

LESSER PULSE HEIGHT ANALYSIS IN
LIQUID SCINTILLATION COUNTING

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Abstract

"Lesser pulse height analysis", an instrumental development in liquid scintillation counting is described and compared with the "summed method" used by most manufacturers. A MKII [®] liquid scintillation counter (Nuclear Chicago Corporation) with lesser pulse height analysis installed was modified to allow direct comparison of the "lesser" and "summed" methods.

The calculation of DPMS in coloured samples using external standard ratio quench curves prepared from chemically quenched standards has been shown to yield appreciable errors. The performance of the "lesser" and "summed" methods with particular regard to this source of error is investigated. The "lesser" method is found to yield considerably smaller errors than the "summed" method. For tritium, the benefit in using the "lesser" method is clearly apparent for all counting efficiencies down to 10%. The "lesser" method is also superior for Carbon-14, but below a counting efficiency of 60% errors become more noticeable.

The unquenched counting efficiencies using the "lesser" method are only marginally smaller than those observed for the "summed" method.

Introduction

A steady progress in the development of improved liquid scintillation counting instruments has been maintained for several years (1,2). Most current commercially available machines employ "summed coincidence"

circuitry to improve the signal to noise ratio of the detection system, and thus enhance the sensitivity of the liquid scintillation method (3,4,5). The external standard ratio method of quench correction has been introduced in order to facilitate the rapid determination of sample counting efficiencies (6).

The calculation of coloured sample activities using external standard ratio quench curves prepared from chemically quenched standards has been shown to yield appreciable errors (7,8). Lang (8) devised a technique to distinguish whether a sample was predominantly colour or predominantly chemically quenched and to make the appropriate corrections. This technique however cannot accommodate those samples that are subject to simultaneous colour and chemical quenching. One way of overcoming this problem is to devise a method so that both coloured and chemically quenched standards give rise to a single quench correction curve. This paper describes the performance of an instrumental development, "lesser pulse height analysis", which is shown to achieve this objective for a wide range of counting efficiencies.

The "summed coincidence" method processes the signals from two horizontally opposed photomultiplier tubes in the following way: If pulses are detected from both photomultiplier tubes within such a short resolving time that they might be regarded as being coincident, then those signals are summed and used for subsequent analysis (3,4,5). The "lesser" method selects only the smallest of the two coincident photomultiplier tube signals for subsequent analysis. The benefit of using the "lesser" method is most clearly demonstrated by comparing the results obtained for both the "lesser" and "summed" methods on the same machine.

Experimental

A Nuclear Chicago Mark II [®] liquid scintillation counter with the "lesser" analysing system installed was modified so that a front panel switch would allow selection of either "lesser" or "summed" modes of operation. The simple modification required is shown in figure 1a. In order to confirm the proper operation of both "lesser" and "summed" circuitry, photomultiplier tube signals were simulated using a test pulse generator (fig. 1b), and the result measured with the single channel

analysers built into the liquid scintillation counter. These single channel analyser levels were plotted versus the appropriate input signals yielding close to linear relationships (fig. 2).

The preset analyser levels set by the manufacturers were used throughout the investigation so that the results obtained would be most relevant to the users of such a machine. A multichannel analyser interface module was also installed in the Mark II [®] so that the pulse height distribution of samples might be viewed using a Nuclear Chicago model 25601 multichannel analyser.

Details of fluor composition, radioactive standards, chemicals and dyes used in the experiment are described in Table I, together with the range of volumes added to the sample vials. In order to minimize variations in activity contained in the test samples, a known amount of activity was added to the stock solution of fluor, and 15 ml of this fluor then accurately pipetted into each vial. These unquenched samples were then counted, and sets of vials containing uniform activity selected for use as test samples.

The test samples were counted repetitively and between each counting period small amounts of the various quenching agents were added each to a particular single vial. Data were obtained giving sample count rate and external standard ratio for both the "lesser" and "summed" methods at each level of quenching. This experimental procedure was performed using first tritium and then carbon-14 as the source of radioactivity. All samples were measured for a preset count of 200000 or a maximum of ten minutes counting time.

Two additional samples were prepared for each isotope giving equal quenched counting efficiencies as measured using the "lesser" method, but quenching one sample with nitromethane and the other with red dye. Thus meaningful comparisons might be made between the pulse height spectra of chemically quenched and coloured samples as observed using the multichannel analyser.

