduces the dynamic range of this method and the statistical precision for samples with strong quench. Also the first 400 channels correspond to approximately 20 keV which makes it impossible to use this method for ^3H samples. Also a small volume dependency can be observed with the SQP(E) parameter.

SIE (Spectral Index of the External Standard)

Older Packard instruments (today PerkinElmer) used the SIE quench parameter (Spectral Index of the external Standard) based on the analysis of the ^{226}Ra Compton spectrum. This method used an average kinetic energy of the spectrum. Because the total spectrum was used to determine the quench parameter this method was also influenced by the vial effect. All methods mentioned so far have been significant improvements compared with the channel ratio method but did not offer the precision and accuracy necessary to fulfill highest demands. This was the reason for the development of the tSIE-method.

tSIE-Value (Transformed Spectral Index of the External Standard)

The tSIE-value can still be used at severe quench levels and is independent on plastic vial and volume effects and used in all current PerkinElmer Tri-Carb models.(B2810,B2910,B3110,B3180) In addition the used ^{133}Ba standard has a low energy which allows better quench correction for the quench critical low energy isotopes. The "Reverse Spectrum transform" is a summation of individual channels (each 0.5 keV) starting at the end of the Compton spectrum to calculate a transformed spectrum. In Figure 6 you can see a transformed Barium spectrum.

The quench parameter will now be determined with the two points P1 and P2 in the spectrum (Figure 7). P1 corresponds to the point where 20% of all counts of the transformed spectrum have been summed starting at the end of the spectrum. P2 will be calculated the same way but this point corresponds to 10% of the total area. A straight line connecting the points P1 and P2 will cross the energy axis in the point defined as the tSIE. By definition this point has a tSIE value of 1000 for an unquenched sample. Figure 7 explains how to determine the tSIE-value. Table 2 demonstrates the calculation of the transformed spectrum using the last channels of the ^{133}Ba Compton spectrum with the help of the reverse summation technique. Using this reverse summation technique the higher energy range without any influence from the plastic vial effect will get a significantly higher and over proportional weight compared to the total spectrum.

Although the tSIE also uses the total spectral distribution for the calculation of the quench level, the plastic vial effect has almost no influence anymore due to the strong weight of the higher energy range. The preparation of a quench curve will be done as usual. In a graph the quench parameters (tSIE) of a standard series will be displayed with the corresponding counting efficiencies as illustrated in Figure 8. Again, each sample has to be measured twice, with external standard and alone to calculate the pure Compton spectrum and the tSIE value of the corresponding sample. Also for unknown samples the tSIE value will be determined in the same way which will give the corresponding efficiency from the quench curve which allows calculating the activity from the CPM value obtained from the measurement of the instrument.

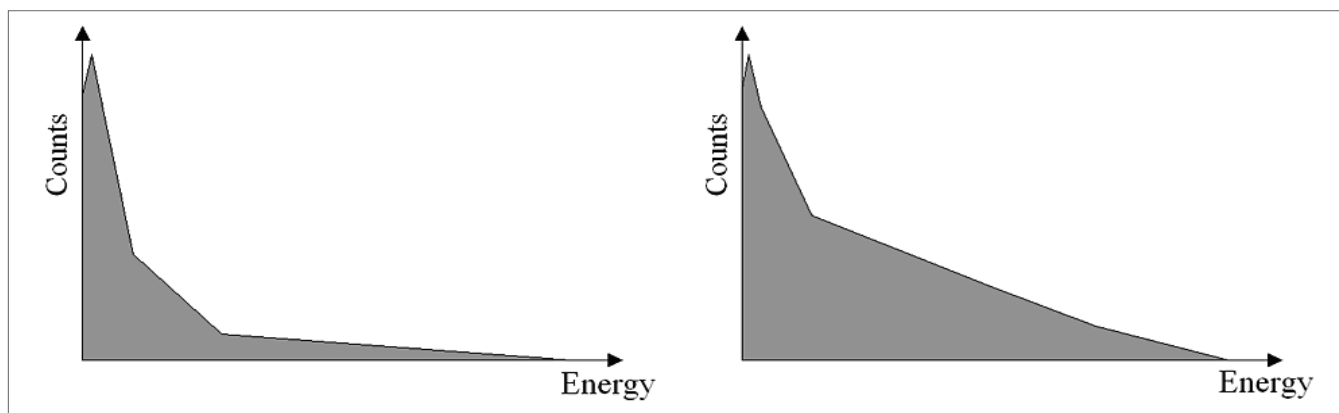


Figure 6. Normal (left) and transformed (right) ^{133}Ba -Compton spectrum.

