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QUENCH MONITORING AND EFFICIENCY CALIBRATION
THROUGH EXTERNAL STANDARDIZATION*

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Liquid scintillation counting makes use of an intimate mixture of radioactive sample and detecting medium which translates atomic radiation into light flashes. The light intensity of such a flash is proportional to the deposited energy in a burst of radiation, but the constant describing this proportionality may change from sample to sample due to chemical differences in various radioactive preparations. This chemical loss in detection efficiency is known as quenching and needs calibration if one is to get quantitatively meaningful results from liquid scintillation counting. Many ways are available for measuring quenching correction, and these have been reviewed by Peng (1).

In this study one of the methods, external source standardization, has been investigated in detail because it seemed capable of fulfilling the need for a rapid, automatic system which monitors quenching chemistry without direct dependence on the internal level of radioactivity.

MATERIALS AND EQUIPMENT

External Sources

The sources were Co^{60} , Cs^{137} , and Ra^{226} (equilibrium), 4 μc unless otherwise noted, each within a plastic sphere; transported from without shield to position next to loaded vial and out again by a pneumatic system; supplied by Packard Instrument Co., Inc.

Internal Isotopes

Standardized isotopes in labeled compounds were H^3 as HTO, C^{14} as aqueous alanine-1- C^{14} , and P^{32} as aqueous triethylammonium orthophosphate- P^{32} .

Liquid Scintillator

The scintillator formulation was 6 g/l. PPO, 0.03 g/l. POPOP, and 100 g/l. naphthalene in p-dioxane, used as 15 ml plus 1 ml H_2O .

Quencher

Nitromethane, spectroscopic-grade.

Vial

Polyethylene; dioxane scintillator does not pass through wall.

Counter

Packard Model 3324 Liquid Scintillation Spectrometer with Automatic External Standardization.

Pulse Analysis

Wide-window, 10X (signifies ratio of upper level to lower level discriminator setting) for each isotope; 2.5X window for C^{14} (when C^{14} is peaked in a 2.5X window, these spectrometer conditions give

zero H^3 efficiency as shown in Figure 1); integral analysis also used with threshold setting just above highest energy C^{14} pulses, designated as $> C^{14}$.

PREPARATION OF COUNTING SOLUTIONS

The liquid scintillator was divided into eight secondary stock solutions each containing a different concentration of nitromethane: 0.0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, and 0.7 volume %. Forty vials were set out in five rows of eight. To each vial in the first row was added 1 ml of H^3 ; similarly in the second row 1 ml of C^{14} ; third row 1 ml of P^{32} ; fourth and fifth rows 1 ml of water. Then, freshly viewing the array as eight ranks of five vials, to each vial in the first rank was added 15 ml of the unquenched scintillator. This was continued with a different level of quenching in each rank until H^3 , C^{14} , P^{32} , and duplicate background quenched series had been completed. In order of increasing quench these eight different solution types were designated as the quenched series 0 through 7. One background series was submitted to Professor G. H. Daub, University of New Mexico, for relative pulse height analysis (2), the standard method for evaluation of liquid scintillator performance. The results are shown in Figure 2; samples 6 and 7 gave too low a response for a valid value.

Figure 1. Relationship between C^{14} and H^3 counting efficiency in various peaked C^{14} windows.

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Figure 2. Dependence of relative pulse height on quenching
in the quenched series.

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COUNTING DATA

Each of the three unquenched radioactive samples was counted at various gain settings in the fixed windows of Table 1 until a maximum count rate was obtained. The maximized gains and counting efficiencies are listed in Table 1. The special requirements for the $> C^{14}$ condition were given above.

All of the quenched radioactive samples were then counted in the appropriate isotope conditions of Table 1, except for $> C^{14}$, and the background series was counted in the 10X windows. Figure 3a presents the relative count rate for the various isotope-window combinations as a function of sample number in the quenched series. Figure 3b shows the relationship of quenching to background for H^3 , C^{14} , and P^{32} in the 10X window. The behavior is different for each isotope, but all three curves can be visualized to fit together to make a single curve on a wide range energy vs. background plot.

Finally, the external sources were counted with the background series in the H^3 -10X window (Figure 4a), the C^{14} -10X window (Figure 4b), the P^{32} -10X window (Figure 4c), and the $> C^{14}$ window (Figure 4d). For calibration of radioactive solutions the first three conditions require a subtracting electronics system to get net external standard counts. The last condition needs an extra channel of analysis but no subtraction for H^3 and C^{14} counting.

