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PROCEEDINGS OF THE UNIVERSITY OF NEW MEXICO CONFERENCE ON

ORGANIC SCINTILLATION DETECTORS

AUGUST 15-17, 1960

U.S. ATOMIC ENERGY COMMISSION • OFFICE OF TECHNICAL INFORMATION

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OF THE UNIVERSITY OF NEW MEXICO
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August 15-17, 1960

EDITORS

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INTRODUCTION

The University of New Mexico Conference on Organic Scintillation Detectors was held in Albuquerque on August 15-17, 1960, and was jointly sponsored by the University of New Mexico, the National Science Foundation, and the United States Atomic Energy Commission. A similar and highly successful conference on liquid scintillators had been held in August of 1957 on the Northwestern University campus, and the more recent conference was held to cover various changes in the field since 1957. Financial assistance was obtained from the National Science Foundation and the United States Atomic Energy Commission through the Office of Special Projects and the Division of Biology and Medicine.

The Conference was attended by 223 delegates and speakers and of these, 19 came from outside the United States with the countries of Germany, England, France, Israel, Canada, Sweden, Norway, and Switzerland being represented.

Dr. Guido H. Daub was the General Chairman of the Conference and represented the host institution. The Program Chairman, who also served in this same capacity at the 1957 conference, was Dr. F. Newton Hayes of the Los Alamos Scientific Laboratory, Los Alamos, New Mexico. Other members of the General Conference Committee were Dr. Ernest C. Anderson and Dr. Donald G. Ott of the Los Alamos Scientific Laboratory, Dr. Carlos G. Bell, Jr., of the Oak Ridge Institute of Reactor Technology, Oak Ridge, Tennessee, and Dr. Frederick Reines of Case Institute, Cleveland, Ohio.

Technical sessions of the Conference were held in the University's new Union Building on the campus. The papers which were presented at the Conference are published in this document in the order in which they appeared on the program.

PART I

THE SCINTILLATION PROCESS

THE EFFICIENCY OF ORGANIC SCINTILLATORS

J. B. Birks*

1. INTRODUCTION.

There are four main types of organic scintillator:

- (a) pure crystals, e.g. anthracene;
- (b) mixed crystal solid solutions, e.g. anthracene in naphthalene;
- (c) liquid solutions, e.g. *p*-terphenyl in toluene; and
- (d) plastic solutions, e.g. *p*-terphenyl in polystyrene.

Except in pure crystals there are always at least two components present, the solvent and the primary solute. The solute concentration is generally small, so that practically all the incident energy of the ionizing radiation is expended in the excitation and ionization of the solvent molecules. A fraction of the resultant solvent excitation energy is then transferred to the solute molecules, and the fluorescence emission of the solute forms the scintillation normally detected by the photomultiplier. In many liquid and plastic solution scintillators secondary solutes, e.g. POPOP, are added to shift the primary solute spectrum to match more closely the photomultiplier spectral response. In such

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systems an additional stage of inter-molecular energy transfer, from primary to secondary solute, is involved.

2. THE PRIMARY PROCESSES.

In the present paper it is proposed to discuss the factors determining the scintillation efficiency of the various types of organic scintillator. The primary events associated with the initial excitation and ionization of the solvent molecules by the ionizing radiation have been discussed more fully elsewhere (1). The alternative primary processes may be summarized as follows:

- (1) excitation into excited π -electron singlet states;
- (2) π -electron ionization;
- (3) excitation of other (σ -electron) excited states;
and
- (4) ionization of electrons other than π 's.

Process 1 is the origin of the main fast scintillation emission (decay time ~ 2 -10 nsec.) since only the de-excitation of the π -electron excited states results in fluorescence.

Ion recombination, following process 2, results in molecules in excited singlet or triplet π -states, and produces the slow scintillation component (decay time ~ 300 nsec.) observed in many organic scintillators, in the absence of oxygen (2). The relatively long decay time of this component arises either from the ion recombination time (3) or from the lifetime of intermediate triplet states populated preferentially on ion recombination (1).

The excitation energy of non- π excited states (process 3) is dissipated thermally and does not result in fluorescence. It is the major cause of the relatively low efficiency of the scintillation process compared with the photo-fluorescence process, where only π -electron states are excited by near ultra-violet radiation.

Process 4, ionization, leads to temporary and permanent molecular damage and to ion recombination. The temporary molecular damage associated with the ionization density along

the track of the ionizing particle is responsible for the ionization quenching effect observed in all organic scintillators (4), which reduces the scintillation efficiency for more heavily ionizing particles. The permanent molecular damage introduces quenching centers which cause a gradual decrease in fluorescence efficiency under prolonged intense irradiation (5). Ion recombination into non- π excited states leads to thermal dissipation of the energy, as in process 3.

The relative probabilities of excitation and ionization in an organic molecule are approximately 2:1. If each electron in the molecule is considered to have the same total excitation and ionization cross-section, then the fraction of the incident energy expended in the excitation and ionization of π electrons (processes 1 and 2) can be evaluated from the fraction of π -electrons in the molecule. The results of this simple model, applied to several molecules of interest, are shown in Table 1.

A more sophisticated model would allow for differences in the excitation and ionization cross-sections of the π - and σ -electrons, and of the K-electrons in the C atoms. This might modify the absolute values of the probabilities, but it should not change their relative order which depends only on the fraction of π -electrons in the molecule.

The scintillation efficiency S for excitation by fast electrons is given by

$$S = PQ \quad (1)$$

where P is the efficiency of the primary π -excitation and Q is the efficiency of the subsequent processes by which the π -excitation energy is converted into fluorescence emission. According to the theoretical model

$$P = \frac{2}{3} \quad (\text{the } \pi\text{-electron fraction}) \quad (1a)$$

Q can be measured and studied using ultra-violet excitation directly into the π -singlet states, and by comparison with similar scintillation studies the primary and subsequent processes can be differentiated. Apart from the major survey of the pure crystal organic scintillators by Sangster and Irvine (6), who compared the relative values of S and Q and hence showed that P is approximately independent of the nature of the scintillator, most experimental studies have been concerned only with a comparison of the relative

TABLE 1

Molecule	No. of π	Electrons Total	Fraction of π 's	π -excitation probability P (Process 1)	π -ionization probability (Process 2)
Anthracene	14	94	0.149	0.099	0.050
Quaterphenyl	24	162	0.148	0.099	0.049
Naphthalene	10	68	0.147	0.098	0.049
p-Terphenyl	18	122	0.147	0.098	0.049
Benzene	6	42	0.143	0.095	0.048
Polyvinyl naphthalene	10n	82n	0.122	0.081	0.041
Polystyrene	6n	56n	0.107	0.071	0.036

magnitudes of S, or, in fewer cases, of Q or quantities related thereto. The similar values of P, the π -excitation probability, for the first 4 compounds in Table 1, confirm the experimental findings of Sangster and Irvine, and show that the differences in S for pure crystal scintillators are due mainly to differences in Q.

For crystalline anthracene it is estimated below that $Q = 0.37$, so that taking $P = 0.099$ from Table 1, $S = 0.037$, which is in excellent agreement with the experimental value of $S = 0.038$ obtained by Birks and Szendrei (7).

The relative magnitudes of the fast and slow components depend on the relative probabilities of π -excitation and π -ionization producing π -singlet states. Since statistically 0.25 of ion recombinations are into singlet states (3), the theoretical ration is 8:1 in reasonable agreement with the measurements of Owen (8) on several scintillators under fast electron (gamma-ray) excitation. With proton excitation the fast component is reduced due to ionization quenching (4), but the slow component associated with ion recombination is unquenched, thus accounting for the dependence of the fast-slow component ratio on the nature of the ionizing particle (8). This has been shown to be in quantitative agreement with the experimental data (1).

The higher value of P for benzene compared with those for the two polymers indicates why liquid solutions are generally more efficient scintillators than plastic solutions, with similar solutes for which the values of Q can be equated by optimum choice of concentration. Liquid solutions have a lower scintillation efficiency than anthracene crystals. As will be shown subsequently, this is due to a lower inherent value of Q, since the values of P are similar in the two cases. The increased value of P for polyvinyl-naphthalene compared with polystyrene indicates that improved plastic solvents can be evolved, by increasing the size of the aromatic ring substituent in the polyvinyl chain, thereby increasing the π -electron function.

3. THE SUBSEQUENT PROCESSES

3.1. Internal Conversion.

The energies of the excited π -electron singlet states of an aromatic molecule can be obtained from its ultraviolet absorption spectrum. The transition moments from the singlet ground state (S_0) to the different excited singlet states (S_1 , S_2 , S_3 , etc.) are related to the magnitudes of the extinction coefficients in the absorption bands associated with each transition. In general it is found that the transition moments to the 2nd and 3rd excited singlet states (S_2 and S_3) are very much larger than to any of the other π -electron states, showing that the π -excitation by ionizing radiation is predominantly into S_2 and S_3 .

The fluorescence emission of the molecule normally occurs from the 1st excited singlet state S_1 , and corresponds to the $S_1 - S_0$ transition. Measurements on a number of organic fluors have shown that the quantum efficiency of fluorescence q_0 is independent of whether the S_1 , S_2 , or S_3 state is initially excited, provided no competitive processes such as photo-chemical dissociation, dimerization, or energy transfer from higher excited states occur. With this restriction, which appears to be valid for most organic scintillator molecules studied, it is thus seen that the primary S_2 and S_3 excitation energy is internally converted with 100 percent quantum efficiency into S_1 excitation energy, the excess energy being dissipated as thermal vibrations to neighboring molecules (Figure 1).

3.2. Pure Crystals.

The processes competing for the S_1 excitation energy in a pure crystal scintillator and their relative probabilities

FIGURE 1

ENERGY LEVELS, PROCESSES, and PROBABILITIES in pure CRYSTAL SCINTILLATOR

are as follows (Figure 1):

- (1) Emission, k_f , ending to processes (3) or (4);
- (2) Internal quenching, k_i ;
- (3) Radiative migration, ak_f ;
- (4) Escape of emission, $(1 - a) k_f$.

The absorption parameter a depends on the overlap of the emission and absorption spectra of the crystal and on the crystal thickness d (9). In anthracene at 290°K, for example, $a = 0.82$ for $d \geq 2$ mm. The additional process,

- (5) Non-radiative migration, k_m

or exciton migration, which occurs with high efficiency in pure crystals does not affect the bulk crystal properties with which we are concerned here.

For $a = 0$ (thin crystal) the molecular fluorescence quantum efficiency is

$$q_0 = \frac{k_f}{k_f + k_i} \quad (2)$$

The technical (thick specimen) fluorescence quantum efficiency (1,10) is reduced by self-absorption to

$$q_p = \frac{q_0(1 - a)}{1 - q_0 a} \quad (3)$$

The energy conversion efficiency Q from the primary excitation to the fluorescence emission of a pure crystal is

$$Q = \frac{E_f}{E_e} q_p = \frac{\lambda_e}{\lambda_f} q_p \quad (4)$$

where E_e and E_f are the mean energies of the primary excitation and the fluorescence emission respectively. These can be obtained from λ_e and λ_f , the mean wavelengths ("centers of gravity") of the absorption and emission spectra respectively.

For anthracene at 290°K, $k_f = 1.4 \times 10^8 \text{ sec}^{-1}$, $k_i =$

$1.6 \times 10^7 \text{ sec}^{-1}$, $a = 0.82$ ($d \geq 2 \text{ mm.}$), $q_o = 0.9$ and $q_p = 0.62$ (1). The crystalline anthracene spectrum below $2,200 \text{ \AA}$ has not been reported, but it is estimated that $\lambda_e = 2500 \text{ \AA}$, and $\lambda_f = 4200 \text{ \AA}$, giving $Q = 0.37$. In conjunction with $P = 0.099$ from Table 1, this yields $S = 0.037$, in agreement with the experimental value of $S = 0.038$ (7).

3.3. Binary Solutions.

In the subsequent discussion we shall use X, Y and Z and corresponding suffixes to refer to molecules of the solvent, primary solute and secondary solute respectively. The quantities [Y] and [Z] represent concentrations of primary and secondary solutes respectively in moles/mole of solvent. The terms k_f , k_i , and k_t [Y] with appropriate suffixes, are defined as rate parameters, corresponding to the probabilities (in sec^{-1}) of emission, internal quenching and non-radiative transfer respectively. To simplify the discussion additional possible quenching processes, such as concentration quenching of the solute, external solute quenching of the solvent, and impurity (e.g. oxygen) quenching, will be omitted, although these can readily be included in a full formal treatment. The quantities a_{xx} , a_{xy} and $(1 - a_{xx} - a_{xy})$ are the fractions of the solvent emission absorbed by X, absorbed by Y, and escaping from the system respectively. The term a_{xx} corresponds to a in Section 3.2., while

$$a_{xy} = 1 - \exp(-\epsilon_{xy}[Y] d) \quad (5)$$

where ϵ_{xy} is the extinction coefficient, in appropriate molecular units of Y averaged over the emission spectrum of X, and d is the thickness. The quantity a_{xy} tends to unity as [Y] or d is increased. In scintillator solutions of normal size, a_{yy} (self-absorption of primary solute emission) is negligible.

The processes competing for the S_{ix} excitation energy in a binary solution scintillator are as follows (Figure 2):

FIGURE 2

- (1) Solvent emission, k_{fx} ;
- (2) Internal quenching of solvent, k_{ix} ;
- (3) Non-radiative migration to solvent, k_{txx} ;
- (4) Non-radiative transfer to primary solute, $k_{txy}[Y]$;
- (5) Radiative migration to solvent, $a_{xx}k_{fx}$;
- (6) Radiative transfer to primary solute, $a_{xy}k_{fx}$; and
- (7) Escape of solvent emission $(1 - a_{xx} - a_{xy})k_{fx}$.

The importance of process (3) is that, by increasing the mobility of the solvent excitation energy, it enhances the efficiency of non-radiative transfer. In a liquid system, where the molecules are mobile, molecular diffusion (Brownian motion) similarly increases the efficiency of process (4).

In the usual liquid or plastic solvents, radiative migration, process (5), is generally negligible, so that $a_{xx} = 0$. In mixed crystals, e.g. naphthacene in anthracene, a_{xx} cannot however be neglected, and radiative migration has been shown to influence the technical efficiency of both radiative and non-radiative transfer (1, 11). The case of $a_{xx} \neq 0$ has been treated in detail previously (1), and hence only the case of $a_{xx} = 0$, which is of practical interest for liquid and plastic scintillators, will be considered here.

In the presence of Y, the molecular fluorescence quantum efficiency of X is reduced to

$$q_{ox} = \frac{k_{fx}}{k_{fx} + k_{ix} + k_{txy}[Y]} \quad (6)$$

The technical fluorescence quantum efficiency (escape of emission) of X is, for $a_{xx} = 0$

$$q_{px} = q_{ox}(1 - a_{xy}) \quad (7)$$

The technical quantum efficiency of radiative transfer to Y is

$$\eta_r = q_{ox} a_{xy} \quad (8)$$

and the technical quantum efficiency of non-radiative transfer is

$$\eta_t = \frac{k_{txy}[Y]}{k_{fx} + k_{ix} + k_{txy}[Y]} \quad (9)$$

Thus the total quantum efficiency of energy transfer from X to Y is

$$\begin{aligned} \eta_{xy} &= \eta_r + \eta_t \\ &= \frac{(q_{ox})_0 a_{xy} + \sigma_{xy}[Y]}{1 + \sigma_{xy}[Y]} \end{aligned} \quad (10)$$

where $(q_{ox})_0$ is the molecular quantum efficiency of X for $[Y] \neq 0$, and

$$\sigma_{xy} = \frac{k_{txy}}{k_{fx} + k_{ix}} \quad (11)$$

The excitation energy transferred to Y by processes (4) or (6) is "trapped", the excess vibrational energy being rapidly dissipated thermally yielding a molecule with S_{iy} excitation energy. The two processes competing for this energy ($a_{yy} = 0$) are (Figure 2),

- (8) Primary solute emission, k_{fy} , and
- (9) Internal quenching, k_{iy} .

The molecular quantum efficiency of fluorescence of Y is

$$q_{oy} = \frac{k_{fy}}{k_{fy} + k_{iy}} \quad (12)$$

Hence the overall energy conversion efficiency from the primary excitation of X to the fluorescence emission of Y is

$$\begin{aligned}
 Q &= \frac{E_{fy}}{E_{ex}} \eta_{xy} q_{oy} \\
 &= \frac{\lambda_{ex}}{\lambda_{fy}} \eta_{xy} q_{oy}
 \end{aligned}
 \tag{13}$$

where E_{ex} and E_{fy} are the mean energies of the primary excitation of the solvent and the fluorescence emission of the solute respectively, obtainable from λ_{ex} and λ_{fy} , the mean wavelengths of the absorption spectrum of the solvent and of the emission spectrum of the solute respectively.

The dependence of η_{xy} on $[Y]$ has been studied using either ionizing radiation or ultra-violet radiation for excitation of the fluorescence. The former method yields relative values only, i.e. S is measured in arbitrary units as a function of $[Y]$, the other factors in equations (1) and (13) not being evaluated. With ultra-violet excitation the intensity I of the solute fluorescence excited indirectly by solvent absorption can be compared with that excited directly by solute absorption, and the absolute value of η_{xy} is determined directly from the ratio (12,13,14). The quantities S and I have been shown to depend in a similar manner on $[Y]$, as predicted by the theory (15).

The dependence of η_{xy} on concentration in a typical plastic solution, TPB in polystyrene of 1 cm. thickness, as evaluated from combined experimental data on I (14) and S (16), is shown in Figure 3. The concentration is expressed in moles/liter, which is approximately 10 $[Y]$ if the styrene molecule is taken as the solvent molecular unit. At low concentrations the energy transfer is purely radiative, increasing to a maximum of $\eta_r \sim (q_{ox})_0$ at about $5 \times 10^{-4} M$. Non-radiative transfer becomes significant about $10^{-4} M$, and as the concentration is increased it competes with the internal quenching and the emission, hence causing a decrease in η_r , and it becomes predominant at high concentrations, where η_t tends towards unity.

Practical plastic and liquid solution scintillators

Fig. 3. Solvent-solute transfer in plastics.

utilize high solute concentrations since thereby η_{xy} and S are maximized, while the scintillation decay time is minimized towards the fluorescence decay time of the solute alone. Two factors limit the maximum concentration that can be used, and hence reduce the practical value of η_{xy} below the theoretical maximum of unity. These are (a) the maximum solubility, and (b) the concentration quenching effect by which the solute fluorescence efficiency q_{oy} is reduced by solute-solute interaction at high $[Y]$. Due to the latter effect $\eta_{xy}q_{oy}$ may decrease as $[Y]$ is increased, so that the optimum concentration is that at which $\eta_{xy}q_{oy}$ is a maximum [equation (13)].

The dependence of η_{xy} on concentration in a typical liquid solution, p-terphenyl in toluene, as evaluated from experimental data on I (12,15,19), is shown in Figure 4. Here the radiative component η_r is negligible because of the low fluorescence efficiency $(q_{ox})_0$ of the pure liquid solvent. As before, η_t tends towards unity at high concentration, the maximum being limited by the solubility, but it is noteworthy that the non-radiative transfer occurs efficiently at lower concentrations than in plastic solutions, corresponding to a higher value of σ_{xy} .

Since $(k_{fx} + k_{ix})^{-1}$ in equation (11), which is equal to the solvent fluorescence decay time, is 14 n sec. for polystyrene and 7.5 n sec. for toluene, it follows that k_{txy} is significantly greater for a liquid solution than for a plastic solution. The k_{txy} value for polystyrene-TPB agrees well with the dipole-dipole transfer probability between static molecules calculated from Förster's theory (17), indicating that non-radiative migration is relatively unimportant in plastic solutions. The non-exponential scintillation decay of plastic scintillators (18), and the observed dependence (16) of σ_{xy} on $\sqrt{J_{xy}}$ for a wide range of solutes, where J_{xy} is the Förster overlap integral, are also consistent with relative immobility of the solvent excitation energy in plastic solutions, and with dipole-dipole non-radiative transfer (single-step). An approximate calculation based on the rather limited data on the overlap of the absorption and emission spectra of polystyrene

Fig. 4. Solvent-solute transfer in liquids.

indicates that the critical Förster dipole-dipole migration distance in polystyrene is probably less than $6.6 \text{ \AA}$, the average spacing between the phenyl groups in the polymer chain, thus indicating why the migration process is inefficient.

In liquid solutions k_{txy} is much greater than is to be expected for single-step dipole-dipole transfer. Thus for p-terphenyl in toluene (12), k_{txy} corresponds to a critical transfer distance of $38 \text{ \AA}$, which is equivalent to a transfer distance of $27 \text{ \AA}$ between static molecules, when the molecular diffusion is allowed for. This exceeds the theoretical value of $15 \text{ \AA}$, indicating that non-radiative migration must also occur and contribute to the transfer efficiency.

Earlier measurements by Birks and Cameron (13) on terphenyl-toluene solutions indicated that η_{xy} varied with the wavelength of the ultra-violet excitation of the solvent, suggesting energy transfer from S_{2x} in competition with internal conversion to S_{ix} , and that η_{xy} tended to a maximum value less than unity as the concentration increased, which was attributed to quenching of the solvent excitation by the solute. These results were at variance with those of Cohen and Weinreb (12) quoted above. A detailed investigation (19) has been made of the cause of the discrepancy, which is found to have been due to the use of a broad divergent light beam for excitation. As the size of the illumination area is reduced, the observed wavelength variation of η_{xy} is correspondingly reduced. For a spot size of 1 mm. diameter and terphenyl-toluene solutions of 5 different concentrations, η_{xy} is found to vary by not more than ± 4 per cent, for excitation wavelengths from $2200 \text{ \AA}$ to $2700 \text{ \AA}$. This result compares with the ± 5 per cent variation observed by Cohen and Weinreb (12) and confirms their conclusion that η_{xy} is independent of wavelength in this spectral range. It is also found in agreement with their results that η_{xy} has a limiting value of 1.0.

3.4. Ternary Solutions.

The processes that compete in the transfer of the primary excitation energy E_{ex} of the solvent X, through the S_{1y} excitation energy of the primary solute Y, to the S_{1z} excitation of a secondary solute Z are shown diagrammatically in Figure 5. The competing processes in the energy transfer from Y to Z are similar to those considered in solvent-solute transfer in Section 3.3. Equations (6) to (12) are directly applicable, substituting Y for X and Z for Y throughout.

The overall energy conversion efficiency from the primary excitation of X to the emission of Z is

$$Q = \frac{\lambda_{\text{ex}}}{\lambda_{\text{fz}}} \eta_{\text{xy}} \eta_{\text{yz}} q_{\text{oz}} \quad (14)$$

where q_{oz} is the molecular fluorescence quantum efficiency of Z, η_{yz} is the total quantum efficiency of energy transfer from Y to Z, and λ_{fz} is the mean wavelength of the emission spectrum of Z.

Recent studies (19) have been made of the energy transfer from *p*-terphenyl to TPB in toluene solutions, TPB being chosen as the secondary solute because its emission can be separated from that of terphenyl with suitable filters. The quantity η_{yz} was determined as a function of [Z] from the ratio of the TPB emission excited by indirect terphenyl absorption and direct TPB absorption respectively. In addition the terphenyl emission intensity was measured as a function of [Z]. The results for solutions of 1.3 cm. thickness, which have been analyzed in terms of equation (10) are plotted in Figure 6. Up to TPB concentrations of 10^{-4} M, the energy transfer is primarily radiative, and both the TPB and terphenyl emission intensities are found to depend on the solution thickness [equation (5)]. The molecular fluorescence quantum efficiency q_{oy} of *p*-terphenyl is observed to be 0.75. Above 10^{-4} M, the terphenyl emission is suppressed, and non-radiative transfer becomes important, increasing toward unit quantum efficiency as the concentration is increased. These

Fig. 5. Energy levels, processes, and probabilities in ternary solution scintillator.

Fig. 6. Energy transfer from primary to secondary solute.

results which throw an interesting light on the mode of operation of secondary solutes will be reported in more detail elsewhere.

4. SCINTILLATION EFFICIENCY.

The basic equation for the scintillation efficiency is

$$S = PQ \quad (1)$$

where, on the simple theory proposed,

$$P = 2/3 \text{ (the } \pi\text{-electron fraction of solvent)} \quad (1a)$$

and Q is given by equations (4), (13) and (14) for pure crystals, binary solutions, and ternary solutions respectively.

The term P has a similar value of about 0.1 for the better crystals and liquid solvents (Table 1). It is inherently lower for a plastic solvent, though it can be improved by introducing larger aromatic substituents in the polymer chain to increase the π -electron fraction.

Considering now the factors influencing Q, the transfer efficiencies η_{xy} and η_{yz} in solution scintillators can be made to approach unity by the use of sufficiently high solute concentrations. Two factors limit the maximum η that can be achieved in practice: the maximum solubility of the solute in the solvent; and concentration quenching which becomes important with some solutes at high [Y] and reduces q_{oy} . Pure crystal scintillators have the advantage that no solvent-solute transfer processes are involved.

The requirements for the final emitting molecule in the system are that it should have a high fluorescence quantum efficiency, and that its emission should match the photo-multiplier spectral response. Crystalline anthracene satisfies the latter requirement, although its quantum efficiency is reduced from $q_o = 0.9$ to $q_p = 0.62$ by self-absorption, yielding $S = 0.037$. If self-absorption were eliminated, i.e. for a thin anthracene crystal at 290°K,

we would obtain $S = 0.054$. Alternatively self-absorption and internal quenching can be reduced by cooling the crystal, thereby increasing S . Data on the variation of S for anthracene with temperature have been presented elsewhere (1). At 0°K with $q_p = 1.0$, we obtain $S = 0.06$. This corresponds to about the maximum theoretical scintillation efficiency attainable with any organic scintillator, since P is about the optimum and the ratio λ_e/λ_f is about the same for all aromatic molecules.

It is of interest to note that the absolute scintillation efficiency of crystalline *p*-terphenyl at room temperature is probably higher than that of crystalline anthracene. It has similar values of P and λ_e/λ_f , with negligible self-absorption and $q_p \sim 0.65$. Its emission is, however, in the near ultra-violet and matches the blue-green photo-multiplier response imperfectly, so that its practical efficiency is inferior to that of anthracene.

Similarly *p*-terphenyl has a high $q_0 = 0.75$ in liquid solution and a similar value in plastic solution, but secondary solutes, chosen also to have a high q_0 , are required to "shift" the emission to match the multiplier response, with a resultant decrease in the absolute scintillation efficiency S due to the further energy degradation from S_{iy} to S_{iz} , but with a gain in practical efficiency. The development of photo-multiplier with a sensitivity in the near ultra-violet comparable with the existing blue-green sensitivity would eliminate the need for secondary solute wavelength-shifters, and would properly utilize the high absolute scintillation efficiency of *p*-terphenyl in the crystalline and liquid and plastic solution phases.

With the optimum λ_f dictated at present by the photo-multiplier response, it is important for λ_e to be as large as possible. The fraction $\lambda_e/\lambda_f \sim 0.6$ is about the same for all aromatic molecules, due to the interdependence of the π -electron singlet energy levels. Hence the largest value of $\lambda_e \sim 2500 \text{ \AA}$ (consistent with $\lambda_f \sim 4200 \text{ \AA}$) is obtained in a single component scintillator like anthracene. The usual liquid and plastic solvents have λ_e in the region of $1500\text{--}2000 \text{ \AA}$, corresponding to only $0.6\text{--}0.8$ of that of

anthracene. It is of interest to note that this approximate to the range of relative scintillation efficiencies attainable, indicating that apart from η , λ_e is the main factor limiting the performance of solution scintillators. Data on the absorption spectra in the vacuum ultra-violet region are sparse, except for the simpler liquid solvents, but since $\lambda_e \sim 0.6 \lambda_f$, λ_e can be estimated from the solvent λ_f . Thus for benzene $\lambda_e \sim 1600 \text{ \AA}$, and for polystyrene $\lambda_e \sim 1850 \text{ \AA}$. The quantity λ_e can be increased by using liquid or plastic solvents having larger molecules or monomer units, preferably containing more than one benzene ring (e.g. polyvinyl-naphthalene) or having suitable substituents which shift with the absorption spectrum to longer wavelengths. With improved solvents the trend should preferably be towards binary solutions, to eliminate one energy transfer process, except where primary solute self-absorption or economic factors are important.

One early binary solution system which merits reconsideration is anthracene in naphthalene (20). These mixed crystals have $P = 0.1$, $\lambda_{ex} \sim 2100 \text{ \AA}$, $\lambda_{fy} = 4200 \text{ \AA}$, $q_{oy} = 0.9$, so that if $\eta_{xy} = 1$ can be achieved, we obtain $S = 0.045$, i.e. a scintillation efficiency about 20 per cent greater than pure anthracene, with an emission matching the photomultiplier response.

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STUDY OF ENERGY TRANSFER BY QUENCHING EXPERIMENTS*

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INTRODUCTION

Four possible processes have been described by which excitation energy produced in the bulk of liquid or solid material can reach a fluorescent solute. These are:

1. Direct energy transfer by a single jump from the excited bulk molecule to a solute molecule over several molecular diameters (Forster mechanism).
2. Migration of excitation energy from bulk molecule to neighboring bulk molecule until the excitation energy comes close enough to a solute molecule for transfer to occur very efficiently. Thus, the final step of process 2 is transfer from the solvent to the solute but this time over considerably smaller distances than process 1.
3. Actual movement of the excited bulk molecule into the neighborhood of the solute molecule (material diffusion) followed by transfer. This diffusion process cannot occur in a rigid medium.

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4. Energy transfer via radiation wherein the bulk molecule emits radiation which is absorbed by the solute which emits in turn with its characteristic spectrum.

All four processes were described in earlier papers (1). Process 4 is found to be insignificant in many cases of interest and especially in liquid and rigid solutions of a single solute in a single solvent. When two emitting solutes are present, a shift in emitted wavelength may occur due to radiation transfer. This wavelength shift was described and interpreted by Kallmann and Furst in 1951 (1,2). However, processes 1, 2, and 3 seem to contribute to energy transfer in varying degrees, depending upon the type of bulk material (for example, whether it is a liquid or a plastic) and also to a certain extent upon the solute (3). It is stated by Birks in a recent paper (4) that we have, in general, abandoned process 3 in favor of process 2; this is not the case. There is evidence that all three transfer processes occur. The purpose of the investigation described herein was to discriminate between the effects of the different processes and to find in which cases each is most significant.

This was carried out by studying the quenching of the bulk material and comparing with processes in which the energy is transferred from the bulk to the fluorescent solute. The significant difference between quenching and fluorescence lies in the existence of an energy state in the fluor which can take over the excitation energy of the bulk; this is not the case for most quenching molecules; they only produce a dissipation of the energy. Process 1 is, therefore, ruled out in the quenching processes discussed here. Processes 2 and 3, however, can be effective for quenching in liquids. Quenching will take place when the excitation energy comes close enough to a quencher molecule for dissipation to occur. In plastics, this can be brought about only by process 2. Otherwise it could occur only when an excited bulk molecule happens to be created near a quencher molecule; this is a rare occurrence at low quencher concentrations.

