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COMPARATIVE STUDY BETWEEN EXTERNAL STANDARD METHOD AND INTERNAL STANDARD METHOD FOR LOW-LEVEL TRITIUM MEASUREMENTS

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ABSTRACT

Quenching is always present in water samples and the degree of quenching can vary from one sample to another even within the same batch. This means that quench correction should be carried out for each sample in order to determine the activity so that comparisons can be made between samples and other batches.

In this paper, a comparative study of tritium measurements between two methods used to correct for quenching is presented. The methods used to determine counting efficiency in the presence of quenching are as follow: Spectral Quench Parameter of External standard method (SQP(E)) and Internal Standard Method.

In this work, a low background liquid scintillation system detector (Quantulus 1220) is used to determine tritium activity concentration in heavy water with different concentration from 99,66 D/H+D% to 1,65 D/D+H %.

A standard calibration curve for the SQP(E) technique has been carried out with ^{3}H low level quenched PACKARD standard set that had an assayed value of 29,240 dpm/std ± 1,6%. Quench correction for Internal Standard Method has been made for each sample of heavy water with Tritiated Water Internal Standard that had a tritium concentration of 2,51 x 10^6 dpm/g ± 3,0%.

A comparison between dilution factors, calculated both for D/(D+ H)% concentration and for tritium activity, measured by the two methods, is discussed in this paper.

Internal Standard Method provides accurate results especially for lower D/(D+H)% concentration, which is the environmental samples case.

Commercial standards set don't fulfill the exigency of an accurate environmental tritium measurement. It must consider the following problems: type of vial, type of scintillant, filled volume and counting geometry. Even if you make your own standard set for quenching calibration you must exceed another problem. The Compton electrons produced by external standard are energetic beta particles and do not have the same behavior of weak beta-particles in the sample itself. Hence a small amount quenching in tritium sample may remain undetected.

1 INTRODUCTION

Tritium analysis is useful in many areas such as nuclear industry monitoring, hydrogeology, dosimetry and health-risk assessment. Tritium occurring in the biosphere originates both from natural and anthropogenic sources. Natural tritium is produced in the atmosphere from the interaction of cosmic radiation with atmospheric gases. Anthropogenic production has disturbed the natural levels of tritium by nuclear weapons tests and, in addition, tritium is released into the atmosphere from weapons manufacturing, operation of nuclear power plants and reprocessing of nuclear fuels.

As tritium is a very soft beta-emitter (maximum energy is 18.6 KeV), the common methods for low-level counting of tritium are either liquid scintillation spectrometry or gas-proportional counting. When analyzing water samples, the measurement by liquid scintillation method offers numerous advantages over gas-proportional counting method: the water sample is directly combined with an appropriate aqueous-accepting scintillation cocktail; minimal sample pre-treatment is required, and the counting efficiency of liquid scintillation method is higher than that of gas-proportional counting.

Liquid scintillation analysis is mostly used for samples that contain only a single isotope, in our case - tritium, and the technique is not considered a spectroscopic but a counting method [1]. There is no spectrum analysis and the total number of counts, or actually the count rate expressed as counts per minutes (CPM), is reported. However, the method may still involve some spectrum analysis. This is because the CPM value may not be a constant fraction of the actual activity. This counting efficiency may vary from sample to sample due to varying degrees of quenching of the scintillation phenomenon.

In this paper, we propose a comparative study between two basic methods for determining the efficiency, using a low background liquid scintillation system detector (Quantulus 1220, Wallac). In order to test the methods, tritium levels were investigated in heavy water samples with different D/ (D+H)% concentration.

2 EXPERIMENT

2.1 Method

In liquid scintillation measurement of tritium, as with most other techniques for measuring radioactivity, efficiency is normally less than 100 per cent and depends on physico-chemical nature of sample. It is necessary to know the value of efficiency in order to determine the absolute activity of sample, or to compare the activities of samples which are counted with different efficiencies. Ideally, conditions under which the measurement efficiency is constant for all types of samples are desirable, but in practice this has not been achieved; one reason being the variation in degree of quenching for different samples, and the efficiency for each measurement must be determined.