TABLE 1. Counting Conditions and Efficiencies for Unquenched Solutions

Isotope Counted	H^3	C^{14}			P^{32}
Window Settings	100-1000	100-250	100-1000	100-∞	100-1000
Window Designation	H^3 -10X	C^{14} -2.5X	C^{14} -10X	$>C^{14}$	P^{32} -10X
Gain, %	75	5.2	15	0.9	1.3
Efficiency, %	31	42	80	0	86

Figure 3. Dependence of (a) internal isotope counting rate and (b) background, on quenching in the quenched series.

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Figure 4. Dependence of external standard count rate on quenching using (a) the H^3 -LOX window; (b) the C^{14} -LOX window; (c) the P^{32} -LOX window; and (d) the $> C^{14}$ window.

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CORRELATIONS

A wide variety of external standard calibration curves can be derived from those shown in Figures 3 and 4 by eliminating the common variable: sample number in the quenching series. The preparation of identically quenched counting solutions has made this possible. Three figures follow which illustrate both the value of external standardization to the user and problems in counter design for the manufacturer.

Extra Channel

Figure 5 results from an electronic system with an optimized C^{14} -10X channel and a second channel with gain set just to the point of eliminating C^{14} from above a lower discriminator level of 100 divisions. A Ra^{226} external standard is counted in the second channel. This system has no memory or subtraction but requires the extra channel and an energetic source. The 100- ∞ curve was obtained by a combination of the C^{14} -10X curve of Figure 3a, the Ra^{226} curve of Figure 4d, and the C^{14} -10X efficiency of Table 1. By progressively moving the upper level discriminator of the external standard channel from ∞ down to 240 divisions, the bow in the curve slowly disappeared leaving the linear 100-240 response.

One-Channel Memory and Subtraction

For Figure 6 the electronic system has three channels set for

Figure 5. External standardization of C^{14} with Ra^{226} in an extra channel.

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Figure 6. External standardization of double-label C^{14} and H^3 with Ra^{226} in a P^{32} -10X channel with memory and subtraction.

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specific isotope counting: H^3 -10X, C^{14} -2.5X, and P^{32} -10X. The H^3 and C^{14} channels are for double-label counting with no H^3 in the C^{14} channel. The P^{14} channel is not only optimized for P^{32} but also counts a Ra^{226} external standard. This channel retains the sample count in its memory, subtracts this from the gross external standard count, and displays the net Ra^{226} count. The C^{14} -2.5X and H^3 -10X curves of Figure 6 were derived from Figures 3a and 4c and from Table 1. In this case, one is not free to improve the response curve by altering the window settings of the Ra^{226} counting channel, since it was preset to optimize P^{32} counting. Figure 6 could also have contained a curve for calibrating P^{32} counting in its P^{32} -10X window.

Two-Channel Memory, Subtraction, and Ratio

The Figure 7 electronics system has three channels set as H^3 -10X, C^{14} -10X, and P^{32} -10X. The C^{14} and P^{32} channels both have memory and subtraction to separate net counts from a Co^{60} source. The electronics further calculate and display the P^{32}/C^{14} channel ratio of net Co^{60} response. This ratio is not only independent of Co^{60} radioactive decay but has a usefully steep response, being the ratio of a descending to an ascending function with increasing quench. The curves of Figure 7 were constructed from data in Figures 3a, 4b, and 4c.

Figure 7. External standardization of P^{32} , C^{14} , and H^3 in 10X windows with Co^{60} using memory, subtraction, and ratio.

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OTHER OBSERVATIONS

Volume Effects

A study of the change in external standard count produced by differences in counting solution volume showed (in percent change per ml): 10-12% at 5 ml, 7-9% at 10 ml, and 1.5-3% at 15 ml.

Memory Counts

In consideration of the possibility that some part of the detector assembly viewed by the photomultipliers might be activated by the external gamma source into long decay time light emission, a 0.5-mc Co^{60} source was used. A 1-minute count immediately following 1 minute with the source next to the vial showed no memory in any of the counting channels.