A measure of the occurrence of 2 can then be obtained by investigating quenching at low quencher concentrations in a rigid plastic. On the other hand, in a dilute liquid solution process 3 is primarily responsible for solute quenching since there is little migration of energy from solute molecule to solute molecule because of their large separation. Thus, the extent of solute quenching in a liquid indicates the degree to which process 3 takes place in the solute. A quantitative comparison between these processes would be

possible only if the effective cross sections for these final steps (dissipation or transfer) were accurately known; this is not the case. It may be conjectured, however, that final step in energy transfer to a fluorescent solute should have a larger cross section than the final step in a quenching process because transfer is a resonance process. Transfer should thus be possible over greater distances than quenching in which no resonance is involved. However, this does not appear to occur since it was observed rather early in liquid scintillator work that efficiencies of energy transfer to a fluorescent solute are in many cases of the same order of magnitude as the efficiency of bulk quenching. This is clearly seen by examining the concentration at which half of the fluorescence transfer occurs (half value concentration); it is not much smaller than the half value of the quenching concentration. These results indicate that migration and/or diffusion contribute significantly in both cases. In order to obtain more information about these processes, quenching was investigated in some detail for three different cases.

Equation 1 gives the amount of quenching as a function of the quencher (degrader) concentration c_D and solute (acceptor) concentration c_A :

$$\frac{I_0}{I} - 1 = \tau_B c_D \delta \frac{N_A(\infty) - N_A(c_A)}{N_A(\infty)} \quad (\text{Eq. 1})$$

In this equation, I and I_0 are respectively the intensities of the fluorescence with and without quencher added to the solution; $N_A(\infty)$ is the number of excited fluorescent solute molecules energized by transfer present at infinite solute concentration, $N_A(c_A)$ is the number at concentration c_A , both in the absence of quencher. Both $N_A(\infty)$ and $N_A(c_A)$ are proportional to the observed light emission extrapolated to zero concentration quenching. In the basic equation for high energy induced fluorescence intensity as a function of solute concentration c_A ,

$$I = \frac{P c_A}{(Q + c_A)(R + c_A)}$$

the N 's are proportional to $\frac{c_A}{Q + c_A}$. δ is the proportionality

factor for processes 2 and/or 3, which lead to quenching; and $\frac{1}{\gamma_B}$ is the probability of the spontaneous decay of an excited bulk molecule. In previous notation, $\frac{N_A(\infty) - N_A(C_A)}{N_A(\infty)}$ becomes $\frac{Q}{Q + C_A}$, where Q is the concentration at which half the energy is transferred to the solute in the absence of quencher. In essentially the latter form, Eq. 1 was used by Burton and Lipsky to determine the quenching of the bulk material by various quenching agents (5).

According to Eq. 1 as c_A increases, the quenching becomes small. Physically, this can be interpreted as coming about because more and more of the energy is transferred to the solute before quenching can occur. If the solute concentration is kept constant while c_D is varied, the quencher expression on the left of Eq. 1 should bear a linear relationship to the quencher concentration c_D . This behavior was found by Burton and Lipsky and was confirmed in our experiments.

In these experiments, the quenching of the bulk material is determined from measurements of the fluorescence while exciting the bulk material either by high energy or by light. Equation 1 does not take into account that energy in the solute molecule may also be quenched by the quenching agent. In many cases, this can be neglected because the quenching of the solute has been found to be considerably smaller than the quenching of the bulk material (7). This point will be discussed further in Section 3. In the experiments herein reported, quenching of the solute by the quenching agent was separately determined by exciting the solute directly by light. From these measurements, the observed light emission can be extrapolated to zero solute quenching by the quenching agent. Equation 1 refers to intensities corrected to zero solute quenching.

Analysis of fluorescence and quenching by Eq. 1 reveals several noteworthy effects: First, as mentioned above, quenching should become very small at large solute concentrations c_A ; this is not always found (see Section 2). Second, it has been observed that the quenching of solute molecules by a quencher is always considerably smaller than the quenching of the usual bulk molecules used in scintillation work. Xylene or benzene, for example, is quenched much more than 9,10-diphenylanthracene, and the same is true for naphthalene molecules when used as bulk material. It was conjectured (6) that this may be due to the effectiveness of processes 2 and/or 3

in quenching the bulk molecules (solvent), whereas quenching of the solute molecules occurs only via process 3. In order to clarify the situation, the efficiency with which the bulk material is quenched was studied as a function of its concentration when dispersed in a poorly transferring medium. Previous experiments over a small concentration range (6) exhibited only a small effect of concentration on solvent quenching. Experiments over wider concentration ranges show that there is an effect, but it is smaller than expected (see Section 3).

Third, there is a difference between quenching in liquid and rigid (plastic) material. In a rigid medium, as pointed out above, only process 2 can bring about quenching at low quencher concentrations. The results of our experiments show, however, that quenching may occur under certain circumstances as strongly in rigid as in liquid media; this is a strong indication for the occurrence of process 2 in rigid media (see Section 4).

DEPENDENCE OF SOLVENT QUENCHING UPON SOLUTE CONCENTRATION

As pointed out, in some instances solvent quenching does not become very small at high solute concentrations, although this is predicted from Eq. 1. Figure 1 shows the quenching under gamma ray excitation of 1-methylnaphthalene by carbon-tetrachloride using 9,10-diphenylanthracene as the light-emitting solute at various carbontetrachloride and solute concentrations. Figure 2 gives the results of similar experiments using p-xylene with fluoranthene as fluorescent solute. Both figures show that small quencher concentrations are sufficient to produce strong quenching at low solute concentrations, whereas quenching almost disappears at high solute and low quencher concentrations. Even large quencher concentrations are relatively ineffective at high solute concentrations. These results are in general agreement with Eq. 1. Cases which deviate from predicted behavior are shown in Figs. 3 and 4. These describe experiments similar to those above and were performed in p-xylene with m-terphenyl and pyrene, respectively, as fluorescent solutes. These solutes were selected because of their high solubility so that the relationship between quenching and solute concentration could be studied up to high concentrations. Figure 3 shows that at m-terphenyl concentrations as high as 200 g/l (0.9 M), 5 g/l carbontetrachloride (corresponding to only 0.03 M) quenches considerably. An

Fig. 1. Effect of CCl_4 on gamma ray induced fluorescence of 9,10-diphenylanthracene in 1-methylnaphthalene.

Fig. 2. Effect of CCl_4 on gamma ray induced fluorescence of fluoranthene in p-xylene.

Fig. 3. Effect of CCl_4 on gamma ray induced fluorescence of m-terphenyl in p-xylene.

Fig. 4. Effect of CCl_4 on gamma ray induced fluorescence of pyrene in p-xylene.

important feature of the results in Figs. 3 and 4 is that quenching decreases only slightly when the solute concentration is increased by a factor of almost 10; whereas, according to Eq. 1, the quenching should be much more reduced. A similar result is observed for pyrene as solute. Although the decrease in quenching at high solute concentration is, in this case, quite noticeable, it is still considerably smaller than expected from Eq. 1. The quenching is reduced only slightly when the solute concentration is increased by a factor of 4. For example, at a pyrene concentration of 25 g/l, the quenching factor $\frac{I_0}{I} - 1$ is 2.8 for 25 g/l carbon-tetrachloride, whereas the quenching at 100 g/l pyrene by the same concentration of carbontetrachloride is still more than 2. According to Eq. 1, a decrease in quenching by a factor of almost 4 is expected for this increase in solute concentration; whereas, the measurements show that

$\frac{I_0}{I} - 1$ decreases only from 1.8 to 1.2.

The explanation for this deviation from the predicted behavior has not yet been ascertained. There are several possibilities which could account for these results. Both m-terphenyl and pyrene are solutes which behave in a somewhat unusual manner with respect to energy transfer; they have large Q values (which indicates smaller transfer efficiencies) compared to other efficient scintillating solutes which have so far been investigated. The paper by Wirth at this meeting indicates that there may be other such substances (8). But this is not enough to explain the results shown in Figs. 3 and 4. It may be that those Q values do not measure the energy transfer in these cases. For example, it may be that at higher solute concentrations, significant self-absorption of the emitted light takes place so that the true energy transfer curve for the solute is quite different from the observed curve. In this circumstance, the Q values determined from the energy transfer curve would be too small and the correct Q values would be larger than those deduced from the curves. In the absence of this hypothetical absorption, the fluorescent light would be considerably greater at high solute concentration. This possible explanation of deviations will be checked by absorption measurements. It would imply that the true Q values of these substances are quite large compared to those of common effective scintillators and certainly larger than those determined from the fluorescence versus concentration curves. Another possible explanation is the formation of m-terphenyl

aggregates at high concentrations. The energy traversing the solvent would not reach one of these aggregates with much greater probability than it would an isolated solute molecule, since the cross section of the aggregate increases relatively slowly with the number of molecules making up the aggregate. Therefore, the effective concentration for energy transfer would be much smaller than the actual concentration. A further lead may come from an investigation of decay time constants of these substances in solution as a function of concentration.

COMPARISON BETWEEN QUENCHING OF SOLUTE AND BULK MOLECULES

There is generally a large difference in the extent to which solute and bulk material molecules are quenched in efficient scintillators. This means that the same molecule (e.g., 1-methylnaphthalene) is quenched differently when used as solvent or solute. This difference in a liquid scintillator may be due at least partially to the occurrence of both transfer processes 2 and 3. Quenching of the bulk molecule thus can occur via both processes. Solute quenching, however, can take place only via material diffusion process 3 because the solute molecules are too far apart for migration.

In solutions in which process 2 is as effective or more effective than process 3, one would expect that quenching of bulk molecules decreases when they are diluted by an inactive medium. (These molecules will be called bulk molecules even after this dilution, although the inactive medium may be the major constituent.) In order to test this hypothesis, solutions using *o*-xylene or 1-methylnaphthalene as bulk material, α -naphthylphenyloxazole as fluorescent solute, *n*-butylphosphate as the diluting inactive substance, and carbontetrachloride or $\alpha, \alpha, \alpha, \alpha', \alpha', \alpha'$ -hexachloro-*p*-xylene as quenchers were investigated under gamma ray excitation. The concentration of fluorescent solute was kept constant during a run but various amounts of xylene or 1-methylnaphthalene, respectively, were present. The quenching of the fluorescent solute is small compared to the quenching of *o*-xylene or 1-methylnaphthalene, so that the quenching of the solution is essentially due to solvent quenching. Preliminary experiments showed that quenching does indeed decrease with greater dilution of the bulk material, but to a smaller degree than expected (6). The results over a wide range of concentration are given in Figs. 5 and 6.

The curves of Figs. 5 and 6 are linear, which is in accordance with Eq. 1. The uppermost curve in Fig. 5 represents the

Fig. 5. Effect of CCl₄ on gamma ray induced fluorescence of 3 g/l of α -naphthyl-phenyloxazole in combinations of n-butylphosphate and 1-methylnaphthalene.

Fig. 6. Effect of $\alpha,\alpha,\alpha,\alpha$ -hexachloro-p-xylene on gamma ray induced fluorescence of 3 g/l of α -naphthylphenyloxazole in combinations of n -butylphosphate and o -xylene.

quenching in the undiluted solvents, whereas the lowest curves give the quenching when only the diluent (*n*-butylphosphate) is present. Quenching in solutions made in *n*-butylphosphate alone is seen to be small even at the largest quencher concentration used, and even part of this is due to solute quenching. The other curves in Fig. 5 show the quenching for various degrees of dilution. At 200 g/l *o*-xylene, a dilution to about 20 per cent, the quenching has decreased by a factor of more than 2; and at 50 g/l *o*-xylene, a dilution to about 5 per cent, the quenching has decreased by a factor of more than 4 compared with no dilution. Figure 6 describes similar experiments for 1-methylnaphthalene. The uppermost curve is for 1 g/l of α -naphthylphenyloxazole; all the other measurements are for solute concentrations of 3 g/l. This group of curves also shows a decrease in solvent quenching with increasing dilution. The two upper curves show that the influence of solute concentration is smaller than expected from Eq. 1. Figure 7 presents the light emission curves of various dilutions of 1-methylnaphthalene in *n*-butylphosphate as a function of the solute concentration in the absence of added quencher. This lowest curve shows that the light emission in *n*-butylphosphate alone is quite small. In solutions containing only 10 g/l of methylnaphthalene, the emission is considerably greater and most of the light emission is due to energy transfer via methylnaphthalene. Thus only a small amount is transferred directly from butylphosphate to the fluorescent solute despite its greater abundance.

These experiments clearly show the decrease in quenching of the bulk molecule with increasing dilution. This behavior can be interpreted in the following way. In methylnaphthalene or *o*-xylene alone, the excitation energy reaches the neighborhood of the quencher mainly by migration, and this process seems to be considerably more effective than the material diffusion. Previously (6) the smaller decrease of quenching than expected between *o*-xylene and 30 per cent *o*-xylene was interpreted to mean that process 3 is of considerable importance; the considerable decrease in quenching observed at still greater dilutions seems to require the interpretation given here. However, the decrease of quenching is certainly much smaller than that calculated, since quenching should be approximately proportional to (H is bulk molecule concentration and n may have the values 2, 4, 8....); n depends upon the mechanism for the exchange of energy between bulk material molecules.

The reason that quenching is smaller than calculated may be understood from Eq. 1. The factor δ is a measure of the effectiveness of migration and/or diffusion. If migration is more important than diffusion in the undiluted solvent, δ should

Fig. 7. Gamma ray induced fluorescence of α -naphthylphenyloxazole in combinations of n-butylphosphate and 1-methylnaphthalene.

decrease as $H^{\frac{n+1}{3}}$, until it reaches the value of the pure diffusion process 3. There are, however, other effects depending on H which influence the factors in Eq. 1. First, the viscosity of the system may change, and this would change δ for the material diffusion process; but this change is too small to account for the observed effects. τ_B and $\frac{N_A(\infty) - N_A(C_A)}{N_A(\infty)}$

also depend on H . The latter increases with decreasing H , as can be deduced from the curves of Fig. 7. If this increase is taken into account in Eq. 1, a change in $\frac{I_0}{I} - 1$ (quenching factor) is obtained which goes in a direction opposite to H , increasing with decreasing H if τ_B is assumed constant. It is difficult to state quantitatively the effect of changing H on τ_B , but there is little doubt that it increases with decreasing H . This would further increase the change of quenching with H .

In summarizing this investigation of the quenching of the bulk material as a function of its concentration in liquids, one comes to the following conclusions. Quenching decreases with decreasing concentration of bulk material. This accounts for the large difference in quenching of bulk molecules and of solute molecules. The discussion of Eq. 1 indicates further that the decrease of quenching is brought about by the simultaneous occurrence of processes 2 and 3 and by the decrease of the efficiency of process 2 with decreasing H . But the observed decrease in quenching is smaller than the decrease in δ because the term $\frac{N_A(\infty) - N_A(C_A)}{N_A(\infty)}$ increases with

decreasing H . The estimated decrease in δ (under the assumption of constant τ_B) is almost proportional to H . This would indicate a considerable preponderance of the migration process over the material diffusion process, in solutions in undiluted bulk material. But final conclusions can be drawn only when the dependence of τ_B upon H has been investigated in detail.

From a practical viewpoint, these results indicate that when a quenching material must be in the solution, it is efficacious to increase the concentration of the solute and possibly dilute the bulk material.

A further remark is in order. In solutions in which an inactive diluent is used in the absence of added quencher, the efficiency of energy transfer decreases (larger Q) with decreasing H , which would also indicate that the migration part of process 2 decreases with increasing dilution. It may,

however, be mentioned that Weinreb (9) did not find this change in Q in his investigations.

QUENCHING IN RIGID MEDIA

Previous investigation of energy transfer in rigid media has produced the following results. It is less effective than in liquids as seen from the general need of larger solute concentrations in order to extract the same amount of energy from plastics (e.g., polystyrene). Furthermore, the shape of the light emission versus concentration curves in polystyrene, for example, is quite different from that found in liquids. These results led to the conclusion that processes 1 and 2 are both effective in polystyrene since material diffusion (process 3) is excluded. The importance of process 2 in polystyrene was deduced from the strong quenching observed with various quenching agents. This quenching is too great at low quencher concentration to be accounted for by the random presence of an excited molecule near a quencher molecule. Solute quenching is smaller in plastics than in liquids. If naphthalene is added, energy transfer to the solute is enhanced as shown by the smaller solute concentration needed to extract equal energy in a plastic containing naphthalene but at the same time quenching is reduced for all quenching agents tested. An interpretation of this behavior is that transfer occurs mostly via process 1 and that the migration, involved in the quenching, is not so effective from naphthalene to naphthalene in the diluted system as from polystyrene to polystyrene. This is the same dilution effect discussed in the previous section for liquids.

In order to study the situation further, a plastic having the naphthalene group in its structure was investigated. In this manner, the concentration of naphthalene groups could be made much greater. It was hoped that discrimination then could be made between changes in migration efficiency brought about by the differences between naphthalene and benzene groups in the structure and those which are due to greater concentration. In a plastic containing naphthalene in its structure, energy migration would be expected to be better than in a system containing only dissolved naphthalene of concentration of a fraction of a mole per liter. Conditions otherwise would be expected to be similar, since in both cases naphthalene transfers the energy to the fluorescent solute.

Polyvinyl naphthalene was tested with various fluorescent solutes in the absence of added quenchers. It was found that these systems were as efficient as the best liquids with respect to the amount of light emitted and the solute concentration needed to extract the energy from the bulk. The initial part of the curves of light versus concentration was very similar to that observed in effective liquids (6). When $\alpha,\alpha,\alpha,\alpha',\alpha',\alpha'$ -hexachloro-p-xylene was added, it was found that quenching is quite small even at higher quencher concentration (see Fig. 8). Since in liquids (inactive media containing large amounts of naphthalene or methylnaphthalene) naphthalene is strongly quenched by this agent, and since this compound also strongly quenches polystyrene without naphthalene, the conclusion would be that, contrary to expectation, migration does (not) occur to any large extent in polyvinyl naphthalene. This result was so surprising that polyvinyl naphthalene scintillators were also tested with diphenylmercury, which had been found to be very effective in quenching polystyrene and polystyrene plus naphthalene (10). Results are presented in Fig. 9. It is seen that quenching is strong even at small quencher concentrations; the molar half value concentration for quenching is close to that for energy transfer. This strong quenching at such low concentrations indicates the occurrence of process 2. These experiments offer strong evidence for the importance of the migration process in rigid media. Process 1 cannot be excluded for the energy transfer, but it is very likely excluded for the quenching reaction because diphenylmercury has no resonance with polyvinyl naphthalene. Since the half value concentration for quenching and fluorescence is relatively close, one may surmise that the migration process is of importance for energy transfer as well.

In order to understand the results with hexachloro-p-xylene, one possibility to be considered may be that quenching in some cases requires not only migration of excitation energy into the neighborhood of a quenching molecule but also the occurrence of a particularly close contact or specific orientation between the quencher and the excited molecule. In a liquid, this can result from reorientation or from the interaction of the two molecules. This may be more difficult in a plastic because of its rigidity. In the particular case of hexachloro-p-xylene, one might assume that the usual proximity of the excited molecule to the quencher is not enough to bring about quenching in polyvinyl naphthalene but is in polystyrene. This additional condition is apparently unnecessary for diphenylmercury, since in both polystyrene and polyvinyl naphthalene, diphenylmercury produces strong quenching.

Fig. 8. Quenching of the gamma ray induced fluorescence of PVN/PPO (0.045 M) by $\alpha, \alpha, \alpha', \alpha', \alpha'$ -hexachloro-p-xylene.

Fig. 9. Quenching of the gamma ray induced fluorescence of PVN/PPO (0.045 M) by diphenylmercury.

The results with plastics can be summarized as follows. Energy migration occurs in polyvinyl naphthalene and in polystyrene. In the former material, it is as good as in liquids assuming that in liquids the diffusion process is less effective than the migration process (Section 3). The closeness of the half value concentrations for quenching and for transfer indicates that process 1 is less important than the migration process. It is found that the mere propinquity of the respective molecules may not always be enough to bring about quenching.

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On the Influence of Brownian Motion on the
Transfer of Energy in Solutions*

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A. INTRODUCTION

Several authors (1-4) have computed the distances over which energy can be transferred from the solvent to the solute by a dipole-dipole interaction in common scintillating solutions. These computations are generally based on a theory which has been developed by Förster (5) and later by Galanin (6). According to this theory the "distance of interaction" is determined by several factors. Most important however are two:

1. The overlap of the energy levels of the transferring solvent and accepting solute molecules, and the respective transition moments of these levels to the ground state.
2. The lifetime of the excited state of the transferring molecules.

As to the overlap, it is easily seen that the greater the range of common energy levels of acceptor and donor the greater the probability of resonance and hence the greater the probability for transfer of energy. This overlap is not easily estimated. Essentially one computes the overlap between the absorption spectrum of the solute and the fluorescence spectrum of the solvent. And since the fluorescence spectrum usually does not give the oscillator strength, one uses instead the mirror image (about the pure electronic transition) of the absorption spectrum of the solvent, relying on the more or less established mirror symmetry between the fluorescence and absorption spectrum. As to the lifetime

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of the excited state of the transferring molecule, it is easily seen that if this lifetime is longer, then the probability for an interaction between the excited donor and unexcited acceptor is greater.

We have thus the means of comparing the theoretical interaction distance with that found experimentally from the transfer efficiency in the solutions. Actually one does not, of course, compare interaction distances. Förster provides a formula which is based on certain statistical assumptions and which connects the "interaction distance" with the concentration of the acceptor. Thus, what one actually does is to compare the theoretical concentration with the actual one for a given efficiency of energy transfer. All authors who have made such computations for the transfer from solvent to solute in liquid scintillating solutions have found that the actual concentrations are usually much lower than the theoretical expectations.

One way to remove this discrepancy is simply to reject the theory and to assume a different process of transfer. In fact the theory was developed for dye molecules which differ in certain aspects from the molecules considered here. Migration of energy through interaction of one solvent molecule with its next neighbors is such a process. There are, however, cases in which this process cannot be the main mechanism of energy transfer. It has been shown (3, 7) that dilution of the transferring solvent to a degree that hardly permits migration of energy through interaction with next neighbors does not impair the transfer efficiency. In these cases, a long-range process has to be assumed.

Now, some authors suggested quite early that the discrepancy between theory and experiment mentioned before could be removed if Brownian motion were taken into account. Förster's formula assumes that acceptor and donor molecules have fixed positions that do not change during the lifetime of the excited donor molecules. However, because of Brownian motion, donor and acceptor molecules could diffuse into the range of interaction during the lifetime of the excited state, even though at the instant the donor became excited they were too far apart to permit energy transfer. Estimates of this effect were somewhat discordant. Belikova and Galanin (2) using a formula developed by Vavilov for fluorescence quenching, showed that Brownian motion would probably account for the differences between the theoretical and experimental

values of the transfer efficiency. For solutions of terphenyl in toluene and anthracene in anisole, Cohen and Weinreb estimated that the effect of Brownian motion would be too small to account for the differences. These estimates depend strongly on certain assumptions which are not too easily verified. One rather arbitrary factor is the molecular radius for diffusion, which can be only very roughly estimated.

Thus, we long ago started to determine experimentally the influence of Brownian motion on the transfer process. In the meantime, other authors also attacked this problem. Hardwick (8) and Knau (9) found that Brownian motion has only an insignificant influence on the transfer process.

B. EXPERIMENTAL

In order to investigate the influence of Brownian motion on the process of energy transfer from an excited solvent to an accepting solute molecule, the transfer efficiency has to be determined as a function of the rate at which these molecules diffuse towards each other. If the transfer is dependent on diffusion, a decrease in the viscosity of the system should be accompanied by an increase in transfer efficiency. One possible way to investigate this influence of changing viscosity might be to compare the transfer efficiencies of a solution in the liquid and the crystalline states by freezing the solution. This has certain difficulties. Usually these crystals are not very uniform; there are cracks which make the crystals rather opaque and reproducibility rather low. But in addition to technical difficulties basic objections might be raised against this procedure. It is possible that the transfer process in the crystal is different from that in a liquid. The probable anisotropy of the process in a crystal, as contrasted to the assumed isotropy in a liquid solution, may be another basic difference. A comparison between the transfer in a monomeric nonviscous solution with the process in a polymeric solid solution is questionable. The chemical change associated with the process of polymerization gives rise to entirely different transfer properties, at least in many cases. The fact that higher solute concentrations are required in common plastic scintillators than in related liquid scintillators in order to obtain equivalent efficiencies might, however, be interpreted as an indication that diffusion plays an important role in the phenomenon of energy migration in liquids.

In this work the viscosity of the system was changed by changing its temperature. Since only moderate changes in viscosity can be

achieved in the aromatic solvents commonly used in energy-transfer experiments, the solution was dissolved in a viscous solvent that is transparent to the exciting and fluorescent radiations. It is thereby possible to obtain much larger changes in viscosity. It has been shown previously (3, 7) that dilution of the transferring solvent in an inert solvent (without appreciable change in diffusion constant) does not change the transfer efficiency as long as the concentration of the solute is kept constant. Therefore, any decrease in transfer efficiency in changing from the undiluted or diluted nonviscous system to the diluted viscous one has to be ascribed to the decrease in diffusion constant.

Several systems were investigated; however the most extensive information was collected for solutions in paraffin oil, in which the acceptor was anthracene and the donor molecules were naphthalene, toluene, or anisole, respectively. Paraffin oil serves as a diluent, the viscosity of which can be considerably varied by changing temperatures. The transfer efficiencies were obtained according to a method employed by several authors. (3, 10, 11) This method consists essentially in comparing the intensity of the solution when the solute is excited via transfer from the solvent with the intensity which is obtained when the solute is excited directly by a wavelength that is not absorbed by the solvent. The anthracene was directly excited by irradiation with wavelength 3340 Å; for excitation via transfer from naphthalene, toluene, or anisole, the exciting wavelength was 2650 Å. The intensity of the exciting light was monitored by measuring the fluorescence of a solution of 1 g/liter aesculin in water. The temperature of the investigated solutions was changed by means of a commercially available thermostatted cell holder, which maintained stability of temperature within about 1°C. Before measurements, and sometimes during measurements, the solutions were deoxygenated by bubbling argon through them. It may be noticed that the quenching effect of oxygen in the viscous solutions is much smaller than in the pure aromatic solvents, an indication that the quenching process depends on diffusion.

In addition to the fluorescence measurements of the solutions in which energy transfer takes place, the fluorescence of the transferring molecules in the absence of acceptor molecules was measured as a function of temperature. We shall see later that these measurements seem indispensable for any understanding of the examined processes.

The viscosities of the solutions as a function of temperature were determined by Cannon-Fenske-Ostwald type viscometers. In order to

allow for long enough times of flow, different viscometers were used for different viscosity ranges. The overlap between the results for different ranges was excellent.

C. RESULTS

If there is any influence of Brownian motion at all, it is more likely to be expected at low acceptor concentrations; so these seem the logical ones to use. This has the additional advantage that the direct excitation of the acceptor is small and no corrections for this effect have to be made. On the other hand, at very low concentrations the importance of radiative transfer of energy may become important, and this process of course cannot be expected to depend on diffusion.

1. Transfer of Energy from Naphthalene to Anthracene

The transfer of energy from naphthalene to anthracene has been the subject of several investigations in the crystalline state, for which a very efficient transfer takes place already at very low anthracene concentrations. We investigated the transfer in a solution of 20 g/liter naphthalene and 0.5 g/liter anthracene in paraffin oil.

Figure 1 shows the variation of the viscosity of the solution with temperature. Figure 2 shows the fluorescent intensity of the solution as a function of temperature when it is excited by light of wavelength 2650 Å (curve 1) and 3340 Å (curve 2), respectively. In the first case anthracene is excited via transfer from naphthalene, in the second case it is excited directly. From these curves the transfer efficiency can be computed as a function of T/η (which is proportional to the diffusion coefficient), where T denotes the absolute temperature and η the viscosity. This function is presented in Fig. 3. From Fig. 3 (full line) it is seen that the efficiency of energy transfer from naphthalene to anthracene increases from a value of 0.53 to 0.70 for an increase in temperature from -5°C to 80°C , corresponding to a variation of the values T/η from 2.2 to $84^{\circ}\text{K/centipoise}$. This increase in transfer efficiency is attributed to the increase in Brownian motion which facilitates the closer approach between the molecules of anthracene and naphthalene. The effect of Brownian motion can be seen also from the comparison between the transfer efficiency in the solution in paraffin oil and the efficiency in a solution of the same concentrations in cyclohexane, which was found to be 0.88 at room temperature.

Fig. 1. Variation of viscosity with temperature of a solution of 20 g/liter naphthalene in paraffin oil.

Fig. 2. Variation of fluorescent intensity with temperature of a solution of 0.5 g/liter naphthalene in paraffin oil. Curve 1: excitation with wavelength 2650 Å (excitation of naphthalene). Curve 2: excitation with wavelength 3340 Å (direct excitation of anthracene).

Fig. 3. Variation of efficiency of energy transfer from naphthalene to anthracene with the diffusion parameter T/η for a solution of 0.5 g/liter anthracene and 20 g/liter naphthalene in paraffin oil.

So far we have only observed the fluorescence of anthracene. It can be shown that practically no fluorescence of naphthalene is transmitted by anthracene under the experimental conditions. It should be stated that the fluorescent intensity of a solution of 20 g/liter naphthalene in paraffin oil is almost identical to the intensity of the same concentration in cyclohexane. From this we may conclude that self-quenching of naphthalene is low since otherwise one would expect the intensity in the much less viscous solution in cyclohexane to be considerably lower. This is an interesting feature of naphthalene. Furst and Kallmann (12) have shown that naphthalene can be used at very high concentrations as a secondary solvent in order to improve the performance of liquid scintillating solutions. This is due to the low self-quenching of naphthalene. It has also been shown by Dammers-de Klerk (13) that beyond a certain concentration an increase in concentration of naphthalene does not result in any decrease of the fluorescent yield. The question now arises as to what happens to naphthalene as a result of the change of temperature and viscosity which led to the above increase in transfer efficiency. This is seen in Fig. 4, which shows the dependence of the fluorescent intensity of 20 g/liter naphthalene in paraffin oil as a function of temperature. The figure shows a marked decrease in fluorescent intensity upon increasing temperature. We now ask to what extent the transfer efficiency is affected by the enhancement of radiationless transitions to the ground state, which manifests itself in the decrease of the fluorescent intensity of naphthalene with increasing temperature. Several authors have assumed a simple competition between energy transfer, fluorescent emission, and radiationless deactivation processes taking place in the transferring molecule. If we assume this competition between the various processes in our system, the influence of increasing temperature can be determined from the observed variation of fluorescent intensity with temperature.

Let I_1 and I_t be the fluorescent intensities of naphthalene at -5°C (the lowest measured temperature) and at temperature t , respectively, η_1 and η_t the respective quantum yields, and Q_1 and Q_t the probabilities for quenching. Let F be the probability for fluorescent emission and T_t the probability for energy transfer at temperature t . Then

$$\eta_1 = \frac{F}{F+Q_1}, \quad \eta_t = \frac{F}{F+Q_t}, \quad \frac{\eta_1}{\eta_t} = \frac{I_1}{I_t}.$$

Fig. 4. Variation of fluorescent intensity with temperature of 20 g/liter naphthalene in paraffin oil.

The transfer efficiency ϵ_t (at temperature t) is given by

$$\epsilon_t = \frac{T_t}{T_t + Q_t + F}.$$

The corrected value ϵ_t' , i.e., the transfer efficiency which would be observed if there were no increase in the quenching process with temperature is given by

$$\epsilon_t' = \frac{T_t}{T_t + Q_1 + F}.$$

The relation between ϵ_t' and ϵ_t is then given by

$$\epsilon_t' = \frac{\epsilon_t I_1}{I_t + \epsilon_t (I_1 - I_t)} \quad (1)$$

The corrected values which were thus computed are shown by the dotted line in Fig. 3.

