

Chapter 19

A New Method of Quench Monitoring in Liquid Scintillation Counting: The H Number Concept^a

Donald L. Horrocks*

Scientific Instruments Division, Beckman Instruments, Inc., Irvine, CA 92713, U.S.A.

INTRODUCTION

The liquid scintillation system is what is commonly called a 'proportional response' system. The response produced (pulse height) is proportional to the energy, from the radionuclide transformation, that is absorbed by the liquid scintillation system. For electron excitation, it has been demonstrated that the response is directly proportional to the electron energy or, at least, to the amount of the electron energy which is dissipated in the liquid scintillation media.

The loss of kinetic energy of the electron (β -particle, conversion electron, Compton electron, etc.) produces excited molecules in the liquid scintillation medium through direction excitations, ionization followed by ion recombination, secondary electrons, and other processes. The excited molecules created in this primary interaction are excited solvent molecules. Excited solvent molecules are not good scintillators. Therefore, small amounts (3-5% by weight) of very efficient fluorescers (solutes) are added. At the proper concentration of these solutes, the excitation energy migrates and transfers, essentially quantitatively, from the solvent molecules to the solute molecules producing excited solute molecules. These excited solute molecules then emit photons (one photon per excited molecule). The number of photons emitted is proportional to the energy of the electron which was stopped within the medium.

The photons are transmitted through the scintillation medium escaping through the walls of the sample container (bottle or vial). From this point on, the light detectors (multiplier phototubes and light guide optics) and electronic system determine the response produced. The photons are collected by a special light collection system onto the face of two multiplier phototubes. The photocathode of the multiplier phototube absorbs a fraction of the photons (quantum efficiency) using that absorbed energy to release electrons from the inside surface of the photocathode. The number of electrons is proportional to the number of photons which strike the face of the multiplier phototube. These electrons, called photoelectrons, are accelerated and focused onto a dynode material which has the property of producing an average of four electrons for each electron which strikes the dynode. These four electrons are then accelerated to a second dynode, and again, each electron releases four electrons giving a total of 16 electrons leaving the second dynode. This process continues through the total number of dynodes of the multiplier phototube. For a ten dynode tube, the total gain would be

$$\text{Gain} = 4^{10} = 1.05 \times 10^6$$

or a total of one million electrons are created for each electron emitted from the photocathode.

^a D.L. Horrocks, patent pending.

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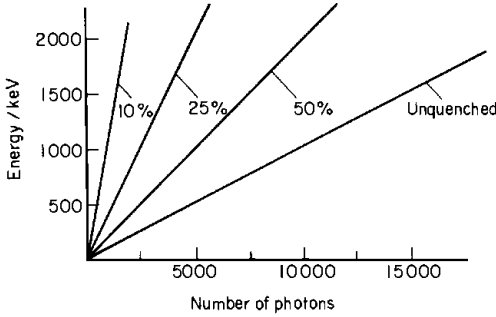


Fig. 1

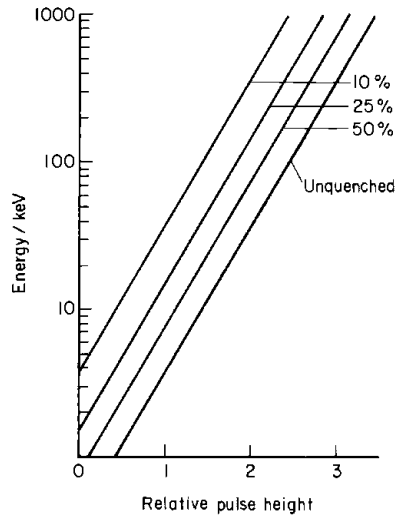


Fig. 2

Fig. 1 Relative quench effect on the photon yield for different electron energies.
 Fig. 2 Relative quench effect on the relative logarithmic response for different electron energies.

Table 1 Relative photon yields as function of electron energy for different amounts of quench.

Electron energy/keV	Relative number of photons produced when sample quench level is			
	Unquenched	50%	25%	10%
1	10	5	2.5	1
18	180	90	45	18
156	1 560	780	390	156
500	5 000	2 500	1 250	500
1 000	10 000	5 000	2 500	1 000
1 710	17 100	8 550	4 275	1 710

Table 2 Relative logarithmic response as a function of electron energy at different quench levels.

Electron energy/keV	Relative logarithm response when sample quench level is			
	Unquenched	50%	25%	10%
1	0.447	0.146	-0.155	-0.553
18	1.702	1.401	1.100	0.702
156	2.640	2.339	2.038	1.640
500	3.146	2.845	2.544	2.146
1 000	3.447	3.146	2.845	2.447
1 710	3.680	3.379	3.078	2.680
Difference	0.30103	0.30103	0.39794	

A constant fraction of the electrons from a single event are collected on the anode of the multiplier phototube, and an electronic circuit integrates the current producing a voltage pulse which is proportional to the total number of electrons produced by the single event.

The voltage pulses from each multiplier phototube of the pair are used to distinguish between real events and random noise. The coincidence circuit will produce a gating pulse for every time that pulses are produced in each multiplier phototube within the resolving time of the system ($15-20 \times 10^{-9}$ s). The voltage pulses from the two multiplier phototubes are also summed to give a truer pulse height representation of the event and to provide a better signal-to-noise ratio.

In commercially available liquid scintillation systems, most factors which determine the measured response for any event are constant. The only variable factor is the response created in the sample itself. Each sample can have varying numbers of photons for equal energy input because of different amounts of 'quench'. Quenching is defined as any process which reduces the number of photons observed for a given amount of energy input to the liquid scintillation solution. The two main types of quenching are:

- (a) Impurity — which reduces the number of photons produced.
- (b) Color — which reduces the number of photons through optical absorption of a fraction of the photons produced. The effect of color quenching is dependent upon the pathlength and the optical density and concentration of the absorbing material.

Within a given liquid scintillation sample, the quenching process(es) are proportional, i.e. if any energy event has a 50% reduction in photon yield, every energy event will have a 50% reduction in photon yield. If all other factors are constant (i.e. MPT gain, electronic amplification, etc.), then the measured response will be reduced by the same fraction. Figure 1 shows the response vs. energy relationships for liquid scintillation samples with different amounts of quench relative to an unquenched sample. The same data are shown in Table 1.

Some commercial liquid scintillation systems (e.g. the Beckman LS-8000 Series) utilize the logarithmic response relationship. In these systems, the pulse height response is converted into a new pulse height response equal to the logarithm of the initial pulse height. This conversion makes it possible to handle pulses that initially differ by a factor of 1000 to 1 in pulse height with a single amplifier and pulse height analyzer.

The effect of quench on the measured pulse height response relationships for a logarithmic system are listed in Table 2, and shown graphically in Fig. 2. It will be noted that a 50% reduction of photon yield due to quenching leads to a constant difference of 0.30103 (the logarithm of 2) between the relative logarithmic response relationships.

THEORY

Compton scattering

For some time it has been common practice to utilize a γ -emitting radionuclide external to the sample to measure the response of liquid scintillation sample mixtures. The response can be calibrated through the use of a set of samples containing a known amount of a given radionuclide but with different levels of quench. The 'quench curve' is a plot of the counting efficiency of the sample containing radionuclide vs. the response produced by the external γ -ray radionuclide on that same sample. Samples with unknown amounts of this radionuclide are then calibrated by measuring the response produced by the external γ -ray radionuclide and calculating the counting efficiency from the quench curve. In this manner, all samples, regardless of their quench level, are corrected to a common quench level for comparison of relative amounts of the radionuclide in different samples.