There are mainly four different types of quenching that may occur in the mixture: absorption or physical quenching, chemical quenching, photon or color quenching and solvent dilution quenching. All four may result in a different relationship between a measured quench index and counting efficiency. An important step in liquid scintillation counting is to determine the amounts of some or all of these quenching modes and to make corrections or adjustments based on the determined amounts [2]. Quench monitoring is the first instance where spectrum analysis is needed.

The counting efficiency E, as a percentage, is defined in Eq. (1), as the ratio of the number of observed counts to the number of disintegrations occurring in the sample:

$$E = CPM/DPM \times 100\% \qquad (1)$$

Due to the varying amounts of quench in each sample, most counters today are equipped with an automatic method to determine the counting efficiency for each sample separately. There are two basic methods available for Quantulus 1220:

a. Internal standard method – After counting the sample, a known amount of non-quenching radioactive standard is added and the sample recounted. The efficiency is then calculated from Eq. (2) [3, 4]:

$$E = (C_S{}' - C_s) / D_s \qquad (2)$$

Where $C_S{}'$ = counts recorded for the combined standard and sample,

C_s = counts recorded for the sample,

D_s = calculated disintegration rate of the standard.

The activity of the added standard should generally be much greater than that of the sample for good statistics. Quenching is automatically corrected if one makes the reasonable assumption that the standard is quenched to the same extent as the sample. Note however that this procedure does not correct for other effects such as chemiluminescence.

b. External standard method – When a scintillation solution is subjected to gamma-rays, a spectrum of Compton electrons is generated within the solution. The external standardization technique depends on the use of a gamma-radiation source (e.g. Europium-152) to generate a spectrum of Compton electrons within the sample vial. These Compton electrons behave as beta-particles in solution and quenching in the sample results in a proportionate quenching of the Compton electrons. The counting efficiency is mostly expressed as a function of a spectrum quench parameter SQP, e.g. as a polynomial:

$$E = A_0 + A_1\, SQP^2 + A_1\, SQP^3 + \ldots \qquad (3)$$

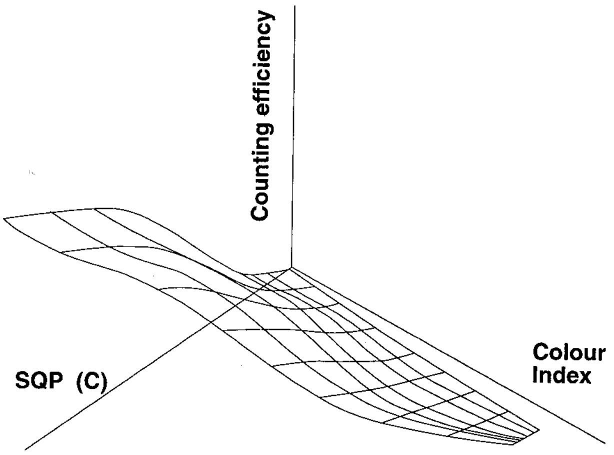


Figure 1: Surface function for counting efficiency in liquid scintillation counting.

Eq. (3) describes a two-dimensional curve. In other counters, the basic counting efficiency function is not a curve but a three-dimensional surface (fig.1) as two spectrum quench parameters are used: the quench index of the external standard SQP(E), and the colour quench index, CI [2]. Hence the efficiency can be calculated according to Eq. 4:

$$E = F[SQP(E), CI] \qquad (4)$$

where F denotes a surface function.

By introduction of the dynamic colour monitor and correction, the external standard quench index became a function of three parameters: p, r, and a.The parameter *p* was equal to the 99% end-point of the external standard spectrum, *r* was equal to the colour index determined by using the external standard and the left-right pulse comparator to establish pulse amplitude disparity and *a* was a volume correction factor determined from the total intensity of the external standard. Finally, the counting efficiency was a spline function of SQP(E), and that is the function used in Quantulus standardization procedure to obtain the calibration curve for tritium quenched standard set.

2.2 Equipment and Materials

A low-level liquid scintillation system Quantulus 1220 (Wallac, Turku, Finland) was used. The detector background is reduced by means of a passive shield (made of lead, cadmium and copper) and an active shield (based on mineral oil scintillator) around the vial chamber. Low activity materials were used in its construction. The system is provided with two pulse analysis circuits that are accessible to the user: a pulse shape analysis (PSA) and a pulse amplitude comparator (PAC) circuit. In order to correct for chemiluminescence, Quantulus 1220 was provided with a delayed coincidence circuit (DCOS). Delayed coincidence pulses are routed to a multi-channel analyzer (MCA), and stored as the chemiluminescence spectrum. The rest of the pulses are routed to a second MCA which is stored as the tritium spectrum. Quenching was quantified with the standard quenching parameter, SQP(E), which was used to determine the counting efficiency for each sample through calibration curves [5].