In order to obtain the transfer efficiency in the absence of Brownian motion the results of Fig. 3 have to be extrapolated to the value $T/\eta \rightarrow 0$. The value thus obtained is about 0.48. The pronounced curvature of the curve at low values of T/η somewhat reduces the accuracy of the extrapolated value. This result shows that, although the influence of Brownian motion is rather significant, the main mechanism of the transfer process is not one of simple collision.

In order to estimate the influence of Brownian motion we have to compare the transfer probability T_0 in the absence of Brownian motion with the value T_B in the presence of Brownian motion. If all the processes that compete with transfer would remain constant we would have

$$\frac{T_0}{T_0 + (F + Q)} = 0.48 \text{ in the absence of Brownian motion}$$

and

$$\frac{T_B}{T_B + (F + Q)} = 0.80 \text{ at the highest measured temperature.}$$

This would mean a change in transfer probability by a factor of 4. The transfer probability in cyclohexane is 6 times T_0 .

The extrapolated value of 0.48 for the transfer efficiency in the absence of Brownian motion may now be examined in relation to the "interaction distance" R_0 defined in Förster's theory. When the respective emission and absorption data of naphthalene and anthracene are introduced in Förster's equation for R_0 , a value of about 40 Å is obtained. This is a much higher value than those obtained for the interaction between anthracene and the solvents usually used in liquid scintillation counters (e.g., toluene). This difference is due to the higher oscillator strength of naphthalene which manifests itself in the greater values of the absorption coefficients. It is also due to the unusually long lifetime of naphthalene (here taken to be 70 mμsec)* which enters into Förster's equation.

From the value of R_0 we can compute the concentration of anthracene that is necessary for a transfer efficiency of 0.48

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* The decay time of naphthalene has been found by Kallmann and Brucker [H. Kallmann and G. J. Brucker, Phys. Rev. 108, 1122 (1957)] to be 76 mμsec for crystals and 34 mμsec for a solution of 10 g/liter in phenylcyclohexane, both under β excitation. After this talk was presented the decay time of naphthalene was measured (as part of a subsequent study) in this Laboratory by the technique described in references 14 and 15. The main decay part of the pulse appeared to be followed by a tail corresponding to a long decay time, which may perhaps result from the particular mode of excitation. The main decay time in deoxygenated solutions of 20 g/liter naphthalene in benzene and in cyclohexane at room temperature was found to be less than 70 mμsec. In paraffin oil, however, it was about 120 mμsec, increasing with decreasing temperature up to about 240 mμsec at -6°C. The longer decay time in paraffin oil is not yet explained, although processes connected with the excitation by the solvent might, perhaps, be involved.

according to Förster's theory. The necessary concentration thus obtained is of the order of the 0.5 g/liter used in the present experiments. These results are thus not in disagreement with Förster's theory.

2. Transfer of Energy from Toluene to Anthracene

The system investigated was a solution of 0.5 g/liter anthracene in a mixture of 1 part toluene and 9 parts of paraffin oil. Figure 5 shows the transfer efficiency in the solution as a function of temperature and of the diffusion parameter T/η . The full line in Fig. 5 shows an initial increase in transfer efficiency with increasing temperature and increasing Brownian motion. For the highest temperatures, however, the transfer efficiency decreases again. This decrease can be explained, as in the case of the solution with naphthalene, by an increased temperature quenching and collision quenching of the transferring solvent, toluene. From Fig. 6 it is seen that the fluorescent intensity of toluene in paraffin oil decreases rapidly with temperature for temperatures higher than 25°C. The transfer efficiency still goes up beyond this temperature, but for the highest temperatures the quenching effect in the solvent outweighs the increase in transfer efficiency due to Brownian motion. If we again assume that the decrease in quantum yield of toluene with increasing temperature is primarily a consequence of the increasingly efficient deactivation process, the probability for emission remaining substantially constant, and if we again assume a simple competition relation between emission, quenching, and transfer of energy to anthracene, then the transfer efficiency can again be corrected according to Eq. (1). The results of this correction are shown by the broken line in Fig. 5.

Again, extrapolation of the transfer efficiency to $T/\eta \rightarrow 0$ yields a value of about 0.28. The highest corrected value is about 0.57. The transfer efficiency in a deoxygenated solution of 0.5 g/liter anthracene in toluene has been found previously (7) to be about 0.7. Comparison of these results with those obtained with naphthalene as a transferring agent shows that in the latter system the transfer efficiency obtained by extrapolating to zero Brownian motion is higher than in the present one. As stated before, this difference can be qualitatively ascribed to the higher transition moments and longer lifetime of naphthalene as compared with toluene. The ratio between the transfer probability at the

Fig. 5. Variation of efficiency of energy transfer from toluene to anthracene with the diffusion parameter T/η for a solution of 0.5 g/liter anthracene in a mixture of 1 part toluene and 9 parts paraffin oil.

Fig. 6. Variation of fluorescent intensity with temperature of a mixture of 1 part toluene and 9 parts paraffin oil.

highest temperature and that in the absence of Brownian motion (corresponding to the extrapolated value of the transfer efficiency) is about 3 for the solution with toluene and about 4 in the solution with naphthalene. Although the parameter T/η at the highest measured temperature is lower in the naphthalene solution than in the toluene solution (85 against 130°K/centipoise), the influence of Brownian motion in the naphthalene solution is higher, since the probability for a molecule to enter the "sphere of interaction" by diffusion increases with the "interaction distance" R_0 and with the lifetime of the excited donor molecule.

In order to obtain the theoretical value for the "interaction distance" the decay time of toluene in paraffin oil was measured at various temperatures by use of an apparatus built by Swank et al. (14, 15). For these measurements the solution was excited by 75-kev electrons. Most of the exciting energy is absorbed by paraffin oil, which then transfers part of the energy to the toluene. It is assumed that the time for this transfer process is short in comparison with the decay time of toluene. The decay time of toluene at the lowest measured temperature was found to be about 32 mμsec.

The theoretical value for the "interaction distance," obtained from the absorption and fluorescence spectra of toluene and anthracene by use of Förster's theory, is about 15 Å. Accordingly, the concentration that would be necessary in order to obtain the extrapolated transfer efficiency should be about 8 times that actually employed. Thus one sees that reduction of diffusion decreases the transfer efficiency considerably, but not enough to bring about quantitative agreement with Förster's theory. The remaining discrepancy may indicate that Förster's theory does not apply quantitatively to this system, or it may have some other cause. For example, since anthracene is much more soluble in toluene than in paraffin oil, it may well be possible that anthracene molecules attach themselves to toluene and that the macroscopic viscosity which is measured does not represent the microscopic viscosity which the anthracene molecules see.

3. Transfer of Energy from Anisole to Anthracene

Since time is running out, I have to confine myself to a few remarks only. A very remarkable increase in transfer efficiency with temperature is observed in this system. However, the fluorescent intensity of anisole (particularly in a solution of 1 part anisole and 9 parts paraffin oil) also increases strikingly with an initial increase in

temperature. We tend to explain this by the assumption that anisole has a strong tendency to form dimers. This effect complicates the interpretation of the results considerably. The dimers may have transfer properties which are different from those of the monomers and much more experimentation is necessary in order to find the influence of dimerization on the transfer process. It may well be that similar effects occur in other systems and that they are masked by competing processes. Thus some of our familiar solutions may also hide many a surprise for the future.

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PART II

SCINTILLATORS

SUBSTITUTED p-OLIGOPHENYLENES

PART I:

Syntheses and Properties of Substituted p-Oligophenylenes

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I. INTRODUCTION

p-Oligophenylenes are defined as initial members of the homologous p-polyphenylene series. A special criterion of this class of material is the inflexible rod-shaped molecular form. In this regard, these substances are very different from all common organic compounds. This fact made them very interesting, especially in the field of polymer chemistry (1). Thus, the investigations to be reported were not begun with the aim to develop organic radiation detectors.

The rapid decline of the solubility (Fig. 1) with increasing degree of condensation, made doubtful the usefulness of these oligophenylenes as model substances with definite molecular form. It was found, however, that their solubility can be strongly increased by substituting methyl or methoxyl groups (2-5).

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FIGURE 1

Structure	S [g/l]
	440
	8
	0,2

s = solubility in toluene at 20°C

Chiefly two reaction procedures were chosen for the synthesis of substituted *p*-oligophenylenes: the Ullmann reaction and the organometallic carbonyl reaction according to Mayer and Schiffner (6).

II. SYNTHETIC PROCESSES

1. The Ullmann reaction

(a) Ullmann himself had already applied this reaction to the synthesis of the unsubstituted *p*-quaterphenyl (Fig. 2) (7).

The simplicity of this procedure made this reaction quite useful. In the course of the investigations we acquired much experience in governing the reaction as well as in working up the reaction mixtures, so that we hope to enlarge the number of compounds sketched on Fig. 3 (8-10).

FIGURE 3

(b) Using our knowledge of Kern's duplication process (12), we could also successfully apply the Ullmann reaction in the sense of a co-condensation (Figure 4). The monoiodo

FIGURE 4

compounds, as here the *o*-iodotoluene, were applied in greater excess, in order to restrain the polycondensation of the bifunctional reaction components. All oligophenylenes, which were prepared according to this principle of synthesis are shown in Fig. 5 (11, 13).

FIGURE 5

(c) To sum it up, the Ullmann reaction presents an efficient method of synthesis for substituted oligophenylenes. The simplicity of the method has already been mentioned. In addition the iodine compounds which are necessary starting materials are very accessible.

2. The organometallic carbonyl reaction

This principle of synthesis was first applied by Mayer and Schiffner for the preparation of *p*-terphenyl (Fig. 6) (6). We have greatly extended this synthetic process, and by variation of the aromatic organometallic compounds, as well as the ring ketones, have prepared 15 methyl substituted and 16 methoxyl substituted *p*-oligophenylenes up to a degree of condensation of 8.

FIGURE 6

(a) The compounds which were prepared by use of monocyclic diketones are grouped in Fig. 7 (10, 13-16). In this

FIGURE 7

case, the middle benzene ring is derived from the appropriate diketones.

(b) By application of bicyclic diketones, we formed the compounds shown in Fig. 8 (9, 10, 16, 17). In this case the

FIGURE 8

two middle rings are produced from the appropriate carbonyl compounds.

(c) We obtained other oligophenylenes inversely through the action of bifunctional organometallic compounds on monofunctional ring ketones, in other words, through exchange of functionality (11, 13, 16, 17). Figure 9 indicates the structure of these compounds. Here, the two middle rings

FIGURE 9

are produced from the organometallic derivatives.

(d) Finally, you can see in Figure 10 (10, 16, 18) all of the compounds by the synthesis of which, monofunctional reaction components were applied.

FIGURE 10

(e) One can say in summarizing, that the organometallic carbonyl reaction presents an efficient method of synthesis for methyl and methoxyl substituted oligophenylenes. The procedure allows, through broad variation of the starting

material, a striving for structures which are not accessible through the Ullmann reaction. Both procedures, however, complement one another excellently. This is natural in so far as both require the same starting compounds. The resulting end-products, however, are different.

3. Substitution reactions

The possibility of dealing more exhaustively with the two processes of synthesis, depended naturally on making iodine compounds easily accessible.

We occupied ourselves, therefore, very closely with the direct iodination of aromatic compounds. During the investigations, we were able to develop a very efficient iodination process, which provides for the application of iodic acid as oxidant (19).

In this iodination process was found the key to our oligophenylenes (9-11, 16, 17, 20). In Fig. 11 you can see

FIGURE 11

a selection of such iodine compounds, whose constitution is clearly secure. Most of these substances were already used for syntheses. A few of them were previously known.

III. SOME PROPERTIES OF THESE COMPOUNDS

1. Solubility and melting point

All of the p-quaterphenyl derivatives which have been produced up until now, are shown with their solubility and melting point data in Fig. 12. To the left you see the

FIGURE 12

$/ = \text{CH}_3$	S	m.p. [°C]	$/ = \text{OCH}_3$	S	m.p. [°C]
	3,7	213		2	224
	51	150		3	241
	55	176		6	192
	110	139		13	184
	135	142		22	160
	190	116		207	98
	490	96	$\Delta = \text{CH}_2$		
	>500	84		0,3	307
	>500	74		1,4	285
	0,22	320		20	194
				84	159

S = Solubility [g/l] (toluene, 20°C)

methyl derivatives, in the upper right hand corner the methoxyl derivatives, and to the lower right, the fluorene derivatives. The compounds are arranged according to their solubilities.

This chart shows forcibly that substituted methyl groups have the aptitude to considerably improve the solubility of the p-quaterphenyl.

This power depends on the number, as well as on the position of the substituents. The relationships are so complicated, however, that we are not as yet in a position to deduct fixed legitimate associations between structure and solubility, despite the mass of available material. We hope that crystallography will continue to be helpful in solving this problem. Those compounds which are, in general, most soluble contain one methyl group per benzene ring. One can generalize this rule extensively.

The power of the methoxyl group in improving solubility is significantly more limited. When one compares analogous substituted compounds with each other, one can establish the fact, that the effect is weaker by about one order of magnitude. It is interesting, though, that fewer, but unsymmetrically arranged, methoxyl groups cause an enormous increase in the solubility.

In connection with this, one has to submit the question. Why is the solubility of p-oligophenylenes so intensely raised by substitution? We can see the cause for that in the destroyed symmetry, which depends on the possibility of rotation of the substituted benzene rings around the longitudinal axis of the molecule. In other words, these molecules can realize more configurations.

According to this conception, a restriction of the rotation with the help of suitable substituents should cause a decrease of the solubility. We synthesized the fluorene derivatives in order to test that and our expectations were confirmed. The solubility of these compounds is very limited, when compared with corresponding methyl derivatives.

While the solubility ascends with increasing degree of substitution, in the same sense the tendency toward crystallization decreases. Therefore, these compounds show a very strong tendency to form supersaturated solutions, and this property makes handling of them especially difficult.

When the solubility increases, the melting point decreases. Solubility and melting point are correlative criteria, since both the occurrence of a solution and melting destroy the lattice. It becomes understandable, therefore, that the tendency toward the formation of a supersaturated solution is connected with the tendency toward the formation of supercooled fusion. In the case of two tetramethyl-*p*-quaterphenyls it appears that a recrystallization of the fusion, which becomes glassy and brittle through cooling, does not take place.

What has been said here about the quaterphenyl derivatives, is also essentially valid for derivatives from other homologs.

2. Ultra-violet spectra

Ultra-violet spectroscopic investigations with unsubstituted oligophenylenes have already been carried out by Gillam and Hey (21).

As is here schematically presented (Fig. 13) (10).

FIGURE 13

These compounds show a broad structureless absorption band, which is displaced toward longer wavelengths when the degree of condensation increases. This displacement takes place, though, in the sense of a converged row with a threshold value of 3210 Å units.

A polyphenylene with a condensation degree of infinity absorbs in the ultraviolet and therefore is colorless.

The absorption behavior of the methyl substituted p-oligophenylenes can also be described with a converged row when one observes the row of the homologous substituted compounds. The range of absorption is much narrower, however, and the threshold value of the corresponding polymethyl-polyphenylene is 287 Å units.

The substituents produce a hypsochromic effect; they disturb sterically the coplanar adjustment or configuration of the molecule and therefore the interaction of the single chromophores.

The conception that the substituents influence the arrangement of the molecules' frame, receives thereby strong support.

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PART II:

Substituted p-Oligophenylenes as Liquid Scintillation Solutes

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The substituted p-oligophenylenes show an extensive fluorescence in dissolved as well as in solid condition. This observation was the reason why they were tested regarding their application as organic scintillation solutes. But not all compounds have as yet been tested.

We used the instrumentation described by Hayes, Ott, Kerr and Rogers (2) in their fundamental work on liquid scintillators. The isotope source was Cs-137, the beakers were made of quartz, practically of the same diameter and height as used in the above mentioned publication. The luminescence was focused by an evaporated aluminum glass reflector and registered by a multichannel analyzer. The scintillator solutes were dissolved in toluene, a reagent of the firm of Merck, Darmstadt, Germany, and compared relatively to a solution of 3 grams per liter PPO in toluene.

The POPOP-TP ratio of the photomultiplier was about 1.2. The optical fluorescence spectra were corrected to give true intensities by means of an especially measured spectral sensitivity curve.

All methyl substituted quaterphenyls shown in Table 1 have a comparable relative pulse height except compound

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TABLE 1

Compound	RPH	$c_{\max}$ (g/l)	s (g/l)	$\bar{\lambda}$ (m μ)	m.p. (°C)
1. p-Quaterphenyl	0.2	0.2*	0.2	--	320
2. 2 ¹ ,3 ⁴ -dimethyl-p-quaterphenyl	1.26 (1.20)⊗	3.7* (6.3)⊗	3.7 (6.3)	392	213
3. 2 ⁴ ,3 ¹ -dimethyl-p-quaterphenyl	1.26 (0.98)⊗	35 (8.6)⊗	51 (36)	373	150
4. 2 ³ ,3 ² -dimethyl-p-quaterphenyl	1.23	55	55	400	176
5. 2 ¹ ,2 ³ ,3 ² ,3 ⁴ -tetramethyl-p-quaterphenyl	1.16	25	>500	390	74
6. 2 ² ,2 ⁴ ,3 ¹ ,3 ³ -tetramethyl-p-quaterphenyl	~0.1	10-20	490	410	96
7. 2 ¹ ,2 ² ,3 ³ ,3 ⁴ -tetramethyl-p-quaterphenyl	1.24	16	110	--	139
8. 2 ³ ,2 ⁴ ,3 ¹ ,3 ² -tetramethyl-p-quaterphenyl	0.90	20	>500	--	84

RPH of 3 g/l PPO equals to unity

s = solubility (toluene 20°C)

* = RPH at the solubility limit

⊗ = as reported by Hayes

No. 6. This is odd since the u.v. spectrum is quite normal (3). The fluorescence spectrum, however, shows almost no intensity.

From a practical point of view compound No. 5 is rather interesting because it is extremely soluble in toluene, more soluble and with higher RPH-value than PPO. There is also an economic advantage: this compound is convenient to synthesize.

The compound No. 3 which is fairly soluble has its mean wave length of the fluorescence spectrum in the same range as p-terphenyl. This was why we tried to add to the optimal concentration 0.5 grams per liter POPOP as a secondary solute. But the efficiency of this secondary solute system was almost the same as we measured for terphenyl with POPOP. Both compounds No. 2 and 3 were earlier tested in Los Alamos. We are sorry, there are some discrepancies in solubility data too (4).

On Table 2 are to be seen the three methyl substituted terphenyls and the phenyl or tolyl substituted fluorenes. The terphenyl derivatives are not as good as the quaterphenyls. Besides they are more difficult to synthesize. The two outer methyl groups, being in m-position to the linking phenylene ring (compound No. 9) show a greater effect than those in p-position (compound No. 10). If the linking phenylene ring is replaced by a cyclohexadiene ring (compound No. 11) the RPH drops to half the value.

The fluorene derivatives No. 14 and 15 were synthesized and measured by Barnett (5) before these compounds were available in our laboratories. However, we found the same relative pulse heights. When our RPH vs. concentration curve for compound No. 15 is extrapolated to a concentration of 0.4 we read exactly the same value.

Number 13 is a good scintillator which is quite soluble in toluene. A better one is compound No. 12 which was unfortunately measured only up to a concentration of 3.5 grams per liter. At this concentration, however, it showed already a relative pulse height of 1.04. This scintillator solute gives reasons for hopeful expectations because at the just mentioned concentration the RPH vs. concentration curve is still rising steeply. These fluorene derivatives are rather easy to prepare.

TABLE 2

Compound	RPH	$c_{\max}$ (g/l)	s (g/l)	$\bar{\lambda}$ ($m\mu$)	m.p. ($^{\circ}C$)
9. 2 ¹ ,3 ³ -dimethyl-p-terphenyl	1.15	12	49	410	141
10. 2 ³ ,3 ¹ -dimethyl-p-quaterphenyl	0.67	10	44	--	145
11. 1,4-di-(<u>m</u> -tolyl)-1,3-cyclohexadiene	0.55	7	very good	--	118
12. 2,7-di-(<u>m</u> -tolyl)-fluorene	1.04	at 3.5	20	--	194
13. 2,7-di-(<u>o</u> -tolyl)-fluorene	1.27	15	85	--	159
14. 2,7-diphenylfluorene	0.95 (0.97) [⊗]	1.4* (1.0)	1.4	--	285
15. 2,2'-bifluorene	0.45 (0.54) [⊗]	0.3* (0.4)	0.3	--	307

RPH of 3 g/l PPO equals to unity
 s = solubility (toluene 20° C)
[⊗] = as reported by Barnett et al.

In Table 3 the compounds No. 16 through 18 are the methoxyl substituted quaterphenyls. Their RPH values are comparable but not better than those for the methyl substituted derivatives. However, their syntheses are more difficult. Compound No. 17 has good solubility. We sent the compounds No. 16 and 17 to Los Alamos and Dr. Hayes was kind enough to have a cross check in his laboratory.

Finally, the compounds No. 17 through 23 are methyl and methoxyl substituted quinqu- and sexiphenyls respectively. The solubility of these substances is poor, and this means the gradient of the RPH vs. concentration curve is limited at the saturated solution. In addition, these compounds are difficult to synthesize.

In summarizing one can say: the quaterphenyl derivatives have the highest RPH values. The attempt to achieve higher pulse heights by a higher degree of condensation has proven useless. The optimal concentrations are, in general, higher than it is the case at the conventional liquid scintillator solutes. In addition these compounds are not as difficult to synthesize.

TABLE 3

	Compound	RPH	$c_{\max}$ (g/l)	s (g/l)	$\bar{\lambda}$ ($m\mu$)	m.p. (°C)
16.	2 ² ,3 ³ -dimethoxy-p-quaterphenyl	1.29 (1.19)⊗	12	18	395	184
17.	2 ¹ ,3 ² -dimethoxy-p-quaterphenyl	1.23 (1.18)⊗	10	207	395	98
18.	2 ¹ ,2 ³ ,3 ² ,3 ⁴ -tetramethoxy-p-quaterphenyl	1.17	13	22	--	160
19.	2 ¹ ,2 ⁴ ,3 ² ,3 ⁵ -tetramethoxy-p-quinquephenyl	0.88	3.5*	3.5	410	165
20.	2 ¹ ,2 ⁵ ,3 ² ,3 ⁶ -tetramethoxy-p-sexiphenyl	0.49	1.8	2	410	210
21.	2 ¹ ,2 ⁴ ,3 ² ,3 ⁵ -tetramethyl-p-quinquephenyl	1.21	7	11	470	186
22.	2 ⁵ ,3 ¹ -dimethyl-p-quinquephenyl	0.76	1.25*	1.25	--	230
23.	2 ¹ ,2 ⁵ ,3 ² ,3 ⁶ -tetramethyl-p-sexiphenyl	1.26	26*	26	430	200

RPH of 3 g/l PPO equals to unity

s = solubility (toluene 20° C)

* = RPH at the solubility limit

⊗ = as reported by Hayes

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A COMPARATIVE SCINTILLATION STUDY OF SOME SELECTED
BIS-BENZOXAZOLE SOLUTES. BENZOXAZOLES III.*

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Summary

Some tentative proof of a hypothesis is presented concerning the energy absorption and emission mechanism of conjugated bis-benzoxazole solutes. Based on the initial assumption, two series of bis-benzoxazoles were prepared and tested as primary and/or secondary scintillators. A few of the compounds yielded favorable light outputs comparable to that of PPO and POPOP. Furthermore, in certain cases, the scintillation performance can be directly correlated with corresponding molecular structures.

Introduction

A favorable relative light output is under report from this Laboratory (1) as the scintillation performance of 2,2'-o-phenylene bis-benzoxazole and trans-1,2-bis(2'-benzoxazolyl)-ethylene. The two compounds can be considered as representative members of a new class, the bis-benzoxazoles. The former substance being a potential primary solute, and the latter a wavelength shifter, yield pulse height values comparable to that of PPO and POPOP (2,3), respectively.

The interest in a comparative scintillation study of bis-benzoxazoles arose when, based on the correlation of light

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absorption and emission properties of analogous substances, it appeared that a tentative interpretation of the relationship between corresponding molecular structures and the mechanism of scintillation can be presented.

In addition, the relative ease of the synthesis of bis-benzoxazoles, as reported earlier (4), facilitated the accessibility of several structurally related compounds to be prepared for spectroscopical investigations.

Development of Theory

A hypothesis was put forward (4) that certain bis-benzoxazoles, having a conjugated double bond system, would acquire quinoid type structures in their lowest excited electronic states, as illustrated in Fig. 1 by the 2,2'-o-phenylene bis-benzoxazole. These structures are, among several others, possible resonant forms of the respective molecular species*, and may contribute in a lesser extent to the ground state.

As the absorption of electromagnetic energy results in the population of various vibrational levels of an upper electronic state(s), according to the Frank-Condon principle, thermal equilibrium will be rapidly established (in ca. 10^{-12} sec.) due to collisional deactivation (5). Thus, prior to radiational deactivation, the lowest vibrational level of the lowest excited electronic state will be occupied by the activated molecules. As the condition of fluorescence of conjugated bis-benzoxazoles, however, it was assumed that their corresponding quinoid structures will be the predominant contributors to this lowest excited electronic state (4), which is then usually involved in the emission of fluorescent photons.

Consequently, the establishment of quinoid structures in the electronically lowest activated state would first effect a single separation of charge accompanied by a transient polarization of the molecules, as seen from Fig. 1. Secondly, it would result in the formation of a more or less

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* for example, about eight resonant forms of 2,2'-o-phenylene bis-benzoxazole can be written which have comparable energies.

Fig. 1. Kekule (A) and quinoidal type structures (B, C) of 2,2'-o-phenylene bisbenzoxazole.

planar type configuration because of the conjugated double bond system of the molecule, which will not only be retained, but altered to a form negating the normal twisting motion of the benzoxazole nuclei. Hence, the arrangement of double bonds in the postulated quinoid structure, as it can be conceived from Fig. 1, might prevent a considerable amount of the absorbed energy to be utilized for internal rotation, viz., to be consumed in processes defined as internal quenching.

As a possible consequence of the latter postulation, it may also be concluded that the persistence of the assumed planar type configuration will then better enhance the re-emission of absorbed energy than favor a radiationless transition of the excited molecule to the ground state. Accordingly, the introduction of inert substituents into positions where they do not electronically interfere with the displacement of double bonds, but might sterically hinder the establishment of the postulated planar structures, is expected to decrease the capability of fluorescence and/or scintillation.

In view of the assumed structural mechanism of energy absorption and emission outlined above, there seem to be two independent prerequisites to efficient scintillation : a) the capability of the formation of polarized quinoid forms in the excited state, and b) that of acquiring a sterically planar structure in the same state. Both of them are also inherent molecular properties. Thus, the $1/\tau_i$ factor which denotes the probability of internal quenching of the scintillation solute in the Kallmann-equation (6), and which has been referred to as being "inherent to the solute molecule", could be defined more precisely. Besides the already suggested solvation effect, there are two other structure dependent parameters to which the constant could be related. It could measure the solute molecule's ability of quinoid structure formation (polarization) and also, the degree of planarity of the configuration present in the lowest excited electronic state. By this interpretation, both of the former parameters would separately contribute to the final value of $1/\tau_i$. References supporting the outlined suggestion will be made in discussing the scintillation efficiency of sterically hindered bis-benzoxazoles.

Finally, it should be pointed out that the hypothesis outlined above appears to be in agreement with the electromagnetic theory of energy absorption, and with previous

concepts relating the property of fluorescence to the compactness of certain molecular structures, rigidity of the molecule in the activated state, etc. (5,7,8,9,10).

Discussion

Ultraviolet Absorption Spectra and the Quinoid Structure

Concerning some tentative proof of the presence of transient quinoid structures in the lowest excited electronic state, it is suggested to consider the first member of the alkenyl bis-benzoxazole series, trans-1,2-bis(2'-benzoxazolyl)-ethylene, as a model. The outlined single separation of charge in this symmetrical molecule might be expected to occur, for example, between either the 6'-6'-positions or the 4'-4'-positions of the two benzoxazole nuclei, as seen from Fig. 2. The diagram depicts the front and the top views of a few approximate patterns of bis-benzoxazolyl ethylene in the ground state. Construction of the molecular patterns was performed with the utilization of known bond lengths and bond angles of analogous heterocyclic compounds, which data is available in the literature (11, 12, 13). The thick solid line illustrates the contours of one of the possible vibrational-rotational forms of the molecule. Two also perceivable structures (out of several others) are shown by thin solid lines. Broken lines represent the oxygen-bridges of the benzoxazole nuclei, which are presumed not to be participating in electronic transitions. Thus, the motion of π -electrons would be restricted to the two benzene rings and to the connecting conjugated double bond system including the two nitrogen atoms of the oxazole rings as well.

Let us allow the first electronic transition to occur with the formation of charge on the 6'-6'-carbon atoms of trans-1,2-bis(2'-benzoxazolyl)-ethylene. The components of the resulting dipole vector, a_x , a_y , a_z , can be calculated from the pattern and will assume values of 2.81, 11.69 and 1.23 Angstrom units, respectively, as noted in the diagram. By considering the data as the dimensions of a box in which the potential has been set equal to zero, the solution of the appropriate free electron Schrödinger equation (14) yields the wavelength of the corresponding transition which is about 371 m μ . The dimensions of another box can be ob-

Fig. 2. Trans-1,2-Bis(2'-benzoxazolyl)-ethylene.

tained from the same pattern, when an electronic transition is allowed inducing a transient separation of charge between the 4'-4'-positions of the bis-benzoxazole skeleton. The vector extending between the latter pair of carbon atoms has components of 1.33, 10.45 and 1.23 Angstroms, respectively. Again, by inserting these values into the proper Schrödinger equation, the wavelength of this so-called 4'-4'-transition will be 338 mμ.

As seen from Fig. 3, the ultraviolet absorption spectrum of trans-1,2-bis (2'-benzoxazoly1)-ethylene exhibits a broad K-band* of considerable intensity in the range of 320 and 380 mμ. The above calculated wavelengths of electronic transitions, which were assumed to be associated with the formation of 4',4'- and 6',6'-quinoidal structures, lay well within the band. As also seen from this curve, there are two distinctive shoulders, displayed by the fine structure of the spectrum, which are located between 336-343 mμ and at 367-373 mμ. The range of these shoulders is then comparable to the calculated single wavelength values of 338 and 371 mμ, respectively.

The fact that calculated and observed wavelengths are in somewhat satisfactory agreement does not necessarily prove the first assumption of this treatment, viz., the exclusion of oxygen atoms from the π -electron transport within the molecule. The approximation of restricting the motion of π -electrons to the two benzo-groups which are conjugated through the connecting unit, including the two nitrogen atoms only of the oxazole rings, appears to be less severe because the free movement of electrons was allowed in a box having a volume almost equivalent to that of the entire molecule. Consequently, the volume of this box includes the formerly excluded oxygen atoms as well. It should be noted, however, that in the solution of the wave-equations another approximation has been made by setting the potential inside the box equal to zero. In fact, the potential inside the box cannot be zero, since the electronegativity values of the carbon and nitrogen atoms are quite different.

Recently, Passerini and co-workers offered an interpretation of the ultraviolet spectra of several benzoxazoles (15). It is based on the assumption that only the benzo-ring should be regarded as the basic chromophore in the compounds

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* K-bands in general, have been ascribed to N-V transitions leading to polarized structures.

