STUDIES OF LOW-LEVEL LIQUID SCINTILLATION COUNTING OF TRITIUM

W. J. Kaufman,* A. Nir,** G. Parks,* and R. M. Hours***

INTRODUCTION

Tritiated water has been demonstrated to be one of the more satisfactory ground water tracers and is finding increasing application by petroleum, hydraulic, and sanitary engineers in the solution of problems involving underground explorations. In instances where the investigation entails the tracing of large volumes of water in conjunction with a resource development for domestic or industrial purposes, it is necessary to employ tritium concentrations well below the current population exposure limits of 3 x 10^{-3} μc/ml (1). Furthermore, the sensitivity of detection or measurement of tritium directly influences the quantity of tracer required for a particular tracing task. Thus for both health and economic reasons, it is desirable to have a highly sensitive yet simple procedure for measuring the tritium content of labeled water. The general objective of this investigation was to develop a counting system allowing the detection of tritium in concentrations of 10^{-6} μc/ml or less with a counting period of no more than 30 minutes.

---

*Division of Hydraulic and Sanitary Engineering, University of California, Berkeley.

**Lawrence Radiation Laboratory, University of California, Berkeley. On leave of absence from the Weizmann Institute of Science, Rehovoth, Israel.

***Commissariat à L'Energie Atomique, Saclay, France.

DETECTION SENSITIVITY

In comparing various systems for measuring tritium, it is desirable to employ a sensitivity criterion that considers the several parameters involved in the measurement and provides a dimensionally meaningful number having a statistical relation to the problem under consideration. Several authors have employed figures of merit, the most common one being the square of efficiency divided by background ($E^2 \div n_b$). Wagner and Guinn (2) have used the term "concentration sensitivity" to designate the smallest concentration of activity determinable with a 10 per cent coefficient of variation, a 30-minute counting period, and a particular sample volume, counting efficiency, and background. This concentration was also designated as the "minimum concentration detectable." Hours and Kaufman (3), in a detailed examination of this question, used a coefficient of variation of 50 per cent to define detectable, and Guinn's 10 per cent value to express the "minimum measurable concentration." The selection of confidence limits is, of course, a matter of individual whim, tempered by the necessities of the problem under investigation. However, for hydrologic studies involving numerous interdependent measurements, a level of confidence of 95 per cent in making the decision of whether a particular sample contained some portion of the original labeled water would seem reasonable. For this reason the 95 per cent limit, i.e., a coefficient of variation of 50 per cent, was chosen to designate detectability throughout the investigation.

For the 95 per cent confidence level, the Minimum Detectable Activity concentration may be obtained from the expression,

$$\text{M.D.A. } (\mu c/ml) = \frac{9.0 \times 10^{-5}}{Ev} \sqrt{\frac{n_b}{t}} \qquad (1)$$

in which E is the efficiency in per cent, v the volume of sample in milliliters, n_b the background in counts per minute, and t the counting time in minutes. The reciprocal of Eq. 1 with a counting time of 30 minutes has been designated Detection Sensitivity (D.S.) and is given by Eq. 2. It has been the general objective of these studies to obtain maximum values of D.S. in the counting of tritiated water samples.

$$\text{Detection Sensitivity (D.S.) (liters/}\mu\text{c)} = 61 \frac{Ev}{\sqrt{n_b}} \qquad (2)$$

If a sample has a concentration of radionuclide corresponding to the M.D.A., there is a probability of 0.5 that it would be rejected as not significant, i.e., the net counting rate would be less than two standard deviations above background. Furthermore, the probability of recording such a concentration as a result of the normal statistical fluctuations in background measurements would only be 0.025. In instances where no limit is placed on the sample volume, most investigators should be concerned with maximizing D.S. rather than simply improving efficiency.

Efforts to improve sensitivity centered around increasing the expression $Ev/\sqrt{n_b}$ by optimizing the scintillator composition and increasing the volume of scintillator placed between the photomultiplier tubes, thus increasing the quantity of sample, v, counted. Since Eq. 2 is a theoretical expression of sensitivity, an investigation of counter performance over a period of several weeks was made to establish the true or operating sensitivity of the counting system. The several experiments related to the general objective of improving sensitivity are described in the following sections.

EXPERIMENTAL PROCEDURES AND RESULTS

The present study employed a commercial Packard Tri-Carb liquid scintillation spectrometer equipped with 2 DuMont 6292 photomultiplier tubes and subsequently modified to receive 2 E.M.I. quartz-faced 6255A photomultipliers. Unless indicated to the contrary, the DuMont equipped instrument was operated with the analyzer photomultiplier at full gain, with a 10-90 volt discriminator channel, and with a photomultiplier voltage of 1300, these values having been selected as generally most suitable for the scintillator used based on the "balance-point operation" method described by Packard (4).

Optimization of the Dioxane-Naphthalene-Water Scintillator

A review of the literature pertaining to tritiated water counting led to the selection of the dioxane-naphthalene-water scintillator suggested by Furst, Kallman, and Brown (5). In the initial phases of the investigation, the proportions of commercial dioxane (containing 4.0 g/l PPO and 0.10 g/l α-NPO), naphthalene, and water were varied systematically with the immediate objective of maximizing the expression $Ev/\sqrt{n_b}$. The 5-dram (20-ml) Crystal Lite vial was employed with the unmodified Tri-Carb shutter-receiver of polished aluminum. The freezer was operated at -7°C during these measurements and in some instances a phase separation occurred prior to completion of a measurement, necessitating the discarding of such observations. A plot of efficiencies and sensitivities of the scintillators containing 60 and 100 g/l of naphthalene is given as Fig. 1 and clearly demonstrates that maximum sensitivity corresponds to a scintillator composition providing considerably less than a maximum efficiency.