There were used 20 mL polyethylene vials from Wallac and high capacity cocktails, OptiPhase Hisafe 3 and Ultima Gold LLT.

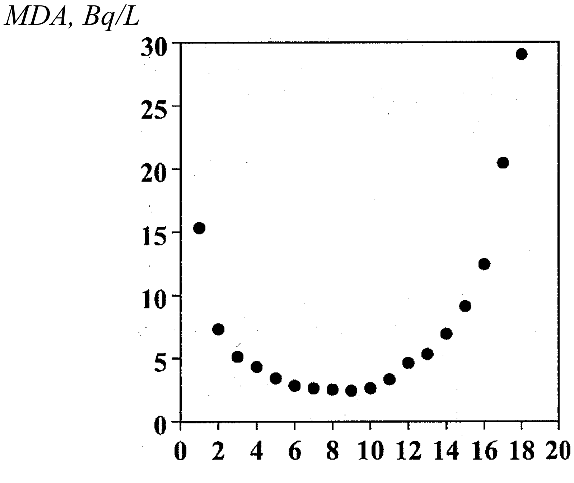


Figure 2: MDA for tritium as a function for sample volume (total volume is kept to 20mL).

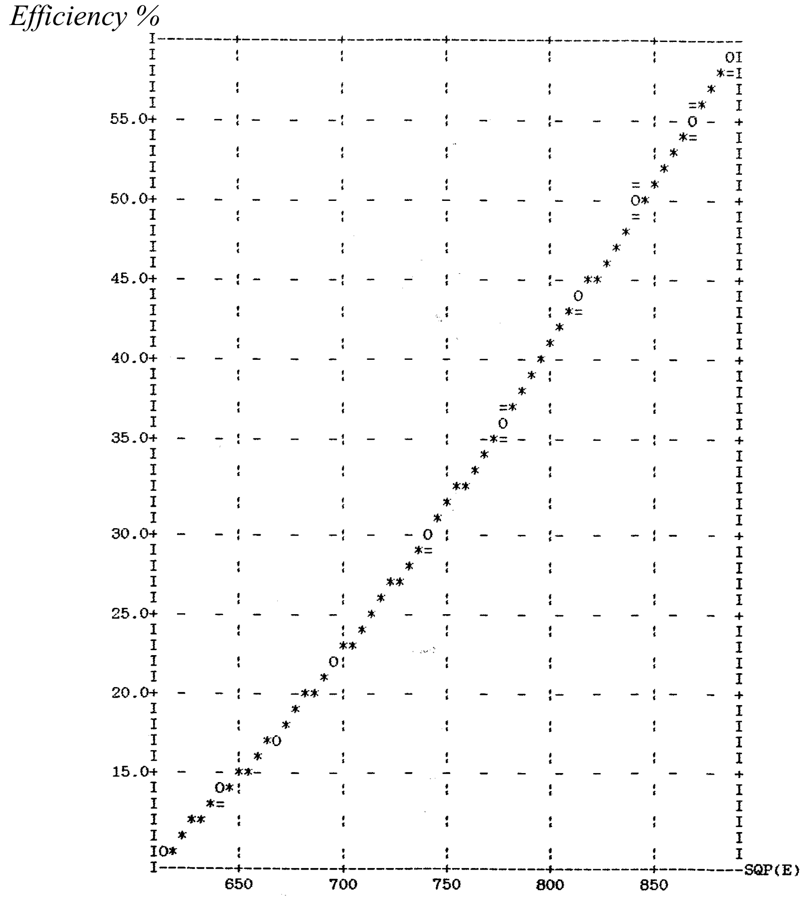
The optimum sample:scintillant ratio was determined, using the total available vial volume of 20 mL. For this, we calculated the minimum detectable activity [6], (MDA) for different ratios of tritiated water and cocktail. The optimum sample volume was found to be 9 mL (Fig. 2), which is about the highest holding capacity of cocktails used in this work for distilled water [7]. However, as environmental samples may induce phase separation, we decide to use a much conservative ratio, 8:12. The same ratio is used by other authors [8].