Fig. 3. Ultraviolet absorption spectra of trans-1,2-Bis(2'-benzoxazolyl)-ethylene (solid line), 1,2-Bis(2'-benzoxazolyl)-ethane (dotted line), and 1,2-Bis(2'-benzoxazolyl)-propane (broken line).

investigated. The aromatic π -shell of the hetero nucleus, particularly the nitrogen atom is stereo-electronically restricted from conjugation with the benzo-ring.

In view of the location and intensity of K-bands, being present in the absorption spectra of alkenyl bis-benzoxazoles, it can be concluded that there is some resonance interaction between the two benzoxazole nuclei necessarily involving the electron shells of the two nitrogen atoms. It can be easily shown that such resonance occurring between the different parts of a molecule would contribute to the formation of polarized quinoid structures and would facilitate the establishment of a planar type configuration.

Furthermore, as shown by a dotted line in Fig. 3, even the formally non-conjugated analog, 1,2-bis-(2'-benzoxazolyl)-ethane exhibits a K-band in the same region, but which is perhaps less intense. In addition, this saturated substance was found to be scintillating to a small extent. The maximum of its relative pulse height is 0.1 at about 2.5 g/l concentration. These two phenomena could be attributed to hyperconjugation extending over the relatively short aliphatic connecting unit and bridging the gap between the two benzoxazole rings.

By increasing the connecting unit with one more methylene group, the resulting 1,3-bis(2'-benzoxazolyl)-propane no longer possesses scintillation properties. Its ultraviolet absorption curve, as seen from the broken line in Fig. 3, does not indicate any resonance interaction between the two heterocyclic nuclei but resembles very much the spectrum of a single benzoxazole molecule.

The Planar Type Configuration and Steric Hindrance

Outlined in the precedings, the establishment of a more or less planar type configuration in the lowest excited state was also assumed besides the formation of quinoidal structures discussed earlier, as an independent prerequisite to efficient scintillation of the bis-benzoxazoles. The introduction of inert substituents which do not electronically interfere with the displacement of double bonds but, due to their relative positions, might distort the planarity of the activated molecule, was accordingly expected to decrease the capability of scintillation. Some experimental proof which can be furnished supporting this postulated condition of light emission,

involves the comparison of light output data of sterically non-hindered bis-benzoxazoles with that of analogous, but sterically hindered ones.

In Fig. 4 the top view of three-dimensional patterns of the trans-1,2-bis(2'-benzoxazolyl)-ethylene, trans-2,3-bis(2'-benzoxazolyl)-propene(-2) and trans-2,3-bis(2'-benzoxazolyl)-butene(-2) molecules are illustrated in the ground state. As pointed out in the preceding chapter, the figures depict only one of the several possible vibrational-rotational forms, however, they can be useful in studying the effect of steric hindrance. Construction of these approximate molecular diagrams was performed as described before and the framework of the 2-propene and 2-butene derivatives was considered to be identical with that of the bis-benzoxazolyl ethylene. Small and big circles in the diagrams indicate areas occupied by the hydrogen atoms and methyl groups, respectively, which are attached to the connecting unit.

Together with the patterns listed are the corresponding scintillation efficiencies. In this respect RPH_{max} refers to a relative pulse height yielded as a primary solute at optimum concentration which is 2.00 g/l (saturated solution) for the first two scintillating substances. The symbol RPH_{max} denotes the relative pulse height as a secondary solute (0.1 g/l) to p-terphenyl (4.00 g/l).

As seen from Fig. 4, a considerably decreased efficiency of scintillation or, even no scintillation, is found for trans-2,3-bis(2'-benzoxazolyl)-propene(-2) and trans-2,3-bis(2'-benzoxazolyl)-butene(-2).

Another pair of compounds having comparable structures but quite different light output values, is presented by the 2,2'-o-phenylene bis-benzoxazole and 2,2'-o-(p-xylenyl) bis-benzoxazole. Relative pulse heights of the latter substances are listed in Table 1.

Structurally, these bis-benzoxazoles are some methylated analogs of the corresponding unsubstituted parent molecules, the latter of which were found to be more or less efficient scintillators. The sharp loss in the light output of the 2-propene and 2-butene derivatives, as compared to that of the trans-ethylene compound, does not seem to be singularly ascribable to the presence of methyl groups.

Fig. 4. Approximate molecular patterns of trans-1,2-Bis(2'-Benzoxazolyl)-ethylene, trans-2,3-Bis(2'-Benzoxazolyl)-propene(-2), and trans-2,3-Bis(2'-Benzoxazolyl)-butene(-2).

Secondly, it appears very improbable that the decreased scintillation efficiency of the methylated analogs would be due to enhanced concentration quenching. It seems unlikely that the relative size of the methyl group(s) would basically alter the collision of activated and unexcited molecules of the same species. Furthermore, this argument could be also disclosed in view of the fact that both the methylated and their unsubstituted parent compounds exhibit optimum scintillation at almost identical concentrations.

But the essential loss in light output might be explained by considering the relative positions of these methyl groups in respect to the establishment of a planar type configuration, which was assumed to be also acquired in the excited state. Such type of substitution does neither interfere substantially with the postulated formation of polarized quinoid structures in the lowest excited state, nor can it be attributed to interference with the displacement of double bonds.

Ultraviolet absorption spectra of both of the methylated analogs of ethylene bis-benzoxazole exhibit a strong K-band in about the same region as that of the parent molecule, as seen from Fig. 5. The presence of the band indicates resonance interaction between the two benzoxazole nuclei and presumably the formation of polarized structures contributing to the lowest excited state. However, by increasing the number of methyl groups substituted into the connecting unit, the main peak of the K-band shifts moderately towards shorter wavelengths. This hypochromic effect could be attributed to the steric hindrance of resonance present to a certain extent even in the ground state. The above interpretation could also be supported by the fact that no fine structure is displayed in the K-band of the 2-butene compound which is sterically a more hindered one than the 2-propene derivative.

In view of the experimental facts presented, it can be easily realized that substitution of inert groups into positions adjacent to the benzoxazole nuclei, in general, would sterically interfere with the suggested establishment of a planar type configuration of the excited molecule. As it can be perceived from the relative position and size of the methyl groups - (big circles) in Fig. 4, forcing one or both benzoxazole nuclei out of plane results in enhanced self-quenching, or in other words, decreased scintillation efficiency. The introduction of the same groups, as seen from Table 2, into electronically significant but sterically non-critical positions, induces only a small alteration in the relative pulse

Fig. 5. Ultraviolet absorption spectra of trans-2,3-Bis(2'-benzoxazolyl)-butene (solid line), trans-2,3-Bis(2'-benzoxazolyl)-propene (broken line), and trans-1,2-Bis(2'-benzoxazolyl)-ethylene (dotted line).

height as compared to that discussed heretofore. Thus, steric hindrance of the activated state could be observed as an argument supporting the assumption described earlier.

However, the initial phases of scintillation and fluorescence are known to be different; it seems that the final stages of the light emission mechanism of conjugated bis-benzoxazoles could be interpreted by the hypothesis outlined in the precedings. This mechanism is pictured in Fig. 6.

Chemical Structure and Scintillation Efficiency

Based on the initial postulation and also on the fact that favorable relative pulse heights were obtained from 2,2'-o-phenylene bis-benzoxazole as a primary solute and from trans-1,2-bis(2'-benzoxazolyl)-ethylene used as a wavelength-shifter, a number of bis-benzoxazoles were prepared and screened for scintillation efficiency.

Our experiments were directed to the replacement of the linkage between the two benzoxazole nuclei by conjugated connecting units varying in structure and in the length of the chain. Also, modification of spectral characteristics by the introduction of various substituents into suitable positions in the benzoxazole nuclei of certain compounds which were found to be already efficient scintillation solutes, appeared to be important as well. The comparison of spectral properties and, in particular, comparison of the relative light output data of members of these two series was expected to yield some information about the relationship between the chemical structure and the scintillation efficiency of bis-benzoxazoles.

The variation of relative light output is reflected in Table I when the connecting unit linking the two benzoxazole nuclei has been varied from simple alkene chains to some heterocyclic systems. Typical members of the already available series of bis-benzoxazoles have been selected and classified according to their connecting units.

The relative efficiency of these substances was determined as being primary scintillators which data is tabulated under the heading of RPH_{max} , or as being secondary solutes

Fig. 6. Assumed structural mechanism of the energy absorption and emission process.

in 0.1 g/l concentration to 4 g/l p-terphenyl, values listed in the third column under RPH_{max} were obtained. Corresponding primary solute optimum concentrations are compiled in the table's first column. The benzoxazole nucleus which can be referred to either as benzoxazole or benzoxazolyl, has been denoted as BOX.

As seen from Table 1, in general, compounds having a straight alkene chain as connecting unit furnish primary solute pulse heights of moderate values only and the respective optimum concentrations indicate limited solubilities in toluene. However, their performance will be increased when used as wavelength-shifters. Solutions containing 0.1 g/l quantities of trans-1,2-bis(2'-benzoxazolyl)-ethylene or trans, trans-1,4-bis(2'-benzoxazolyl)-butadiene as secondary scintillators to p-terphenyl yield pulse heights of 1.34 and 1.18, respectively with an average grade DuMont 6363 tube. These light outputs are comparable to that of the same amount of POPOP (1.23) which data has been found as the performance of the latter substance in connection with the use of average grade photomultiplier tubes (3).

Replacement of the connecting unit by different aromatic nuclei results in an increase in the light output when the corresponding compounds are tested as primary solutes. In this respect, however, the efficiency of 2,2'-o-phenylene bis-benzoxazole is less than that of PPO, viz., 0.95 versus 1.00.

Regarding the approximate patterns of the o-phenylene bis-benzoxazole, it seems to be likely that due to their mutual ortho-positions, the two benzoxazole nuclei might sterically hinder each other to a certain extent in attaining the previously postulated establishment of a planar type configuration in the lowest excited state.

The cause of steric hindrance referred to was expected to be eliminated by introducing the benzoxazole nuclei into para-positions of an aromatic system, like it is in 2,2'-p-phenylene bis-benzoxazole or in the 2,2'-(4,4'-biphenylene) bis-benzoxazole. These two compounds then can be considered as heterocyclic analogs of p-terphenyl and p-quaterphenyl respectively, and would also be potential primary scintillators. The relative light output versus the concentration curve of both aromatic bis-benzoxazoles has a steep slope, and considerable pulse heights are found for even relatively low concentrations. Unfortunately, the solubility in toluene of both substances is a very limited one.

Table 1.

EFFECT of the VARIATION in the CONNECTING UNIT (R) on
SCINTILLATION EFFICIENCY

	Conc. (g/l)	RPH _{max} *	RPH _{max} **
1.1. R = ALKENE CHAIN			
trans-1,2-Bis(2'-BOX)-ethylene	2.00 (s)	0.70	1.34
trans-2,3-Bis(2'-BOX)-propene(-2)	2.00 (s)	0.20	0.31
trans-2,3-Bis(2'-BOX)-butene(-2)	---	0.00	0.00
trans,trans-1,4-Bis(2'-BOX)-butadiene	0.86 (s)	0.80	1.18
1.2. R = AROMATIC NUCLEUS			
2,2'-o-Phenylene BisBOX	6.00	0.95	0.97
2,2'-o-(p-Xylenyl)BisBOX	5.00	0.55	0.93
2,2'-p-Phenylene BisBOX	0.17 (s)	0.30	1.01
2,2'-(4,4'-Biphenylene)BisBOX	0.10 (s)	0.27	1.24
1.3. R = HETEROCYCLIC NUCLEUS			
2,3-Bis(2'-BOX)-pyridine	5.00	0.04	0.75
3,4-Bis(2'-BOX)-pyridine	5.00	0.30	0.54
2,5-Bis(2'-BOX)-pyridine	0.35 (s)	0.35	0.98

RPH_{max}*, Relative Pulse Height as primary solute

RPH_{max}**, Relative Pulse Height as secondary solute
 (0.1 g/l) to p-terphenyl (4.0 g/l)

(s) saturated solution

The biphenylene bis-benzoxazole, however, appears to be an efficient secondary scintillator to the primary solute p-terphenyl by yielding a relative light output of 1.24 in this respect.

The decreased scintillation efficiency of 2,2'-o-(p-xylyl) bis-benzoxazole, a sterically hindered dimethyl analog of the parent 2,2'-o-phenylene derivative, has already been discussed in the preceding chapter.

Substitution of benzoxazole nuclei into a heteroaromatic system, such as pyridine, decreases the scintillation efficiency, as compared to that of the corresponding aromatic isomers. In agreement with other available data (16), this effect can be attributed to a transition of an electron of the unshared pair in the pyridine nitrogen atom to an antibonding π -molecular orbital.

In a second approach to the modification of spectral properties of certain bis-benzoxazoles having an established scintillation efficiency, a series of symmetrically substituted bis-benzoxazolyl ethylenes as well as o-phenylene bis-benzoxazole derivatives was prepared and tested. Relative pulse height values of some selected members of these two series are presented in Table 2. The arrangement of data compiled is the same as in the preceding table.

As seen from this table, the introduction of methyl groups into sterically non-critical but electronically significant positions, viz., positions in the benzoxazole rings, results only in a less pronounced modification of the relative light output. As a result of an inductive effect on the displacement of double bonds, substitution of an electron-donating group(s), slightly decreased the scintillation efficiency of the corresponding 5,5'-dimethyl derivatives as compared to that of the parent trans-ethylene and o-phenylene compounds. For the same reason, introduction of the same groups into 6,6'-positions effects a slight increase in the pulse height when the respective 6,6'-dimethyl derivatives are tested as primary solutes.

Electron withdrawing groups, as expected, decrease the efficiency of scintillation in general, like it is found for the 5,5'-dichloro- and 5,5'-dinitro members of both series. The presence of the same substituents in 6,6'-positions cancels the fluorescence and/or scintillation ability of such substances.

Table 2.

EFFECT of SUBSTITUTION in the BENZOXAZOLE NUCLEI on
SCINTILLATION EFFICIENCY

SUBSTITUENTS ($R_1=R_2$)	Conc. (g/l)	RPH* max	RPH** max

2.1. SYMMETRICALLY SUBSTITUTED BIS-BENZOXAZOLYL
ETHYLENES

R ₁ = R ₂ = H, H	2.00	0.70	1.34
,5,5'- Dimethyl	4.00	0.57	0.95
,6,6'- Dimethyl	2.50	0.81	1.10
,5,5'- Dichloro	0.80 (s)	0.22	0.68
,5,5'- Dinitro	0.75 (s)	0.18	0.55
,6,6'- Dinitro		insignificant	

2.2. SYMMETRICALLY SUBSTITUTED 2,2' -o- PHENYLENE
BIS-BENZOXAZOLES

R ₁ = R ₂ = H, H	6.00	0.95	0.97
,5,5'- Dimethyl	7.00	0.83	1.16
,6,6'- Dimethyl	8.00	0.98	1.05
,5,5'- Dichloro	3.50	0.66	0.85
,5,5'- Dinitro	2.80	0.23	0.65
,6,6'- Dinitro		insignificant	

RPH*_{max}, Relative Pulse Height as primary solute

RPH**_{max}, Relative Pulse Height as secondary solute
(0.1 g/l) to p-terphenyl (4 g/l)

(s) saturated solution

In summarizing, based on the relative pulse height data presented of this selected series of bis-benzoxazoles, it appears that members of this molecular species having a straight alkene chain as connecting unit might have also some practical value as being secondary solutes to p-terphenyl. In addition, it could be concluded that certain bis-benzoxazoles having an aromatic connecting unit might be useful as primary scintillators.

Method of Evaluation

All of the phosphors prepared were evaluated with the use of a detecting system containing no specific components.

Accordingly, an average grade 3" DuMont 6363 photomultiplier tube was utilized as light detector. The 90% sensitivity of this type of tube occurs in the range of 390 and 490 mμ which corresponds to S-11 characteristics (17).

Samples for testing were covered only with an aluminum reflector having a highly polished inner surface, and then were excited with 662 KeV γ-rays from a Cesium-137 source built into the top of the reflector.

In contrast to the simple detecting system, the unit analyzing and recording the resulting line spectra was a RCL 256-channel pulse-analyzer.

Since there are many critical variables involved in the quantitative evaluation of liquid scintillation solutes, a standardized procedure was followed. To obtain reliable results, which would be also comparable to that of other scintillators published, the calculation of pulse height values was based on a reference curve. The curve which was determined both before and after the measurement of each set of new samples, is a plotting of pulse height versus the width in millimeters of the registered spectra, and is defined by two calibration points each having a fixed value. These fixed points were the actual widths of spectra registered by two arbitrary standards in presence of the aluminum type reflector. Used as standards were a) a 3 g/l PPO solution in toluene, and b) a 4 g/l p-terphenyl solution containing 0.1 g/l of

POPOP as secondary solute. The spectrum width of the former solution was regarded equivalent to a pulse height of 1.00. That of the latter reference standard was considered to be 1.23 under the experimental conditions described and in agreement with the value recorded as the performance of PPO under similar conditions (3).

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HEXAFLUOROBENZENE LIQUID SCINTILLATORS AND THEIR APPLICATION
TO GAMMA AND FAST NEUTRON DOSE RATE MEASUREMENTS*

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INTRODUCTION

The measurement of gamma ray and fast neutron dose rates in a mixed radiation field poses some interesting problems. If the rates are to be measured by means of liquid scintillators, probably the most important of these is the fact that all of the common liquid scintillators are basically hydrocarbon in composition and consequently respond to both types of radiation.

A method has been described by Berlman and Marinelli (1) for the estimation of fast neutron rates in the presence of gamma rays. This system makes use of "twin" detectors having liquid scintillators of equal electron but dissimilar hydrogen content. The solvents used were xylene and 1,4-bis(trifluoromethyl)benzene. By suitable adjustment of solute concentrations, volumes of liquid scintillator and photomultiplier voltages, the Compton electron pulse-height spectra of the two solutions can be made to coincide satisfactorily under the action of gamma rays. In the presence of neutrons, the proton pulse-height spectra will differ in magnitude because of the different number of proton recoils produced in each liquid scintillator.

In the case of gamma radiation, scintillations are produced in the liquid scintillator by ionizing particles which arise as electrons from Compton scattering of gamma rays.

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When fast neutrons are involved, the ionizing particles arise as recoil protons from the collision of fast neutrons with hydrogen in the solvent. As a consequence, a solvent which contains no hydrogen should respond only to gamma radiation, and one which contains hydrogen should respond to both gamma rays and fast neutrons. In the method which is to be described, simultaneous gamma ray and fast neutron rate measurements are made by means of "paired" liquid scintillators, one of which is only gamma-sensitive and another which responds to both gamma rays and fast neutrons. With the two detectors in the same geometry with respect to the radiation source, the gamma rate is obtained from the hexafluorobenzene liquid scintillator. Based upon the calibrated ratio of gamma sensitivities, an equivalent gamma response is calculated for the hydrocarbon solution. Then, by difference, the net nongamma response of the latter scintillator represents the fast neutron component.

PREPARATION OF HEXAFLUOROBENZENE SOLVENT

Synthesis of Hexafluorobenzene

Of the organic compounds which do not contain hydrogen, perfluoro- compounds such as perfluorohexane, perfluorotoluene, and hexafluorobenzene (C_6F_6) looked most promising as liquid scintillator solvents. Perfluorohexane was prepared but was an extremely poor chemical solvent for scintillator solutes. Perfluorotoluene has been obtained in small yield only as a by-product in various reactions. Hexafluorobenzene is not, at present, a commercially available chemical. In fact, specialty laboratories apparently were not interested in synthesizing this compound, probably because of the lengthy and inconvenient procedure, low yield, and high cost of catalytic materials. Consequently, the material used was prepared according to the procedure of Hellman et al. (2), which involves the pyrolysis of tribromofluoromethane in a platinum tube at 530 to 550° C under 4.5 atmospheres nitrogen pressure. Conditions (2) for optimum yields of product are given in Table 1. The contact time should be about 15 seconds with a nitrogen flow rate of about 100 cc per minute (3).

Purification of Hexafluorobenzene

The crude product from the pyrolysis reaction contained

TABLE 1. PYROLYSIS OF TRIBROMOFLUOROMETHANE

Temp., °C	Press., atm.	Feed Rate, g/min	Total Recovery, per cent	Bromine Liberated, per cent	Gross Yield C ₆ F ₆ , per cent	Recovery CFBr ₃ , per cent	Net Yield C ₆ F ₆ , per cent
530	4.5	5.1	99	50	29	43	50
540	4.5	7.0	95	62	38	30	55
550	4.5	3.5	96	67	40	25	52

free bromine (~57 per cent by weight), unreacted tribromofluoromethane (~28 per cent by weight), and other bromofluoro- compounds. Bromine removal was effected by washing the crude product with bisulfite solution. Preliminary distillation of the product through a Snyder column gave two fractions: impure hexafluorobenzene (boiling range 60 to 92° at 585 mm) and recovered tribromofluoromethane. The product fraction was dissolved in ether, treated with 2N sodium hydroxide for 51 hours, washed with water, and dried over Drierite. This step was essential, since bromine was liberated in the subsequent fractionation from an unstable compound, probably symtetrabromodifluoroethane, and complete removal of this compound in the later gas chromatographic purification was difficult. The dry solution was then fractionated in a helices-packed column, and final purification of the hexafluorobenzene was accomplished by gas chromatographic resolution of 1- to 4-ml aliquots on a preparative-scale column.* Purity of the finished product was checked by gas chromatography on two analytical columns with different packing materials. The analytical columns indicated a small amount of a second component, which was trapped from the gas stream and subjected to mass spectrometric analysis. Bromine was absent, but the -CF₃ group was present; hence, the contaminant was thought to be perfluorotoluene. The relative anode current measurement (4) obtained with 2,5-diphenyloxazole (PPO, 5 g/l) solute and a Cs-137 source was 23 per cent of that shown by a standard solution of PPO (5 g/l) in toluene.

EVALUATION OF SOLUTES IN THE HEXAFLUOROBENZENE LIQUID SCINTILLATOR SYSTEM

Based upon light output, the radiation damage from a given total gamma dose to solutions of various solutes in hexafluorobenzene is considerably greater than to solutions

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* The column, which was operated at a temperature of 80°C with a helium flow of 1400 cc per minute, was designed and constructed by R. N. Rogers of the Los Alamos Scientific Laboratory. This 10-ft column, 2 in. in diameter, was packed with Dow-Corning silicone high vacuum grease on C-22 fire brick support.

of the same solutes in hydrocarbon solvents such as toluene, xylene, and triethylbenzene. Since the damaged solutions are yellow in color, regardless of which solute is employed, transmittance of the solutions has been reduced. In addition, noncolored chemical substances which quench the scintillation process may also be present.

Although 2,5-diphenyloxazole (PPO) appeared to be the solute of choice for use with C_6F_6 because of good solubility and scintillation characteristics, it was found experimentally (5) that exposure of C_6F_6 -PPO (5 g/l) scintillator to a total gamma dose of 3.2×10^5 roentgens,* resulted in a 45 per cent reduction in scintillator response. Other solutes were then evaluated on the basis of the following criteria: solubility in C_6F_6 ; relative anode current measurements; radiation damage to solutions in C_6F_6 , as indicated by relative current measurements; and effect of oxygen on the rate of radiation damage. Results for a number of solutes are shown in Table 2.

Based upon the results obtained with the irradiations in vacuo, a solution of 9,10-diphenylanthracene (D7) in C_6F_6 , free of oxygen and saturated with an inert gas, is considered to be the liquid scintillator of choice for monitoring high gamma dose rates; especially when the accumulated dose becomes large, i.e., $> 10^4$ r. In C_6F_6 -D7 solutions, the average increase in sensitivity due to removal of the oxygen quenching factor (6), by saturating the solutions with argon, was 64 per cent. An oxygen-free solution of PPO offers greater sensitivity and would, therefore, be of interest for monitoring low gamma dose rates.

The deterioration process involved in radiation damage is probably one of free radical formation from molecules of the solvent with subsequent chemical reactions involving the solute. The result obtained when no solute was dissolved in the C_6F_6 during irradiation suggests that substances were formed in the solvent which were either capable of quenching the scintillation process or of reacting with the added solute to form a scintillation-quenching or light-absorbing product.

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* Gamma rays from a 25.5 kc barium-lanthanum source; average energy 1.1 Mev.

TABLE 2. RADIATION DAMAGE TO HEXAFLUOROBENZENE SOLUTIONS OF VARIOUS SOLUTES

Accumulated Dose, (a) roentgens	Solute (b)	Relative Currents (c)		Ratio (d)
		Before Irradiation	After Irradiation	
<u>In Air</u>				
1.46 x 10 ⁶	D7 (3 g/l)	0.160	0.014	0.088
1.6 x 10 ⁵	PPO (5 g/l)	0.230	0.190	0.825
1.46 x 10 ⁶	PPO (5 g/l)	0.223	0.091	0.408
1.46 x 10 ⁶	G127 (2 g/l)	0.124	0.023	0.185
<u>In Vacuo</u>				
1.24 x 10 ⁶	PBD (3 g/l)	0.190	0.124	0.654
1.24 x 10 ⁶	D7 (3 g/l)	0.165	0.128	0.776
1.24 x 10 ⁶	PPO (3 g/l)	0.205	0.092	0.448
1.24 x 10 ⁶	None (e)	0.205	0.188	0.917

(a) Cobalt⁶⁰ 1.3-Mev gamma rays.

(b) The solutes represented by these designations are: D7, 9,10-diphenyl-anthracene; PPO, 2,5-diphenyloxazole; Gl27, 3,3'''-dimethyl-p-quaterphenyl; and PBD, 2-(4-biphenyl)-5-phenyl-1,3,4-oxadiazole.

(c) PPO in toluene (3 g/l) was used as the standard. Air-saturated solutions were used.

(d) This is the ratio of relative current after irradiation to that before irradiation.

(e) PPO (3 g/l) was added after irradiation of the solvent.

In this regard, it is of interest that hexafluorobenzene recovered, by high vacuum distillation, from a radiation-damaged solution gives the original relative current value when fresh solute is added.

PHOTOVOLTAIC CELL AND PHOTOMULTIPLIER TUBE DETECTORS

Photovoltaic Cell Detectors

A procedure has been described (7) for monitoring fairly high dose rates of pure gamma radiation. In this system, photons which are emitted from a liquid scintillator and impinge on a selenium photocell give rise to a measurable current by means of the photovoltaic effect. An adaptation of this method was used in designing our high dose rate detectors.

The design of the photovoltaic detector and especially the volume of the liquid scintillator chamber are directly related to the range of radiation dose rates to be monitored. The use of a glass container for the liquid scintillator is not satisfactory when high dose rates or large accumulated doses are to be encountered, because of browning of the transparent window facing the photovoltaic cell. Cerium-stabilized glass has been used satisfactorily, but it seemed preferable to have no glass at all. Consequently, detectors were made as shown in Fig. 1, in the form of a right cylinder with the photovoltaic cell cemented in place as one end of the container. Armstrong A-6 epoxy resin is a satisfactory adhesive and was found not to affect the liquid scintillator adversely. The detector barrel was made of steel and was coated on the inside with reflecting TiO_2 epoxy resin paint (8). A step or shelf in the steel barrel and a spring contact make the necessary electrical connections to the collector ring and the back plate of the PV cell, respectively. Current from the PV cell is fed through a BNC connector and coaxial cable to the galvanometer system.

The size of the detector, i.e., the volume of liquid scintillator, is a function primarily of the dose rate range to be monitored and secondarily of the efficiency of the liquid scintillator in use. In order to preserve linearity of response of the PV cell with a safe margin, the maximum current from IRC-A5* selenium PV cells should not exceed 300 μa

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* International Rectifier Corporation, El Segundo, California.

Fig. 1. Photovoltaic cell detector.

with an external resistance of 10 to 100 ohms and $10\text{ }\mu\text{a}$ with an external resistance of 1000 to 1100 ohms. The acceptable minimum current from the PV cell is considered to be $10^{-2}\text{ }\mu\text{a}$, since noise pick-up may occur below this level. The gamma dose rate range of a 20-ml detector, having a typical sensitivity of $1.3 \times 10^{-3}\text{ }\mu\text{a/r/min}$, would, therefore, be 7.7 r/min to $2.6 \times 10^5\text{ r/min}$. It also follows that for a detector with a 10 fold increase in volume, the sensitivity is increased by a factor of 10, and both the minimum and maximum measurable dose rates are decreased by the same factor. Since maximum current limits apply as described above, the high dose rate range of a detector can be extended somewhat by reducing its gamma sensitivity. This may be accomplished in a number of ways, which include: reduction in the volume of scintillator solution; reduction in the concentration of solute; and selection of the solvent and/or the solute, on the basis of relative pulse height or relative anode current measurements.

Gamma Calibrations

In our work, gamma sensitivity, in $\mu\text{a/r/min}$, of the PV gamma detectors, was determined with a Co-60 source. As already mentioned, a typical sensitivity for the $\text{C}_6\text{F}_6\text{-D}_7$ liquid scintillator is $1.3 \times 10^{-3}\text{ }\mu\text{a/r/min}$. When these detectors are to be used in mixed radiation gamma-neutron fields, calibrations are made in double-walled aluminum cans with 0.04 in. of Li-6 shielding against thermal neutrons. Gamma sensitivity of the PV gamma-neutron detectors was determined in a similar manner, also with Li-6 shielding. A typical sensitivity is $1.32 \times 10^{-3}\text{ }\mu\text{a/r/min}$, when the liquid scintillator is mineral oil/D7 (2 g/l).

In a mixed gamma-neutron field, the fast neutron contribution to the response of hexafluorobenzene solutions, due to hydrogen in the solute, is considered to be negligible. For example, in a solution of hexafluorobenzene-D7 at a concentration of 2.25 g/l, the weight of hydrogen per liter is 0.124 g. This weight of hydrogen is 0.15 per cent of that in 1 liter of xylene-D7 (3 g/l), or 0.1 per cent of that in 1 liter of mineral oil/D7 (2 g/l). Since the gamma sensitivities of hexafluorobenzene and mineral oil solutions of D7 are approximately equal, i.e., $1.3 \times 10^{-3}\text{ }\mu\text{a/r/min}$, and the ratio of neutron to gamma sensitivity of the latter solution is 0.22, the fast neutron response due to hydrogen in the C_6F_6 solution should not exceed 0.02 per cent of the gamma response.

Fast Neutron Calibrations

Fast neutron sensitivity, in $\mu\text{a}/\text{rad}/\text{min}$, was determined at the Los Alamos Godiva II reactor. Paired detectors, shielded with Li-6, were placed at identical distances from the reactor. At a given power level, the gamma response of the gamma detector and the gamma plus neutron response of the gamma-neutron detector were read simultaneously. The integrated fast neutron dose for each run, from which a dose rate was calculated, was determined with sulfur monitors. From the gamma dose rate obtained, with the gamma detector and the previously calibrated gamma sensitivity ratio of the two detectors, an equivalent gamma response was calculated for the gamma-neutron detector. Then, by difference, the neutron response in microamperes was equal to the total response of the gamma-neutron detector minus its calculated gamma response. The neutron sensitivity of the detector was then obtained by dividing the net neutron response by the neutron dose rate. The ratio of gamma sensitivity to neutron sensitivity thus obtained for the PV gamma-neutron detectors was 4.6.

When a gamma-neutron detector is employed in a mixed radiation field, dose rate limits are dependent upon the composition of the radiation since the sensitivity of the detector toward gamma rays and fast neutrons, respectively, differs by the factor 4.6. For example, in a pure neutron field, using a typical fast neutron sensitivity of $2.87 \times 10^{-4} \mu\text{a}/\text{rad}/\text{min}$, the rate range would be from 35 to 10^6 rads/min. Applying the above-mentioned gamma sensitivity, the range of the same detector for gamma rays only would be 7.6 to 2.3×10^5 r/min.