Gamma-rays interact with matter in one of three ways: (1) pair production, (2) Compton scattering, or (3) photoelectric effect. Figure 3 shows the relationship between the relative probability of these three types of interactions as a function of the energy of the γ -rays. The process of pair production has an energy threshold of 1.02 MeV (twice the energy equivalent of the rest mass of an electron). Any γ -ray of energy

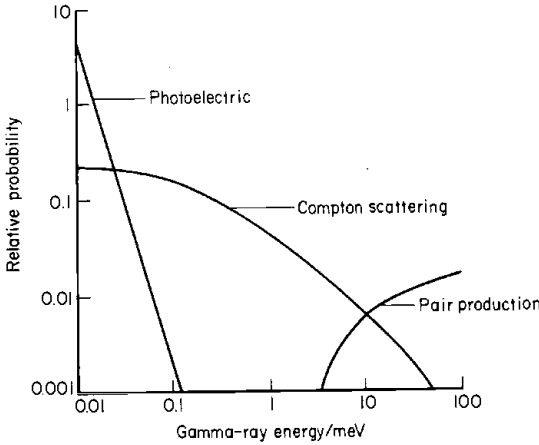


Fig. 3

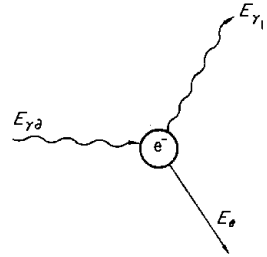


Fig. 4

Fig. 3 Relative probabilities of pair production, Compton scattering, and photoelectric effect as a function of γ -ray energy.

Fig. 4 Diagram of the Compton scattering process for γ -ray of energy E_{γ_0} .

less than 1.02 MeV cannot interact with matter by the process of pair production. At the other end of the energy scale, the photoelectric effect is predominant only at γ -ray energies below 20 keV. Compton scattering is the predominant mode of interaction for γ -rays with energies between 20 keV and 10 MeV. Thus by choosing the γ -emitting radionuclide to have γ -ray energies between 0.1 and 3.0 MeV, the Compton scattering process will be the predominant mode of interactions of the γ -rays with the interacting media (in this case, the liquid scintillation solution).

The Compton scattering process is independent of the scattering media. The γ -rays collide with essentially free electrons in the media imparting part of their kinetic energies to the electrons. This results in scattered γ -rays of energies less than the initial γ -ray energy, E_{γ_0} . Total energy (and momentum) is conserved:

$$E_{\gamma_0} = E_e + E_{\gamma_1} \tag{1}$$

where E_e is the energy of the scattered electron and E_{γ_1} is the energy of the scattered γ -ray. The Compton scattering process is shown diagrammatically in Fig. 4.

The division of the energy E_{γ_0} between E_e and E_{γ_1} is only a function of the angle at which the γ -ray collides with the electron. The number of scattering events is a function of the γ -ray flux and the number of electrons (electron density) in the scattering medium.

Because of their difference in mass (essentially zero for the γ -ray and 5.486×10^{-4} amu for the electron) the γ -ray will never impart its total energy to the electron. A maximum amount of energy, E_{max} , will be transferred to the electron for a direct head-on collision with the γ -ray scattered at 180° and retaining the residual amount of energy ($E_{\gamma_0} - E_{\text{max}}$). The value of E_{max} is given by the expression

$$E_{\text{max}} = \frac{\left(2 E_{\gamma_0} \right)^2}{2 E_{\gamma_0} + 0.51} \tag{2}$$

Table 3 Values of E_{-max} for different γ -ray energies, E_{γ_0} .

E_{γ_0}	E_{-max}
0.356	0.207
0.510	0.340
0.662	0.478
1.280	1.067
2.750	2.517

where energies are expressed in MeV and 0.51 MeV is the energy equivalent of the electron at rest. It is evident, from Eqn. 2, that the value of E_{-max} is only dependent upon the energy of the γ -ray, E_{γ_0} . Table 3 lists the values of E_{-max} for several

E_{γ_0} values.

The probability of any value of E_{-e} is equal up to the value of E_{-max} . Thus a theoretical plot of the number of scattered electrons of given energy vs. the energy of the scattered electron would be represented by Fig. 5. There will be no electrons of energy greater than E_{-max} . (This fact is predicated in the assumption that only a single Compton scattering per γ -ray will occur.)

Pulse height response

The measured distribution of Compton scattered electrons will be different from the theoretical distribution because no detection system is theoretically perfect. Any detection system (including a liquid scintillation system) will produce a spread of responses for the same energy event which is detected by that system. Figure 6 shows the distribution of pulses from a liquid scintillation solution for detection of essentially monoenergetic electrons. Electrons of 0.369 MeV energy from ^{113m}In are measured for a source of ^{113m}Sn - ^{113m}In (as an organic complex) dissolved in a liquid scintillation solution. The pulse height spectrum was obtained on a Beckman liquid scintillation system with logarithmic response (i.e. the linear pulse height response

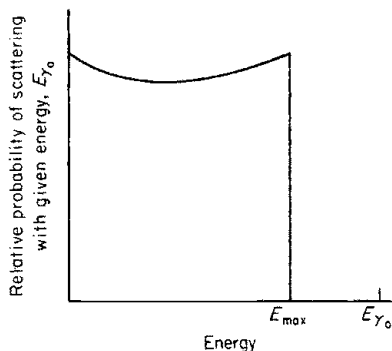


Fig. 5 The number of Compton scattered electrons of given energy for γ -ray of energy E_{γ_0} .

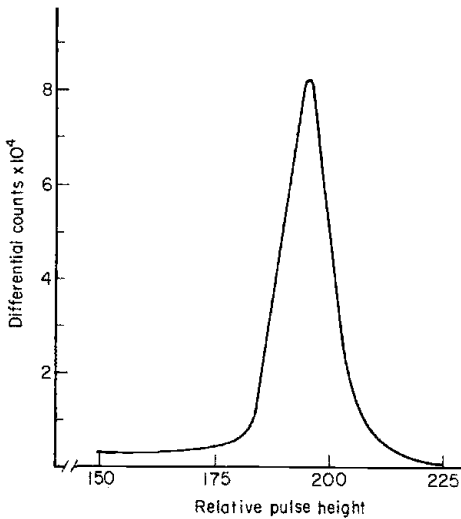


Fig. 6

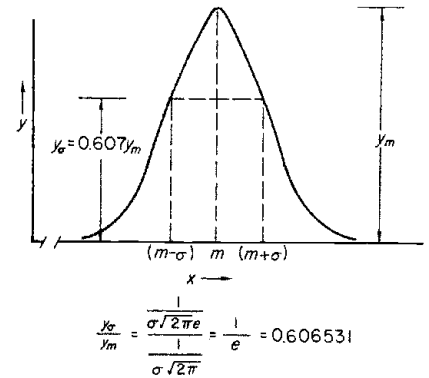


Fig. 7

Fig. 6 Pulse height distributions for 0.369 MeV electrons from ^{113m}In in a liquid scintillation system.

Fig. 7 Gaussian distribution plot of y vs. x showing the relationships for the values of σ , y_m and y .

is converted to a pulse height proportional to the logarithm of the linear pulse height response).

Since the spread of pulse height responses is statistically random, the distribution can be described by the equation for a Gaussian distribution:

$$y = (\sigma\sqrt{2\pi})^{-1} \exp [-(x - m)^2 / 2\sigma^2] \quad (3)$$

where the terms of the equation are illustrated in Fig. 7.

From Eqn. 3 several relationships can be derived. First it is necessary to define the term σ as the variance of the Gaussian distribution and 0.6827 of the total area of the distribution will fall between values of x equal to $(m - \sigma)$ and $(m + \sigma)$. (In measurement of radioactivity rates, σ is referred to as the standard error.) At the values of x equal to $(m + \sigma)$ a Gaussian distribution has some unique properties which are not repeated at any other x values. The first derivative (or slope) of the equation gives a maximum value at x equal to $(m + \sigma)$:

$$\frac{dy}{dx} = \frac{-2(x - m) / 2\sigma^2}{\sigma\sqrt{2\pi}} \exp [-(x - m)^2 / 2\sigma^2] \quad (4)$$

Substituting $x = (m + \sigma)$ gives

$$\frac{dy}{dx} = + [\sigma^2 \sqrt{2\pi e}]^{-1} \text{ (a maximum)} \quad (5)$$

Substitution of any other value of x will give a value of dy/dx less than this.