Quench correction for Internal Standard Method was made for each sample of heavy water with Tritiated Water Internal Standard that had a tritium concentration of 2,51 x 10^6 dpm/g ± 3,0% (reference date December, 1998).

To obtain the heavy water sample with different concentration we start from 99.66 D/(D+H) % heavy water concentration, and by dilution method we obtain the amount needed for the three types of measurement: infrared spectroscopy, liquid scintillation counting by internal and external standard methods.

3 RESULTS

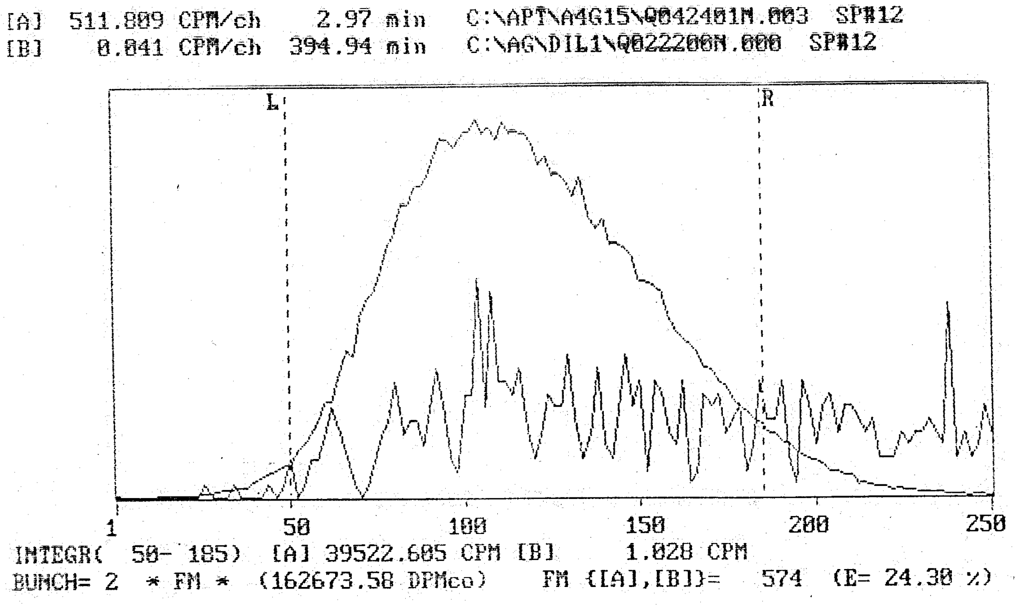
Standard calibration curve was carried out with ^{3}H low level quenched Packard standard set, with an assayed value of 29,240 dpm/std ± 1,6% (Fig. 3). Heavy water samples prepared to be measured by SQP(E) technique used Ultima Gold LLT liquid scintillation cocktail.



Useful SQP(E) range: 614 – 884

Figure 3: Quench standard curve for ten standard points fitted by smooth spline calculation method

For Internal standard method we used the automatic program of Quantulus 1220, Spectrum Analysis Program to calculate the efficiency, optimum window for maximum figure of merit, and the tritium concentration in heavy water samples. It is illustrated in Fig.4 and Fig.5 the automatic calculation of efficiency and tritium concentration activity for 99,66 D/(D+H) % heavy water concentration.