Photomultiplier Tube Detectors

A more sensitive system for low radiation rates was devised by cementing the cathode of a 1 in. diameter DuMont No. 6467 photomultiplier tube into a standard 20-ml steel chamber,* with reflecting inner surface. A variable high voltage supply is used with this type detector. By adjustment of the total resistance in the photomultiplier tube

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* Chambers made for photovoltaic detectors may be used with slight alteration.

bleeder network, the currents developed in this detector are made compatible with the limits imposed by the galvanometer assembly.* The resistance was set at 3.4 megohms.

The current produced may become significantly nonlinear if it exceeds 0.1 of the current flowing in the bleeder network. Hence, the maximum usable current at any given high voltage is:

$$I_{\max} (\mu a) = \frac{\text{voltage (volts)}}{\text{resistance (megohms)}} \times 0.1$$

Since the measurable radiation rates are limited by the maximum and minimum allowable currents, as well as the sensitivity of the detector, there is a maximum and minimum value of dose rate measurement at each high voltage available. Using typical sensitivity values, the range of the PM-type detector for gamma radiation is from 1.87×10^{-4} r/min to 295 r/min, when the liquid scintillator is hexafluorobenzene-D7 (2.25 g/l). The PM-type gamma-neutron detector, filled with hydrocarbon liquid scintillator, may also be used to measure gamma dose rate in a pure gamma field and has a typical range of 6.4×10^{-5} r/min to 129 r/min, when the scintillator is p-xylene-D7 (3 g/l).

Gamma Calibrations

Gamma sensitivities, in $\mu a/r/min$, of the PM gamma and gamma-neutron detectors was determined with a Co-60 source over a wide range of high voltages applied to the tube. These calibrations were also made with Li-6 thermal neutron shielding. The calculated values of maximum and minimum measurable dose rates cover more than a thousand fold range of dose rate at a given high voltage. Since it is often necessary to pre-set the high voltage, a suitable range can be selected to cover the estimated dose rate with considerable room for error in the estimation.

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*The recording galvanometer assembly may be used interchangeably with either the PV- or the PM-type of detector.

Fast Neutron Calibrations

Fast neutron sensitivity of the PM gamma-neutron detectors was determined at the Godiva II reactor essentially as described for PV detectors. The ratio of gamma sensitivity to neutron sensitivity for the PM detectors filled with mineral oil/D7 (2 g/l) was 4.2. Using this ratio of response, fast neutron sensitivity for each high voltage setting may be calculated as a function of the gamma sensitivity calibration.

INSTRUMENTATION

The currents generated by either the PV- or PM-type detector are measured by means of a transistorized galvanometer* (Fig. 2). This instrument is equipped with a choice of external resistance parallel to the input such that voltages are developed across a net input resistance of either 10 or 1000 ohms. By this means, that resistance which both develops the voltages to be measured in the galvanometer and is part of the load across the PV cell is altered to coincide with the range of current to be measured and still preserve linearity of response of the PV cell. Low-impedance coaxial cable carries current from either type detector to the galvanometer.** The output from the galvanometer is fed through a voltage divider into a strip chart recorder,*** with 100 mv full-span. A voltage regulator is used to supply power at constant voltage to the galvanometer. Since this is a low current device in which the output from the detector is not amplified before transmission, it has been found advantageous to operate the detector-galvanometer circuit as a full floating ground system.

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* Kintel Model 204A electronic galvanometer and amplifier.

** RG58/U coaxial cable, impedance 0.014 ohm/ft, has been used to transmit signal over distances up to 2 miles.

*** Model G-11A, Varian Recorder.

Fig. 2. Photovoltaic cell detector and galvanometer.

DOSE RATE INDEPENDENCE

Linearity of response over the entire dose rate range of a detector is considered to be a primary requisite of these devices. Thus, a calibration at a given dose rate is effective over the entire rate range.

Linearity of response of the PV gamma and gamma-neutron detectors was demonstrated, with a 25.5 kilocurie barium-lanthanum source, to be very good over a dose rate range from about 10^2 to 10^4 r/min. Similar good linearity was shown by: a PV gamma-neutron detector to fast neutrons in a mixed radiation field from the Godiva II reactor, over a range from 28 to 74 rads/min; a PM gamma-neutron detector to Co-60 gamma rays over a range from 10^{-1} to 10^2 r/min; and a PM gamma-neutron detector to 3 Mev neutrons over a range from 2.5×10^{-1} to 7.4×10^{-1} rad/min.

FACTORS AFFECTING DETECTOR RESPONSE

Photomultiplier Tube Fatigue

In the case of photomultiplier-type detectors, one limitation must be observed in adjusting the sensitivity of the detector for the probable dose rate range which is to be monitored. When relatively large anode currents, those greater than $1 \mu\text{a}$, are delivered for more than a few minutes, a change in the response of the photomultiplier tube is observed. Different brands of tubes behave differently under these circumstances. For example, DuMont No. 6467 tubes show an increase in sensitivity, whereas RCA No. 6199 tubes decrease in sensitivity. From a study of this feature with PM detectors under gamma ray excitation, the following generalizations may be made for DuMont No. 6467 tubes. At $2 \mu\text{a}$ anode current, the tubes are stable for about 15 minutes; near $1 \mu\text{a}$, the response is constant for at least 30 minutes; and below $0.5 \mu\text{a}$, stability is good over several hours. Tubes which have had a change in response recover over a period of time, which is roughly proportional to the magnitude of the change.

Radiation Damage to Liquid Scintillators

Radiation damage to liquid scintillators becomes a serious factor when high dose rates are encountered, especially if monitoring is on a continuous basis. As illustrated in Fig. 3, the damage resulting from a given integrated gamma dose from Co-60 is greater to a hexafluorobenzene solution of D7 (2.25 g/l) than to a solution of the same solute in p-xylene (3 g/l). These results were obtained in each case with PV detectors filled with oxygen-free argon-saturated solutions.

An effect which has been noted in instances of alpha and beta particle damage to polystyrene scintillator (9) and with cathode rays (10) was observed in the case of damaged hexafluorobenzene scintillator. When irradiation was interrupted, partial recovery of sensitivity took place, reaching a maximum in about 24 hours. The maximum recovery amounted to about 14 per cent, based on the sensitivity of the damaged solution. When irradiation was resumed, however, the damage rate was much faster than at the time of interruption but soon dropped to the former rate.

Temperature Effect

The effect of temperature on the sensitivity of photovoltaic- and photomultiplier-type detectors was determined over the range of most probable practical application, 22 to 32° C. The results for both hexafluorobenzene-D7 and p-xylene-D7 solutions are shown in Fig. 4. These data were obtained with oxygen-free argon-saturated solutions and include the effect of temperature on response of the photomultiplier tube or the photovoltaic cell.

It has been demonstrated by Seliger and Ziegler (11) that the temperature effect is linear and inverse with changes in temperature. Response curves were obtained, in their case, for solutions of several solutes in the same solvent; the slopes of the curves differed considerably. The effect of temperature on photomultiplier tube response was of about the same magnitude and opposite in sign to the effect on the scintillator solution. In the present work, the decrease in sensitivity with temperature was considerably larger in hexafluorobenzene than in p-xylene solutions of D7 solute. The lesser effect in the photomultiplier-type detector, for both

Fig. 3. Effect of large doses of gamma radiation on PV gamma detector response (dose rate $\sim 10^3$ r/min). The lower C_6F_6 -D7 curve is a continuation of the upper curve from the 50 per cent response point after time was allowed for recovery; add 1.04×10^6 r to the abscissa units for the lower curve.

Fig. 4. Effect of temperature on detector response to gamma radiation.

solvents, probably reflects the positive effect of temperature on the tube response.

Response to Thermal Neutrons

Thermal neutron response of a photovoltaic cell gamma-neutron detector, liquid scintillator triethylbenzene-terphenyl-POPOP,* was observed in the north thermal column of the Los Alamos Homogeneous Reactor. The lithium extrapolation method (12) was used to determine the thermal neutron sensitivity of the PV-type detector. In terms of gamma-equivalent r per tissue rad of thermal neutrons, the sensitivity was 6.9. In actual practice, this factor is virtually eliminated by shielding with Li-6.

Energy Dependence to Fast Neutrons

Energy dependence of the photomultiplier gamma-neutron detector was studied with monoenergetic fast neutrons from the Los Alamos Van de Graaff accelerator. Two detectors with different wall materials, iron and beryllium, in the liquid scintillator chambers were used. The liquid scintillator in each case was p-xylene-D7 (3 g/l).

As illustrated in Fig. 5, with beryllium wall material the response per tissue rad of fast neutrons steadily increases with energy in the region from 1 to 8 Mev. The difference in response of the two detectors may be due, in part, to neutron-induced activity in the iron chamber. Since equal volumes of the same liquid scintillator were used in the two detectors, the other factors affecting sensitivity were light-gathering efficiency and the sensitivity of the photomultiplier tube.

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* 2,2'-p-Phenylenebis 5-phenyloxazole .

Fig. 5. Effect of neutron energy on PM gamma-neutron detector response to fast neutrons (p-xylene-D7 scintillator).

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SOLID AND LIQUID SOLUTION SCINTILLATORS CONTAINING
MONOISOPROPYLBIPHENYL

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We have recently investigated the use of monoisopropylbiphenyl (MIPB) in the preparation of plastic scintillators which show pulse shape discrimination (1), and for liquid scintillators which are particularly suitable for direct counting on filter paper. A further investigation of the role of this solvent appeared desirable in order to elucidate the mechanism by which this compound affected the scintillation process and thereby made possible a differentiation in detection between light and heavy ionizing particles in the plastic scintillator. Similarly, observation of the low quenching action exhibited in liquid scintillators employing MIPB as solvent, prompted an investigation of the kinetics of quenching in such liquid scintillation systems. Although the behavior in liquid and plastic scintillators is probably not directly related, the results are nevertheless being combined in this report on the scintillation properties of MIPB.

PLASTIC SCINTILLATORS

We at first assumed that MIPB acted as a high boiling solvent or plasticizer in plastic scintillators. One would thus postulate that the polymer chains were merely diluted and to some extent disentangled by the presence of this solvent, and that energy transfer would take place through the combined aromatic medium. However, such a postulate requires the molecular weight of the polymer to be relatively unchanged for samples prepared with or without MIPB, and we have already shown that the molecular weight is not affected by the presence of familiar

scintillating solutes (3). When samples of plastic scintillator similar in composition to those employed in pulse shape discrimination measurements were dissolved, and their molecular weights measured, it was found that a great reduction in molecular weight had occurred in comparison with polymers prepared in the absence of MIPB. These results indicated that MIPB was participating in the polymerization process, probably as a chain transfer agent. A formal investigation of the role of MIPB as a chain transfer agent was therefore initiated with the aim of determining: (a) the kinetic constants for chain transfer (b) their temperature dependence and hence activation energy (c) the relationship between the intrinsic viscosity and the number average molecular weight of polyvinyltoluene.

Before proceeding with the preliminary report of this investigation, it is probably advisable to review the basic steps in a vinyl polymerization reaction. The general features of these polymerizations are well established and are known to occur via a free radical mechanism involving the steps, initiation, propagation and termination. Once a free radical is formed by an initiator or by thermal means the whole process proceeds to completion with extreme rapidity, and the individual polymer radical has merely a fleeting existence. Consequently the reaction mixture at any instant consists of monomer and dead polymer together with an exceedingly small population of growing radicals. The dead, or full grown, polymer does not participate further in the reaction mechanism.

The reactions are succinctly summarized in Table I.

Table I

REACTION SCHEME FOR A VINYL POLYMERIZATION

	Rate Constant	Step	
$I \rightarrow 2R$	k_d	Initiation	1
$R. + M \rightarrow M_1.$	k_p	Propagation	2
$M_1. + M \rightarrow M_2$	k_p		
$M_x. + M \rightarrow M_{x+1}$	k_p		3
$M_x. + SH \rightarrow M_xH + S$	k_p		
$S. + M \rightarrow SM.$	k_{tr}	Chain Transfer	4
$M_x. + M_y. \rightarrow M_{x+y}$	k_t	Termination	5
or $M_x + M_y$			

The kinetics of chain transfer to solvents have been thoroughly investigated and it can be shown that

$$\frac{1}{\bar{x}_n} = C_m + C_s [S] [M] + \frac{k_t}{k_p^2} \frac{R_p}{[M]^2} + C_I \frac{k_t}{k_p^2 k_d} \frac{R_p^2}{[M]^3} \quad \underline{6}$$

where C_m , C_s , C_I are chain transfer constants to monomer solvent and initiator respectively,

k_t , k_p , k_d are rate constants for termination, propagation and initiation.

$[S]$, $[M]$ are molar concentrations of solvent and monomer. R_p is the rate of the propagation reaction and $\bar{x}_n$ is the number average of monomer segments in the polymer.

If the third term is held constant, and chain transfer to monomer and initiator is negligible, (as is the case with styrene) then

$$\frac{1}{\bar{x}_n} = \left(\frac{1}{\bar{x}_n} \right)_0 + C_s \frac{[S]}{[M]} \quad \underline{7}$$

The latter equation is readily susceptible to experimental test. By plotting the reciprocal of the number average molecular weight against the solvent monomer ratio, S/M one can obtain C_s , the chain transfer constant from the slope of the linear relationship.

The term $\frac{k_t}{k_p^2} \frac{R_p}{[M]^2}$ in equation 6 can be maintained constant

by adjusting the initiator concentration, by diluting with inert solvent which does not show chain transfer in a manner which does not alter the initiator or monomer concentrations, or by conducting a thermal polymerization with diradical initiation, as in styrene (4)(5).

EXPERIMENTAL

Vinyltoluene monomer (Dow) was freed of inhibitor and distilled under reduced pressure. MIPB was acid washed, chromatographically purified, and distilled. For the thermally initiated samples, vials containing a total of 20 ml. of various ratios of monomer and MIPB were subjected to a series of freezing thawing cycles and sealed under vacuum. The samples were placed in thermostatted baths and allowed to polymerize to approximately 10% conversion at the chosen temperature.

Initiated samples were prepared as above, but contained a fixed concentration, 0.0609M of 2, 2'azobisisobutyronitrile, 10 ml of vinyl toluene and varying ratios of benzene and MIPB to furnish a total volume of 25 ml.

Molecular weights were determined by measurement of intrinsic viscosity and by direct determination employing a series of five Zimm-Myerson osmometers. Methyl ethyl ketone was used as solvent in each case.

RESULTS

The results of thermal measurements are summarized in Table II for experiments performed at three temperatures. For the samples prepared at 60 and 100°C the polymerization was stopped at approximately 10% conversion and the samples were isolated by two precipitations from methyl ethyl ketone using methanol as precipitant. The 125°C samples were obtained from samples prepared previously in conjunction with pulse shape discrimination work and were completely polymerized. The results of the 125°C samples cannot strictly be compared with the other samples, because of complicating side effects at high conversion which partially invalidate the simple vinyl polymerization kinetic scheme here employed.

The chain transfer data are presented graphically in Figure 1, and it is seen that the results demonstrate the occurrence of chain transfer and allow a determination of the chain transfer constants. From these data and the temperature dependence of the chain transfer constants, it is in principle possible to predict the molecular weight of the polymer formed at any ratio of vinyl toluene to MIPB and at any temperature. The magnitude of the chain transfer effect

Table II

EVALUATION OF CHAIN TRANSFER CONSTANTS FOR THERMALLY INITIATED POLYMERS

<u>Code</u>	<u>S</u> <u>Moles/l</u>	<u>M</u> <u>Moles/l</u>	<u>S/M</u>	<u>Viscosity</u> <u>Molecular</u> <u>Weight</u>	<u>$10^5/X_n$</u>	<u>%</u> <u>Conversion</u>	<u>Intrinsic</u> <u>Viscosity</u>

(60°C Thermal Sample)

#1	0	9.506	0	1,371,000	8.63	11.6	1.414
#2	.520	8.555	.0608	1,358,000	8.75	11.2	1.408
#3	1.041	7.605	.1368	1,014,000	11.58	11.4	1.188
#4	1.561	6.654	.2346	904,000	13.00	10.8	1.110
#5	2.081	5.704	.3649	832,000	14.18	11.5	1.059
#6	2.602	4.753	.5474	617,000	19.15	11.5	.890
#7	3.122	3.802	.8210	513,000	23.05	10.2	.800
#8	4.162	1.901	2.184	169,000	69.97	9.9	.420
#9	4.683	0.9506	4.926	66,700	177.3	7.1	.245

$$C_s = 1.76 \times 10^4$$

(100°C Thermal Samples)

#31	0	9.506	0	594,000	20.09	9.8	.871
#32	0.520	8.555	.0608	513,000	22.46	10.4	.800
#33	1.041	7.605	.1368	456,000	26.00	9.4	.748
#34	1.561	6.654	.2346	405,000	29.55	9.2	.698
#35	2.081	5.704	.3649	363,000	33.10	6.2	.656
#36	2.602	4.753	.5474	295,000	40.19	7.0	0.580
#37	3.122	3.802	.8210	220,000	53.19	8.5	.501

$$C_s = 3.9 \times 10^4$$

Table II
(continued)

EVALUATION OF CHAIN TRANSFER CONSTANTS FOR THERMALLY INITIATED POLYMERS

<u>Code</u>	<u>S</u> <u>Moles/l</u>	<u>M</u> <u>Moles/l</u>	<u>S/M</u>	<u>Viscosity</u> <u>Molecular</u> <u>Weight</u>	<u>10⁵/X_n</u>	<u>%</u> <u>Conversion</u>	<u>Intrinsic</u> <u>Viscosity</u>
(125°C Thermal Samples)							
IP-10	0	9.506	0	515,000	22.46	100	.801
IP-11	0.520	8.555	.0608	258,000	44.92	100	.554
IP-12	1.041	7.605	.1368	224,000	53.19	100	.494
IP-14	2.081	5.704	.3649	117,000	101.65	100	.342
IP-15	2.602	4.753	.5474	85,700	137.11	100	.283

$$C_S = 21.5 \times 10^4$$

Fig. 1. Chain transfer with MIPB.

is surprisingly large, and indeed it can be seen that a sixfold reduction in molecular weight was obtained for sample IP-15 in Table II at a relatively low S/M ratio of .55 . The chain transfer constant at 60° is exactly 100 times that of benzene with styrene at this temperature.

We expect to complete the measurement of the initiated samples in the near future, and thus obtain an independent check of the chain transfer constants and also a better value for the energy of activation. However, the general pattern of these systems is already clear and we are confident that chain transfer plays a major role in the polymerization of samples containing MIPB.

Detailed investigations of plastic scintillators have often been hampered by the lack of any reported value relating the intrinsic viscosity of polyvinyltoluene to the molecular weight of this polymer. If the constants K and α in the Staudinger equation

$$N = KM^{\alpha} \quad \underline{8}$$

are known then for many investigations simple viscosity measurements for a series of concentrations serve to determine molecular weight.

As part of this work we undertook the evaluation of these parameters employing the osmometers which we are using in our laboratory (7). Only preliminary values can be presented at this time, since the measurements required lengthy equilibration times and the work was initiated quite recently. However the relationship

$$N = 2.86 \times 10^{-6} M_n^{.99}$$

appears to be a satisfactory one for relating number average molecular weight to intrinsic viscosity of polyvinyl toluene. The logarithmic plot of log M vs log N from which this was obtained by the method of least squares is shown in Figure 2.

QUENCHING STUDIES IN LIQUID SCINTILLATORS

A systematic study has been made of the kinetics of the quenching process in liquid scintillators containing MIPB or toluene as solvents. The kinetic scheme and rate constants shown in Table III were postulated and by the application of a steady state treatment the following relationships were obtained.

Fig. 2. Dependence of number of average molecular weight on intrinsic viscosity.

Table III

KINETIC SCHEME FOR ENERGY TRANSFER

$S + h\nu$	S^*		Excitation
$S^* + S$	$2S$	k_s	Solvent quenching
$S^* + S$	$S^* + S$	k_t	Propagation
$S^* + F$	$F^* + S$	k_p	Transfer to solute
F^*	$F + h\nu$	k_r	Solute emission
$F^* + F$	$2F$	k_i	Internal quenching
$F^* + Q$	FQ	k_q	External quenching of solute
$S^* + Q$	$S + Q$	k_m	External quenching of solvent
S^*	$S + h\nu$		Solvent emission

$$V = \frac{k_r k_p I [F]}{k_r + k_i [F] + k_p [F] + k_s [S] + k_m [Q]} \quad 10$$

and

$$\frac{V}{V_o} - 1 = \frac{k_m [Q]}{k_p [F] + k_s S} \quad 11$$

where S, F and Q refer to the molar concentrations of solvent, phosphor and quencher and I is the incident flux of ionizing radiation and V, V_o are the intensities of emitted light, in the presence or absence of Q.

Equation 11 is formally similar to the Stern Volmer equation (8) employed in fluorescence studies and the quenching constant

$$y'' = \frac{k_m}{k_p [F] + k_s [S]} \quad 12$$

It is evident that a plot of 1/y'' vs F should be linear and its slope will determine k_p/k_m and intercept k_s S/k_m. The slope to intercept ratio serves to evaluate k_p/k_s S and this ratio should thus be independent of the quenching agent employed but should be influenced by the nature of the solvent. This ratio is similar to the ratio E/A employed by Hardwick (9). The experimental work was undertaken in order to test this point and to obtain quenching constants and other rate constants in these liquid scintillator systems.

EXPERIMENTAL

Procedures and apparatus were identical to those reported in previous papers (3)(2). The choice of quenching agents reflected our interest in "loading liquid scintillators with elements of high atomic number. Diphenyl mercury (DPHg), and lead 2-ethyl-hexanoate were therefore chosen for this study as well as CCl₄. The latter was employed for comparison with existing data on the high quenching action of halogenated compounds.

RESULTS

From the work with two solvents, three quenching agents and two solutes, twelve sets of quenching curves were obtained. Two representative sets of data are shown in Figure 3 and 4 where the data for the quencher diphenyl mercury are plotted as a function of quencher concentration at the inscribed concentrations of terphenyl as primary solute. The concentrations on POPOP was maintained at 0.05 g/l.

It is immediately obvious from the slopes of the various lines that the quenching constants are significantly lower in MIPB than in toluene and the various quenching constants are assembled in Table IV. These quenching constants have been plotted against phosphor concentration in order to test the validity of equation 12. A typical plot is shown in Figure 5 and the data for all the systems investigated are summarized in Table V. The ratio of intercept to slope is found to be independent of the quencher employed and is interpreted as being the ratio of k_s/k_m . This ratio differs significantly for MIPB and toluene and in view of the difficulties of comparison of quantities based on a slope of a slope the agreement in results appears quite satisfactory. The data are consistent with results obtained by other workers (9) (10).

In conclusion we can state that MIPB behaves as an efficient chain transfer agent in plastic scintillators and one can conjecture that the pulse shape discrimination properties shown by these are related to the lower molecular weights which they possess and its different distribution. The chain length constants obtained and their temperature dependence make possible a prediction of the number average molecular weight for any composition of polymer over a wide range of polymerization temperatures.

For liquid scintillators based on MIPB as solvent, quenching constants have been determined and compared with the higher values obtained for toluene. A kinetic scheme has been postulated which has been substantially verified by the experimental results obtained by variation of the concentration of solute and quencher.

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Fig. 3. Quenching by diphenyl mercury at the inscribed concentration of terphenyl in toluene.

Fig. 4. Quenching by diphenyl mercury at the inscribed concentration of terphenyl in MIPB.

Table IV

QUENCHING CONSTANTS

Solvent		Toluene			MIPB		
System		Conc'n F	V		V		
		(Moles/l)	(%)	Vo/V	(l/Mole)	(%)	Vo/V
					y''		y''
					(l/Mole)		(l/Mole)
-155-	Terphenyl- CCl ₄ (.005 Moles/l)	.001	10.9	1.818	163.6	21.9	1.378
		.002	17.1	1.695	139.0	25.7	1.359
		.004	23.8	1.547	119.4	30.0	1.335
		.006	27.9	1.462	92.4	33.0	1.290
		.008	31.4	1.415	83.0	35.2	1.263
		.010	33.4	1.381	76.2	37.6	1.242
		.014	35.4	1.353	70.6	40.1	1.191
		.020	39.3	1.286	57.2	41.7	1.186
	PBD - CCl ₄ (.005 Moles/l)	.001	11.8	1.807	161.4	23.4	1.524
		.002	17.4	1.647	129.4	27.3	1.412
		.004	25.9	1.493	98.6	33.9	1.315
		.006	31.6	1.383	76.6	36.9	1.277
		.008	35.0	1.312	62.4	38.7	1.240
		.010	35.9	1.286	57.2	39.9	1.205
		.014	39.5	1.254	50.8	43.4	1.168
		.020	43.6	1.175	35.0	43.6	1.150

Table IV - Page 2QUENCHING CONSTANTS

System	Solvent	Toluene				MIPB	
	Conc'n F (Moles/l)	V (%)	Vo/V	y'' (l/Mole)	V (%)	Vo/V	y'' (l/Mole)
Terphenyl Pb-2-Et- Hex. (.005 Moles/l)	.001	15.2	1.295	59.1	26.6	1.130	26.0
	.002	22.9	1.265	52.9	30.6	1.127	25.0
	.004	30.6	1.197	40.4	35.7	1.110	22.0
	.006	35.2	1.151	30.4	38.7	1.098	20.0
	.008	39.3	1.130	26.1	40.6	1.092	18.4
	.010	42.0	1.107	21.7	43.0	1.084	16.9
	.014	44.4	1.085	17.0	44.8	1.072	14.8
	.020	47.0	1.078	16.0	47.7	1.048	12.0
PBD Pb-2-Et- Hex. (.005 Moles/l)	.001	17.1	1.254	49.9	31.8	1.112	22.4
	.002	23.8	1.233	46.4	34.8	1.105	20.5
	.004	32.6	1.181	35.7	41.0	1.087	17.2
	.006	38.0	1.143	28.3	43.4	1.083	16.6
	.008	41.1	1.120	24.4	44.7	1.075	14.5
	.010	41.8	1.113	22.5	45.5	1.067	13.3
	.014	46.2	1.080	15.1	47.2	1.054	10.9
	.020	47.8	1.068	12.5	48.0	1.043	9.0

Table IV - Page 3QUENCHING CONSTANTS

System	Solvent	Toluene			MIPB		
	Conc'n F (Moles/l)	V (%)	Vo/V	y'' (l/Mole)	V (%)	Vo/V	y'' (l/Mole)
Terphenyl DPHg. - (.005 Moles/l)	.001	11.5	1.715	143.0	27.0	1.112	22.4
	.002	18.7	1.547	109.4	31.6	1.107	21.4
	.004	26.5	1.387	77.4	36.3	1.097	19.4
	.006	31.2	1.304	6	39.2	1.085	17.0
	.008	35.0	1.269	53.8	41.3	1.080	16.0
	.010	37.4	1.237	47.4	43.5	1.075	15.0
	.014	39.8	1.206	41.2	45.0	1.061	12.2
	.020	43.7	1.157	31.4	47.4	1.049	9.8
PBD - DPHg. - (.005 Moles/l)	.001	14.1	1.510	102.0	31.6	1.126	25.2
	.002	20.1	1.425	85.0	35.2	1.097	19.4
	.004	29.2	1.322	64.4	41.4	1.077	15.4
	.006	35.0	1.252	50.4	44.2	1.067	13.4
	.008	37.7	1.222	44.4	45.3	1.060	12.0
	.010	39.1	1.180	36.0	45.7	1.055	11.0
	.014	43.4	1.146	29.2	47.6	1.046	9.2
	.020	45.5	1.127	25.4	48.8	1.037	7.4

Fig. 5. Dependence of quenching constants on phosphor concentration.

Table VEVALUATION OF PARAMETERS FROM QUENCHING DATA

Solute- Quenching System	TOLUENE		MIPB			
	Intercept ksS/km (moles/l)	Slope kp/km	Intercept/slope		Intercept/slope	
			ksS/kp = Q (moles/l)	Intercept ksS/km (moles/l)	Slope kp/km	ksS/kp=Q (moles/l)
PBD - CCl ₄	5.0×10^{-3}	1.24	4.0×10^{-3}	9.5×10^{-3}	1.44	6.3×10^{-3}
PBD - Pb-2- Et-Hex	15.0×10^{-3}	3.48	4.3×10^{-3}	42.2×10^{-3}	3.36	12.6×10^{-3}
PBD - DPHg	8.0×10^{-3}	1.95	4.3×10^{-3}	49.0×10^{-3}	4.18	11.7×10^{-3}
Terphenyl - CCl ₄	5.1×10^{-3}	0.97	5.3×10^{-3}	12.2×10^{-3}	0.84	14.5×10^{-3}
Terphenyl - Pb- 2-ET-Hex	13.5×10^{-3}	3.17	4.3×10^{-3}	35.2×10^{-3}	2.47	14.3×10^{-3}
Terphenyl - DPHg	6.5×10^{-3}	1.51	4.3×10^{-3}	40.7×10^{-3}	2.98	13.7×10^{-3}

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PROGRESS IN PLASTIC SCINTILLATORS

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There are three general classes of luminescent substances used as scintillation detectors; inorganic crystals, organic compounds, and inert gases. Plastic scintillators can be considered as solid solutions of luminescent organic compounds in a transparent plastic medium. Thus they can be classed as a special group among organic scintillators.

The development of plastic scintillators began in 1950 when Schorr and Torney (1) reported that solid solutions of p-terphenyl in polystyrene produced scintillations upon excitation with ionizing radiation. Since that time there has been a considerable accumulation of data on such categories as

- 1) recipes for producing plastic scintillators of various sizes and compositions,
- 2) luminescent properties of solutes in a plastic medium,
- 3) effects of the plastic medium on the mechanism of energy transfer in the scintillation process, and
- 4) the use of plastic scintillators to detect ionizing radiation.

1. PREPARATION OF PLASTIC SCINTILLATORS

The most common method of preparation of a plastic scintillator is by the thermal polymerization of a solution of the solute in the monomer. (2-5) Polymerization procedures vary with the composition

and size of the sample desired. For large samples, polymerization is initiated slowly at lower temperatures ($90-100^{\circ}\text{C}$) and then completed at a higher temperature. (6, 7)

It has been found that a higher luminescent efficiency can be obtained if the monomer is purified to eliminate inhibitors. This is generally done by vacuum distillation of the monomer before use. The removal of oxygen before starting the polymerization will also produce a more efficient scintillator. The use of initiators such as benzoyl peroxide tends to reduce the luminescent efficiency. (8)

Other methods for the preparation of plastic scintillators include such techniques as molding a mixture of polymer with some solute, or casting ready made plastic scintillators. Plastic scintillators prepared by these methods are usually found to be slightly less efficient.

The most common monomers used to prepare plastic scintillators are styrene or vinyl toluene. In order to find a more efficient monomer, a systematic study of different monomers has been carried out. The results of the study will be presented in the following paper.