Further, the second derivative (slope of the slope) gives a value of zero at the values of \underline{x} equal to $(\underline{m} \pm \sigma)$:

$$\frac{d^2 \underline{y}}{d\underline{x}^2} = \left(\frac{-2 (\underline{x} - \underline{m}) / 2 \sigma^2}{\sigma \sqrt{2\pi}} \right) \left(\frac{-2 (\underline{x} - \underline{m})}{2 \sigma^2} \right) \exp [-(\underline{x} - \underline{m})^2 / 2 \sigma^2] + \left(\frac{-2 / 2 \sigma^2}{\sigma \sqrt{2\pi}} \right) \exp [-(\underline{x} - \underline{m})^2 / 2 \sigma^2] \tag{6}$$

Substituting $\underline{x} = (\underline{m} + \sigma)$ gives

$$\frac{d^2 \underline{y}}{d\underline{x}^2} = \left(\frac{-2 \sigma / 2 \sigma^2}{\sigma \sqrt{2\pi}} \right) \frac{-2}{2 \sigma^2} \underline{e}^{-\frac{1}{2}} + \left(\frac{-2 / 2 \sigma^2}{\sigma \sqrt{2\pi}} \right) \underline{e}^{-\frac{1}{2}} = ([\sigma^3 \sqrt{2\pi}]^{-1} - [\sigma^3 \sqrt{2\pi}]^{-1}) \underline{e}^{-\frac{1}{2}} = 0 \tag{7}$$

Similarly, $d^2 \underline{y}/d\underline{x}^2 = 0$ upon substituting $\underline{x} = (\underline{m} - \sigma)$.

And finally the value of \underline{y} at \underline{x} equal to \underline{m} is

$$\underline{y}_{\underline{m}} = [\sigma \sqrt{2\pi}]^{-1} \tag{8}$$

The value of \underline{y} at \underline{x} equal to $(\underline{m} \pm \sigma)$ is

$$\underline{y}_{\sigma} = [\sigma \sqrt{2\pi}]^{-1} \underline{e}^{-\frac{1}{2}} \tag{9}$$

The ratio of $\underline{y}_{\sigma} / \underline{y}_{\underline{m}}$ will be equal to

$$\frac{\underline{y}_{\sigma}}{\underline{y}_{\underline{m}}} = \frac{[(\sigma \sqrt{2\pi})^{-1}] \underline{e}^{-\frac{1}{2}}}{(\sigma \sqrt{2\pi})^{-1}} = 0.606531 \tag{10}$$

Thus for any Gaussian distribution, the value of \underline{y} for which $d^2 \underline{y}/d\underline{x}^2$ is equal to zero is \underline{y}_{σ} or

$$\underline{y}_{\sigma} = 0.606531 \underline{y}_{\underline{m}} \tag{11}$$

The distribution plotted in Fig. 6 is replotted in Fig. 8 along with plots of $d\underline{y}/d\underline{x}$ and $d^2 \underline{y}/d\underline{x}^2$. It will be noted that $d\underline{y}/d\underline{x}$ gives a maximum value at \underline{x} equal to about 200. The value of $d^2 \underline{y}/d\underline{x}^2$ is equal to zero at a value of \underline{x} equal to 200.25. Using the relationship

$$\underline{y}_{\sigma} = 0.607 \underline{y}_{\underline{m}}$$

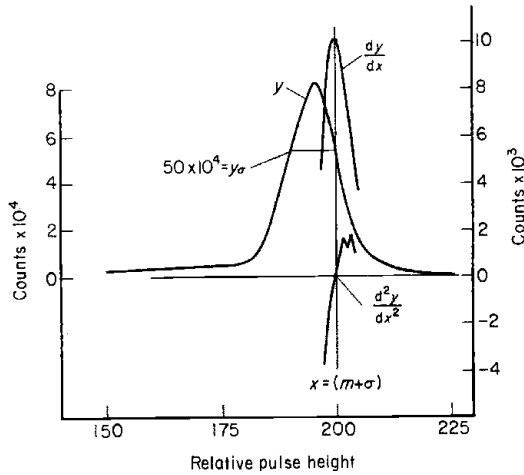


Fig. 8 Pulse height distribution for 0.369 MeV electrons along with $\frac{dy}{dx}$ and $\frac{d^2y}{dx^2}$ plots and evaluation of \underline{x} .

Table 4 Evaluation of value of \underline{x} equal to $(\underline{m} + \sigma)$ for plots in Fig. 8.

For criteria	Value of \underline{x}
$\frac{dy}{dx} = \text{maximum}$	200
$\frac{d^2y}{dx^2} = 0$	200.25
$\frac{y}{\sigma} = 0.607 \frac{y_m}{\sigma}$	200.74

and the value of \underline{y} equal to 8.24×10^4 , the value of \underline{y}_σ is calculated to be 5.00×10^4 . The value of \underline{x} for $\underline{y}_m = 5.00 \times 10^4$ is 200.74. Table 4 summarizes the values of \underline{x} for which each of the criteria for a Gaussian distribution is evaluated at \underline{x} equal to $(\underline{m} + \sigma)$. It can be seen that all values of \underline{x} are, within experimental error, the same. Thus the distribution obtained for measurement of essentially monoenergetic electrons in a liquid scintillation system can be fitted to the equation for a Gaussian distribution.

Figure 9 shows the distribution of pulses obtained for the Compton scattered electrons produced in a liquid scintillation solution by the γ -rays (0.662 MeV) from a ^{137}Cs - ^{137m}Ba source. (The only γ -rays which escape the source holder are the 0.662 MeV γ -rays. The 32 keV Ba X-rays are totally absorbed in the source tube holder.) The use of a radionuclide which gives a single γ -ray energy will give a single Compton distribution while a radionuclide with two or more γ -ray energies will produce two or more Compton scattered electron distributions with an E_{max} for each γ -ray energy. Figure 10 shows the distributions obtained with a single E_{max} energy γ -ray source (^{137}Cs - ^{137m}Ba) and a source of γ -rays of two different energies (^{22}Na). Table 5 summarizes the expected values of E_{max} for these radionuclides.

Since each different energy γ -ray produces its own distribution of Compton scattered electrons from zero energy to E_{max} , the spectrum for ^{22}Na shows one distribution superimposed upon another. In order to utilize the Compton distribution for quench monitoring it is best to have a single energy γ -ray source which will present no

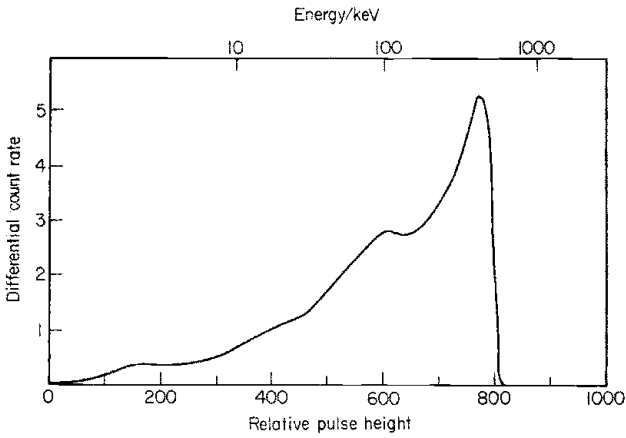


Fig. 9 Pulse height distribution for Compton scattered electrons produced by the 0.662 MeV γ -rays from ^{137}Cs - $^{137\text{m}}\text{Ba}$ interactions with a liquid scintillation solution.

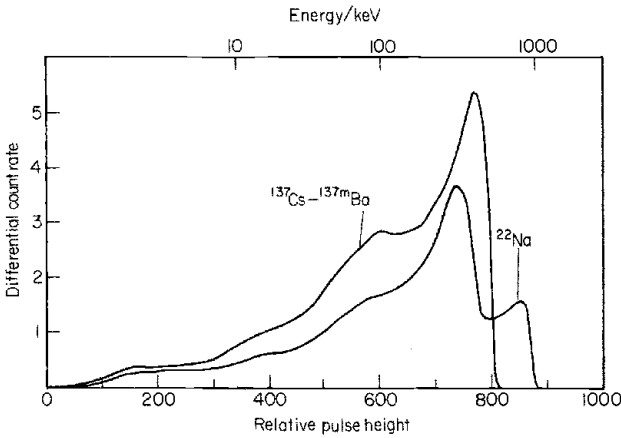


Fig. 10 Pulse height distributions for Compton scattered electrons produced in a liquid scintillation solution by γ -rays from (a) ^{137}Cs - $^{137\text{m}}\text{Ba}$ (0.662 MeV) and (b) ^{22}Na (0.51 MeV and 1.28 MeV).