Results

The count rate data for all samples at all levels of quenching were expressed as a % counting efficiency. These counting efficiencies were then plotted versus the corresponding external standard ratio values in figures

LIQUID SCINTILLATION COUNTING

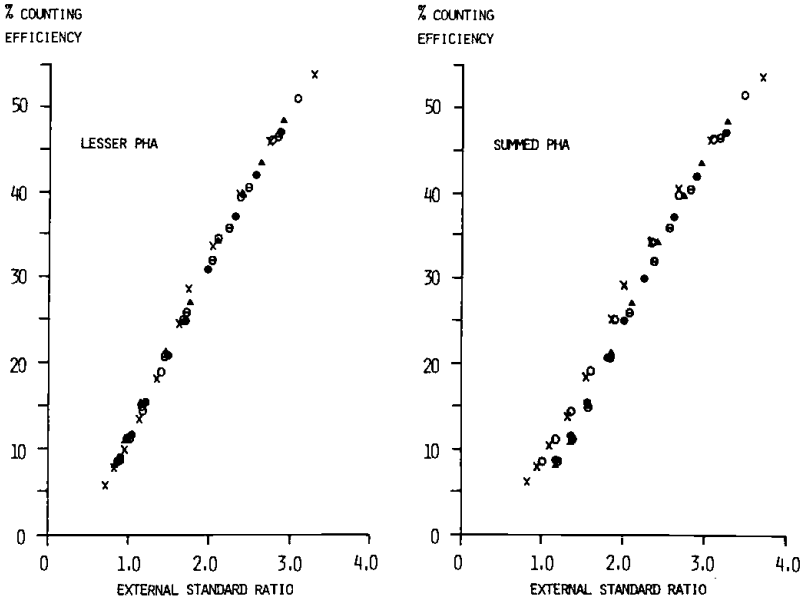


FIGURE 3. LESSER AND SUMMED TRITIUM COUNTING EFFICIENCY CORRECTION CURVES
 QUENCHING AGENTS: - NITROMETHANE (x), CARBON TETRACHLORIDE (o),
 YELLOW (theta), RED (delta) AND BLUE (bullet) DYES

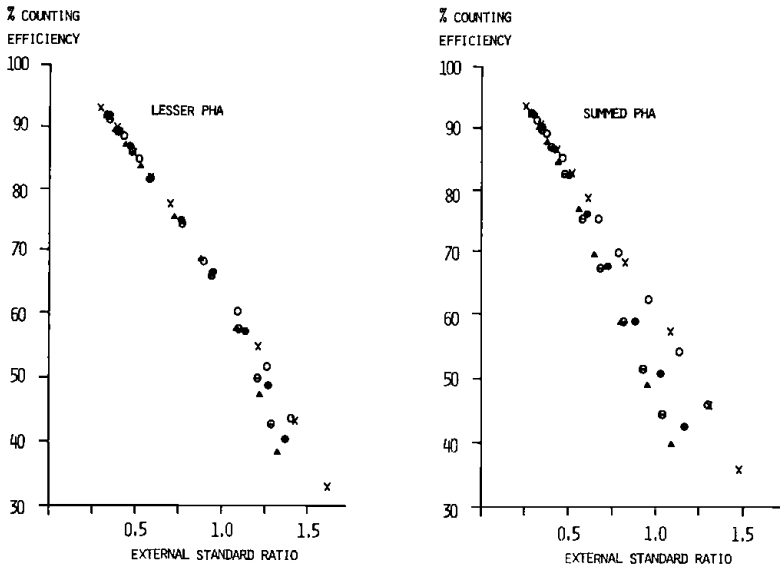


FIGURE 4. LESSER AND SUMMED CARBON 14 COUNTING EFFICIENCY CORRECTION CURVES
 QUENCHING AGENTS: - NITROMETHANE (x), CARBON TETRACHLORIDE (o), YELLOW (theta), RED (delta) AND BLUE (bullet) DYES

3 and 4. Using the data obtained for nitromethane, quench correction curves were generated using two methods; firstly by fitting polynomials according to the method of Carol and Houser (9), and secondly by straight line fitting between the standard points. The apparent activities in the remainder of the samples were calculated using counting efficiencies interpolated from the appropriate quench correction curves. The % error in calculating the activities using polynomial quench correction curves are shown in figures 5 through 8. Very similar results were obtained when counting efficiencies were linearly interpolated between the standard points.

The pulse height spectra for the carbon-14 isotope are shown in figure 9 for nitromethane quenched and red coloured samples of equal counting efficiency. The external standard spectra in these samples are shown in figure 10.

Discussion

The counting efficiency data for tritium shown in figure 3 indicate visually that all the quenching agents used give rise to a single quench curve for the "lesser" method. For the "summed" method however, chemically quenched and coloured samples give rise to distinctly separate curves.