A further investigation of the scintillator system containing 100 g naphthalene per liter of dioxane led to the selection of PPO and POPOP at 6.0 g/l dioxane and 0.3 g/l dioxane, respectively, as providing the greatest sensitivity. POPOP was found superior to α-NPO as a secondary phosphor and PBD was less satisfactory than PPO as the primary phosphor. Although these studies were far from exhaustive,* they demonstrated that further examination of combinations of dioxane, naphthalene and water, together with the four phosphors, would afford little additional benefit as measured by improved sensitivities. It is interesting to note that a second lot of commercial dioxane gave an 18.4 per cent improvement in efficiency, confirming reports concerned with the purity of the scintillator components. Unless otherwise indicated, all measurements reported subsequently herein were carried out with 81.4 per cent by volume of the second lot of dioxane (containing 100 g/l naphthalene, 6.0 g/l PPO, and 0.3 g/l POPOP) and 18.6 per cent water. This scintillator has been designated ΔN7-100.

Studies of Counting Cell Geometry

Recognizing that the optimum scintillator composition for the 5-dram counting cell would not necessarily be the most satisfactory for other and larger cells, the study was continued with the ΔN7-100 scintillator with the objective of selecting a scintillator volume (V) and a suitable container and reflector that would afford a maximum value of $Ev/\sqrt{n_b}$, yet be readily adaptable for use with the Tri-Carb instrument. In

*Further details of these studies were reported in Ref. 3.

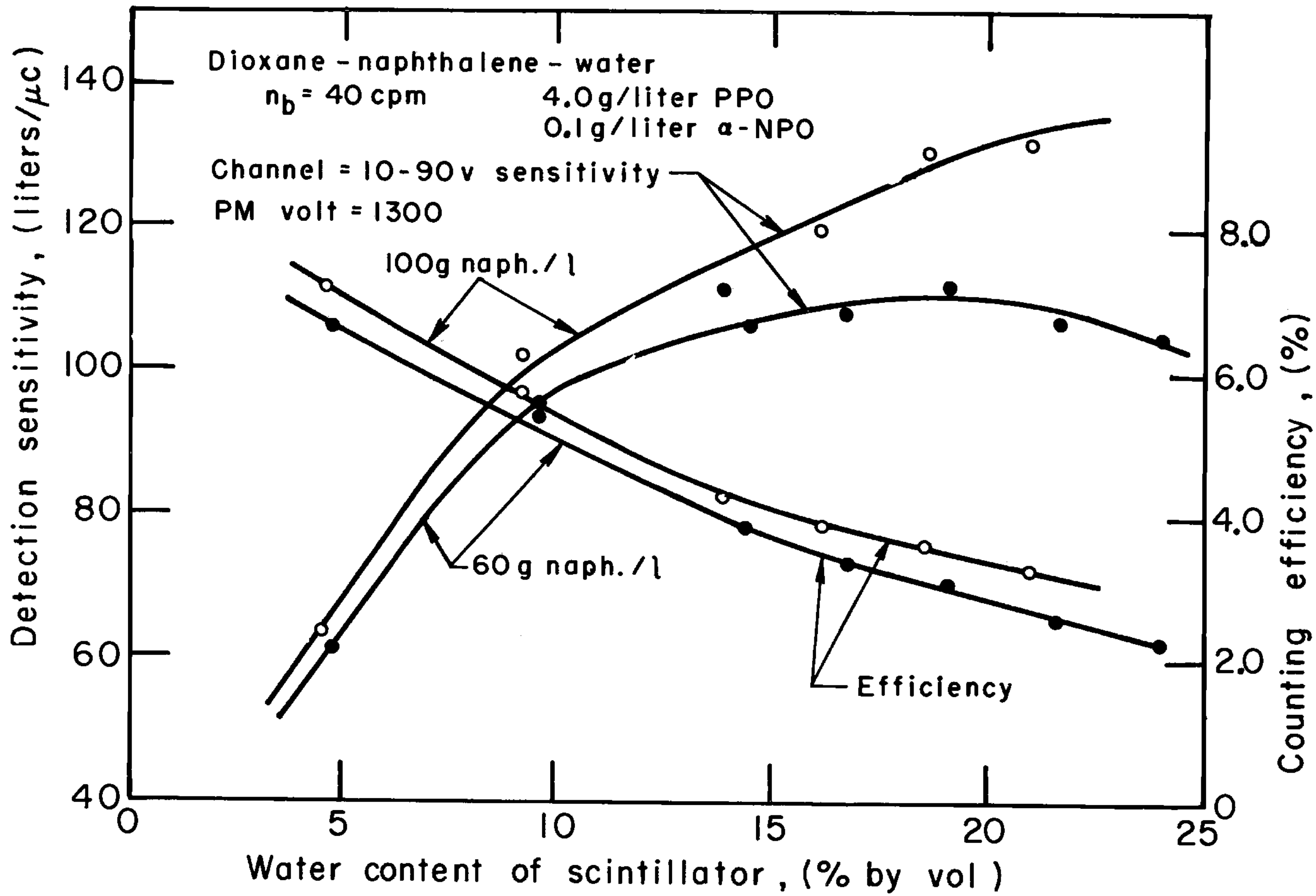

Fig. I Influence of scintillator composition on detection sensitivity and efficiency.

order to ensure indefinite temperature stability of the scintillator, a refrigerator temperature of +3°C was chosen for these measurements and all subsequent studies. The cells examined included the commercially available 60-ml Crystal Lite vial, 60-ml quartz and 140-ml Pyrex vials of similar configuration, and 3 cylindrical vials of Vycor, quartz, and Pyrex. The characteristics and performance of these several cells have been summarized in Table 1. The 3 cylindrical cells were placed in a specially constructed receiver and aligned coaxially with respect to the photomultipliers. The advantages of a silicone-bath optical couple over air are clearly apparent from the values in parentheses in Table 1.

The advantages of the cylindrical geometry were further investigated with a special photomultiplier holder allowing separation distances ranging from 20 to 100 mm and with the scintillator in direct contact with the face plates of the DuMont photomultipliers. The photomultipliers were connected with a polished aluminum sleeve (internal diameter = 52 mm) that formed a cylindrical cavity containing the scintillator. Measurements of efficiency were made at several photomultiplier separations with each of 3 scintillators:

(1) the DN7-100 - 18.6 per cent water and 81.4 per cent of the "first lot" of dioxane containing 100 g naphthalene, 4.0 g PPO, and 0.1 g POPOP per liter.