A large number of different organic luminescent materials have been tried out as solutes for preparing a more efficient plastic scintillator. (2-5, 8-9) Some solutes have been fairly successful, e. g., p-terphenyl, 2-phenyl-5-(4-biphenyl)-1,3,4-oxadiazole (PBD), 9,10-diphenylanthracene, etc. Pichat and Koechlin (2) increased the luminescent efficiency by adding small amounts of 1,1,4,4-tetraphenylbutadiene as a secondary solute. Since this report, numerous combinations of primary and secondary solutes have been tried in order to produce a more efficient scintillator. Thus far the most efficient primary solute known to the author is PBD; the most efficient secondary

solute is p,p-diphenylstilbene. Typical results of light output vs concentration of solute are given in Fig. 1. The light output values are relative to a standard anthracene crystal. The best commercially prepared plastic known to the author contains a combination of p-terphenyl and p,p-diphenylstilbene.

In doing work with plastic scintillators, one must be extremely careful that the solutes are of very high purity. This can be easily checked by measuring the absorption and emission spectra of the solutes. Unfortunately some of the confusing data in the literature can be traced to using compounds of questionable purity.

Various attempts to increase the photosensitivity by incorporating heavy metals in plastic scintillators have had very limited success. (2,5,10) This is due to the large quenching action of the heavy metal. However, a plastic scintillator that Hyman (11) successfully loaded with 5% lead gave a pulse height equal to 70% of that of the unloaded plastic. This lead-loaded plastic did give a measurable photoelectric peak. Results are shown in Fig. 2.

2. LUMINESCENT PROPERTIES OF PLASTIC SCINTILLATORS

An excellent review of the luminescent properties of plastic scintillators has been written by Rozman and Kilin. (12) In the short time allowed, it is impossible to review all the work that has been turned out so only some arbitrarily selected topics will be discussed.

The luminescent yield of a plastic scintillator is temperature dependent for some solutes. Rozman (13) investigated this phenomenon

Fig. 1. Light output vs. concentration of solutes in polyvinyltoluene. Source: beta rays from Cs^{137} . All light output values are relative to a standard anthracene crystal. (Reprinted from reference 5 with the kind permission of the editor.)

Fig. 2. Pulse height spectrum of lead-loaded plastic scintillator vs. unloaded plastic scintillator. Source: Co^{57} ; $E_\gamma = 123 \text{ kev.}$ (Reprinted from reference 11 with the kind permission of M. Hyman.)

for several different solutes. For p-terphenyl in polystyrene the luminescent yield changed very little over a wide temperature range. For other solutes (e. g. , 1, 1, 4, 4-tetraphenylbutadiene) the temperature coefficient is larger and may even change sign.

The principal results of fluorescence studies on plastic scintillators are as follows. The emission spectrum observed for a plastic scintillator usually corresponds to the fluorescence spectrum of the solute added. In most cases the observed spectrum is the same for both plastic and liquid solutions. Exceptions to this are for anthracene and p-terphenyl in polystyrene. Several authors have shown that anthracene enters into a chemical bond (i. e. , copolymerizes) with styrene during polymerization. (14-16) It has been reported that the fluorescent spectra of concentrated solutions of p-terphenyl in polystyrene contain the bands of the crystal. (17) This suggests that p-terphenyl is imbedded in the plastic medium as microcrystals.

As expected, the fluorescent intensity increases with increasing solute concentration. Maximum intensity is usually reached at a solute concentration of 1 to 4%. In a system consisting of a primary plus a secondary solute, the emission spectrum corresponds almost entirely to the fluorescent spectrum of the secondary solute. The fluorescent spectrum is influenced by the reabsorption processes. The degree of reabsorption depends on the dimensions of the plastic scintillator.

3. USE OF PLASTIC SCINTILLATORS TO STUDY THE PROCESS OF ENERGY TRANSFER

In investigating the luminescent properties of plastic scintillators,

a question that arises immediately concerns the mechanism by which the relatively high energy of a charged particle is transferred to some fluorescent solute. It has been convenient to divide this over-all process into two separate categories. The first process includes the deceleration of the charged particle and transfer of its energy to molecules of the medium. The second phase includes all processes that occur until the activated molecules lose their excitation energy. Thus far, the larger amount of work in plastic scintillators has been centered around the second of these two categories so the first (and possibly more fundamental) is still very imperfectly understood.

There are several advantages, or disadvantages (depending on the particular viewpoint), to using the plastic medium for studying energy transfer processes. The most notable characteristic of a plastic is that the medium is rigid so that the Brownian motion of molecules and radicals is limited. Moreover, mechanisms involving collisions and diffusion of molecules can be excluded. One can also exclude such problems as oxygen quenching. However, there does appear to be some surface deterioration of plastics left standing in air. It is important to have a freshly cut surface on a plastic if meaningful measurements are to be made.

Using a plastic scintillator for studying energy transfer processes is complicated by the fact that the polymer, e. g. , polystyrene or polyvinyl toluene, has a relatively high fluorescent quantum yield. This enhances the possibility of a radiative transfer mechanism. For the polystyrene-anthracene system, Koski (18) suggested a radiative transfer mechanism involving polystyrene fluorescence followed by absorption by anthracene. The anthracene molecule then emits its characteristic

radiation. However, further study (19-21) soon indicated that such a mechanism could account for only 20% of the luminescent yield of a plastic scintillator.

Swank and Buck (20) carried out an experiment comparing the change in pulse height with solute concentration for different modes of excitation. In one series of experiments the plastic scintillators were excited by either α or β particles. In the other series of experiments the samples were excited by radiation produced by a thin polystyrene disk which in turn was excited by α particles (indirect excitation). From an analysis of their data, the authors concluded that a nonradiative transfer mechanism is operating in the plastic medium. Andreeshev and Rozman (22) quantitatively analyzed the luminescent spectra of thin plastic scintillators and arrived at similar conclusions.

Krenz (14) investigated the polystyrene-anthracene system in detail by use of high-energy excitation. He concluded that at low solute concentration a radiative transfer process predominates, but at higher solute concentrations the transfer is predominantly nonradiative. Birks and Kuchela (23) arrived at similar conclusions for the system 1,1,4,4-tetraphenylbutadiene in polystyrene.

The plastic medium is known to be a heterogeneous mixture of long chain molecules. The role that the polymer chain plays in the energy transfer process is not too well understood. Shimizu, Hirayama, and Okamoto (24) have shown that the transfer efficiency in the system polystyrene - p-terphenyl decreases with an increase in the temperature of polymerization. This is attributed to a decrease in the average length of the polymer chain. Funt and Hetherington (25) found that for average

molecular weights lower than 100 000, the light output depends on the chain length. Krenz (14) suggests that the nonradiative energy transfer process in polystyrene-anthracene is an intramolecular process. The increase in efficiency with solute concentration is partly explained by anthracene being chemically bound to the polymer chain. Avivi and Weinreb (26) measured the transfer efficiencies for two different types of solution. One solution was a polystyrene plastic scintillator (the solute being anthracene or 2,5-diphenyloxazole) dissolved in ethyl acetate. The other consisted of the particular solute added to a solution of polystyrene in ethyl acetate. In the former solution, chain attachment was possible; in the latter solution chain attachment was highly improbable. The authors concluded that chain attachment is not necessary for increased efficiency. Also, while anthracene is attached to the polymer chain, nonradiative energy transfer may still be an intermolecular process. Brown, Furst, and Kallmann (27) studied the effect that naphthalene has on the energy transfer process in polystyrene and polymethyl-methacrylate. They report that naphthalene enhances the energy transfer process in the rigid medium in a manner similar to that found for the liquid media. The authors were not able to distinguish between a migration process, involving transfer along the polymer chain, and a single-step process involving relatively long distances. They tentatively concluded that perhaps a combination of both processes were involved.

An investigation of the lifetimes of the excited molecules can be an important means of helping to clarify the mechanism by which energy is transferred to the fluorescent solute. Lifetime studies on p-terphenyl in polystyrene excited by high-energy radiation have shown that the decay

does not follow an exponential decay law. (28) Comparative studies of p-terphenyl in toluene show that the luminescent decay does follow an exponential decay law. Thus we see an important difference between the rigid and the liquid medium. Kilin and Rozman (29) studied the photofluorescent lifetime of 1,1,4,4-tetraphenylbutadiene and 1,3,5-triphenyl- Δ^2 -pyrazaline in polystyrene. Using a phase fluorometer, they found that for direct excitation of these solutes the decay does obey an exponential decay law. There is an increase in the lifetime of these solutes with an increase in concentration. This is what one would expect if self-absorption processes are operating.

Recently Basile and Weinreb (30) have made a detailed study on the lifetimes of anthracene and 9,10-diphenylanthracene in polystyrene. Samples were excited both by uv and electron excitation. The authors analyzed the shapes and duration of the light pulse that was produced by these different modes of excitation. By such an analysis it was shown that a radiative transfer process takes place at low solute concentrations. At higher solute concentrations the much faster nonradiative transfer process predominates. However, data obtained by the two modes of excitation did not differentiate between an intermolecular and an intramolecular process of energy transfer.

The shape of the light pulse obtained for both electron and uv excitation did not obey a simple exponential decay law. For dilute solutions, they could successfully describe the shape of the light pulse as a cascade of two exponentials. Essential to their analysis was the assumption that the fluorescent decay of polystyrene follows an exponential decay law. (28) Numerous measurements on electron excitation of pure polystyrene have shown this to be true for at least two thirds

of the decay curve. Kilin and Rozman (31) have published data showing that the luminescence of polystyrene does not decay according to a simple exponential law. These authors, using a phase fluorometer for their measurements, observed a change in lifetime with a change in modulation frequency. The difference between these results may be due to the different techniques used. However, the lifetime values that Kilin and Rozman report for polystyrene are 10-25% lower than values obtained by Basile (32) for both thick and thin samples. The reason for the discrepancies in the lifetime studies is not understood at this time. It is obvious that more study is needed in this field to help understand the energy transfer process.

The work on energy transfer can be summarized briefly as follows. The transfer of energy from the excited solvent molecule to the solute molecule is concentration dependent. A radiative transfer takes place at low solute concentration. As the concentration increases the transfer becomes predominantly nonradiative.

Some attempts have been made to see how the polymer chain is involved in the transfer process, if indeed it is involved at all. This has not been too successful. Thus far it has not been possible to distinguish between a migration (intramolecular) process or a single-step jump (intermolecular) process of energy transfer.

4. APPLICATIONS OF PLASTIC SCINTILLATORS

While plastic scintillators form a somewhat special group among organic scintillators, they are widely used in the detection of ionizing radiation. The increasing use of plastic scintillators has demonstrated that these detectors have great value both in scientific experimentation

and for technical measurements. A very brief discussion of a few of their uses will be given.

Plastic scintillators are widely used for β -particle counting. (33, 34) Their mechanical properties adapt them to the construction of very sensitive well-type counters. One use of these well-type counters has been the measuring of exchangeable K^{42} in man. (35) For soft β -radiation, it was reported that it is possible to obtain counting efficiencies two to three times as great as that obtained by use of gas counters.

Plastic scintillators can also be used in coincidence circuits, for β spectrometry, and also for studying nuclear transformations. For studying nuclear phenomena a serious shortcoming is the low cross section for the photoelectric effect. By using thin films it is possible to count fission fragments. Thin scintillators in conjunction with thick scintillators have proved useful for particle identification. (36) Since they have a high hydrogen content, plastic scintillators can also be used for studying fast neutrons.

Large plastic scintillators are being used more and more in the study of cosmic rays. (37) In contrast, thin filaments of plastic scintillators can act as light pipes and a counter made up of a large number of these filaments can serve to register particle tracks. (38-40)

There are a number of distinct advantages to using plastic scintillators as detectors. They are fairly simple to prepare in a large variety of sizes and shapes. They are fairly easy to machine and have high mechanical strength. They possess good optical properties and good temperature stability. Plastic scintillators have been used in

the temperature range from -190°C to $+70^{\circ}\text{C}$. They require very little in the way of special packaging to protect them from adverse effects of the atmosphere. Also plastic scintillators can be used inside vacuum equipment.

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THE DEPENDENCE OF PULSE HEIGHT ON THE MOLECULAR STRUCTURE OF
THE SOLVENT AND FLUOR IN ORGANIC SCINTILLATORS

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Recent papers by the authors (1) have shown that a correlation exists between pulse height (β and γ radiation) and the molecular structure of the solvent and fluor in plastic and liquid scintillators. The purpose of the present paper is to review some of the published material and to extend this correlation by presenting some recent results.

It is known that in order to have an efficient solid or liquid scintillator a conjugated double bond system is necessary. This suggests that electron mobility and electron density are important factors in the absorption of energy which can be potentially emitted as light. The electrons in the conjugated double bond system may also be important in the transfer of this energy possibly by a π bond overlap between the solvent and the solute (1). Dipole-dipole interactions might also be a factor in the transfer of energy from the solvent to the solute and this would be favored by electron displacements within the molecule. Therefore, it is reasonable to expect that a suitable parameter which characterizes electron density distribution in a solvent or fluor molecule would bear some relation to the observed pulse height.

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For the aromatic systems used in this work it was possible by means of the Hammett (2) or Taft sigma (σ) values (3) to place a relative numerical value on the extent to which the substituents either donate or withdraw electrons from the benzene ring as compared to the hydrogen atom. Substituents donating electrons to the benzene ring have a negative sigma value and substituents withdrawing electrons have a positive sigma value.

Taft (3) has recently shown that the Hammett sigma (σ) value can be divided into inductive (σ_I) and resonance (σ_R) components such that $\sigma = \sigma_I + \sigma_R$.

The object of this paper is to determine whether the R.P.H. versus σ correlation can be generally applied to plastic, liquid and crystalline scintillators. The dependence of pulse height on the molecular structure of the aromatic solvent (plastic, liquid or crystalline) and fluors was studied by using ring substituted aromatic solvents and fluors with substituents which differ greatly in their ability to either donate electrons to or withdraw electrons from the aromatic ring.

RESULTS

I. Plastic Scintillators

A. The Effect of Solvent Structure

Plastic scintillators were prepared from a series of substituted styrenes whose substituent groups differed considerably in electronegativity. Paraterphenyl at 3% by weight and 0.05% POPOP were used throughout as the primary fluors and waveshifter, respectively.

The values of the relative pulse heights and σ , σ_I and μ , the dipole moment, for the ring substituents used on the styrene monomers which produced plastics with good optical properties are given in Table 1 and are plotted in Figures 1, 2 and 3 respectively.

TABLE 1. RELATIVE PULSE HEIGHT (α , β , γ RADIATION), SIGMA VALUES AND DIPOLE MOMENTS OF SUBSTITUTED STYRENE PLASTIC SCINTILLATORS^a

Styrene Substituent	R.P.H. ± 2			Reference for σ , σ_I	σ	σ_I	μ
	α	β	γ				
None	15	39	39		0	0	0
Methyl	22	45	44	7,8	-0.16	-0.045	0.4 (4)
Mixed dimethyl	25	53	-				
3,4-Dimethyl	-	58	52	7,8	-0.23	-0.090 ^b	-
2,4-Dimethyl	-	61	55	7,8	(-0.32) ^c	-0.090 ^b	-
2,5-Dimethyl	-	54	-	7,8	(-0.23) ^c	-0.090 ^b	-
p-Isopropyl	-	43	-	12,7	-0.151	-0.0563	-
p-Ethyl	-	39	-	12,7	-0.151	-0.0517	-
p-Benzyl	-	38	-	7	-	+0.036	-
p-Methoxy	6	24	20	7,8	-0.26	+0.25	1.28 (5)
p-Chloro	0	2.5	0	7,8	+0.226	+0.47	1.73 (6)
m-Chloro	0	1.8	0	7,8	+0.373	-0.47 ^d	-

^aResults for β and γ radiation are presented in reference 1.

^bFor disubstituted styrenes the σ_I was obtained by taking the sum of the σ_I for two methyl groups.

^cValues obtained by assuming that the o-methyl and p-methyl values are the same and that the values are additive.

^d σ_I was assumed to be the same as for p-chloro substituent.

Figure 2. Pulse heights of substituted styrene plastic scintillators versus σ_I .
(1) 2,4-DMS, (2) 3,4-DMS, (3) 2,5-DMS, (4) Methylstyrene, (5) p-isopropylstyrene, (6) p-ethylstyrene, (7) styrene, (8) p-benzylstyrene, (9) p-methoxystyrene, (10) p-chlorostyrene, (11) m-chlorostyrene, (12) diethylstyrene.

Figure 3. Pulse heights of monosubstituted styrene plastic scintillators versus dipole moments (μ).

The values of the relative pulse height (β -radiation) for a series of plastic scintillators based on substituted α -methyl styrenes are listed in Table 2.

TABLE 2. RELATIVE PULSE HEIGHT VALUES (β -RADIATION) FOR A SERIES OF SUBSTITUTED α -METHYL STYRENES

Structural Formula	R.P.H.* $\pm$ 2
α-Methyl styrene	5
p-Methyl-α-methyl styrene	6
p-Isopropyl-α-methyl styrene	3

*These values were obtained by extrapolation of copolymer data (see reference 1).

B. The Effect of Fluor Structure.

Two series of polyvinyltoluene scintillators were prepared, one of which contained various substituted naphthalenes and the other various substituted biphenyls as the fluor. The relative pulse heights (β -radiation) are listed in Table 3 and are plotted against ϕ in Figure 4.

TABLE 3. RELATIVE PULSE HEIGHTS (β -RADIATION) OF POLY-VINYL TOLUENE SCINTILLATORS CONTAINING (A) SUBSTITUTED NAPHTHALENES AND (B) SUBSTITUTED BIPHENYLS AS THE FLUOR.*

(A) Naphthalene Substituent	No. in Fig. 4	R.P.H. $\pm$ 2
none	1	19
1-methyl	2	13
mixed dimethyl**	3	14
1-methoxy	4	23
1-cyano	5	14
(B) Biphenyl Substituent		
none	6	18
4-phenoxy	7	17
4-cyano	8	25

*All samples contain 0.05% POPOP.

**This material was obtained from the Eastman Organic Chemical Co. and the distilled fraction that was used had the following physical constants: b.p.₁ 93° n_D^{28°} 1.6040.

Figure 4. Pulse heights of polyvinyltoluene scintillators containing (A) substituted naphthalene, and (B) substituted biphenyls versus σ .

II. LIQUID SCINTILLATORS.

A. The Effect of Solvent

The correlation between R.P.H. and ϕ has also been found to hold for aromatic liquid scintillators. In Figures 5 and 6 the ϕ response data (7) on seven aromatic liquids with nine different fluors are presented as a plot of limiting relative pulse height versus ϕ values (1). The limiting relative pulse height is equal to the extrapolated pulse height which one would obtain in the absence of fluor self-quenching at infinite concentration of fluor. This approximates the conditions under which the plastic scintillators were tested, since the fluor self-quenching with PTP is low and since the concentration of PTP is at a level where a further increase will not significantly increase the R.P.H. (8).

B. The Effect of Fluor Structure

Values of the maximum R.P.H. of a series of substituted 2,5-diphenyl-1,3-oxazoles (9) and 2,5-diphenyl-1,3,4-oxadiazole (10) fluors in toluene scintillators are plotted versus ϕ in Figures 7(A) and 7(B) respectively.

Recently a paper by Shvaika and Grekov (11) has come to the authors' attention wherein they also point out that electron donating substituents in substituted 2,5-diphenyl-1,3,4-oxadiazoles increase their efficiency as solutes in toluene scintillators.

III. CRYSTALLINE AROMATIC SCINTILLATORS

Values (12) of the average pulse height for a series of substituted benzene crystalline scintillators are plotted against ϕ and ϕ_I in Figures 8 and 9. It is suggested

Fig. 5. Limiting relative pulse height versus σ for the indicated solutes in the following solvents:
 (B) benzene, (P) phenylether, (C) cumene, (T) toluene,
 (X) xylene, (Y) p-cymene, (E) phenetole.

Figure 6. Limiting relative pulse height versus $\bar{O}$ for the indicated solutes in the following solvents: (B) benzene, (P) phenylether, (C) cumene, (T) toluene, (X) xylene, (Y) p-cymene, (E) phenetole.

Figure 7. Maximum relative pulse height versus σ for (A) substituted 2,5-diphenyl-1,3,4-oxadiazoles, and (B) 2,5-diphenyl-1,3-oxazoles in toluene.

Figure 8. Average pulse height versus σ for crystalline substituted benzene compounds. (1) Benzene, (2) p-cymene, (3) 1,2,4,5-tetramethylbenzene, (4) phenylether, (5) pentamethylbenzene, (6) hexamethylbenzene.

Figure 9. Average pulse height versus σ_I for crystalline substituted benzene compounds. (1) Benzene, (2) *p*-cymene, (3) 1,2,4,5-tetramethylbenzene, (4) phenylether, (5) diphenylmethane, (6) pentamethylbenzene, (7) hexamethylbenzene.

that the reason that the points for hexa and penta methyl benzene fall off the correlation line for σ is due to steric effects in these compounds and that the σ values for meta and para methyl substituents are no longer applicable when applied to ortho methyl groups. The plot of average relative pulse height versus σ_I is better than the σ plot because the inductive effects (σ_I) may not be influenced by steric effects.

DISCUSSION

The variation in pulse height with solvent and fluor structure can best be discussed in terms of the general pulse height equation (1,8,13).

$$P.H. = \frac{E}{w_0} q_f \sigma \frac{(q_0 + k_c)}{1 + k_c} \frac{1}{1 + mc} \quad (1)$$

where $k_c = p_t/(p_{ss} + p_{es})$, $mc = p_{ff}/(p_{ef} + p_i)$, $q_f = p_{ef}/(p_{ef} + p_i)$ is the quantum efficiency of the fluor exclusive of fluor self-quenching, c is the concentration of the fluor, p_t , p_{ss} , p_{es} , $p_{ff} = \beta c$, p_{ef} and p_i are respectively, the probabilities of transfer from the solvent to the fluor, solvent quenching, direct emission by the solvent (very small), self quenching of the fluor, emission by the fluor and internal quenching by the fluor, β is a constant, E is the particle energy which is completely absorbed by the scintillator, w_0 is the average dissipated particle energy required to produce one fluorescent excitation in the solvent, q_0 is the quantum yield of the solvent (very small in comparison to k_c) and σ is a factor (includes photocathode efficiency, instrument factors, etc.) which converts the number of emitted quanta from the scintillator to an observed pulse height voltage. The various parameters in equation (1) will be considered in greater detail in the discussion of results obtained with the plastic and liquid scintillators.

From the data of Figures 1, 2 and 3 for plastic scintillators and Figures 5 and 6 for liquid scintillators it is

seen that there is an approximate linear correlation between the pulse height and $\bar{\sigma}$ or $\bar{\sigma}_I$. For the liquid and plastic scintillators since fluor self quenching is unimportant and therefore the pulse height is equal to $E/w_0 q_f$ or stated mathematically $(q_0 + kc)/(1 + kc) = 1$. Since in both cases the fluor was constant for a given series of solvents, it is suggested that the variation in pulse height can be accounted for by a variation in w_0 , the dissipated average particle energy required to produce one fluorescent excitation in the solvent, and/or $q_f = p_{ef}/(p_{ef} + p_i)$ the fluorescent quantum yield of the fluor exclusive of fluor self quenching.

It is postulated here that by varying the solvent the major change in the pulse height arises from a change in the absorption process as characterized by w_0 . With the rather great changes in fluor structure for the liquid scintillators it seems unlikely that the interactions between each fluor with each solvent would be the same as indicated by the similarity of slope in the $\bar{\sigma}$ correlations unless the probability of internal quenching p_i was small.

It was of further interest to determine something about the locus of absorption of energy in the plastic solvent molecule.

Substitution of a methyl group for the α -hydrogen in polystyrene to give poly- α -methyl styrene, reduced the R.P.H. from 39 to 5 (Table 2). On the other hand it has been shown that substitution of a methyl group in the ring caused an increase in R.P.H. On this basis, it might be expected that substitution of a methyl group in the ring of poly- α -methyl-styrene would increase its R.P.H., but the data in Table 2 show that the expected increase was not obtained. These results suggest that the α -hydrogen is a preferred locus of energy absorption. Furthermore, it appears that the α -hydrogen must be in the backbone of the polystyrene chain since the R.P.H. (Table 1) of p-isopropyl styrene which has two α -hydrogens was no greater than that obtained with methyl styrene. The primary absorption process in liquid organic scintillators would appear to be different from that in plastic scintillators, since many aromatic solvents which have good scintillation properties do not have an α -hydrogen of the type discussed here, e.g., benzene and other solvents in Figures 5 and 6.

The role of the substituents with negative σ_I values in enhancing the R.P.H. values may, however, be similar in both liquids and plastics.

When the solvent type was kept constant and the aromatic substituents of the fluor were varied a σ versus maximum relative pulse height correlation was also obtained for solutes in plastic and liquid scintillators (Figures 4 and 7). A comparison of the slopes of the line of Figures 1, 2, 5 and 6 with Figures 4, 7 shows that the pulse height varies much more with a change in the σ value of the solvent than with an equal change in the σ value of the fluor. The variation of pulse heights in Figures 4 and 7 can be attributed on the basis of equation (1) to a change in p_t , w_o or q_f . Since the solvent composition is fixed it is reasonable to assume, on the basis of the previous discussion, that w_o does not account for the variation in pulse heights. From the data it is presently not possible to distinguish whether changes in q_f or p_t are responsible for changes in the observed pulse height.

It is interesting to note that aromatic crystalline scintillators also gave a R.P.H. versus σ correlation such that the pulse height increased with an increase in the electronegativity of the substituents on the benzene ring. In this case no fluor was present thus the absorption and transfer step may both depend on the electron donating power of the substituents.

In summary, an overall scintillation mechanism for plastic, liquid and crystalline scintillators which would be in harmony with the present observation requires first, an absorption of a fraction of the dissipated particle energy by the solvent and secondly, a transfer of the energy to the fluor molecule. The presence of nuclear substituents donating electrons to the benzene conjugated system probably facilitate the primary absorption process. The transfer of energy from the excited solvent molecules to the fluor molecules may, however, be facilitated by a favorable electron density distribution between the two.

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PART III

INTERNAL SAMPLE COUNTING

PHOTOMULTIPLIERS FOR THE SCINTILLATION COUNTING
OF C^{14} AND TRITIUM

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1. The efficiency of a counting assembly for the scintillation assay of compounds tagged with a low energy beta emitter such as C^{14} or H^3 , which can be dissolved (or suspended) in a liquid phosphor, is very greatly dependent on the quality of the Photomultiplier tube used. This is illustrated by the bias curves of Fig. 1, which shows the curve given by 10 μ curie of H^3 in a standard phosphor *, d, the thermionic electron curve from a tube with a standard S-11 cathode, a, and the much more useful performance of tubes made specially for H^3 counting (b & c)

It is the purpose of this paper to consider the steps by which acceptable performance has been achieved, to report on results obtained in various designs of counting head and to outline those areas in which improvement may still be obtained.

2. In a standard * liquid phosphor, the average energy from a tritium disintegration to give a photoelectron from a semitransparent Cs Sb cathode with a phosphor vial designed to give effective light coupling to the cathode, is about 2500 eV, so a large proportion of the disintegrations will give only a single photoelectron and an appreciable proportion (which turns out to be between 30 and 50%, will fail to give a detectable signal. The rate of emission of thermionic electrons from a 2" diameter Photomultiplier tube with a typical S-11 cathode of photosensitivity 70 μ A/L, which has a peak quantum efficiency of about 15% at 4200 AU and a red threshold around 6800 AU, is about 30,000 electrons per second at 20°C and about one tenth of this at -20°C.

* Toluene + 5g/litre p-terphenyl & 16 mg/litre POPOP

Fig. 1. Bias curves 6097B, 6097S, modified 6097S and 10 mpc H³ scintillator at 23°C.

If a tube of this type is to be used for tritium counting in a single tube assembly (with which we are at the moment solely concerned) it is obvious that a bias point corresponding to a signal amplitude much greater than one electron must be chosen and the counting efficiency will be relatively low. In fact, for a tube background of 1 count per second at 20°C an efficiency of 0.7% is obtained for a 10 ml sample.

The first step, then, in making a Photomultiplier tube more suitable for tritium counting is to modify the cathode processing to reduce the thermionic emission as much as possible without unduly depressing the quantum efficiency of the cathode in the spectral region of interest, which for most phosphors is between 3500 and 4500 AU. Since the high value of thermionic emission from a standard S-11 cathode is associated with an appreciable sensitivity in the red region of the spectrum, our initial criterion for improvement was a decrease in the ratio of red to blue sensitivity and work along these lines was reported at the 1958 Scintillation Counter conference (1). It was soon found essential, however, to introduce an operational tritium counting test, since neither the red-blue ratio, nor the tube dark current, gave an adequate guide to a tube's performance. This test is carried out in a counting head at room temperature with a sealed 10 ml hemispherical vial containing tritiated toluene phosphor mounted over the tube face, with an interposed shutter assembly (the optical coupling is relatively poor). After an adequate period in the dark (between 1 and 4 hours usually), the tube is adjusted to a standard overall sensitivity and the bias is adjusted until the count rate with the shutter open is an arbitrary figure of 90 counts per second. The shutter is closed and the tube background rate is measured. The tube performance is then expressed as a ratio, e.g. 90/7 and the smaller the background the better the tube. The correlation between the performance rating and the tube dark current is shown in Fig. 2 and at the present time more than half of the 'S' tubes made are rated 90/10 or better, while 15 to 20% are rated 90/5 or better. These latter tubes give efficiencies of 15-17% for a tube background of 180 cpm with a 10 ml sample at 20°C.

3. In order to put the results summarised above into proper perspective in the field of Photomultiplier tubes, it is desirable to consider the characteristics of various dynode structures and their influence on tube background. Three types of dynode structure

Fig. 2. Correlation between dark current and thermionic background for specified count rate from H^3 scintillation source in standard test jig.

are in common use; the linear focussed design (used in the RCA 6810A and EMI 9593B), the box and grid structure, (used in the DuMont 6292 and EMI 9524B) and the venetian blind dynode (used in the EMI 9536, 9514 and 6097). Two types of secondary emitting surface are in general use; Cs Sb, mainly used in EMI tubes, and Ag-MgO-Cs.

The variation of gain with voltage for representative tubes is shown in Fig. 3 and the increase in gain with a larger number of stages will be noted. This is important, since, in order to reduce the complexity of apparatus used to process the signal after the anode of the Photomultiplier tube, it is desirable to operate with as high tube gain as possible, provided this does not in turn produce feedback effects which increase the background signal.

A measure of the feedback stability of a given structure is provided by a plot of anode dark current divided by tube gain, which may be expressed in terms of cathode dark current, or in terms of the input light level to give an anode current equal to the dark current. However expressed, this parameter is found to be roughly independent of tube gain up to some critical value, as shown in Fig. 4. While the limiting value of gain varies from tube to tube, as does also the cathode dark current, nevertheless typical values may be given to particular tube designs and it is found that the box and grid type of structure has a relatively low limiting gain, around 5×10^7 , independent of the number of dynodes (above 10), while the venetian blind structure has a limiting gain which increases with the number of dynodes, values of 10^9 with 13 stages being readily obtained. The focussed structure appears to lie midway between the other two designs in its behaviour. (The above comparisons refer to tubes with S-11 cathodes.)

Recently, a statistical study of the variation of dark current among tubes of a given type, has shown that there appears to be a median value characteristic of a given dynode structure, for tubes made with S-11 cathodes of very similar parameters. This is illustrated by the distribution curves of Fig. 5, from which it will be seen that the venetian blind structure gives the lowest value of dark current, while the linear focussed structure is worse by a factor of 20. The fact that the curves appear to be Gaussian when plotted against the log of the dark current suggests that the variation is due to a statistical spread in the work function of the cathode, but there is no obvious explanation for the difference in the median values, since the S-11 cathodes were all very similar. The results are not due in any obvious way to feedback processes, since the tubes were all operating well below the limiting value of gain and it may

Fig. 3. Variation of gain with voltage for representative tubes.