Similar results are apparent for carbon-14 (fig. 4) for counting efficiencies above 60%. Below this counting efficiency differences between coloured and chemically quenched samples also become apparent for the "lesser" method. It is interesting to note that even though the "lesser" method always rejects information from one photomultiplier tube and thus might be expected to lose sensitivity, the unquenched counting efficiencies for the "lesser" method are very close to those obtained for "summed" (fig. 3,4).

Figures 6 and 8 show clearly that the "lesser" method reduces the error in determining coloured sample activities. This effect is particularly useful for samples that are quenched partly by chemicals and partly by colour.

The errors observed cannot be attributed to a volume dependancy effect, since it was found that a change in sample volume from 15 to 16 mls caused less than 1% change in both observed count rate and external standard

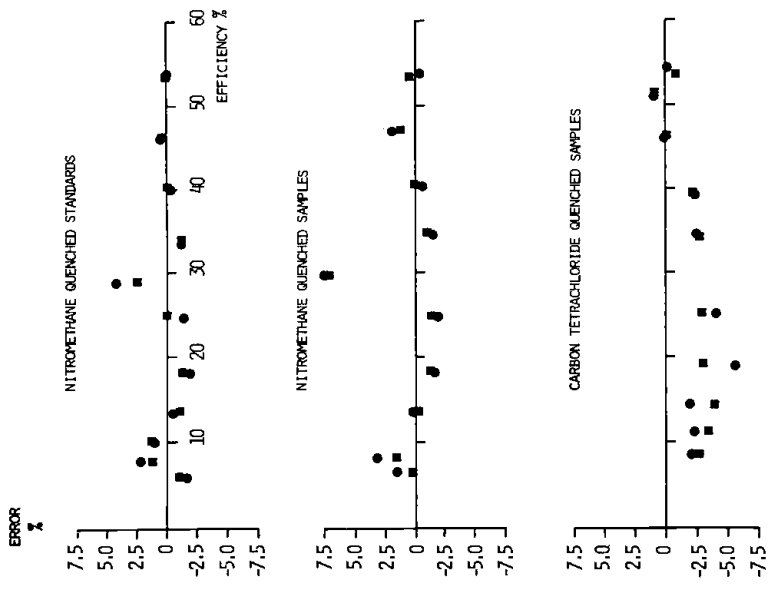


FIGURE 5. DIFFERENCES BETWEEN APPARENT TRITIUM DPM AND KNOWN DPM EXPRESSED AS A % ERROR FOR LESSER (●) AND SUMMED (■) METHODS COUNTING EFFICIENCIES INTERPOLATED FROM POLYNOMIAL QUENCH CORRECTION CURVES

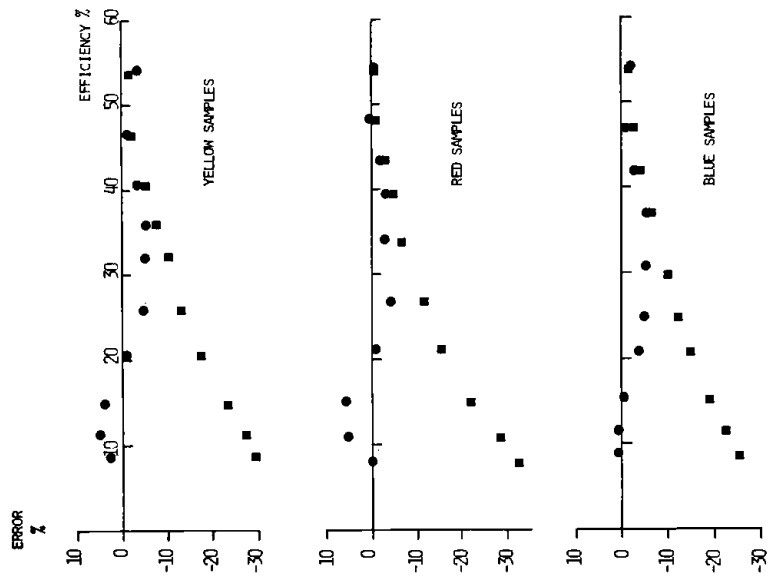


FIGURE 6. DIFFERENCES BETWEEN APPARENT TRITIUM DPM AND KNOWN DPM EXPRESSED AS A % ERROR FOR LESSER (●) AND SUMMED (■) METHODS COUNTING EFFICIENCIES INTERPOLATED FROM POLYNOMIAL QUENCH CORRECTION CURVES