(2) the ΔN7-100 - 18.6 per cent water and 81.4 per cent of the "second lot" of dioxane containing 100 g naphthalene, 4.0 g PPO, and 0.1 g POPOP per liter.

(3) the Kinard system (6) - solvent: 5 parts 1,4-dioxane, 5 parts xylene, and 3 parts ethanol and solute: 80 g naphthalene, 5.0 g PPO, and 0.05 g α-NPO, all per liter of solvent. The final scintillator was 7.14 per cent water by volume.

The relation of efficiency and sensitivity to photomultiplier separation for the 3 scintillators is shown in Fig. 2. As noted earlier, optimum sensitivities occur at appreciably less than optimum efficiencies. Furthermore, the ΔN7-100 system, at somewhat lesser PPO and POPOP concentrations than employed in the previously discussed dioxane system, was definitely superior to the DN7-100 and Kinard systems. A maximum sensitivity was observed for the Kinard scintillator but was not apparent for the two dioxane-naphthalene systems. In all cases, the efficiency decreased with increased

TABLE 1. CHARACTERISTICS AND PERFORMANCE OF VARIOUS COUNTING CELLS

Cell	Photomultiplier Gap (mm)	Background n_b (cpm)	Efficiency E (per cent)	Detection Sensitivity (Eq. 2) (liters/μc)
20-ml, Crystal Lite	47	49	5.01	160
60-ml, Crystal Lite	67	49	2.17	210
60-ml, quartz	67	49	2.61	260
140-ml, Pyrex	67	112	2.00	300
180-ml,* Vycor (aluminum foil covered)	105	291 (348)	3.43 (7.61)	410 (840)
180-ml,* Pyrex (silvered)	105	168 (242)	3.16 (7.95)	500 (1020)
87-ml,* quartz	105	60 (103)	4.10 (7.04)	530 (680)

*Cylindrical cell coaxially mounted with respect to photomultipliers. Values in parentheses were determined with an optical coupling. All measurements were made with the ΔN7-100 scintillator at +3°C, 1300 V, and with the 10-90 volt channel.

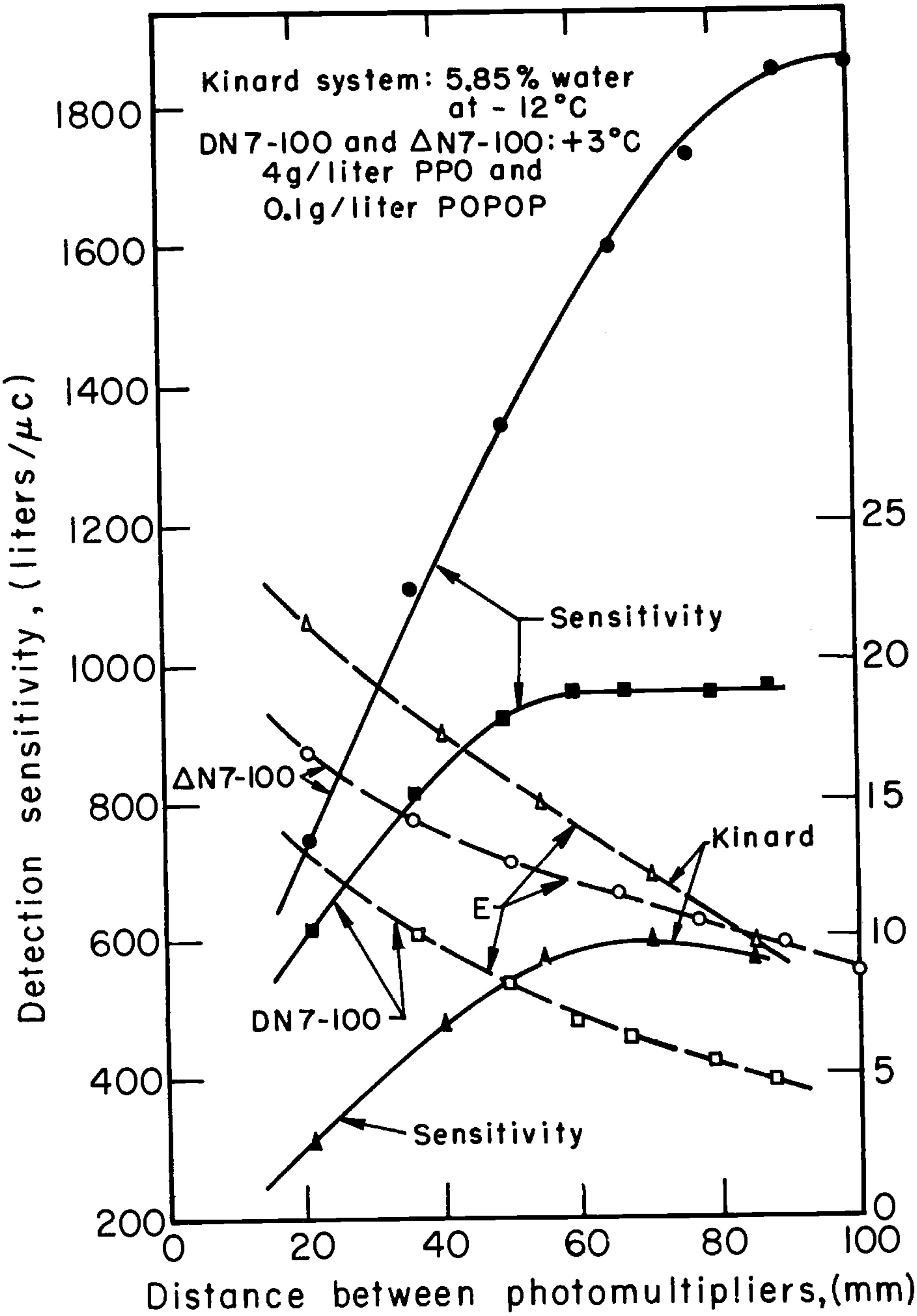

Fig. 2 Effect of photomultiplier separation on efficiency and sensitivity.

photomultiplier separation. In a long cylindrical cell, a release of 30 to 40 photons near one photomultiplier might well go undetected by the more distant photomultiplier and, in a coincidence system, pass unrecorded by the scaler serving the 10-90 volt channel. The greater the number of photons produced, the greater the efficiency at small photomultiplier separations. Similarly, the greater the photon production, the greater the photomultiplier separation corresponding to maximum sensitivity, providing the scintillators under comparison have identical optical transmissibilities. This relationship is shown to exist for the DN7-100 and ΔN7-100 systems, but not for the Kinard system. This anomaly might be explained by the greater light absorption occurring in the Kinard scintillator.