Table 5 Gamma-ray energies, E_{γ_0} , and E_{max} values for two radionuclides, ^{137}Cs - $^{137\text{m}}\text{Ba}$ and ^{22}Na .

Radionuclide	E_{γ_0} /MeV	E_{max} /MeV
^{137}Cs - $^{137\text{m}}\text{Ba}$	0.662	0.478
^{22}Na	0.510 1.280	0.340 1.067

Table 6 List of some desirable properties of ^{137}Cs - $^{137\text{m}}\text{Ba}$ radionuclides for use as a source for this new method of quench monitoring.

Desirable Property	Property of ^{137}Cs - $^{137\text{m}}\text{Ba}$
Single energy	0.662 MeV ^a
E_{max} sufficiently high to provide dynamic range	0.478 MeV
Long halflife	30 y
Moderate Compton scattering yield	40 μCi source yields about 10^6 Compton scattered electrons min^{-1} with Beckman LS-8000 geometry and 16-18 ml of liquid scintillation solution

^a The 32 keV Ba X-rays are not detected as they are not energetic enough to penetrate the mounting for the γ -ray source.

interfering Compton distributions. It is also desirable to have the γ -ray energy sufficiently high enough to provide a wide dynamic range of quench monitoring but not too high an energy as to require a very large amount of the radionuclide in order to have a sufficient number of Compton scattered electrons produced (per unit time) in the finite volume of the liquid scintillation solution. Figure 3 shows the relative probability of Compton scattering as a function of γ -ray energy. It is also desirable to have a source which will not decay too rapidly. One radionuclide which seems to satisfy these criteria is ^{137}Cs - $^{137\text{m}}\text{Ba}$. Subsequent discussions will deal with the use of ^{137}Cs - $^{137\text{m}}\text{Ba}$ but any radionuclide which satisfies these criteria could also be used. Table 6 summarizes some of the properties of ^{137}Cs - $^{137\text{m}}\text{Ba}$.

If this method is to be viable, it is necessary that the pulse height distribution for a monoenergetic electron excitation gives a Gaussian distribution at different quench levels. Figure 11 shows pulse height spectra for 369 keV electrons from $^{113\text{m}}\text{In}$ in a liquid scintillation solution at different quench levels. As predicted by the Gaussian theory, the value of $\frac{y}{x}$ decreases with decreased pulse height value of x and the distribution becomes $\frac{y}{x}$ broader (i.e. σ becomes larger). Also, the $\frac{y}{x}$ higher pulse height side of the distribution satisfies all the criteria of the Gaussian equation. Table 7 summarizes the values of pulse height for which x is equal to $(\bar{x} + \sigma)$ for each quench level. The most quenched sample exhibited a greater than 50 decrease

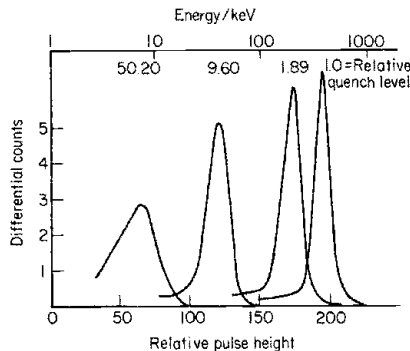


Fig. 11 Pulse height distributions for 0.369 MeV electrons in a liquid scintillation solution with different amounts of a quenching agent.

Table 7 Pulse height values for which each of these Gaussian criteria are satisfied at four different quench levels.

Relative quench level	Energy equivalent ^a	$\underline{y}_\sigma = 0.607 \underline{y}_m$	Pulse height for which $\frac{dy}{dx} = \max$	$d^2 \underline{y}/dx^2 = 0$
1.00	369	200.74	200	200.25
1.89	195	180.54	181	180.37
9.60	38.4	129.22	130	129.51
50.20	7.4	76.60	76	75.10

^a Electron energy which would produce the same pulse height response in a sample with relative quench level of 1.00.

Table 8 Evaluation of pulse height which evaluates the Gaussian parameters for the scintillation solution shown in Fig. 12.

Value of pulse height for which			
$\underline{y} = 0.607 \underline{y}_m$	$\frac{dy}{dx} = \text{maximum}$	$d^2 \underline{y}/dx^2 = 0$	
169.3	169.5	169.6	
Actual count data			
Pulse height	Counts	Δ^a	$\Delta^2 \frac{b}{b}$
172	976		
171	1110	134	
			42
170	1286	176	
			116
169	1578	292	
			-176
168	1694	116	
			- 87
167	1723	29	
$\underline{y}_m = 2440$			
$\underline{y} = 0.607 \underline{y}_m = 1481$			

^a $\Delta = \frac{n}{n} - \frac{n}{n-1}$

^b $\Delta^2 = \Delta_n - \Delta_{n-1}$

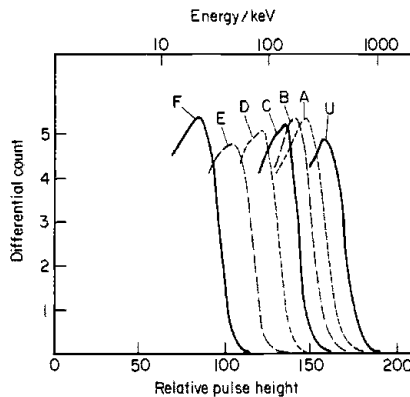


Fig. 12 Pulse height distributions of the upper edge of Compton electron distributions from scattering by 0.662 MeV γ -rays in set of ^3H samples with different levels of quench.

in light yield. The fact that all three values of pulse height, at a given quench level, according to different criteria are nearly the same prove that the Gaussian distribution is valid over a very wide dynamic quench range.

Compton edge measurement

These same criteria can be used in evaluating the pulse height distribution for Compton scattered electrons of energy E_{max} . The electrons of energy E_{max} are monoenergetic and there are no electrons of energy greater than E_{max} . Thus the upper edge of the Compton distribution can be considered as the upper half of a Gaussian distribution for electrons of energy E_{max} . Actually, there are Compton electrons of energy just less than E_{max} which also will contribute to the pulse height distribution of the Compton edge. However, in practice the contributions from these electron energies do not render the shape of the Compton edge non-Gaussian. There is still only one pulse height value for which the value of $d^2y/dx^2 = 0$. Figure 9 shows the pulse height distribution for the Compton electrons produced by the 662 keV γ -rays from a ^{137}Cs - ^{137m}Ba source. Table 8 summarizes the actual count data and the pulse height values obtained by three methods of determining the inflection point of the Compton edge: (1) $y_{\sigma} = 0.607 y_m$, (2) $dy/dx = \text{maximum}$ and (3) $d^2y/dx^2 = 0$. Since all values are the same, it is evident that the Compton edge is indeed described by the Gaussian equation.

Figure 12 shows the Compton edge spectra obtained for a series of ^3H quenched samples which were exposed to the γ -rays from the ^{137}Cs - ^{137m}Ba source. These spectra (like those shown in the previous figures) were obtained using a multichannel analyzer as described previously. Table 9 summarizes the data obtained with these samples. Figure 14 shows a plot of the ^3H counting efficiency vs. the two methods of quench monitoring: external standard channels ratio (ESCR) and Compton edge inflection point pulse height value.

H# definition

In a logarithmic energy-response relationship, the following equation

$$\text{PH} = a + b \log E \quad (12)$$

relates the measured pulse height (PH) on some arbitrary scale (discriminator divisions, channels, etc.) as a function of the excitation energy (E) in keV, where 'a' is the pulse height response for a 1 keV electron and 'b' is the slope. For each level of quench there will be a different equation with the same value of 'b' but different values of 'a'.