Contributors to the External Sample Count

The Ra^{226} external standard was counted in the C^{14} -10X window and also in a higher energy window at 1.3% gain between 100 and 240 divisions with empty chamber only, empty glass vial, vial with 15 ml toluene, and vial with 15 ml unquenched toluene scintillator. The C^{14} -10X window gave 7,300 cpm for chamber, another 200 cpm for empty vial, another 11,000 cpm for 15 ml toluene, and another 200,000 cpm for scintillation solutes dissolved in the toluene. In contrast, the higher energy external standard window showed 90,000 cpm with the scintillator and no cpm with bottle, vial, or chamber.

Statistics of Source Repositioning

A sample was left loaded in the counting chamber while the Ra^{226} source was repeatedly blown into its counting position and back to its storage position. Eleven consecutive 1-minute counts at times when the source was in gave an average 71,812 cpm. The standard deviation of a single determination was 283 cpm, calculated from the counting data. Since this number is very close to 268, the standard error, the source was positioned very reproducibly.

DISCUSSION

It is shown in Figure 3a that counting efficiency is a monotonic function of quenching over a wide range for H^3 , C^{14} , and p^{32} . Thus a means of monitoring quenching should be capable of indicating counting efficiency without ambiguity, although in a differently performing relationship for the three isotopes. Figure 4 shows the counting performance of three external standards Co^{60} , Cs^{137} , and Ra^{226} as a function of quenching under four representative counting conditions. Both Cs^{137} and Ra^{226} were incompetent for quench monitoring under C^{14} counting conditions because their responses go through a maximum and are, therefore, ambiguous. Under p^{32} counting conditions and in a channel just above the C^{14} end point, Cs^{137} fails because of deficient range of response. Under H^3 counting conditions, Ra^{226} is poor because of the small slope of its response.

Otherwise, good relationships remain, and because identically quenched series were prepared for all the counting it is possible to derive many external standard vs. counting efficiency calibration curves from those shown in Figures 3a and 4 and from Table 1. The few examples shown in Figures 5-7 illustrate three modes of electronic handling of the sample and external standard counts.

The extra channel approach, i.e., an analysis window not used for sample counting, offers versatility in tailoring the shape of the curve such that a linear response may result. Such an extra channel set above the C^{14} end point and using the high energy extending Ra^{226} external source was manipulated in Figure 5 to give a remarkably linear and steep relationship.

Another approach makes a sample-counting channel double as external standard channel. This requires the sequence: sample count, memory, external standard count, subtraction, and display of the net external count. If the sample counting time is different from that for the standard, the memory must be accompanied by a normalization calculation. Here one has no freedom to independently adjust the external standard response curve. Such a system is shown in Figure 6, where H^3 and C^{14} double-label counting conditions are both calibrated by the net count rate of a Ra^{226} external standard in an optimized P^{32} counting channel.

A more complicated system is one in which two sample-counting channels also count the external standard. This requires memory

and subtraction in each channel as before plus calculation of a ratio of the two net standard counts. Just such a system is shown in Figure 7, where the counter has three channels optimized for wide-window H^3 , C^{14} , and P^{32} counting. The external standard is Co^{60} , and it is counted in both the C^{14} and P^{32} channels. The quantity calculated is the channel ratio: P^{32}/C^{14} . Calibration curves for H^3 , C^{14} , and P^{32} vs. the Co^{60} ratio are shown. Decay corrections for Co^{60} are unnecessary, and a steep relationship is obtained through taking a ratio.

The external standard method does not depend on sample counts directly as in the channel ratio standardization method, and low-level samples are no harder to calibrate for efficiency than hot samples. The external method is so independent of sample radioactivity that background samples can be calibrated for quenching.

The external standard method does what the internal standard method used to do with much greater ease and without irreversibly altering the sample, but the internal standard method is not eliminated from use. External standardization must be calibrated and periodically recalibrated by carefully prepared internal standard solutions of the same volume and preferably of the same quenching chemistry as the routinely counted samples.

Volume effects are severe enough with external standardization to warrant careful control over sample volume, a normal chemistry skill.

It has been demonstrated in this study that in a variety of ways external standardization not only monitors quenching but also calibrates counting efficiency for H^3 , C^{14} , and P^{32} over a wide range of quenching. The method does not alter the sample and it operates free of dependence on sample activity. One-minute counting times give a standard deviation less than 0.5% for unquenched samples, so that the method is not time-consuming and is capable of high precision. The external standard method can be as accurate as the internal standard samples used for calibration.

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