Characteristics of the Insert Counting Cell

The insert cell shown in Fig. 3 represents an effort to optimize those factors exerting a major influence on sensitivity, while retaining a high degree of versatility of instrument use. The cell has a volume of 170 ml and creates a polished cylindrical cavity between the photomultiplier tubes, the face plates of the latter comprising the ends of the cell. By employing threaded aluminum photomultiplier tube holders and rubber O-rings, it was possible to contain the scintillator without leakage, yet to easily remove or shift the photomultipliers without fear of breakage. The cell interior was polished silver, while the remainder of the cavity was polished aluminum. The photomultiplier separation was 90 mm. The cell may be easily removed and replaced with the normal Tri-Carb shutter-receiver assembly for use with the 20-ml vials.

The efficiency and sensitivity of the insert cell operated with the ΔN7-100 scintillator and 2 DuMont 6292 photomultipliers were 6.34 $\pm$ 0.09 per cent and 1220 liters/μc, respectively, the latter quantity computed from Eq. 2. In 16 independent 30-minute measurements over a 4-day period, the background was 100.5 $\pm$ 1.8 cpm, clearly demonstrating the conformance of operation to the variance expected from Poisson statistics. The operating temperature during the test series was 3°C.

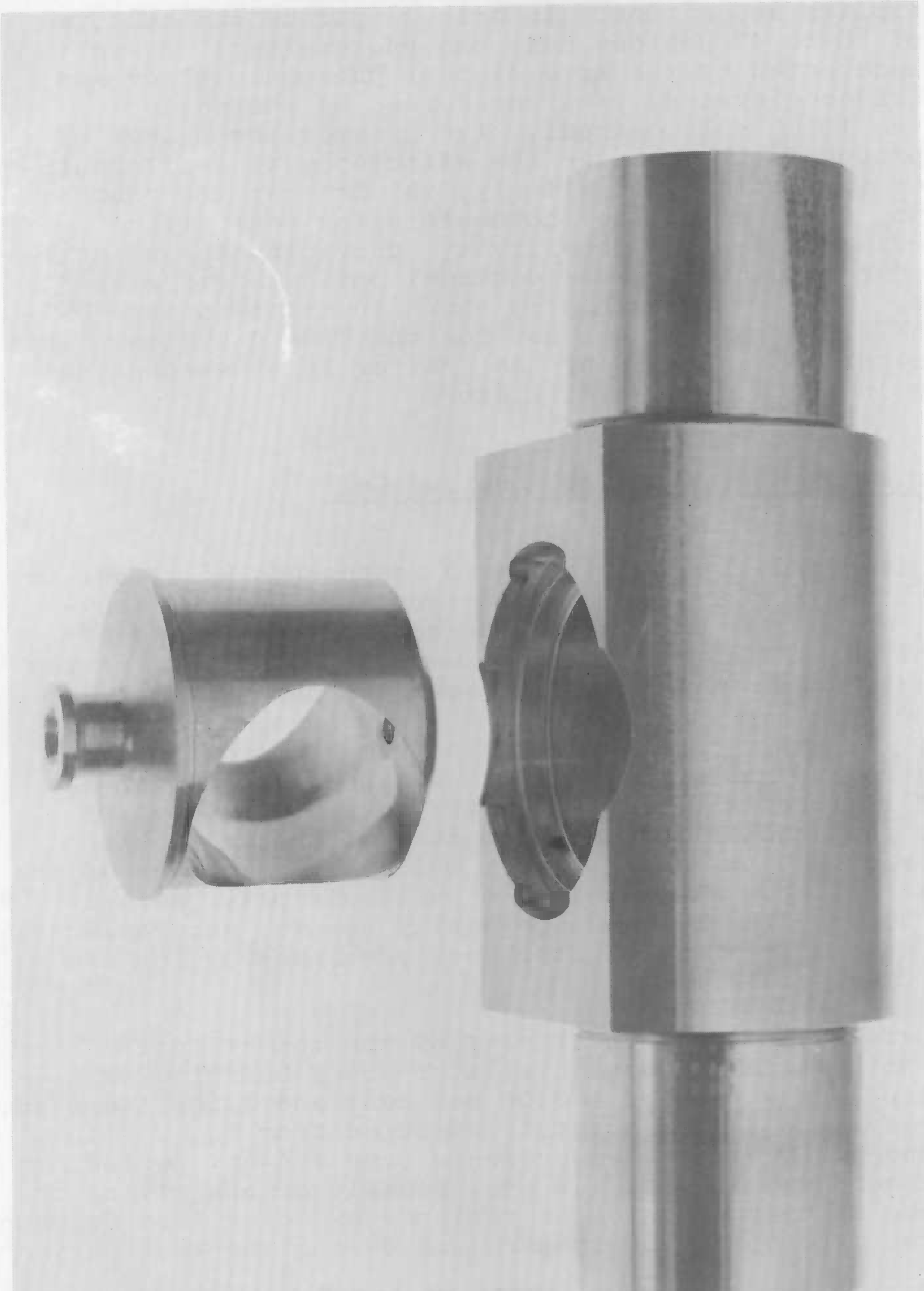

Fig. 3. Insert cell and modified Tri-Carb receiver.