Fig. 4. Variation of dark current with over-all sensitivity for various tube types.

Fig. 5. Distribution curves of dark current for various tube types.

be that the phenomenon is associated with particular processing techniques which are individual to a dynode design, but the fortunate fact remains that the venetian blind structure, with which EMI has most experience, appears to be very suitable for low dark current tubes.

When tubes are made with 'S' cathodes, the dark current is reduced by a factor of 10 or more and it is found that the $1\frac{1}{2}$ " diameter 9524S box and grid tube (with Cs Sb dynodes) becomes very competitive with the 9514S, only partly due to its smaller cathode area. This reinforces the suggestion that the difference shown in Fig. 5 may in part be due to processing.

A further observation relating to dark current is illustrated in Fig 6. (2). A tube was fitted with a fine grid parallel and close to the cathode so that a small negative PD sufficed to bias off electrons from the end window deposit. Under these conditions it was found that whilst 92% of the anode current produced by illumination of the cathode was cut off, only 14% of the dark current was affected, showing that the major part of the tube background was generated by regions of the cathode-D1 space which were of little utility for the production of photoelectrons. This result was not entirely unexpected, since the production of a uniform deposit of antimony on the window requires that the source of this material be situated in a position ideally suited for coating the walls of the cathode screen with antimony, which will absorb caesium to become an efficient generator of thermionic electrons.

Various artifices have been considered for the reduction or elimination of this undesirable wall coating and in recent months an ingenious arrangement has been developed by V.A. Stanley, at Ruislip. This consists of lining the cylindrical wall with a fine mesh, of small shadow area, spaced away by a millimetre or so. A small amount of Sb is deposited on the inner facing of this mesh but the greater part passes through onto the wall of the tube. After sensitisation, the small area of CsSb on the mesh can emit electrons into the C-D1 space for collection into the first dynode, but the electrons from the wall coating are biased back by the contact potential between the suitably chosen mesh material and the cylinder of the cathode screen.

The electron bias curves of tubes of this type have an unexpected shape. In place of the nearly linear relationship between amplitude and log-count-rate, exemplified by curve b of Fig. 1, which is found with a conventional 'S' cathode tube (and which was the subject of some controversy at the last Scintillation Counter Conference in Washington), a pronounced fall-off in the number of counts as low amplitude is observed, (curve c, Fig. 1), although at higher amplitudes the two

Fig. 6. Characteristics of 6097 with grid control of cathode emission.

curves are similar. This suggests that the majority of the thermionic electrons from the tube wall are incident on D1 in a position which gives a lower value of stage gain than those coming from the cathode, while a porportion may skip D1 and produce still smaller pulses from D2, so that the linear curve b is, in fact, made up of superposed distributions similar to curve c, but having a much wider statistical variation due to the inclusion of many signals of amplitude down to a fraction of one secondary electron, in place of the median value of 5 given by electrons from the cathode. In fact, analysis of the two curves shows that the average D1 gain for curve b is only half of that for curve c and in the latter case one electron amplitude is equivalent to 10 V bias.

4. We are now in a position to consider the results obtained on single tube assemblies by various workers. Fig. 7 shows a plot of tritium counting efficiency versus tube background at 20°C obtained at the Thornton Research Centre of the Shell Petroleum company. Using a standard 6097S (rating 90/7), a limiting efficiency of about 48% is obtained with a tube background of 200 counts per second and 14% for 3 counts per second. Using a modified tube with a mesh mounted around the cathode screen as described above, the background rate for efficiencies below 25% is about the same as for a standard 6097S, but above this level the effect of reduction in the small pulse background becomes very noticeable and a limiting value of 52% for 70 counts per second is obtained.

Fig. 8 shows the results obtained by Ekco Nucleonics, using a 9514S in an arrangement similar to that of the Shell counting head but cooled to -20°C and having better optical coupling. The limiting efficiency, using a tritiated toluene sample, has now increased to 64% for a tube background of 10 cps, while at 3 cps the efficiency is about 50%. It will be interesting to see the shape of curve given by a mesh lined tube when cooled, but this test has not been carried out at the time of writing.

It may perhaps be deduced from Fig. 9, which shows similar curves obtained by Nuclear Enterprises of Edinburgh, using a 9524 tube of 1 $\frac{1}{8}$ " diameter, that cooling performs much the same function as the interposition of a mesh, since the small amplitude pulses seem to be reduced more than the larger background signals. Fig. 10 shows a bias curve of the arrangement, which differs from those mentioned previously, in having a cylindrical vial of height rather greater than its diameter and uses a newly developed phosphor type NE 213. The limiting efficiency is 64% at about 1 cps and is 20% at 0.15 cps from the tube. A comparison of the bias curves of Fig. 1 and of

Shell Counting Head

H^3 Counting Efficiency vs Tube background

20°C. 10 ml Scintillator. Hemispherical vial

Amersham Hexadecane -1:2T in Toluene + 5 g/litre p-terphenyl + 16 mg/
litre POPOP

Fig. 7. Variation of tritium counting efficiency with tube background: Shell Petroleum Company.

Fig. 8. Variation of tritium counting efficiency with tube background: Ekco Nucleonics.

Nuclear Enterprises Tritium Counter

H³ Counting Efficiency Vs Tube background

NE 5503 and 9524A
15 ml Scintillator Cylindrical Vial
28 mm dia. Photomultiplier tube.

Fig. 9. Variation of tritium counting efficiency with tube background: Nuclear Enterprises.

Bias Curves - NE 5503 & 9524A

Source 10 μmc H^3 in 15 ml
NE 213 Scintillator
Vials - Silica
NE 5503 Shielded Head
Operating Temperature -10°C
NE 5202 Amplifier Gain 5000
9524A No. 7141 EHT 750 V.
Bias Curves taken with 20 V gate

Fig. 10. Bias curves: Nuclear Enterprises.

Fig. 10, normalised to an equal electron amplitude scale, suggests that the amplitude of primary signals from the Nuclear Enterprise assembly at -10°C is about 20 to 30% higher than from the Shell assembly at 20°C . Part of this increase is undoubtedly due to the fact that the NE head is designed to give rather tighter optical coupling than is the Shell head which was designed for rather less onerous requirements. The tube background given by the particular 9524A appears to be 8 times lower than that of the 9514S used in the Ekco equipment and while part of this is undoubtedly due to the 4:1 reduction in area of the 9524 compared with the 9514 (23 mm diameter of 44 mm diameter), some part must also be due to the spread in tube parameters.

From the above it will be seen that for a single tube assembly, operating with an efficient phosphor and vial assembly, the limiting efficiency for H^3 counting lies between 48 and 64%. In all of the above measurements great care was taken to ensure that measurements were not falsified by phosphorescence of vial or phosphor. This was done by handling in light shields or dark rooms and by the use of identically handled blanks.

5. The disturbing effects of phosphorescence may be sufficient to demand the use of a coincidence arrangement for their elimination, particularly with some types of sample. From the data given above, we can see that a vial tightly coupled to two Photomultiplier tubes, so that the light from a scintillator is shared equally between the two cathodes will give a maximum efficiency for H^3 of between 25 and 40% (single tube efficiency squared.) Any reduction in the optical coupling will markedly reduce this efficiency.

The fact that two tubes are 'looking' at each other now immediately brings in the complication of tube interaction. In a preliminary set-up using two 9514S tubes, the random coincidence rate at room temperature (about 23°C) with the tubes optically isolated has been measured at 0.3 c/s. With the tubes coupled through an empty cylindrical vial with plane parallel end windows, a coincidence rate of 2 counts per second was obtained due to tube interaction and with a blank phosphor in the vial an extra background of 1.5 cps was obtained. These figures refer to an H^3 counting efficiency of about 15% (the arrangement was not optimised for light coupling) and the interaction count rate varied linearly with H^3 counting efficiency, which suggests that signals from the cathode are of only 1 or two electrons. The resolving time of the coincidence unit was about 0.5 usec.

Work has just begun on a study of this interaction and of means for reducing it but we have, as yet, little to report. Up to the moment, it has seemed reasonable to assume that the interaction is due to the passage of light from the anode region of one tube where excitation of Cs vapour will occur, to the cathode of the second tube. If this is the case, the use of a coincidence unit of resolving time shorter than the electron transit time (about 60 μ sec) should greatly reduce the effect. The observations that interaction is proportional to cathode area (checked by blacking out parts of the cathode) and also to H^3 detection efficiency, would not be inconsistent with such an explanation, but these would be equally consistent with a mechanism not involving anode light feedback. A very recent private communication from J.F. Cameron and I.S. Boyce at A.E.R.E., Harwell, suggests that they have made observations which, although tentatively, support a theory not involving anode light as a primary cause, since the coincidence rate is not affected by cooling, which materially reduces the anode current. If these observations are confirmed, many of the possible lines of work, involving modifications to tube structure, which we have in hand at the moment, will be fruitless and it is regretted that time has not permitted clarification of this point before the presentation of this paper.

One other aspect of tubes which must be examined in connection with coincidence arrangements is a possible advantage of tubes with tri-alkali cathodes (S-20) such as EMI 9558B. These have high photo-sensitivities with up to 20% quantum efficiency in the blue and rather lower thermionic emission than an S-11 cathode (between one quarter and one sixth, at 20°C).

Tested in our single tube head, such tubes are rated at 90/25, which compares unfavourably with the modern specially made 'S' cathode tubes, but they have not yet been checked by us in a coincidence head. The possibility also exists that re-examination of phosphors operating with quartz window versions of the 9558 and also with quartz window 'S' cathode tubes may lead to some improvement in counting efficiency.

6. CONCLUSION

At the present moment, Photomultiplier tubes are available capable of giving counting efficiencies for 10 ml samples of tritiated toluene phosphors of between 10 and 15% with a tube background of 3 counts per second at 20°C and of 50 to 60% for this background at -10 to -20°C. At this reduced temperature 30% is obtainable with tube backgrounds of only a few counts per minute.

Much work remains to be done to improve the performance of tubes in coincidence arrangements but significant improvements are hoped for in the next few months.

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NEW ACCESSORIES FOR LIQUID SCINTILLATION COUNTING

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New accessories will broaden the scope and usefulness of coincidence type liquid scintillation techniques, both by enabling the investigator to perform measurements which he could not do in the past and also by simplifying and facilitating existing liquid scintillation counting techniques.

THE COUNTING VIAL

The first accessory which merits discussion is the counting vial. It has long been recognized that the typical glass counting vial offers some difficulties, particularly to those interested in low level counting. The most widely used vial not only contains a significant amount of radioactivity which contributes to increased background, but also it would appear, does not permit all of the photons generated in a counting solution to pass through and evenly distribute themselves to the photomultipliers.

Agranoff (1) some years ago recognized that the glass of the vial contributed to the over-all background, and studied the use of quartz counting vials. As would be anticipated, significant background reduction was noted. However, quartz vials have not come into widespread use because, apart from their expense, it is difficult to make a satisfactory closure. Attempts to obtain quartz vials with rolled threads at reasonable cost have been rebuffed by the various manufacturers of

quartz equipment. Polyethylene snap caps which have been used by some workers with glass vials can be used with quartz, but in our experience it is sometimes difficult to obtain a good fit. Kaufman (2) has, of course, gone even farther than Agranoff by eliminating the sample container altogether.

After receiving suggestions from several interested parties, and particularly at the insistence of Dr. Herbert Jacobsen of the University of Chicago, we decided to evaluate seriously the use of medium density polyethylene as a material of construction for liquid scintillation counting vials. This plastic was adjudged to be best from the standpoint of inertness, moldability, transparency, and cost. Polyethylene would appear to offer some attractions as well as some severe shortcomings. There is no significant background contribution from polyethylene since any natural radiocarbon has long since decayed. In fact, with the Tri-Carb® Spectrometer set at the tritium peak, background reductions as shown in Fig. 1 exceed 30 per cent when a polyethylene container is compared to a glass container of identical size and shape. As is to be expected, background reduction in the region of the tritium peak is a maximum, since the K^{40} counts of both photomultipliers and glass counting vial show up here.

Counting efficiency for polyethylene containers, as shown in Fig. 2, is also significantly higher than for glass containers, particularly when the weakest beta emitters such as tritium are counted. Using the same instrument settings, a tritium efficiency increase of over 10 per cent was noted for polyethylene containers while for carbon a decided spectral shift was evidenced.

In the case of tritium, more of the lowest energy events could be noted and so when counted on the Tri-Carb Liquid Scintillation Spectrometer more tritium events were noted in the lower (10-50) channel. Also, more events of higher energy were noted in the upper (10- ∞) channel, and this must be due to more complete photon passage through the container for events which formerly showed up as being of lower energy.

In carbon counting a decided spectral shift was evidenced. As seen from the data shown in Fig. 2, the C^{14} peak shifted down by a full high voltage tap. In the lower channel, with the instrument set at the C^{14} peak for normal glass counting vials, actually fewer counts were observed on the 10-50 scaler with a plastic container than with glass. However, in the 10- ∞ channel there were significantly more events recorded when the plastic container was employed. This implies that the

Fig. 1. Comparison of glass to polyethylene vials (background reduction for polyethylene is expressed as a percentage of the background for glass vials at the same high voltage settings).

Fig. 2. Comparison of glass to polyethylene vials (counting efficiencies for C^{14} and H^3 activity).

walls of the glass container do not prevent a carbon event from being recorded but do interfere with some of the photons from that event. The plastic, on the other hand, must be more "transparent" and so we see a particular event with an apparently greater energy and this must be more akin to reality.

It must be emphasized that data presented in Fig. 2 imply that one ought not use the same instrument settings when counting with plastic vials, as when counting with glass vials. If a particular background can be tolerated with glass vials, then with plastic vials much wider window settings could be used in order to achieve this same background. With the increased efficiency thus obtained, one can expect to significantly shorten counting times.

A study of the phosphorescence of medium density polyethylene was also made. Figure 3 indicates that medium density polyethylene exhibits significantly more phosphorescence than glass. Both sample containers were exposed at a distance of 6 in. from the center of a 20-watt fluorescent lamp for a period of 5 minutes and then measured in "single channels" in the Tri-Carb Liquid Scintillation Spectrometer. A fast decay component is noted, followed by a prolonged slow fall-off of phosphorescence. After 14 hours, over 4000 counts above background were noted for the polyethylene vials. However, in coincidence after about 3 minutes, no spurious counts were observed due to phosphorescence. These figures indicate that for single channel operation, the use of plastic vials must be ruled out since the phosphorescence decay seems to require a prolonged period of dark adaptation before counting can begin.

Polyethylene containers, although advantageous from the counting standpoint, have decided disadvantages which must be noted. The melting point of polyethylene is low and it is unwise to attempt to heat strongly any material in one of these containers as is sometimes necessary to effect solution. Furthermore, solvents such as toluene tend to diffuse through polyethylene and at room temperature this diffusion occurs quite rapidly. At 0°, diffusion of toluene from a full 20-ml container occurs at the rate of about 100 milligrams during a 24-hour period. It is, therefore, necessary to use a polyethylene container and then discard it promptly. Sample storage in these containers is out of the question. It should be recognized that large molecules will not diffuse, and since Davidson (3) has demonstrated that count rate is independent of solvent volume, a slight amount of solvent loss would not be expected to interfere with counting.

Fig. 3. Comparison of glass to polyethylene vials.

Finally, some speculations are in order as to the reasons for increased counting efficiency. It has been surmised that either polyethylene is more transparent than glass or it disperses light more uniformly, thus ensuring that each photomultiplier receives approximately the same number of photons. We have not an answer to this question, but Ott (4) has indicated that by roughening typical glass counting vials with crocus cloth he has improved counting efficiency about 5 per cent for tritium, and so this might tend to support the second hypothesis.

CONTINUOUS LIQUID FLOW MONITOR

We would like to turn next to a device for the continuous measurement of radioactivity in liquid streams. Following the published suggestions of Steinberg (5), we have evaluated the use of a solid suspended scintillator in aqueous solution for the measurement of radioactivity in that solution. Steinberg has demonstrated that crystalline anthracene is a superior scintillator for such measurements. He has suspended scintillators in aqueous solution containing activity and obtained remarkably good results. Table 1 confirms Steinberg's work using 6 levels of activity of carbon-14 benzoic acid in aqueous solution. The amount of anthracene was always in excess and the counting efficiencies are in fairly good agreement.

TABLE 1. COUNTING EFFICIENCIES OF AQUEOUS SOLUTIONS OF C¹⁴ BENZOIC ACID

<u>Anthracene</u>			<u>Pilot Beads</u>		
Activity	CPM*	Eff.	Activity	CPM*	Eff.
dpm	above bkg.	%	dpm	above bkg.	%
1016	480	47.5	3560	444	12.6
1524	735	48.2	5340	693	13.0
2032	761	37.5	7110	909	12.8
2540	1043	41.2	8885	1180	13.2
3048	1175	38.5			
3557	1455	40.8			

*20-ml glass vials; tap 5, 10- ∞ ; background 40 cpm.

We also decided to evaluate a plastic scintillator (Pilot "B" beads) for the same purpose, and Table 1 also shows the results. With 4 levels of activity, a 12 per cent efficiency for C^{14} was obtained but this efficiency is only about one-third of that which can be obtained with anthracene. With either scintillator, it is necessary to count at higher than usual voltages and with integral settings in order to maximize efficiency. At these settings, background is somewhat elevated.

We next turned our attention to a prototype liquid flow system, and this is shown in Fig. 4. The detection element illustrated has been somewhat modified and for this work consisted of a straight glass tube, about the size of a cigarette, packed with crystals of anthracene and placed between two photomultipliers. This "Tri-Carb Cartridge" contained about 1 gram of scintillator and had a free space of about 1 milliliter. The photomultipliers were connected to an Automatic Tri-Carb Liquid Scintillation Spectrometer. For purposes of this preliminary work, the spectrometer was read out repeatedly as a solution of activity was continually circulated through the detection zone. Table 2 shows efficiencies for carbon-14 using both anthracene crystals and plastic scintillator beads (Pilot "B"). The values noted were similar to those experienced in the counting vials and indicate that for uncolored aqueous solutions continuous flow measurements appear to be practical. Backgrounds are substantially lower than with glass counting vials, since little glass is involved in the system.

TABLE 2. CONTINUOUS FLOW MONITOR -- COUNTING EFFICIENCIES OF AQUEOUS SOLUTIONS

Anthracene			Pilot Beads		
Activity	CPM*	Eff.	Activity	CPM*	Eff.
dpm/ml	above bkg.	%	dpm/ml	above bkg.	%
340	155	45	510	84	16.5
846	326	48	1195	151	12.7
1040	428	41	1530	235	15.3
2040	837	41	3810	491	12.9

* Tri-Carb Cartridge; tap 5, 10- ∞ ; background 22 cpm.

Fig. 4. Continuous Flow Detector (prototype unit). In the unit actually tested, a straight tube replaced the coil shown. The photomultipliers are in a refrigerated housing, and the preamplifiers are mounted on a separate chassis.

Although continuous flow measurements of carbon-14 activity give results approaching the same order of magnitude as that which can be obtained in the more usual liquid scintillation solvent systems, tritium counting would seem to be marginal. Table 3 shows results obtained by circulating tritiated water at 4 levels of activity over both anthracene crystals and Pilot beads. Again, the Pilot beads are only a fraction as good as the anthracene crystals. But here, in contrast to the situation for C¹⁴, maximum efficiency does not approach that of homogeneous systems.

TABLE 3. CONTINUOUS FLOW MONITOR -- COUNTING EFFICIENCIES OF TRITIATED WATER

Anthracene			Pilot Beads		
Activity	CPM*	Eff.	Activity	CPM*	Eff.
dpm/ml	above bkg.	%	dpm/ml	above bkg.	%
2.1×10^4	278	1.3	3.3×10^4	104	0.3
10.3×10^4	3093	3.0	16.5×10^4	360	0.2
41.3×10^4	5870	1.4	66.0×10^4	779	0.1
82.5×10^4	8081	1.0	136×10^4	661	0.05

*Tri-Carb Cartridges; tap 8, 10-∞; background 60 cpm.

Table 4 indicates, with arbitrarily selected accuracy and confidence levels, the minimum detectable activities which can be ascertained with a continuous flow system using the efficiencies and backgrounds previously experienced. These projections are based on the assumption that a constant activity level is maintained in the detection zone for the time noted.

Care should be exercised in attempting to apply conventional criteria of good counting statistics to a continuous flow system, such as that described, since the time of measurement cannot be governed by statistical considerations but rather by the rate of flow of liquid passing through the system.

TABLE 4. MINIMUM COUNTING LEVELS DETECTABLE WITH 10 PER CENT ACCURACY AND 62% CONFIDENCE

<u>C¹⁴</u>			<u>H³</u>		
Time min.	CPM*	DPM	Time min.	CPM**	DPM
1	67	168	1	143	14,300
5	32	80	5	46	4,600
10	20	50	10	30	3,000
30	10	25	30	16	1,600

* 40 per cent efficiency; background 20 cpm.

** 1 per cent efficiency; background 60 cpm.

GAS CHROMATOGRAPHY EFFLUENT DETECTION

The detection of radioactivity in the effluent of a gas chromatography column has received considerable attention. In general, attempts to trap effluent streams by refrigeration have met with failure due to the formation of aerosols which were swept through the trap by the carrier gas. Even with complete trapping, quantitative transfer of minute quantities of material to a suitable counting system may become a significant problem. Attempts to trap in liquid scintillation counting vials containing toluene have also met with failure, since the bubbles of carrier gas breaking the surface have been found to contain activity which was, therefore, not trapped. Popjak (6) has described a satisfactory trapping device for use with a single photomultiplier counter and has recently adapted his system for use with a coincidence-type instrument (7).

Karmen (8), noting Steinberg's suggestion that anthracene is an excellent scintillator, has made worthwhile use of this material for measurement of gas chromatography

effluents. Figure 5 shows a gas chromatography fraction collector patterned after Karmen's suggestions. The effluent leaving the mass detector of a typical gas chromatography column is brought through a heated tube to the heated head of the fraction collector. The stream passes over crystals of anthracene, generally coated with 5 per cent by weight of silicone oil (Dow-Corning 550). The anthracene is held in a glass Tri-Carb Cartridge which has at its lower end a cigarette filter to permit passage of carrier gas. The Tri-Carb Cartridge, being at room temperature, will condense components of the effluent stream. The cartridge is removed from the fraction collector, placed in a sample adapter, and counted directly in the Automatic Tri-Carb Liquid Scintillation Spectrometer. No further sample preparation is required and counting efficiencies for carbon are on the order of 50 per cent, while for tritium about 10 per cent efficiency has been noted. Backgrounds are quite low, as little glass is involved in the system.

Karmen (8) has demonstrated that trapping is quantitative by passing the effluent from typical gas chromatogram fatty esters down a length of anthracene crystals. After cutting the collecting tube into segments, he noted that all activity was collected in the uppermost portion.

Fraction collection offers the advantage of permitting precise measurement, since one can measure for as long as is necessary to obtain good statistics. For the very lowest level work, the fraction collector undoubtedly is the method of choice. However, fraction collection suffers from a serious shortcoming in that data are not obtained until some time after the gas chromatogram has been run.

Using the principles described above, Karmen has constructed a device to give continuous indication of radioactivity as it leaves the detector of a gas chromatography column. Again, activity is trapped on anthracene crystals coated with silicone oil, but in this case the collecting cartridge is placed between 2 photomultipliers which continually observe scintillations as they occur. A recording ratemeter, operated from the output of the Tri-Carb Spectrometer, gives an indication of activity as it accumulates on the surface of the anthracene crystals. A 4-component mixture is shown in Fig. 6. The lowest boiling material came out first, was trapped, and followed by the 4 successive higher boiling fractions. The difference in step-heights is a measure of total activity in each peak.

Fig. 5. Gas Chromatography Fraction Collector.

Fig. 6. Typical trace obtained from a Cumulative Gas Chromatography Detector. A 4-component mixture of fatty acid methyl esters is shown. The run required about 40 minutes, and there was no evidence of tailing in an additional 2 hours.

With carbon-14 activity, counting efficiencies are quite high as was previously indicated. With tritium, there is a noticeable decrease in activity as more and more silicone oil is employed. With no silicone oil, counting efficiencies are actually higher than is usually obtained in toluene solution, but significant losses in counting efficiency were experienced when 5 and 10 per cent levels of Dow-Corning 550 were used. It is, therefore, suggested that particularly when tritium activity is to be measured, the amount of silicone be reduced to the minimum required to trap the most volatile component in the system.

There is no question as to the capacity of a typical cartridge containing approximately 1 gram of crystalline anthracene for trapping the effluent of a typical analytical gas chromatograph run. Columns were loaded with over 10 times the useful weight which they could handle, and all activity was trapped by a single cartridge.

The cumulative-type detector is, of course, fast but it suffers the decided disadvantage that small amounts of activity would be lost as they came through the column after a large amount of activity had already been accumulated. Of course, one can change cartridges rather quickly and overcome a part of this problem. The best over-all solution might be a combination of both the fraction collector and continuous device, using the continuous monitor as an indication of which fractions need be measured and which could be passed over.

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SOME RECENT DEVELOPMENTS IN LIQUID
SCINTILLATION COUNTING OF BIOCHEMICAL SAMPLES

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The purpose of this presentation is to review and comment upon a few of the more recently developed techniques that have been found useful in applying liquid scintillation counting to the assay of beta emitter activity in samples typical of biochemical research. This does not attempt to be comprehensive and represents this author's experience.

A year and a half ago we reported (1) on our use of suspensions of barium carbonate in toluene, gelled with Thixcin, for counting C^{14} derived from hemoglobin. Use of this technique has continued and well over 2000 such samples have been prepared. Our technique evolved from replacing the aluminum stearate, used by Funt and Hetherington (2), with the Thixcin as employed by White and Helf with gels for substances other than barium carbonate (3). The resultant counting samples look opaque and bizarre with all sizes of clumps of precipitate but they count reproducibly. We attribute this to the probability that the barium carbonate is really in microcrystalline form of rather uniform size, that the large aggregates of such crystals are permeated by scintillator solvent, and that the solid is an efficient reflector for the light of the scintillations. The absolute efficiency of the system depends upon the amount of barium carbonate in the bottle and runs linearly from 60 per cent with no suspension to 41 per cent with one gram of barium carbonate in 20 ml. of gel. The method is especially convenient for samples that inherently arise as CO_2 gas. The barium carbonate is weighed into the bottles and this weight provides the appropriate efficiency factor from previously established data.

We have tried the Cab-O-Sil gels described by Ott et al. (4). The efficiency did prove to be somewhat superior to that of Thixcin. For our particular production line this seemed less important than the convenience of the single-step addition of fluid Thixcin-toluene

to the barium carbonate, as compared with separate additions of Cab-O-Sil and toluene. We have also been concerned over the possible health hazard with Cab-O-Sil because it is silica, it tends to dust into the air, and it could readily be inhaled. Cab-O-Sil, however, would seem to be a real convenience for those needing only an occasional suspended sample--a sort of "instant" scintillator gel. The choice between barium carbonate gel counting of CO₂ and counting the CO₂ as Hyamine-carbonate in toluene solution (5, 6) seems to be very much one of personal preference and economics. The counting efficiencies, the quantities of carbonate that can be incorporated per bottle and the labor of sample preparation seem very similar. The Hyamine technique is significantly more expensive. It costs about nine cents per millimole for the commercially prepared solution of the Hyamine base in contrast with a half a cent for the Thixcin necessary to gel 20 ml. of toluene and support 5 millimoles of barium carbonate.

Both gel counting and Hyamine counting have numerous applications beyond carbonate assay. Helf, White and Shelley (7) have reported the use of gels for counting various solid compounds involving a number of isotopes. Shapira and Perkins have recently used Thixcin gels for counting aqueous materials in emulsion form (8). Hyamine is equally versatile since it can solublize in toluene almost any acidic sample material as well as compounds such as proteins and polysaccharides that are susceptible to alkali digestion (9, 10, 11, 12).

In instances where specific activities are sufficiently high for small samples to be adequate, specially tailored scintillation solvent mixtures may be ideal. Along these lines the author reported the use of a dioxane-anisole-dimethoxyethane mixture (DAM) for counting purines dissolved in water or ethylene glycol (13). This same mixture has been extensively employed since for counting tritium water and a variety of water-soluble compounds. Like other mixtures of organic solvents with water, the water is prone to separate out if there are appreciable quantities of salts in the sample. This, for example, caused us difficulties in testing for radioactivity in fractions from a Dowex-1-formate ion exchange column being eluted with formic acid-ammonium formate. Formic acid up to 4 normal made fine counting samples with 4 parts of DAM but when ammonium formate-formic acid buffer was used to elute columns, similar DAM counting samples all became diphasic. Treatment of the eluates with sufficient Dowex-50 hydrogen resin to remove the ammonium ion resulted in solutions that were again miscible with DAM.

In another instance a 30 per cent methanol in toluene scintillator solution was employed to prepare samples containing up to 0.1 mg. of C¹⁴-dextran and C¹⁴-carboxylinulin. These difficultly soluble substances were in 0.1 ml. of aqueous solution that was counted with 10 ml. of the organic

scintillator with 58 per cent absolute efficiency. The same type of alcohol-toluene scintillator has been employed at the level of 18 ml. to dissolve 0.2 ml. of aqueous alkali containing CO_2 or digests of protein (14). Herberg has used a blend of toluene, dioxane, methanol and naphthalene to dissolve alkali digests of tissue samples (10).

Another point to keep in mind is the fact that some non-scintillation solvents, which may be useful as extractants to isolate material for counting, can themselves be mixed with a scintillation solvent without much loss of counting efficiency. Dr. Thomas Butler and I employed this device for counting dimethyloxazolidinedione- C^{14} , DMO. This compound was readily extractable into ethyl acetate from aqueous homogenates of tissues. One part of such ethyl acetate extract was counted in 5 parts of toluene scintillator solution with nearly the same efficiency as a pure toluene solution. It did require two taps higher voltage on the Tri-Carb photomultipliers to show the peak differential counting rate.

One of the more agreeable developments of the past few years, so far as our counting in DAM solvent goes, is the availability of adequately pure solvents from commercial sources. The former need for elaborate purification of the ethers discouraged many workers from using this system. Now we find that the spectroscopic grade of dioxane manufactured by the Matheson Co. yields very satisfactory results when used with 1, 2-dimethoxyethane from the same manufacturer and anisole from Distillation Products Industries.

Dr. Daniel Steinberg is responsible for a novel and most useful approach to the problem of counting aqueous samples (15). He explored the possibility of reversing the phases of the suspended sample technique and put his aqueous samples in bottles containing solid scintillator particles. The object is to provide a large surface area of scintillator to come in contact with the sample solution. The best form of scintillator to date is blue-white fluorescence grade anthracene. For C^{14} solutions this can provide 54 per cent absolute efficiency when the anthracene is less than saturated with sample. This efficiency is difficult to control so Dr. Steinberg recommends using a fixed excess of sample solution with a specific weight of anthracene, a procedure analogous to infinitely thick barium carbonate Geiger-Mueller counting. For 3.0 ml. of aqueous sample and 1.00 gm. anthracene the absolute efficiency is about 22 per cent. A nonionic wetting agent is added in preparing the samples. This technique seems applicable to any water solution of adequate optical clarity and its rather moderate efficiency is compensated for by its relatively large capacity for aqueous sample material. Full details have recently been published (16) and I shall merely vouch for the fact that we have confirmed the reported efficiency and reproducibility.