Table 9 Data for set of ^3H quenched samples relating counting efficiency, ESCR and pulse height of inflection point (from Gaussian parameters).

Sample	ESCR ^a	^3H counting efficiency/%	Pulse height of inflection point	Relative ^b quench	Energy ^c equivalent/keV
U	.737	60.0	169.3	1.00	487.0
A	.682	54.1	159.0	1.46	328.0
B	.646	49.7	150.0	2.03	236.0
C	.586	41.4	142.0	2.71	176.5
D	.509	32.2	130.5	4.12	116.0
E	.376	20.5	115.0	7.24	66.0
F	.081	9.9	95.5	14.71	32.5

^a External standard channels ratio.

^b The amount by which the quench has reduced the light output for the 478 keV Compton electrons.

^c The energy equivalent of an electron which would produce the same response in the unquenched liquid scintillator as the 478 keV electrons do in the quenched liquid scintillator.

For an unquenched system (N_2 - saturated, flame-sealed standards) the relationship could be represented by

$$\underline{\text{PH}}_0 = a_0 + b \log \underline{E} \quad (13)$$

Likewise for any quenched sample the relationship will be given by

$$\underline{\text{PH}}_q = a_q + b \log \underline{E} \quad (14)$$

The value of 'a' will be different for different amounts of quench in the samples. The difference between the measured pulse height responses for a given energy will be

$$\underline{\text{PH}}_0 - \underline{\text{PH}}_q = a_0 - a_q + b \log \underline{E} - b \log \underline{E} = a_0 - a_q \quad (15)$$

This is the definition of the H#, namely

$$\underline{\text{PH}}_0 - \underline{\text{PH}}_q = \text{H\#} \quad (16)$$

Upon substitution of the H# definition into Eqn. (15), the following relationship is obtained

$$a_q = a_0 - \text{H\#} \quad (17)$$

The pulse height-energy relationship for any liquid scintillator sample (quenched or unquenched) thus becomes

$$\underline{\text{PH}} = a_0 - \text{H\#} + b \log \underline{E} \quad (18)$$

Consider a liquid scintillation system which has an arbitrary pulse height scale of 0-1000 divisions and values $a = 58$ and $b = 270$. The typical pulse height responses for electrons of energies of 1, 10, 100 and 1000 keV at selected quench levels, designated by H# values of 0, 58, 98, 198 and 298 are shown in Table 10 and Fig. 13. If any pulses which exceeded the zero threshold were counted, then the theoretical minimum detectable energy for the different quench levels would be as shown in Table 11. As quenching becomes greater, it requires more energy to produce enough photons to give a measurable response.

An advantage of the use of H# is evident from the fact that any sample can have only one H# value. This is different from other methods of quench monitoring such as

Table 10 Relative pulse height response (log conversion) at different quench levels as measured by the $H\#$ value.

Electron energy/keV	Pulse height response at $H\#$ equal to				
	0	58	98	198	298
1	58	0	- 40	-140	-240
10	328	270	230	130	30
100	598	540	500	400	300
1000	868	810	770	670	570

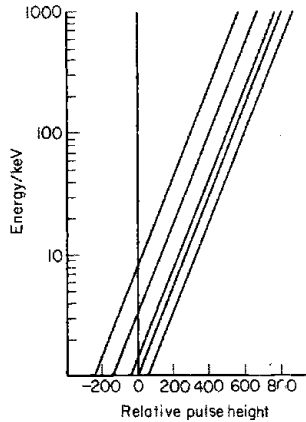


Fig. 13 Pulse height response vs. log of electron energy at different quench levels.

Table 11 Theoretical minimum detectable energy of electrons at different quench levels as measured by the $H\#$ value (based on Table 10 and Fig. 20).

$H\#$	Theoretical minimum detectable energy/keV at zero pulse height
0	0.34
58	1.00
98	1.40
198	3.30
298	7.80
400	18.50

sample channels ratio (SCR), external standard count rate (ESCPM) and external standard channels ratio (ESCR). These three methods can give essentially large and varied numbers of values of the quench measuring value, depending on the choice of the settings for the counting channels used. Figures 14 and 15 show different quench curves for the same samples with different choices of counting channels for ESCR and SCR methods of quench monitoring.

Both SCR and ESCR methods have a limited range because, at some point, they become invariant with changing quench. Figures 16 and 17 show how a ratio can become constant at a given quench level and remain constant at all greater quench levels. The dynamic range of the $H\#$ method is only limited by the quench level at which the inflection point of the Compton edge is no longer measurable.

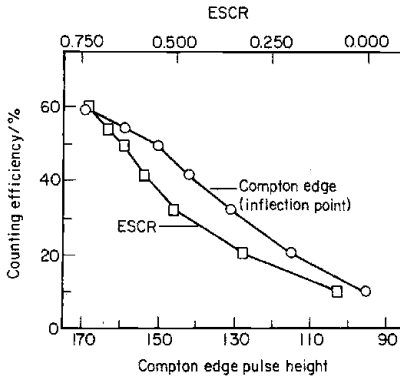


Fig. 14

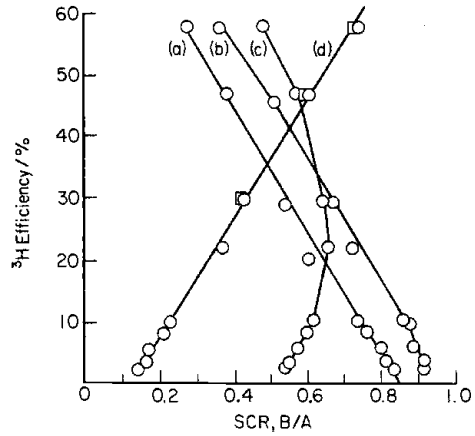


Fig. 15

Fig. 14 Different plots of ESCR values vs. ^3H -counting efficiency for the same samples but different choices of the window settings for the two counting channels for Compton generated pulses.

Fig. 15 Different plots of SCR values vs. ^3H -counting efficiency for the same samples but different choices of the window settings for the two counting channels for ^3H -generated pulses.

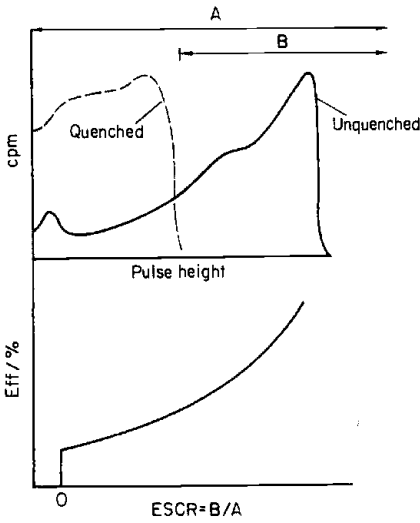


Fig. 16

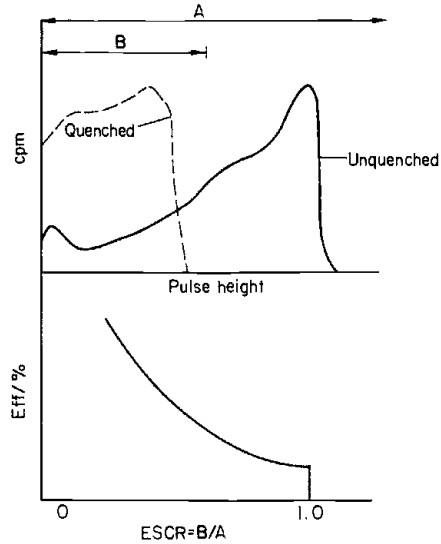


Fig. 17

Fig. 16 Selection of window settings and count ratio as function of quench showing limiting range.

Fig. 17 Selection of window settings and count ratio as function of quench showing limiting range.