Comparison of DuMont 6292 and E.M.I. 6255A Photomultiplier Tubes

The purpose of this phase of the investigation was to compare the performance of the more commonly used DuMont 6292 photomultiplier tubes with the E.M.I. 6255A and to modify the scintillator and cell reflectivity to conform more nearly with the spectral sensitivity of the E.M.I. tubes. Bibron (7), using a coincidence system equipped with E.M.I. 6255 photomultipliers, has reported tritium efficiencies of 25.5 per cent with a 20-ml quartz vial optically coupled to the photomultipliers. The corresponding background was only 15 cpm. There are several potential advantages of these photomultipliers over the DuMont 6292. The 6292, having the S11-type photocathode, is more sensitive in the visible portion of the spectrum and consequently there is an advantage in employing a wave length shifter with PPO, such that the scintillator spectrum more nearly matches the spectral response of the photomultiplier. Undoubtedly some loss occurs in the additional energy transfer from primary to secondary phosphor. On the other hand, the E.M.I. 6255A tubes with the S13 photocathode and quartz face plates are more sensitive in the ultraviolet region, thus possibly removing the need for POPOP. An incidental advantage of the visible region is the longer mean absorption path of the photons and a lower susceptibility to impurity absorption (8).

A comparison of the two types of photomultipliers was made employing the ΔN7-100 scintillator and is reported in Table 2. The high voltage and amplifier settings were selected to achieve a maximum value of detection sensitivity. The higher gain of the 13-stage E.M.I. photomultipliers required the addition of an external attenuator to the Tri-Carb system in order to bring the spectrum within the 10-90 discriminator channel. This modification also served to enhance discrimination of line and tube noise originating in the freezer and preamplifiers.

Performance of the E.M.I. 6255A Tubes in the Ultraviolet Region

The efficiency and sensitivity of the E.M.I. 6255A photomultipliers were determined as a function of tube separation and with the ΔN7-100 scintillator, with and without POPOP. A cylindrical Teflon reflector was used in this comparison, since

TABLE 2. EFFICIENCY AND DETECTION SENSITIVITY OF E.M.I. 6255A AND DuMONT 6292 PHOTOMULTIPLIER TUBES

Tube and Cell	Background, cpm 10-90	90-∞	Efficiency (per cent)	Detection Sensitivity (liters/μc)
E. M. I.				
20-ml vial	24	49	2.6	112
170-ml cell	57*	202	6.9*	1680*
DuMont				
20-ml vial	40	--	2.7	99
170-ml cell	100	250	6.3	1220

*In a subsequent statistical study of the E.M.I. tubes, the background was 43 cpm, the efficiency 5.6 per cent, and the detection sensitivity 1620 liters/μc.

it has been reported to have good ultraviolet diffuse reflection characteristics (9). The results are given in Fig. 4 and demonstrate little practical advantage of one scintillator over the other. Maximum sensitivities with Teflon are less than those reported in Table 2 for both E.M.I. and DuMont photomultipliers employed with the polished silver insert cell, this being largely due to the greater backgrounds. The highest efficiency was achieved with the ΔN7-100 less POPOP solution at 10 mm separation, while the highest detection sensitivity was equal for both solutions, but at different photomultiplier separations. This may be explained by the different transmission and reflection characteristics of both systems. This would also explain the superiority of the 170-ml insert with the ΔN7-100 solution as having a better average combination of transmission and reflection coefficients. The lower background in both counting channels, obtained for the 170-ml insert compared to that found with the Teflon-lined cell, although the former has higher counting efficiency, was not readily explained on the basis of the foregoing experiments and needs further investigation. These results indicated that the measurement in the ultraviolet spectral region was inferior under the present conditions, although it might be of certain advantage when sample volume was limited.

The Use of an Internal Cobalt^{57} Standard as a Counting Efficiency Monitor

One of the factors influencing detection sensitivity in tritium counting was the varying counting efficiency, caused often by small amounts of quenching impurities introduced into the scintillator solution at some stage of sample preparation. The sample itself has often varying chemical composition, which affects the quenching and light transmission properties of the scintillator solution. In order to account for these variations in counting efficiency, the common method is to "spike" the solution with known amounts of tritiated sample. This method has the disadvantages that care must be taken not to change the counting efficiency while "spiking" and that the original sample activity is destroyed.

In searching for a suitable efficiency monitor that would be free from these disadvantages, the use of Co-57 as an internal solid source was investigated. Cobalt-57 decays by electron capture with 270 days half-life, with two predominant gamma radiations in cascade: γ_1 = 14 kev, and γ_2 = 122 kev, with