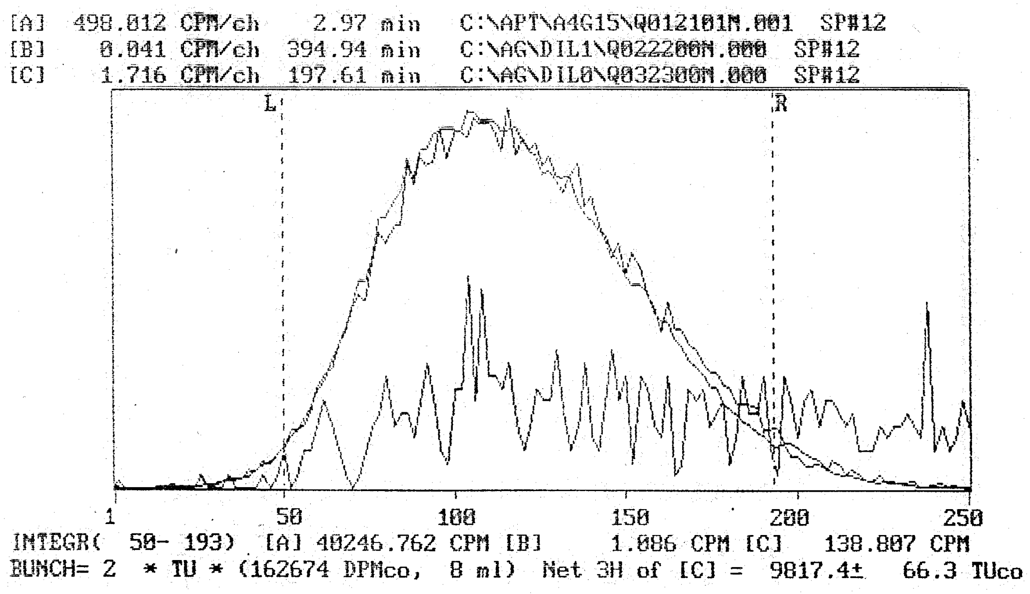


```
[A]  511.809 CPM/ch    2.97 min   C:\APT\A4G15\Q042401M.003  SP#12
[B]    0.041 CPM/ch  394.94 min   C:\AG\DIL1\Q022200M.000  SP#12
```

```
INTEGR(  50- 185)  [A] 39522.605 CPM [B]     1.028 CPM
BUNCH= 2  * FM *  (162673.58 DPMco)    FM {[A],[B]}=   574  (E= 24.30 %)
```

Figure 4: Efficiency determination by internal standard method of 99.66 D/(D+H) % heavy water

The three spectrums shown in figure 5 represent the sample and tritiated water mixture spectrum and the background spectrum. During the measurements, background was around 1 CPM.

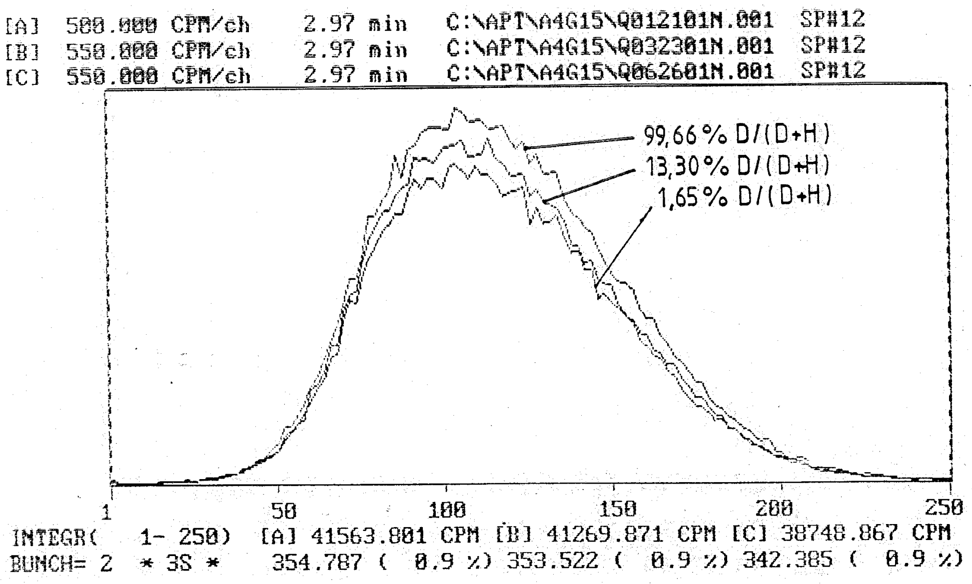


```
[A]  498.012 CPM/ch    2.97 min   C:\APT\A4G15\Q012101M.001  SP#12
[B]    0.041 CPM/ch  394.94 min   C:\AG\DIL1\Q022200M.000  SP#12
[C]    1.716 CPM/ch  197.61 min   C:\AG\DIL0\Q032300M.000  SP#12
```

```
INTEGR(  50- 193)  [A] 40246.762 CPM [B]     1.086 CPM [C]   138.807 CPM
BUNCH= 2  * TU * (162674 DPMco,  8 ml)  Net 3H of [C] =  9817.4±   66.3 TUco
```