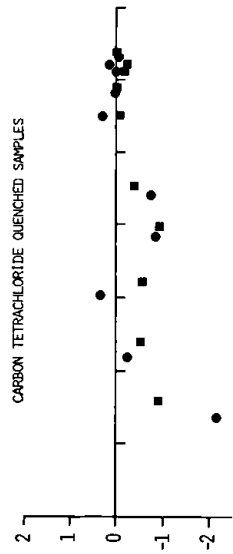
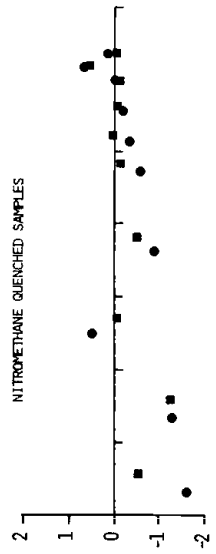
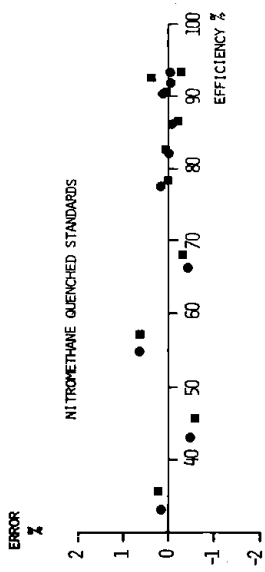


FIGURE 7. DIFFERENCES BETWEEN APPARENT CARBON 14 DPM AND KNOWN DPM EXPRESSED AS A % ERROR FOR LESSER (●) AND SUMMED (■) METHODS COUNTING EFFICIENCIES INTERPOLATED FROM POLYNOMIAL QUENCH CORRECTION CURVES

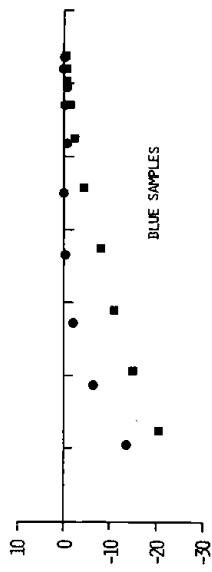
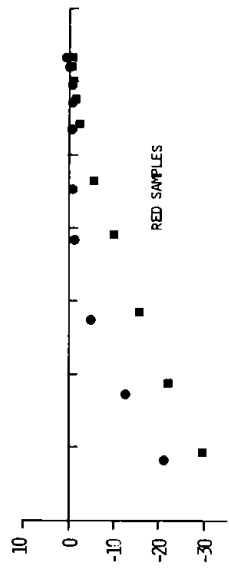
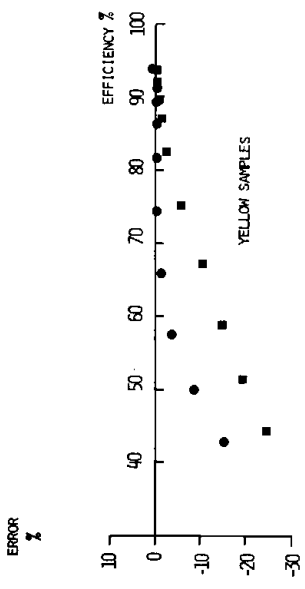


FIGURE 8. DIFFERENCES BETWEEN APPARENT CARBON 14 DPM AND KNOWN DPM EXPRESSED AS A % ERROR FOR LESSER (●) AND SUMMED (■) METHODS COUNTING EFFICIENCIES INTERPOLATED FROM POLYNOMIAL QUENCH CORRECTION CURVES

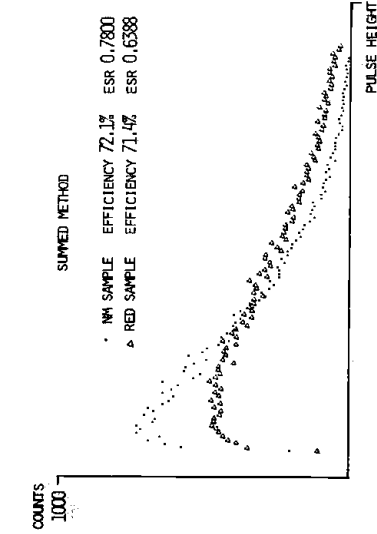
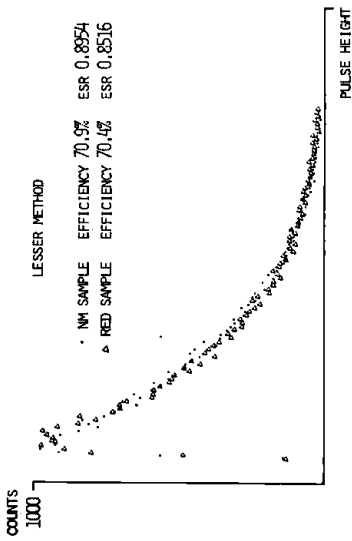