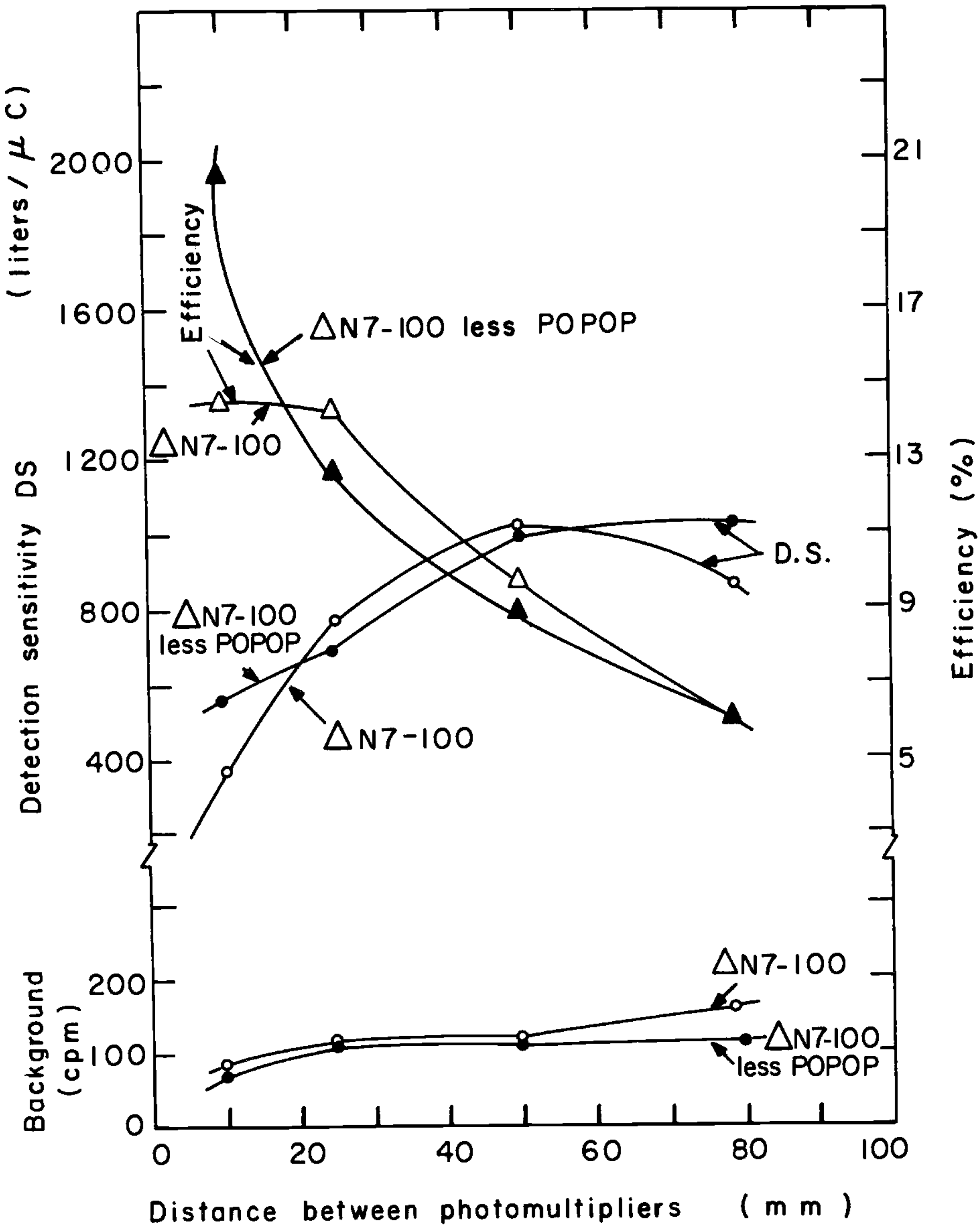

Fig. 4 Efficiency, detection sensitivity, and background as a function of photomultiplier separation for the ΔN7-100 and ΔN7-100 less POPOP systems.

the γ_1 undergoing high electron conversion ($E/\gamma = 15$) (10). It was expected that, with the 2-channel system of the Packard Scintillation Counter set for tritium counting in the lower channel, the lower energy radiation would be counted predominantly in the lower channel while the higher energy radiation would be counted in the higher channel, the exact channel count ratio depending on efficiency. This ratio could be an effective tritium counting efficiency monitor provided a definite dependence between the two variables could be shown, which would be reproducible and independent of the cause of efficiency change within reasonable limits. Furthermore, it should not affect the activity and composition of the sample. The advantage of using the channel count ratio rather than single channel count rate is that the ratio is independent of the activity of the Co-57 source and no correction for decay is required. The activity level was selected so as to give statistically significant ratios within 3-5 minutes counting times, but not so high as to cause count loss due to dead time in associated apparatus.

The source was deposited at the tip of a 2-in. long platinum wire. This portion of the wire was then gold-plated in order to reduce loss of Co-57 to the solution. The upper end of the platinum wire was mounted in an aluminum holder in the center of a plastic cap which served as the cover for the 170-ml insert cell. When in use, the active tip of the platinum wire was in the center of the cell and about 3/4 in. from its bottom.

The experiment consisted of measuring the counting efficiency of tritium in a particular scintillator and then determining the channel ratio, R, for the Co-57 source in the same sample, where $R = n_{(90-\infty)}/n_{(10-90)}$. In order to vary the efficiency, increasing amounts of water, hydrogen peroxide, pyridine, and "O-ring contamination" were added to the ΔN7-100 solution. The range of efficiency variation was then increased, through the use of tritiated toluene, as a scintillator solvent with 3 g/l PPO and 0.3 g/l POPOP, and with pyridine as the quencher. The results of repeated runs performed with different scintillator solutions, quenchers, and photomultiplier tubes are given in Fig. 5. The result of a typical repeated measurement of the R value was 0.920 ± 0.006, while the calculated statistical standard deviation was 0.003. The actual counting rate of Co-57 was about 40,000 cpm in each channel. Good reproducibility of R values was obtained only with careful placing of the Co-57 source holder in the same position in the insert cell. The need for this precaution was caused probably by improper centering