Table 2. Calculation of the transformed spectrum with the tSIE-method.

Sum x_i+x_{i+1}	176	119	69	37	16	6	0
Counts in Channel x_i+x_{i+1}	57+119	50+69	32+37	21+16	10+6	6+0	0
Counts in Channel x_i	75	50	32	21	10	6	0
keV	277.0	277.5	278.0	278.5	279.0	279.5	280.0

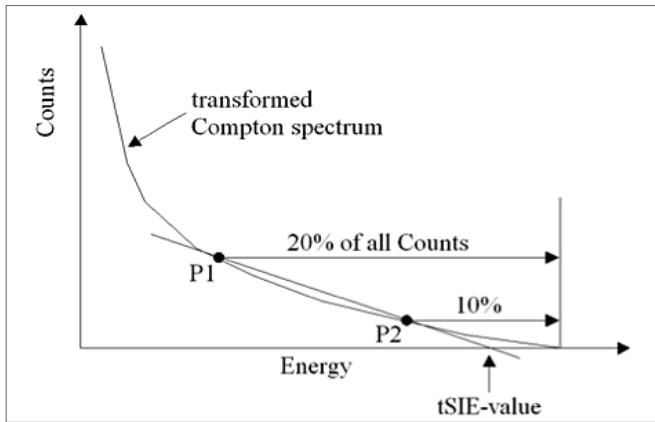


Figure 7. Determination of the tSIE-value with the transformed ^{133}Ba -Compton-spectrum.

The straight line between the two points P1 and P2 are comparable with a very sensitive long hand. With increasing quench this line is not only shifted to the left towards lower energies but also the slope of the line is increasing. This results in changes of the tSIE value even for small changes in the quench level. Therefore the tSIE-value is especially helpful for critical samples with strong quench and/or low activities and for dual and triple labeled samples.

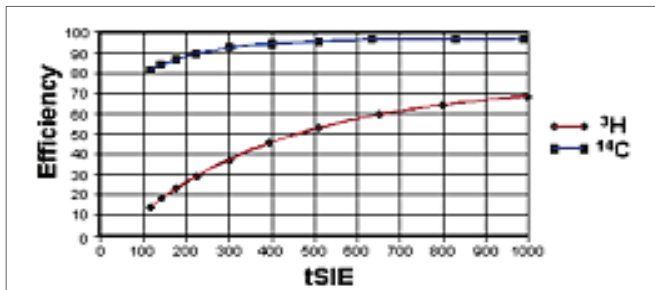


Figure 8. Quench curves for ^3H and ^{14}C using the tSIE as quench parameters for single labeled samples.

tSIE/AEC (transformed Spectral Index of the External Standard with Automated Efficiency Control)

This method uses the tSIE quench parameter but in addition a method to adapt the energy windows, especially for dual labeled samples, to the quench level. In dual labeled samples with strong quench and fixed energy windows increasing quench will result in increasing spill down of the higher energy nuclide into the window of the lower energy nuclide.

Especially in cases with a large excess of the higher energy nuclide the basic tSIE has limited possibilities to calculate correct quench levels for heavily quenched samples. The shift of energy windows depending on the quench level extends the dynamic range of the tSIE method significantly for samples with strong quench and for dual labeled samples.

Other Methods

Other methods include the "Direct DPM" and the "Full-Spectrum DPM". For a more comprehensive review of all existing methods including TDCR, CIEMAT-NIST, 4pbq-counting please read the available literature.

References

1. PerkinElmer (Germany) GmbH, 63110 Rodgau-Jügesheim, LSC Application Note, Use and Preparation of Quench Curves in Liquid Scintillation Counting, July 2004.
2. PerkinElmer (Germany) GmbH, 63110 Rodgau-Jügesheim, LSC Application Note, Efficiency Tracing and Direct DPM, July 2006.
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4. R. H. W. Edler, Eine Einführung in die Szintillationstechnik zur Messung von Radionukliden, in Vorbereitung (2009), ISBN-10: 3-00-020422-9, ISBN-13: 978-3-00-020422-7

The application note information enclosed is used to illustrate the technique and may not represent the latest instrument, reagents and cocktails. Customers should validate the technique in their laboratory. Contact Customer Care at www.perkinelmer.com/contact to find the current PerkinElmer instruments, reagents and cocktails.

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