FIGURE 9. COMPARISON OF LESSER AND SUMMED C14 PULSE HEIGHT SPECTRA FOR COLOURED (RED) AND NITROETHANE (NI) QUENCHED SAMPLES (MCA INTERFACE COARSE GAIN B. FINE GAIN MAX. SIGNALS GATED THROUGH C14 WINDOW)

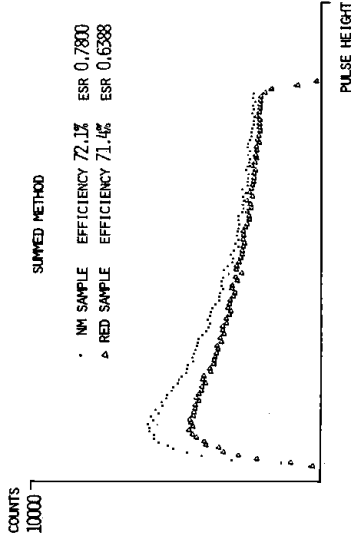
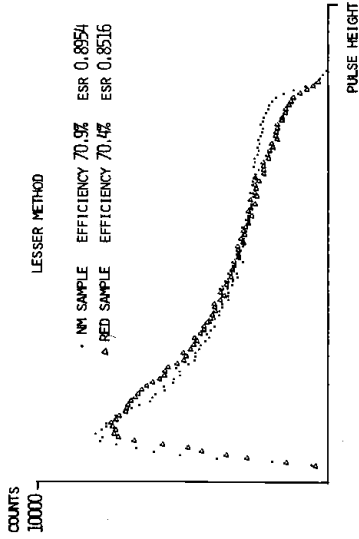


FIGURE 10. COMPARISON OF LESSER AND SUMMED EXTERNAL STANDARD PULSE HEIGHT SPECTRA THROUGH C14 ESR \square WINDOW FOR COLOURED (RED) AND NITROETHANE (NI) QUENCHED SAMPLES. SAMPLE CONTRIBUTION ELIMINATED. (MCA INTERFACE COARSE GAIN A. FINE GAIN 80%, COUNTING TIME 1.7 MINS)

ratio. Furthermore since the "lesser" and "summed" measurements were performed on the same vial at each level of quenching, any differences must be attributable to those two methods.

The pulse height spectra of carbon-14 (fig. 9) shows dramatically the differences between the "lesser" and "summed" methods. For the "lesser" method the spectra for samples quenched to the same counting efficiency by chemicals and dyes very nearly coincide. For the "summed" method large differences are evident. Despite these changes in spectral shape, the integral counting efficiencies for the summed method do not differ greatly for the two quenching agents. The corresponding external standard ratios however do differ greatly, and figure 10 shows the associated spectral shapes of the external standard. It would appear therefore that the deviations of the "summed" data from a homogenous quench curve are due predominantly to displacements in the external standard ratio values.

Conclusions

The authors conclude from this investigation that the "lesser" method is a useful instrumental development in liquid scintillation counting. The reliability in determining the activities in samples that are both coloured and chemically quenched is improved by the application of this method.

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Table I. Materials Used

- A. Fluor Composition:
4 g/l PPO, 50 mg/l POPOP in toluene
- B. Radioactive Standards:
 - (i) Tritiated Toluene NES 004 lot 552-220
3.12 x 10⁶ DPM/ml - 25th April 1972
 - (ii) Carbon-14 Toluene NES 006 lot 552-285
4.15 x 10⁵ DPM/ml - 8th March 1972
- C. Chemical Quenching Agents:
 - (i) Nitromethane - maximum of 0.12 ml added to vials
 - (ii) Carbon Tetrachloride - maximum of 0.28 ml added to vials
- D. Dyes - colour quenching agents:
 - (i) Carotene Yellow - 47.2 mg/100 ml fluor
maximum of 0.27 ml of solution added to vials
 - (ii) Scarlet Red - 115.9 mg/100 ml fluor
maximum of 0.31 ml of solution added to vials
 - (iii) Oracet Blue - 89 mg/10 ml fluor
maximum of 0.27 ml of solution added to vials