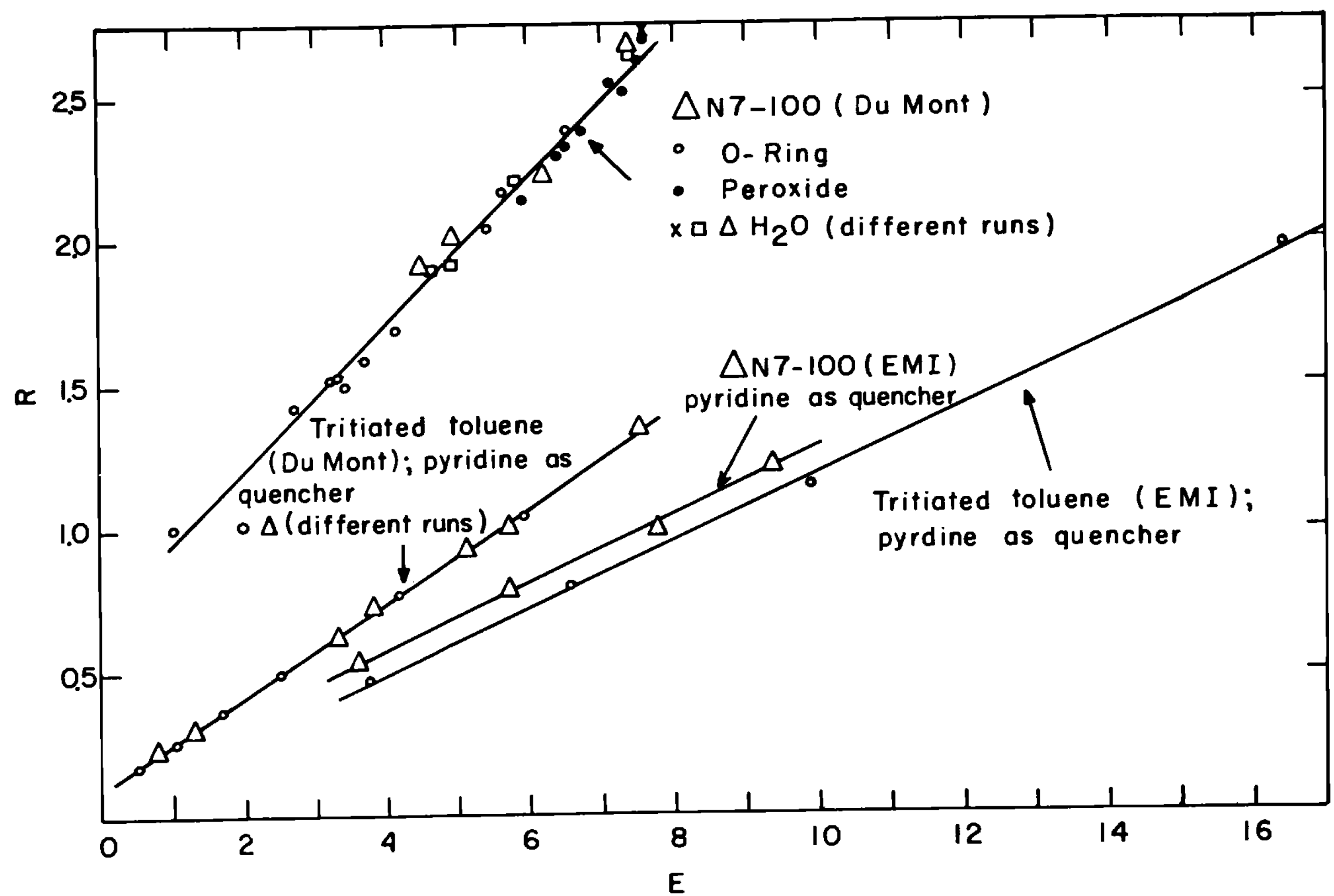

Fig. 5. Cobalt^{57} channel ratio (R) as a function of counting efficiency (E) for different scintillator solutions, quenchers, and photomultiplier tubes.

of the wire and the source on the wire. The activity of the scintillator increased considerably during the first day of application of the Co-57 standard, but on subsequent days this increase was reduced to about 4 cpm following each measurement.

The foregoing results indicate that Co-57 may serve as an effective efficiency monitor for tritium in liquid scintillator solutions. The ratio was independent of the source of quenching and its reproducibility was satisfactory. The contamination of the sample was slight and could probably be avoided with better source preparation. Present results indicate that with an accurately determined R versus efficiency curve, the efficiency can be ascertained within 0.1 per cent for a series of runs performed within several hours. Long-term accuracy of this method depends on instrumental stability and was illustrated by the results of the next section.

As evidenced from Fig. 5, the R values and slopes of the R versus efficiency curves vary when basic components of the system such as gain settings, photomultiplier tubes, or cell shapes are changed. This should be expected as these changes affect the counting efficiency of γ_1 and γ_2 in a differing manner. The change in scintillator solution would influence the R versus efficiency curve only to the extent that the absorption efficiency for γ_2 would be changed, as γ_1 is fully absorbed in most cells of conventional sizes. This indicates that care should be exercised with quenchers that would be used in large quantities so as to change the effective absorption characteristics for gamma radiation of the resulting scintillator.

Performance Stability of the 170-ml Insert Cell and the Tri-Carb Counter

A series of 31 background and 21 low-level tritium measurements were made over a 2-week period employing the ΔN7-100 scintillator, the 170-ml insert cell, and the Tri-Carb instrument equipped with E.M.I. 6255A photomultiplier tubes. All scintillator solutions were prepared daily from distilled water and a stock dioxane solution of naphthalene, PPO, and POPOP. The scintillator samples were cooled to 3°C, introduced into the insert cell, and immediately counted for 30 minutes. Generally three background and two active samples were counted daily, and no effort was made to decontaminate the cell between measurements. Measurements of the Co-57 channel ratio were made after each tritium observation. The mean values and "measured" standard deviations are shown in Table 3 together with the theoretical standard deviation as computed from Poisson statistics. The mean net counting rate was 108.7 cpm. The individual observations plotted against time are shown in Fig. 6.

The measured standard deviation of each quantity shown in Table 3 exceeded the theoretical. This is to be expected, since the error computed from the Poisson distribution reflects only the random nature of radioactive decay while the measured error includes such effects as variations in sample preparation, Co-57 source position, cell reflectivity, and of course the over-all instrument performance. As the theoretical error is reduced by increasing the number of counts recorded, the ratio of theoretical to measured error must be expected to increase. The measurements are considered to demonstrate an adequate instrument reliability for low-level measurements, but do indicate an appreciable discrepancy between the theoretical and actual detection sensitivities. The theoretical detection sensitivity from Eq. 2 had an average value of 1660 liters/μc.

ACKNOWLEDGMENTS

This research was conducted by the Sanitary Engineering Research Laboratory of the University of California, Berkeley, under a contract with the U. S. Atomic Energy Commission. The authors gratefully acknowledge the assistance and advice of Dr. Joseph A. Lieberman, Chief, Environmental and Sanitary Engineering Branch, Division of Reactor Development, U. S. Atomic Energy Commission.