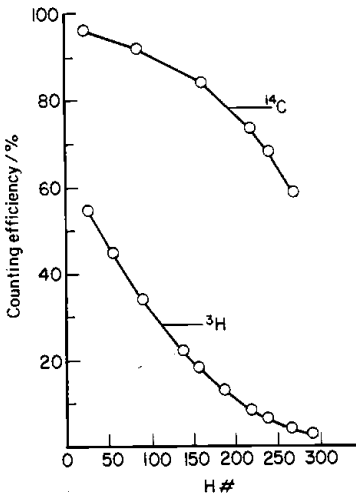


Fig. 18

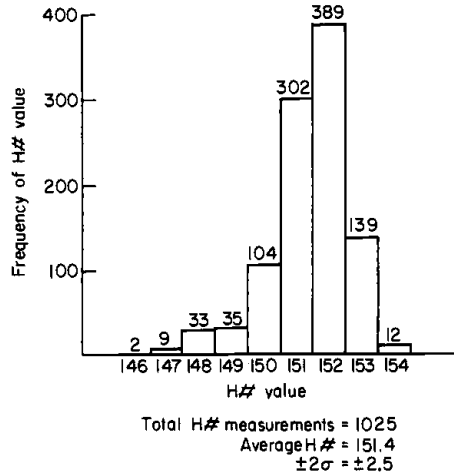


Fig. 19

Fig. 18 Plots of counting efficiencies of (a) ^3H - and (b) ^{14}C -containing samples of different quench levels as a function of the H#.

Fig. 19 Frequency pattern of H# values for single sample of moderate quench measured for 2.5 d.

Since the H# is unique, it can be considered to be the universal quench parameter. Any properly calibrated system with H# capabilities should give, within statistical limits, the same H# value for equally quenched samples. Thus different laboratories now have a parameter which can be used to correlate experimental results. Also experiments done at different times can easily be compared through the H# values. Two instruments may not have the same counting efficiencies due to differences in multiplier phototubes, but the H# values should be the same, within statistical limits, at the same quench level.

RESULTS

The following results were obtained using a commercially available liquid scintillation system which has the H# concept as an integral part of the system, the Beckman LS-8000 liquid scintillation system. Figure 18 shows typical plots of H# vs. counting efficiency for tritium- and ^{14}C -containing samples.

H# repeatability

The Beckman LS-8000 Series systems are designed to give H# repeatability such that the calculated counting efficiency based on the spread of H# values will be statistically ($\pm 2\sigma$) within $\pm 1\%$ efficiency of the average calculated counting efficiency. This requires comparison of the H# spread to a counting efficiency vs. H# plot for the particular radionuclide and quenching agent used in the experiment.

Figure 19 shows the experimental data obtained for a quenched ^3H -containing sample (18.68% counting efficiency). The sample was counted repeatedly (uninterrupted) over a period of 2.5 d with each H# determination followed by a 2 min sample count. The 2 min sample count is desirable to prevent fatigue of the multiplier phototube by continuous exposure to the γ -ray source. Using the average H# value, the H# value plus 2σ error value and the H# value minus 2σ error value, the counting efficiency based on the quench curve were calculated. The results are given in Table 12. The total spread of H# values is from 146 to 154. However, this distribution can be described as a normal distribution of values about some average value. The average value was calculated to be 151.4 and the $\pm 2\sigma$ error (95% confidence level) was

Table 12 Quench curve equation and calculated counting efficiencies for H# frequency plot of Fig. 19.

Quench Curve	Eff (%) = A + B (H#) + C (H#) ² + D (H#) ³								
	A = 65.894301								
	B = - 0.455973								
	C = 0.001099								
	D = - 0.00000097								
<table style="width: 100%; border-collapse: collapse;"> <thead> <tr> <th style="text-align: left;">H# Value</th> <th style="text-align: left;">Counting Eff/%</th> </tr> </thead> <tbody> <tr> <td>Average = 151.4</td> <td>18.68</td> </tr> <tr> <td>Average + 2 = 153.9</td> <td>18.21</td> </tr> <tr> <td>Average - 2 = 148.9</td> <td>19.17</td> </tr> </tbody> </table>		H# Value	Counting Eff/%	Average = 151.4	18.68	Average + 2 = 153.9	18.21	Average - 2 = 148.9	19.17
H# Value	Counting Eff/%								
Average = 151.4	18.68								
Average + 2 = 153.9	18.21								
Average - 2 = 148.9	19.17								
<p>Average Eff = (18.68 + 0.49) % - 0.47 %</p> <table style="width: 100%; border-collapse: collapse;"> <tbody> <tr> <td style="width: 50%;">Maximum = 154</td> <td style="width: 50%;">18.18%</td> </tr> <tr> <td>Minimum = 146</td> <td>19.73%</td> </tr> </tbody> </table>		Maximum = 154	18.18%	Minimum = 146	19.73%				
Maximum = 154	18.18%								
Minimum = 146	19.73%								

calculated to be ± 2.5 H# units. This gives a range of 148.9 to 153.9 with a 95% confidence level. This means that only 5% (51) of the measured values should be outside this range. Indeed there were 44 values outside the range 149-154 although the distribution seems skewed to the low H# values.

The total 2σ error spread of counting efficiency was less than + 0.5%. This is well below the quoted specification of $\pm 1.0\%$. Even the total spread from lowest to highest measured H# values was only 1.55% counting efficiency.

Another sample of low quench (namely an air-saturated, unquenched sample) was counted under the same conditions for 1.6 d. A total of 652 H# values were measured. The frequency of H# values are plotted in Fig. 20. Table 13 lists the calculated efficiencies for the H# values measured. The ± 2 error of the H# values produced only a $\pm 0.39\%$

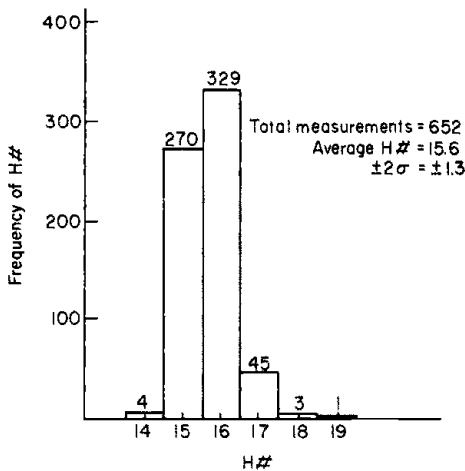


Fig. 20 Frequency pattern of H# values for single sample of low quench measured for 1.6 d.

Table 13 Quench curve equation and calculated counting efficiencies for H# frequency plot of Fig. 20.

Quench Curve	Eff (%) = A + B (H#) + C (H#) ² + D (H#) ³	
	A = 60.720351	
	B = - 0.289077	
	C = - 0.000237	
	D = 0.00000205	
H# Value	Counting Eff/%	
Average = 15.6	56.15	
Average + 2 = 16.9	55.76	
Average - 2 = 14.3	56.54	
Average Eff = (56.15 ± 0.39)%		
Maximum = 19	55.23	
Minimum = 14	56.63	
Difference = 5	1.40	

counting efficiency error. The total spread of H# values (14-19) correspond to a change of 1.40% counting efficiency.

The H# value was measured for a single sample 100 times uninterrupted. After about 16 h (overnight) the 100 measurements were repeated. Finally, after another 16 h (overnight) the 100 measurements were repeated a third time. Figure 21 shows the frequency distributions of the three experiments. The average H# values and calculated $\pm 2\sigma$ error values are in very good agreement.



Fig. 21 Frequency patterns for H# values for a single sample measured for 100 times on each of three successive days.

Table 14 Calculated counting efficiencies for ^3H quench set based on frequency distribution of H# values.

Number of measurements	Average H# $\pm 2\sigma$	Average counting Eff/% $\pm 2\sigma$ /%
65	21.7 \pm 2.8	54.35 +0.84 -0.82
65	31.5 \pm 2.3	51.43 +0.70 -0.67
65	57.0 \pm 2.8	43.85 +0.83 -0.83
65	84.5 \pm 3.3	35.84 +0.95 -0.94
65	135.5 \pm 4.0	22.30 +0.97 -0.95
65	194.5 \pm 2.8	10.60 +0.43 -0.40
65	227.2 \pm 3.1	6.85 +0.26 -0.23
65	268.4 \pm 8.4	5.70 +0.32 -0.13

In another experiment, each bottle of a series of quenched samples containing ^3H was measured 65 times. The samples were moved in the sample changing mechanism between each group of 10 measurements. Table 14 lists the data obtained along with the 2σ spread of H# values and counting efficiencies. In every case, the $\pm 2\sigma$ spread of H# values produced less than $\pm 1\%$ spread in calculated counting efficiencies.