Figure 5: Determination of tritium activity concentration in 99.66% D/(D+H)% heavy water

Studying spectrums obtained for the mixture of internal standard and different concentration of heavy water, Fig. 6, we observe a left shift spectrum and a decreasing of counting rate. The action of the dilution is the same like a quenching agent.



```
[A]  500.000 CPM/ch     2.97 min   C:\APT\A4G15\Q012101N.001  SP#12
[B]  550.000 CPM/ch     2.97 min   C:\APT\A4G15\Q032301N.001  SP#12
[C]  550.000 CPM/ch     2.97 min   C:\APT\A4G15\Q062601N.001  SP#12
```

```
INTEGR(   1- 250)  [A] 41563.801 CPM [B] 41269.871 CPM [C] 38748.867 CPM
BUNCH= 2  * 3S *    354.787 (  0.9 %) 353.522 (  0.9 %) 342.385 (  0.9 %)
```

Figure 6: Left shift spectrum and decreasing of counting rate for tritium concentration in different heavy water samples

To compare the two method described above we measured a number of seven samples, obtained by dilution, to determine tritium concentration activity. In table 1 is shown the results.

Table 1: Dilution factors comparison of tritium and deuterium. Experimental values with uncertainty reported ± 1σ.

Sample	Infrared spectroscopy. Densimetry		Liquid scintillation counting Internal Standard Method		Liquid scintillation counting External Standard Method	
	D/(D+H)% concentration	Dilution factor for Deuterium	TU	Dilution factor for Tritium	Tritium Activity TU	Dilution factor for Tritium
G1	99.66± 0.005	-	9817.1 ± 62.5	-	9719.9 ± 65.0	-
G2	51.32 ± 0.02	1.9419	5026.3 ± 44.2	1.9531	4993.7 ± 47.3	1.9464
G3	26.36 ± 0.02	3.7807	2455.6 ± 30.9	3.9974	2312.8 ± 32.1	4.2026
G4	13.30 ± 0.02	7.4932	1272.9 ± 17	7.7123	1115.7 ± 18.2	8.7119
G5	6.30 ± 0.02	15.8191	639.5 ± 12.5	15.3512	587.4 ± 14.0	16.5473
G6	3.30 ± 0.02	30.2	351.7 ± 10	27.9132	301.7 ± 11.0	32.2171
G7	1.65 ± 0.02	60.4	164.2 ± 7.3	59.8603	127.3 ± 8.3	76.3542

For our counting conditions (8 ml of sample with 12 ml of scintillation cocktail, counting window from channels 50 to 200, background 0.8 – 1 CPM), the best match between dilution factors is for that obtained by internal standard method. Tritium values for pure heavy water sample measured by the two methods are in the uncertainty reported range (G1), but if we compare the values from the samples that contain less deuterium, the differences are noticeable. External standard method is not so sensitive to the amount of water in the sample because the efficiency of the measurement was around 29 %. Internal standard method has a wide range of efficiency values, from 24.31% for G1 to 22.80 % for G7 (which is mostly a water sample, and contains only 1.65 D/(D+H) % heavy water). The value of efficiency isn't discussed here because there are different liquid scintillation cocktails involved in this study, but we discuss the sensitivity of the two methods. This lack of sensitivity for external standard method can be explained by two reasons:

- The basic process, which produces Compton electrons is the interaction of gamma-ray photons with the planetary electrons of atoms, and is mass dependent. Therefore the process, as used in liquid scintillation measurements, is dependent upon the volume of the sample. The filled volume for Packard standard set is 15 ml.
- The Compton electrons produced by external standard are energetic beta-particles and do not mimic exactly the behavior of weak beta-particles in the sample itself. Hence a small amount of quenching in a tritium sample may remain undetected (e.g. tritium values for G5, G6 and G7 samples).

4 CONCLUSION

Internal Standard Method provides accurate results especially for lower D/(D+H)% concentration, which is the case of environmental samples.

Commercial standards set don't fulfill the exigency of an accurate environmental tritium measurement. The following problems must be considered: type of vial, type of scintillate, filled volume and counting geometry. Even if you make your own standard set for quenching calibration you must exceed another problem. The Compton electrons produced by external standard are energetic beta particles and do not have the same behavior of weak beta-particles in the sample itself. Hence a small amount quenching in tritium sample may remain undetected.

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