TABLE 3. PERFORMANCE STABILITY OF INSERT CELL

Quantity	Mean	Measured Standard Deviation	Theoretical Standard Deviation
Background, n_b	42.8 cpm	2.1 cpm	1.2 cpm
Efficiency, E	5.62%	0.18%	0.14%
Channel Ratio Co-57, R	0.755	0.015	0.003

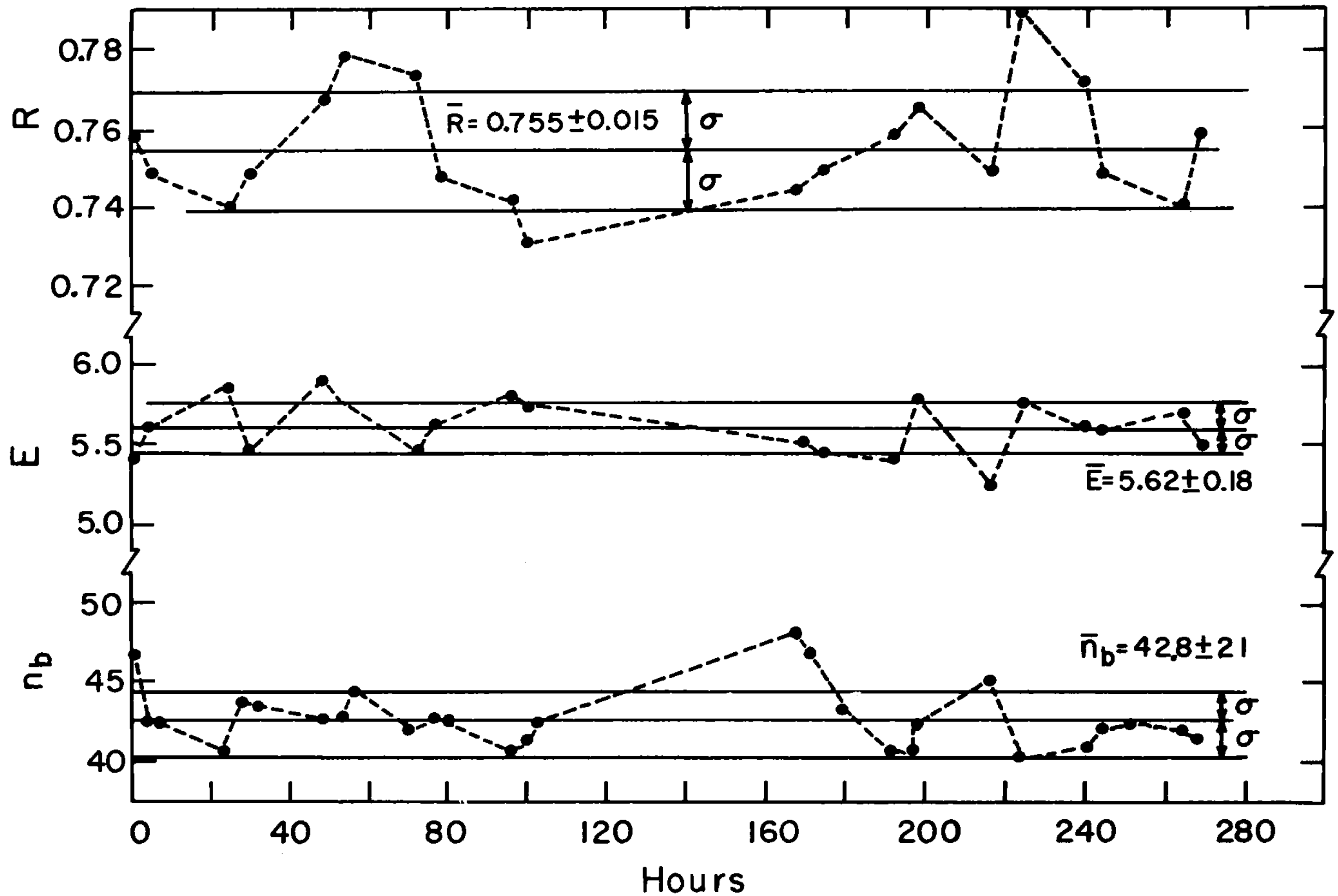

Fig 6 Co^{57} channel ratio (R), counting efficiency (E), and background (n_b), for a long-term measurement

REFERENCES

(1) Maximum Permissible Body Burdens and Maximum Permissible Concentrations of Radionuclides in Air and in Water for Occupational Exposure. N. B. S. Handbook 69 (June 5, (1959).

(2) Wagner, C. D. and Guinn, V. P. For Low Specific Activity: Use Scintillation Counting. Nucleonics 13:56 (October 1955).

(3) Hours, R. M. and Kaufman, W. J. Low-Level Tritium Measurement with the Liquid Scintillation Spectrometer. Progress Report No. 1, October 1, 1959. Sanitary Engineering Research Laboratory, University of California, Berkeley.

(4) Packard, L. E. Liquid Scintillation Counting. Proceedings of the Conference held at Northwestern University, August 1957, Pergamon Press, New York (1958).

(5) Furst, M., Kallman, H., and Brown, F. H. Increasing Fluorescence Efficiency of Liquid Scintillation Solutions. Nucleonics 13:58 (April 1958).

(6) Kinard, F. E. Liquid Scintillator for the Analysis of Tritium in Water. Rev. Sci. Instr. 28:293 (April 1957).

(7) Bibron, R. Measurement of Weak Activities in Carbon-14 and Tritium by a Scintillation Method. L'Onde Electrique 39:382 (January 1959); AEC-TR-3849.

(8) Swank, R. K. Liquid Scintillation Counting. Proceedings of the Conference held at Northwestern University, August 1957, Pergamon Press, New York (1958).

(9) E. I. DuPont de Nemours and Co., Eng. Res. Lab. Personal communication.

(10) Strominger, D., Hollander, J. M., and Seaborg, G. T. Table of Isotopes, Rev. Mod. Phys. 30:630 (1958).