Quench curve repeatability

A set of quenched samples containing ^3H were measured a total of ten times and the best fit cubic equation was derived for each measurement of the set. Table 15 lists the coefficients for the equation of efficiency vs. H# according to

$$\text{Eff} (\%) = A + B (\text{H}\#) + C (\text{H}\#)^2 + D (\text{H}\#)^3$$

There is some difference between the values of the coefficients, but calculation of the counting efficiencies at the same H# values for each of the ten equations gives, basically, the same efficiencies. Table 16 lists the ten calculated efficiencies with the average efficiency, the maximum spread of percent efficiency and the percent error due to the measured spread. The spread in efficiency calculated from these ten quench curve equations is less than the quoted $\pm 1\%$ spread in counting efficiency. It is not considered accurate to calculate the efficiency based upon an H# value outside the range of H# values of the quench set. The limits of H# values for these data were the lowest H# of 26 and the highest H# of 300.

Efficiency calculation repeatability

Using a single quench curve equation

$$\text{Eff} (\%) = 66.624937 - 0.447602 (\text{H}\#) + 0.000969 (\text{H}\#)^2 - 0.00000064 (\text{H}\#)^3$$

a set of quenched samples, each with the same amount of ^3H , was counted ten times. The H# value was used to calculate the counting efficiency of each sample of the set based upon the above equation. The sample dpm was calculated from the measured cpm (background corrected) and calculated counting efficiency.

$$\text{dpm} = \frac{(\text{measured cpm} - \text{background}) \times 100}{\text{Eff} (\%)}$$

Table 15 Values of the constants of cubic equation for best fit of H# vs. ^3H counting efficiencies plots obtained from ten different sets of data.

No.	A	B	C	D
1	67.315940	-0.460974	0.001027	-0.00000071
2	64.219007	-0.391243	0.000623	-0.00000001
3	65.952075	-0.443017	0.000962	-0.00000064
4	65.894301	-0.455973	0.001099	-0.00000097
5	65.403666	-0.422358	0.000830	-0.00000042
6	66.309376	-0.453936	0.001039	-0.00000078
7	63.836877	-0.373475	0.000483	+0.00000028
8	64.598544	-0.411766	0.000785	-0.00000035
9	67.184785	-0.471673	0.001142	-0.00000097
10	66.624937	-0.447602	0.000969	-0.00000064

Table 16 Calculated ^3H counting efficiencies at specific H# values using each of the ten sets of values of the constants given in Table 15.

Equation	Efficiency at H# equal to						
	30	50	100	150	200	250	300
1	54.39	46.75	30.78	18.88	10.53	5.18	2.29
2	53.04	46.22	31.32	19.52	10.81	5.19	2.75
3	53.50	46.13	30.63	18.99	10.71	5.33	2.34
4	53.17	45.71	30.31	18.95	10.90	5.43	1.82
5	53.47	46.31	31.04	19.31	10.77	5.13	2.05
6	53.61	46.11	30.53	18.97	10.84	5.58	2.57
7	53.08	46.42	31.60	19.64	10.70	5.04	2.83
8	52.95	45.94	30.92	19.32	10.85	5.25	2.27
9	54.03	46.34	30.46	18.86	10.77	5.48	2.27
10	54.04	46.58	30.89	19.12	10.74	5.28	2.27
Average	53.53	46.25	30.85	19.16	10.76	5.29	2.35
Spread Total	1.44	1.03	1.29	0.78	0.37	0.54	1.01
± %	0.72	0.52	0.65	0.39	0.19	0.27	0.51

Table 17 Calculated ^3H counting efficiencies based on single quench curve for actual repeated (ten times) measurement of H# values.

Sample no.	H# spread	Average H#	Average Eff/%	Eff/% spread ^a	Average dpm ratio ^b
1	27 - 28	27.4	55.04	0.39	0.971
2	50 - 54	52.6	45.89	1.41	1.002
3	85 - 89	86.7	34.60	1.18	0.988
4	135 - 140	137.6	21.75	1.09	0.972
5	151 - 156	154.0	18.45	0.97	0.974
6	183 - 189	187.8	12.79	0.92	1.013
7	217 - 224	219.6	8.21	0.79	1.062
8	235 - 241	238.3	6.39	0.57	0.992
9	260 - 266	263.6	4.32	0.42	0.940
10	287 - 297	293.8	2.66	0.45	0.985

^a Maximum calculated Eff minus minimum calculated Eff.

^b Average calculated dpm/real dpm.

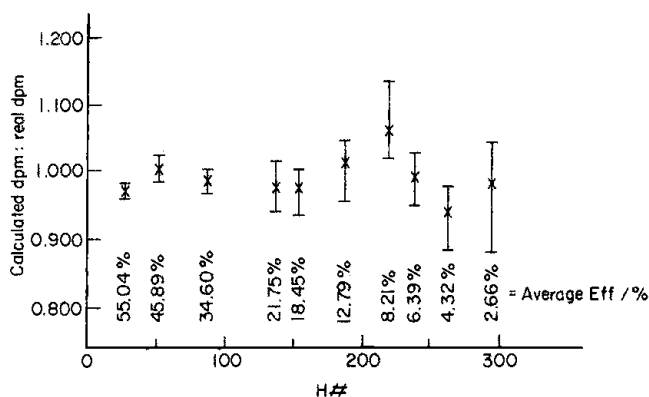


Fig. 22 Ratio of calculated dpm to real dpm as function of H# value as presented in Table 17.

A constant background of 27.0 cpm was used for all H# values. Table 17 lists data obtained from the actual measurements.

The ratio of the calculated dpm to the known dpm was obtained for each of the ten determinations of each sample of the set. Figure 22 shows a plot of the relative dpm ratio at each average H# value for the ten measurements.

The average of the relative ratio is indicated by an 'X' while the bar indicates the spread of relative dpm ratios obtained within the set of ten measurements.

Repeatability for ¹⁴C efficiency

A set of ¹⁴C-containing standards was counted and the H# values measured to obtain the quench curve shown in Fig. 23. The best fit equation for this quench curve was calculated as

$$\text{Eff (\%)} = 97.975905 - 0.99460 (\text{H\#}) + 0.000421 (\text{H\#})^2 - 0.00000216 (\text{H\#})^3$$

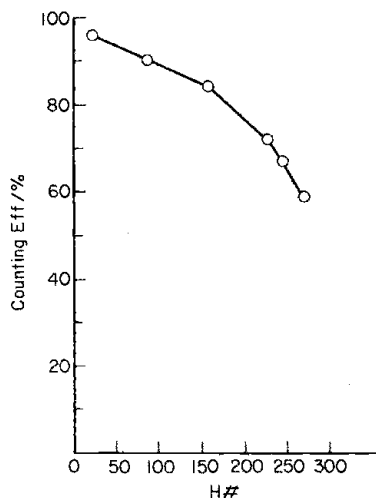


Fig. 23 Counting efficiency of ¹⁴C vs. H# value for set of samples of different quench level.

Table 18 Data showing calculated ¹⁴C-counting efficiencies for repeated measurement of samples of different quench as measured by the H# value based upon two different quench curves: Test No. 1 and Test No.2.

Test No. 1

Sample no.	H# spread	Average H#	Average Eff/%	Eff/% spread	Average dpm ratio
1	22 - 25	23.4	95.67	0.25	1.000
2	82 - 85	83.9	91.14	0.22	1.005
3	158 - 164	159.7	83.88	0.79	0.995
4	219 - 226	221.4	73.03	1.63	1.006
5	239 - 243	241.3	68.04	1.09	1.001
6	267 - 272	269.5	59.39	1.71	1.001

Test No. 2

Sample no.	H# spread	Average H#	Average Eff/%	Eff/% spread	Average dpm ratio
1	22 - 25	23.4	95.88	0.31	0.998
2	83 - 85	84.1	90.90	0.14	1.009
3	158 - 164	159.9	84.08	0.50	0.992
4	220 - 226	222.6	73.10	0.43	1.003
5	237 - 244	240.7	68.40	1.98	0.991
6	269 - 277	273.2	57.72	3.02	1.028

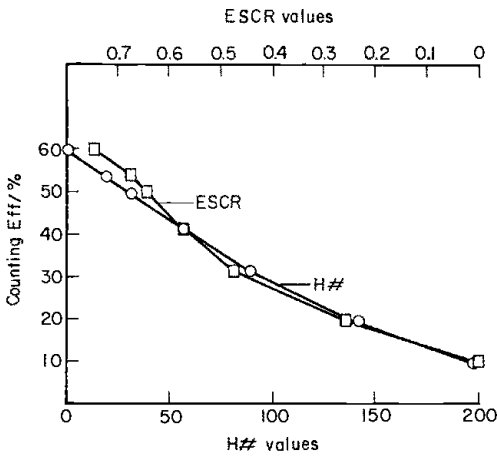


Fig. 24

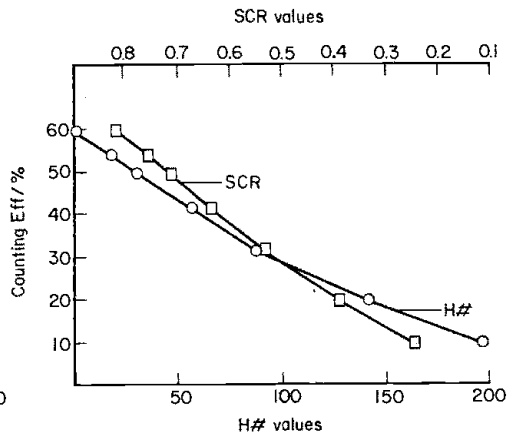


Fig. 25

Fig. 24 Comparison of ³H-counting efficiency plots vs. ESCR and H# values.

Fig. 25 Comparison of ³H-counting efficiency plots vs. SCR and H# values.

Using this quench curve equation, this set of ^{14}C samples was counted nine more times. The measured H# values were used to calculate the counting efficiencies and the counting efficiency was used to calculate the dpm values of the samples. These results are listed in Table 18 as Test No.1.

The set was again counted and a second quench curve calculated. Using this new quench curve the sample set was again counted nine more times. The measured H# values were used to calculate the counting efficiencies and dpm values of the samples. These results are listed in Table 18 as Test No.2. The results are within experimental error of those obtained in Test No.1.

Comparison with ESCR and SCR

Figure 24 shows the plot of ^3H -counting efficiency vs. H# and ESCR values obtained with the same set of samples. It is noted that the ESCR value is zero at ^3H -counting efficiency of 10% and remains zero for any lower ^3H -counting efficiency. This data represents only one choice of external standard counting channels.

Figure 25 shows the plot of ^3H -counting efficiencies vs. H# and SCR values obtained with the same set of samples. To cover the same range of quench the SCR window settings were selected to give a ratio of 0.815 for an unquenched sample. To obtain the same statistical accuracy of the ratio for the most quenched sample (SCR = 0.248) the sample had to be counted six times longer than the unquenched sample. Again this data represents only one choice of sample channels ratio counting channels.

CONCLUSIONS

The concept of the H# has been shown to be theoretically valid. Based upon this proof, the features of the H# concept as embodied in the Beckman LS-8000 Series liquid scintillation systems have been demonstrated. It has been shown that the H# is unique, provides a method of instrument calibration and provides wide dynamic quench range measurements. Further, it has been demonstrated that the H# concept provides a universal quench parameter.

The H# concept provides a statistically repeatable measure of the quench level of any sample. Counting efficiency vs. H# plots are repeatable within the statistical limits of + 1% counting efficiency. The H# concept has made possible a very accurate method of automatic quench compensation (AQC).

The H# concept has introduced a new method of measuring sample quench level and will lead to accurate corrections of sample cpm to the actual dpm.

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1. D.L. Horrocks, Nucl. Instrum. Methods 30, 157 (1964).
2. D.L. Horrocks, Nucl. Instrum. Methods 117, 589 (1974).

DISCUSSION

J.F. STOUTJESDYK: Did you compare chemical and color quenches?

M.T. O'NEILL: Yes.

J.F. STOUTJESDYK: How do you explain the good results in view of the different effects of color and chemical quenchers on the pulse height spectra of β -emitters of higher energies than ^3H ?

M.T. O'NEILL: I know that quench curves were obtained for ^{14}C samples which consisted of different cocktails and quenchers. The curves obtained were essentially superimposable despite differences in quenching agents and type of sample.

D. SAMPSON: How in practice is the H number measured?

M.T. O'NEILL: By dividing the pulse height scale into small discrete channels and accumulating counts in each channel. By use of the microprocessor it is possible to compare the counts in each channel and precisely locate the inflection point.

C. PALAIS: Does H number give universal quench curve for color and chemical quenchers?

M.T. O'NEILL: In one experiment nine separate quench curves were obtained from tritiated samples exhibiting varying degrees of chemical and color quench. All curves were within $\pm 2\%$ of each other.

G.W.A. NEWTON: What checks does the user have that the microprocessor has found the correct inflection point in the Compton edge?

M.T. O'NEILL: The inflection point of the Compton edge is factory set at 780 discriminator units; this setting is also used for the automatic calibration. If for some reason the calibration number changes the instrument will automatically re-adjust the operating parameters.

B.E. GORDON: When an isotope of equal or larger energy is present in an amount of much higher count rate than the energy or count rate of the ^{137}Cs , how does this affect the H number precision? It must go down for purely statistical reasons, but how much?

M.T. O'NEILL: Experiments have been carried out using high activity ^{32}P samples and valid H number measurements were obtained. I am not in possession of actual statistical data giving error values on these measurements but I am sure these could be obtained from Dr Horrocks.

B.W. FOX: I assume that this system of measuring quenching is only valid for homogeneous systems? Has Dr Horrocks had an opportunity to examine the so-called 'operationally homogeneous' zone of colloid counting systems using this Compton edge shift measurement?

M.T. O'NEILL: I believe Dr Horrocks has done work on this aspect and the results may be available in some publication but I am not in possession of those data at this time.

L. BURKINSHAW: I should have thought that in computational terms, it would have been easier to find the peak of the Compton edge, rather than the point of inflection, and would have given the same information. Can you explain why the point of inflection is used, rather than the peak?

J.A.B. GIBSON: The Compton 'peak' is not in fact a true peak in the sense of a photoelectric interaction and because of this its position will show more variation with quenching than the position of the inflection point. The H factor represents a direct measure of the 'gain' of the system and the position of the inflection point ($d^2y/dx^2 = 0$) is the most precise measurement of E_{max} and hence its change with quenching represents the best measurement of the gain of the system.

L. BURKINSHAW: I agree that the Compton edge is not a 'true' peak in the sense that the photopeak is. Nevertheless; its position on the pulse-height scale is linear with the maximum energy of the Compton electrons, and I should have thought its position would be a good indication of the depression of light output in a quenched phosphor.

H. PROCHAZKA: How did you take account of the intensities of the gamma lines? The example of ^{137}Cs is simple because the gamma line intensity is about 100%. How is it possible to measure and calculate other gamma lines - for example ^{134}Cs ?

M.T. O'NEILL: If I understand the question correctly other external gamma sources could be used provided they satisfy the criteria as previously presented. However, the properties of ^{137}Cs are such that it makes it the most desirable source.

C. HORNE: Would the author care to comment on what experiments have been carried out using color and chemical quenching agents using ^{14}C activity, what the results were and how the accuracy of dpm calculation from experimental samples is affected?

M.T. O'NEILL: Dr Horrocks has carried out experimental work and the results are found to be satisfactory.