Last fall a brief note by Wang and Jones (17) reported that radio-activity deposited on squares of filter paper could be counted by immersing them in especially constructed bottles containing conventional toluene scintillator mixture. This came to our attention six months ago when we were separating C^{14} -labeled purines and nucleotides on Whatman 3 MM paper by high voltage electrophoresis. We tested a 1" x 1 1/4" piece of paper wedged vertically in a standard 5 dram vial and were amazed at the 50 per cent counting efficiency. This technique quickly became our standard one and the 2-11 per cent variation in counting rate for repeated automatic counts on the same samples was not excessive for much of our work. In April, Geiger and Wright (18) published a study of this counting technique and reported their experience with a manual Tri-Carb counter, where the orientation of the paper in the bottle with respect to the photomultiplier tubes could be controlled. Their data showed 10-17 per cent of the mean as the range of observed counts at different angles of rotation of the sample. The correlation of low values and high values with certain orientations supported our belief that much of our variation was due to the random positioning inherent in automatic counting. Last month we received the June issue of "Atomlight", issued by New England Nuclear Corporation. This carried an article by Dr. Robert Loftfield in which he reported attempts to obviate the sample paper orientation problem by forming the paper into a vertical cylinder within a 10 mm. diameter test tube filled with solvent. This very substantially reduced the variability of the counting rates with a concomitant 20 per cent reduction in efficiency. At just this time we had also given a little thought to the asymmetry problem characteristic of the vertical square type of paper sample and decided that a recumbent circle or disc of paper on the floor of the bottle might look the same to the phototubes from any rotational angle. The fact that we, like Loftfield, lost only 20 per cent of our counts in going to a disc sample was encouraging. A set of ten replicate paper disc samples was prepared using a few micrograms of hypoxanthine- C^{14} in 10 μ l of water as the load. Papers were dried, put in bottles of toluene scintillator solution and counted for ten cycles of the automatic Tri-Carb counter with the accumulation of sufficient pulses to provide for a 95/100ths error of less than one per cent on each count. The data in terms of the variation between the highest and lowest of the ten counts on each bottle, as a percentage of the average of the ten counts, are given in Table 1 in the "circles" column. The maximum variation for any ten counts on random repositioning of a bottle was 2 per cent. The column headed "squares" shows analogous data for 10 of our wedged-in, 1" x 1 1/4", vertical pieces of paper. The average variation here is over three times as great as with the circles. Truly homogeneous, dissolved C^{14} samples under these conditions show variation that amounts to the statistical error of the counting or about 1 per cent in this case. The absolute efficiencies are 70 per cent for dissolved samples, 50 per cent for

squares and 40 per cent for circles. To obtain this last efficiency for circles it is necessary to count them at one or two high voltage taps (85-170 volts) greater photomultiplier voltage. The disparity in efficiencies for dissolved as compared with "on paper" samples makes it essential to know whether samples do dissolve. If they dissolve readily off paper, samples will count as homogeneous samples and the phototubes seem to be unaware of the presence of either a square or circle of paper. A simple test for what has happened is to count, remove the paper and count again. With truly insoluble compounds the "used" sample bottle and solvent give a blank counting rate and may be used for the next piece of paper.

A number of the factors influencing this counting technique have been examined. The volume of toluene overlying a paper disc is inconsequential between 5 and 15 ml. except as larger volumes increase the background. At 18 ml. of toluene about 4 per cent of counts is lost. If solvent and bottle are reused, the background of the solvent eventually builds up due to small bits of fiber accumulating. Simple filtration removes these and restores the original background. Reuse of solvent also accumulates color. Our sample bottles for electrophoresis papers, which are dried from Varsol, showed this and any color extractable from sample papers might be expected to accumulate similarly. Such color betrays itself by a shift of the pulse spectrum. Small pencil notes on sample papers, on the other hand, do not influence the counting rates. The translucency of filter paper to scintillation photons is so good that a blank disc of Whatman 3 MM on top of a disc containing a C^{14} sample causes only a 3 per cent reduction in count rate.

Since this paper counting appears to be an infinitely thin sample technique we sought to determine the maximum mass of a safe load. With glucose solutions and C^{14} , 10 lambda spots applied to blotted water-wet papers showed no self-absorption up to 5 per cent glucose in the loading solution; this was the highest concentration tested. In one calibration of our disc counting efficiency, 0.1 ml. of sodium hydroxide-carbonate containing 5.1 mg. of salts was dried on a 24 mm. disc and gave the same 40 per cent efficiency calibration as did a 3 μ g. sample of hypoxanthine- C^{14} . The 24 mm. disc may be conveniently cut from papers using a silver quarter dollar as a template. When spots on papers from electrophoresis or chromatography exceed this size, overlapping circles can be employed to count the large spots as several samples. This is not as convenient as dicing papers into squares, which should suffice for manual counter operators, who can provide uniform orientation of their samples. As might be expected, color in a paper sample does quench its counting and this cannot be measured with an internal standard in solution.

Table 1

COMPARISON OF VARIABILITY OF AUTOMATIC
COUNTS ON PAPER SAMPLES IN BOTTLES

Sample No.	<u>Squares</u>	<u>Circles</u>
	(% variation)	
1	11	1.4
2	8	1.2
3	4	1.6
4	1	2.0
5	11	1.0
6	4	1.6
7	11	1.0
8	7	1.4
9	10	2.0
10	4	1.6
Average	7.1%	1.5%

Ten samples each of C^{14} -hypoxanthine on 1" x 1 1/4" squares mounted vertically and 24 mm. diameter discs lying horizontally in 20 ml. bottles were counted for 10 automatic cycles in a Tri-Carb counter. All bottles contained toluene with 0.3% PPO and 0.05% POPOP, 18 ml. for the squares, 15 ml. for the circles. 40,000 or more counts were recorded at "peak" high voltage thru a 10-100 volt window for each counting. The % variation is the % ratio of the difference between the highest and lowest values of ten counts on the sample to the mean of the ten counts.

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STUDIES OF LOW-LEVEL LIQUID SCINTILLATION COUNTING OF TRITIUM

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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 $3 \times 10^{-3} \mu\text{c/ml}$ (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 $10^{-6} \mu\text{c/ml}$ or less with a counting period of no more than 30 minutes.

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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,

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

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.

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

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 $\Delta\text{N7-100}$.

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 $\Delta\text{N7-100}$ 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

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

Fig. 1 Influence of scintillator composition on detection sensitivity and efficiency.

order to ensure indefinite temperature stability of the scintillator, a refrigerator temperature of $+3^{\circ}\text{C}$ 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 Δ N7-100 - 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 Δ N7-100 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/ μ c)
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 Δ N7-100 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 Δ N7-100 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 Δ N7-100 scintillator and 2 DuMont 6292 photomultipliers were 6.34 ± 0.09 per cent and 1220 liters/ μ c, respectively, the latter quantity computed from Eq. 2. In 16 independent 30-minute measurements over a 4-day period, the background was 100.5 ± 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 Δ N7-100 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 Δ N7-100 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		Efficiency (per cent)	Detection Sensitivity (liters/ μ c)
	10-90	90- ~~oo~~		

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/ μ c.

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 $\Delta N7-100$ 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 $\Delta N7-100$ 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 Cobalt⁵⁷ 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: $\gamma_1 = 14$ kev, and $\gamma_2 = 122$ kev, with

Fig. 4 Efficiency, detection sensitivity, and back-ground as a function of photomultiplier separation for the Δ N7-100 and Δ N7-100 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 $R = n_{(90-100)} / n_{(10-90)}$. In order to vary the efficiency, increasing amounts of water, hydrogen peroxide, pyridine, and "O-ring contamination" were added to the $\Delta N7-100$ 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. Cobalt⁵⁷ 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 $\Delta N7-100$ 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/ μ c.

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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

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CORRECTION FOR QUENCHING IN LIQUID SCINTILLATION

COUNTING OF HOMOGENEOUS SAMPLES

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In liquid scintillation counting of homogeneous solution samples, the organic phosphor is mixed with a small amount of the radioactive solution to be assayed. The introduction of foreign material into the phosphor system frequently causes a diminution of the maximum light output that is obtained from radiation energy dissipated in the system by the beta particles. In theory, the radiation energy is transferred molecularly through the solvent to the phosphor which becomes excited and then de-excites with the emission of light as fluorescence (1,2). When non-fluorescent materials are present, degradation of the excitation energy may take place without emission of light. This quenching of fluorescence reduces the counting efficiency of the liquid scintillation system, and leads to erroneous results in assaying the radioactive samples if the extent of quenching is not considered.

Correction for the loss of sample counts due to quenching may be achieved either by an internal standard method (3-6), by the extrapolation method (7,8), or by comparing the pulse-height distribution in terms of the ratio of counts in two channels in the liquid scintillation spectrometer (3). In the latter method the two channels must be especially adjusted for this purpose. This report is concerned with the merits and shortcomings of the first two methods.

The internal standard method, which is widely used for correcting quenching loss, involves the addition of a radioactive compound to the counted sample, followed by a recount; the increment in counts thus observed is attributed to the added internal standard which is presumably being quenched to the same extent as the sample. From the ratio of the known counts of the added standard to the observed increment in counts

in the sample, the true counting rate of the sample may be computed. The accuracy and precision of this method under varied conditions have not been evaluated despite the earlier observation by Davidson and Feigelson (3) that the internal standard technique is useful in calculating a correction for slight quenching but is of doubtful validity when the quenching correction is large. Whisman and his co-workers (6) applied the internal standard technique to the radioassay of some tritiated hydrocarbons and studied the precision of the method but their evaluation did not take into consideration the conditions of varying degrees of quenching under which the internal standard method may not apply.

The extrapolation method consists of radioassaying the sample at several different sample concentrations in the liquid scintillator. Since quenching is concentration dependent (9), decreasing the sample concentration causes a corresponding increase in the counting efficiency of the system or the counts observed per unit sample. If the counting rate per unit weight (or volume) of the sample at each sample concentration is plotted against the corresponding concentration on semi-log paper, a linear relationship results. By extrapolation to zero sample concentration where, theoretically, no quenching takes place, the true activity of the sample per unit weight (or volume) is obtained. The validity of this method in application for quenching correction has been reported earlier (7,8).

Since the extrapolation method uses many points for extrapolation thereby giving proper weighting to each observation, it is therefore inherently more accurate than the internal standard method which relies on a single observation and is consequently more liable to experimental error. In Table 1, the merits and shortcomings of the two methods, based upon the results of the present study, are listed.

The precision of the internal standard method versus the extrapolation method was studied under comparable but varying conditions of quenching with samples containing succinic-2,3-C¹⁴ acid and tritiated methyl stearate of high specific activity. The method employed is as follows:

Azobenzene, Apiezon wax, iodine and para-nitroaniline were dissolved in toluene to a concentration of 315.7, 52.1, 67.6, and 50.3 mg. per ml. respectively, and the solutions were used as quenching agents. A known number of counts of C-14 and H-3 was added separately to each solution of the quenching agents and the solution was then assayed by the extrapolation method using sample concentrations ranging from 10

Table 1

COMPARISON OF MERITS AND SHORTCOMINGS

<u>Internal Standard Method</u>	<u>vs.</u>	<u>Extrapolation Method</u>
1. Single counting sample required.	1.	Multiple counting samples required.
2. Results more prone to experimental error.	2.	Results plotted according to equation. $S_a = S_o \exp. (-qC)^*$ thereby leading to more accurate weighting of each observation.
3. Selection of an adequate radioactive compound for internal standard necessary.	3.	No internal standard required.
4. Accuracy affected by the concentration of quencher present.	4.	Applicable to high concentration of quenchers, if the above equation is obeyed.
5. Accuracy affected by the level of radioactivity added as internal standard.	5.	Quenching constant, q , is independent of specific activity of sample.

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* S_a is the apparent specific activity of the sample at concentration C ; S_o , the specific activity of the sample in the absence of quenching; q , the quenching constant, equal to $0.693/C_{1/2}$, where $C_{1/2}$ is the sample concentration that will reduce the counts to half of initial value by quenching. See Ref. (8).

microliters to 0.5 ml. in 10 ml. of a mixed liquid scintillator.* Upon completion of counting, a known number of counts of C-14 or H-3 in 50 microliters of toluene was added as internal standard to the counted samples containing the respective isotopes and the samples were then re-counted. All the samples were integral-counted in 10- ∞ channel in a Tri-Carb automatic liquid scintillation spectrometer** at the balance point repeatedly for several 10-minute periods. This yields a statistical accuracy of 0.5% or better. The various background samples were counted at the same settings at 10-minute intervals.

In the experiments studying the effect of quencher concentration and likewise the number of counts added as internal standard, four replicate samples were employed. In this manner, the accuracy and validity of quenching factor was established.

Results and Discussion

Figures 1, 2, 3 and 4 are displays of the counting results of sample containing azobenzene, Apiezon wax, iodine and para-nitroaniline as quenchers, plotted according to the extrapolation method. Figure 2 and 4 show on an expanded scale the initial portion of each curve; the lines are regression lines for points corresponding to sample concentration of 10, 20, 40, 60, 80 and 100 microliters in 10 ml. scintillator, and the intercepts represent the counting rate of the sample in the absence of quenching. The average numerical value for the calculated intercepts from these four sets of samples are given in Table 2.

It can be seen that the plots for C-14 samples containing azobenzene and para-nitroaniline exhibit a linear relationship at low concentrations of the quencher but deviate significantly from that relationship at high concentrations; this deviation may seriously limit the usefulness of the extrapolation method in assaying radioactive solutions containing high concentrations of strong quenchers. In contrast, the plots of C-14 samples containing Apiezon wax and iodine as coloring and quenching agents remain linear throughout the concentration used. This discrepancy in the behavior of these sets of samples may be explained on the basis that in addition to fluorescence quenching there is also an "optical" quenching as a result of the coloring of the solution which may reduce the transmission of light produced in the system disproportionately from that due to fluorescence quenching alone.

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* The mixed scintillator consists of a mixture of equal volumes of the toluene scintillator (3.0 g./l.) and the dioxane scintillator (7.0g. PPO, 0.05 g. POPOP, and 50 g. naphthalene to 1 l. with purified dioxane) (10).

**Manufactured by the Packard Instrument Company, LaGrange, Ill.

Fig. 1. Apparent specific activity versus sample concentration for C^{14} samples (APZ for Apiezon wax; AZB for azobenzene; NA for para-nitroaniline, and I_2 for iodine).

Fig. 2. Replot of Fig. 1 on expanded concentration scale.

Fig. 3. Apparent specific activity versus sample concentration for H^3 samples.

Fig. 4. Replot of Fig. 3 on expanded concentration scale.

Table 2

COMPARISON OF ACCURACY OF RESULTS

	C ¹⁴	H ³
	Counts / 10 min. / 0.1 ml. sample	
True value	46,400	511,094
Value obtained by:		
1) Internal standard method		
Apiezon wax	48,177 $\pm$ 3%*	563,674 $\pm$ 10%
Azobenzene	46,358 $\pm$ 13%	581,133 $\pm$ 7%
Iodine	46,339 $\pm$ 8%	451,829 $\pm$ 18%
<u>para</u> -Nitroaniline	46,750 $\pm$ 4%	543,180 $\pm$ 11%
Av.	46,906	509,979
2) Extrapolation method		
Av. intercepts of regression lines	47,415	497,633

$$*\text{Standard deviation} = \sqrt{\frac{n \sum X^2 - (\sum X)^2}{n(n-1)}}$$

Another plausible explanation for the discrepancy is that at high sample concentrations, the solution may deviate from an ideal solution in that the solute molecules tend to associate thereby decreasing the effective concentration of the quencher present; consequently, a positive deviation from the predicted straight line as evidenced in Figures 1 and 3 results.

Apparently, this deviation is energy dependent and varies inversely with the intensity of light produced in the system, because under identical conditions, the plots for H-3 samples were found to deviate more from the linear relationship than the C-14 samples.

The precision of the extrapolation method in determining the sample counts in the absence of quenching is 2.1% for C-14 samples and 2.5% for H-3 samples. The variation among the values of the intercept of the regression line from the four sets of samples is within 1.7% and 7.3% of the standard deviation of the mean for samples containing C-14 and H-3 respectively.

When all the counted samples were "spiked" with an internal standard and recounted, the increment in counts in each sample was used to compute the counts initially present without quenching. The results obtained from samples containing 10, 20, 40, 60, 80 and 100 microliters of azobenzene, Apiezon wax, iodine, and para-nitroaniline in 10 ml. scintillator are given in Table 2. It may be noted that the values obtained from C-14 samples were identical within the experimental error to the counts added initially while those obtained from H-3 samples showed a greater dispersion of the data and were approximately 9% higher than the true value. The value from H-3 samples containing iodine was not included in this computation.

When the factor derived from samples containing concentration of quenchers in excess of 100 microliters in 10 ml. scintillator was used for quenching correction, higher values of sample count than that added initially were obtained. In general, the deviation from the true sample count becomes greater as the concentration of the quencher increases, with the exception of H-3 samples containing iodine which showed a trend in the direction of negative deviation.

The dependence of the accuracy of radioassay by internal standard method upon the concentration of the quencher present was studied using C-14 samples containing different quantities of azobenzene in 10 ml. scintillator. The results are given in Table 3. Ratio of the sample

Table 3

ACCURACY VS. CONCENTRATION OF QUENCHER IN SCINTILLATOR

Counts initially present, C_0 :	59,187 c/10 min.
Counts added as internal standard in 0.05 ml. toluene, C_{IS} :	39,212

Mg. of azobenzene in 0.1 ml. toluene added to 10 ml. scintillator	Ratio: counts remaining after quenching to C_0	Ratio: counts derived from correction to C_0
3.95	0.032	1.85
1.58	0.264	1.96
0.789	0.526	1.15
0.158	0.888	1.03

counts derived from quenching correction to the sample counts initially added shows a significant deviation from unity as the concentration of azobenzene increases. This finding confirms the observation of Davidson and Feigelson (3) that the internal standard technique is valid only under conditions of minimal quenching.

The level of activity added as internal standard may also affect the accuracy of the factor for quenching correction. Table 4 shows the

Table 4

ACCURACY VS. LEVEL OF RADIOACTIVITY ADDED AS INTERNAL STANDARD

Counts initially present, C_0 :	82,219 c/10 min.	
Counts remaining after addition of 0.394 mg. azobenzene in 0.1 ml. toluene:	59,871	
Counts added as internal standard in 0.05 ml. toluene, C_{IS}	Ratio: C_{IS} to C_0	Ratio: counts derived from correction to C_0
998,961	12.4	1.03
212,858	2.59	1.03
29,201	0.356	1.06
19,166	0.233	1.25
5,790	0.07	1.45

results of a study in which internal standards of varying levels of activity from 0.07 to 12.4 times the initially added sample counts were used. The ratio of the sample counts obtained by correction to that initially present also showed a deviation from unity. Conceivably, the extent of this deviation is dependent upon the concentration of the quencher. It is clear that under the quenching conditions prevailing in this experiment, in order to determine accurately a sample count in the absence of quenching by correction, an internal standard of comparable or higher activity than that of the true sample counts should be added.

Background counts

Domer and Hayes (11) observed that background counts are quenched differently from the sample counts. Therefore, the accuracy in assaying weakly active, strongly quenched, colored samples such as those

containing biological specimens depends largely upon an exact knowledge of the background counts of the sample. Herberg (12) measured the background counts of a colored sample accurately by using a colorimetric technique. Under varying conditions of fluorescence and "optical" quenching, the individual sample background counts may vary; but in cases of severe quenching, the unquenched portion of the background counts tends to approach a limiting value.

The composition of background counts in liquid scintillation counting was reported (8) to be attributable to 1) chance coincidence, 2) reciprocal sensitization of the photocathodes of the multiplier phototubes, 3) potassium-40 in glass, 4) Cherenkov radiation, 5) cosmic radiation, and 6) environmental radioactivity. In a clear, transparent sample containing quenchers, the fraction of the total background counts of the sample due to cosmic radiation and environmental radioactivity will be quenched proportionately as the sample counts, provided that the background counts have a comparable pulse-height distribution as the sample counts; whereas, the remaining fraction of the background counts due to chance coincidence, reciprocal sensitization of photocathodes, potassium-40 in glass, and Cherenkov radiation will not be quenched. However, in a colored quenching sample, in addition to fluorescence quenching, there is also an attendant "optical" quenching, which diminishes the transmission of light from Cherenkov radiation and potassium-40 in glass thereby reducing the background counts of the sample to a value, attributable mainly to chance coincidence. The results of a series of samples studied are given in Table 5.

Fluorescence Quenching in Liquid Scintillator vs Sources of Excitation

In order to determine whether the fluorescence excited by ionizing radiation is quenched similarly as that excited by ultraviolet light in the presence of a quenching agent in another approach to quenching correction in liquid scintillation counting, scintillator solutions containing varying amounts of quenchers were measured in an Aminco fluorospectrophotometer. For the particular composition of the mixed scintillator solution used in this experiment, the exciting wavelength used was found to be 3900 Å., and the wavelength of the main band of the fluorescence spectrum was 4200 Å. When the reciprocal of the fluorescence readings at 4200 Å was plotted against the concentration of the quencher on semi-log paper, a linear relationship was obtained. Scintillator solutions of identical composition were also used to count C-14 or H-3, and the ratio of the sample counts added initially to that observed was similarly plotted against the concentration of the quencher. Straight or nearly straight lines as shown in Figure 5 were obtained.

Liquid scintillators containing ferric chloride or Apiezon wax as quenching agents showed comparable quenching of fluorescence in solution,

Table 5

BACKGROUND COUNTINGS

Sample	C ¹⁴ Settings	H ³ Settings	
<u>No.</u>	<u>Counts per 10 min.</u>		
	(Channel width: 10 - ∞ volts)		
1	Dark vial	63 ± 24*	148 ± 33
2	Blank sample well	129 ± 20	405 ± 56
3	Empty glass vial	141 ± 17	612 ± 53
4	Toluene**	209 ± 19	859 ± 50
5	Mixed scintillator**	499 ± 21	1131 ± 63
6	FeCl ₃ solution I ⁺	93 ± 19	287 ± 47
7	FeCl ₃ solution II ⁺	87 ± 20	323 ± 57
8	FeCl ₃ -scintillator solution I ⁺⁺	110 ± 32	379 ± 45
9	FeCl ₃ -scintillator solution II ⁺⁺	130 ± 22	505 ± 73

* Average of at least 16 readings. Standard deviation calculated by

$$\sqrt{\frac{n \sum X^2 - (\sum X)^2}{n(n-1)}}$$

**10 ml. solution, not de-oxygenated.

+ I and II containing 340.4 mg. and 22.4 mg. FeCl₃·6H₂O, respectively per 10 ml. solution of equal volumes of para-dioxane and toluene.

++ I and II containing 123.5 mg. and 24.7 mg. FeCl₃·6H₂O, respectively, per 10 ml. mixed scintillator.

irrespective of the means of excitation, although the slope of the two lines differed slightly. With azobenzene as a quencher, quenching is approximately four times more severe with ionizing radiation as the exciting source than with uv light; whereas, with para-nitroaniline, the opposite is true. In liquid scintillators containing increasing amounts of hyamine hydroxide or phenyl isothiocyanate, the intensity of fluorescence at 4200 Å remained practically unaltered while these same solutions showed strong quenching properties as counting systems.

These interesting but fragmentary observations serve to emphasize again the complexity of the energy transfer mechanism in liquid scintillation systems. Only when this mechanism is completely understood can a more accurate correction for quenching in counting samples be made.

Fig. 5. See text. (F) and (C¹⁴) indicate data obtained using ultraviolet light and ionizing radiation, respectively, as sources of excitation.

Summary

The results of this study indicate the following:

- 1) The internal standard method and the extrapolation method yield equally valid and accurate results in quenching correction in liquid scintillation counting under conditions of minimal quenching or dilute sample concentration.
- 2) The accuracy of the results is dependent upon the beta energy of the isotope.
- 3) In cases of severe quenching, the internal standard method tends to yield inaccurate but consistently high results; whereas, under identical experimental conditions, the extrapolation method may or may not apply depending upon the degree of severity of quenching involved.
- 4) At high sample concentrations of the quencher, the extrapolation method may not apply if a deviation from linearity of the semi-log plot of apparent specific activity vs. sample concentration is observed.
- 5) In order to obtain an accurate factor for quenching correction in the internal standard method, comparable or higher activity than sample activity should be used as internal standard.
- 6) For colored or transparent samples containing stronger quenchers, the background count is lower than that of liquid scintillator alone and tends to approach a limiting value.

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PART IV

EXTERNAL SAMPLE DETECTORS

LANDSTUHL 2 π HUMAN COUNTER

1. Measurement of Cesium-137 and Potassium

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The 2 π liquid scintillation counter which was designed and built at the Los Alamos Scientific Laboratory for demonstration at the Second International Conference on the Peaceful Uses of Atomic Energy has been in operation at Landstuhl, Germany for a little more than one year.

The US Army Medical Research Unit, Europe was activated for the specific purpose of operating the counter. Under the supervision of F. Newton Hayes and with the assistance of Alexander Pfau the counter was reassembled at its present location in May 1959.

Briefly, to review some of the characteristics of the counter; it is designed so that the subject walks into the counter and stands erect during the measuring process. The tank is six feet high and is filled with 280 liters of terphenyl-POPOP in triethylbenzene. There are six photomultiplier tubes, sixteen inches in diameter, which are inserted directly into the tank without windows. The shielding is composed of lead three inches thick (1).

One of the primary uses of the counter has been to survey the European population for their cesium-137 content. At the same time, the potassium is also determined by measuring the potassium-40.

In order to make an accurate determination of the quantity of these two isotopes, calibration is the primary requisite. Fortunately, both of these isotopes are fairly well uniformly distributed throughout the human body. Therefore, the calibration standards were prepared by placing a known amount of each isotope in plastic bottles filled with

distilled water. Our initial calibration efficiency factors were based solely on weight. Bottles of uniform diameter and twelve inches high were placed one on top of the other in the position which was to be occupied by the subject. The efficiency graphs thus obtained are shown in Fig. 1 and 2.

It is obvious, however, that height is of some importance. Unfortunately, not everyone who weighs 150 or even 190 lbs has the same or similar geometry. Some 190 lbs individuals are tall and thin, others of that weight are not tall and obviously not thin. To apply the same efficiency factor to both individuals can cause more error than we would like.

Therefore, the present calibration method was introduced. Isotope containing plastic bottles of six different diameters were used, thereby obtaining efficiency points for six weights each at heights from 3 feet to 6 feet 4 inches. These were obtained at 2 inch intervals. By applying calculus, Dr. Oberhausen was able to calculate an accurate calibration factor based on each subject's height as well as his weight. Fig. 3 and 4 were prepared from the efficiency charts thus obtained.

An examination of this data shows that identical net counts per second in two subjects of the same weight - one tall and thin; the other short and fat - can result in differences of up to about ten per cent in the calculated amount of the isotope present.

The potassium concentration levels plotted in Fig. 5 were obtained using our latest method of calibration. The lines represent the findings reported by Anderson and Langham (2) while the points are our results. Higher values found during adolescence with gradual decreasing levels among the older age groups were noted at both Los Alamos and Landstuhl.

Unfortunately, the newer method of calibration has not yet been applied to our cesium measurements. Fig. 6 shows the distribution of our first one thousand German residents. The average level was 80 μ curies cesium-137/gm potassium.

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Fig. 1. Cesium¹³⁷ efficiency versus weight.

Fig. 2. Potassium⁴⁰ efficiency versus weight.

Fig. 3. Cesium¹³⁷ counting efficiency versus subject's height and weight

Fig. 4. Potassium⁴⁰ gamma counting efficiency versus subject's height and weight.

Fig. 5. Potassium concentration in gm/kg of body weight versus age.

Fig. 6. Distribution for males and females in $\mu\mu\text{c Cs}^{137} / \text{g}$ potassium.

2. MEASUREMENT OF CONTAMINATED INDIVIDUALS

Erich Oberhausen*

The human counter with its superior geometric design offers the possibility of detecting incorporated gamma emitting isotopes at a level much lower than the maximum permissible concentration (MPC). Therefore, a number of German companies working with radioactive isotopes have taken advantage of the situation and periodically send their employees to be measured in the human counter. In several cases, incorporations much below the maximum permissible concentration were found.

Also, in the normal measurements of cesium-137 and potassium, about which Dr. Onstead has just spoken, a few individuals have been seen with high counts which could not be explained by their cesium-137 and potassium-40 content. Usually, these people had never worked with radioactive isotopes and had never even realized that they had had an incorporation. In those cases, the personal history was thoroughly checked and it was usually found that the individual has had an illness 20 or more years ago at which time thorotrast might have been administered. A special measurement was then made to be certain that it was thorotrast.

In order to make measurements which show what isotope was present in the contaminated individual and in what quantity, the counter was calibrated with the different

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isotopes in question. As very often there was an incorporation of more than one isotope, a way to separate the counts of the different isotopes had to be found. As the resolution in such a large liquid scintillation counter is very poor, one might think that this is impossible.

Figure 1 shows the gamma spectrum of different isotopes as measured in the counter. These spectra show a resolution of about 40% for the potassium-40 peak and of about 50% for the cesium-137 peak. As for cobalt-60, the two peaks at 1.1 and 1.3 MeV were not separated; but a big help in identifying cobalt-60 is the small peak at a higher energy which results from the summation of the two energies. Both radium-226 and thorium-228 have a large number of gamma lines in the spectrum and no differentiating peaks, but an overall energy distribution is characteristic, especially for thorium-228 with its high energy end. For these reasons, a particular energy measurement was never tried, but instead, measurements in several channels were made. From the ratio of the counting rates in the different channels, it was attempted to calculate which isotopes were present. Usually, measurements were made in three channels. One channel was fixed for the energy peak of cesium-137, the second for potassium-40, and the third covered an energy range from 1.8 to 3 MeV. With the first two channels fixed at the peak energies of cesium-137 and potassium-40, a correction for the normal potassium-40 and cesium-137 content of the human body could be obtained. With three channels there was the possibility of separating three different isotopes, providing the ratio of the counting rates was known. In most instances, not more than three isotopes would be incorporated. Up to now, there were no cases in which the isotopes present could not be identified. There would be a possibility that, by using a multichannel analyzer, four or five gamma emitting isotopes could be separated.

Now, I will present two examples of these measurements. The first was an isotope handler who was working with cesium-137, cobalt-60, radium and thorium. From his counting results in the first two channels, it was clear that he had an incorporation of cesium-137 and cobalt-60. The ratio of the counting rates in the second and third channels was the same as was found by an earlier calibration with just cobalt-60 in these channels. This shows that the individual had no appreciable amount of radium-226 and thorium-228 incorporated. These results were checked with several urine samples. The urine samples were ashed and then measured

Fig. 1. Gamma spectra from the Landstuhl Human Radioactivity Detector.

for alpha and gamma activity. However, only normal alpha activity was found in the urine. This would not have been the case if radium or thorium had been incorporated.

From measurements of exhaled radon, a second isotope handler was seen to have radium-226 incorporated. When this individual was measured in the human counter, the ratio of the counting rates for three channels was not as expected from the previous calibrations with radium-226. The counting rate in the first channel was much too high as compared with the second and third channel. Therefore, an incorporation of a second isotope with an energy similar to that of cesium-137 was suspected. A measurement of an ashed urine sample in a well type scintillation crystal showed clearly the cesium-137 peak. With a second measurement five months later, a biological half life of 144 days was calculated which was a second indication that it was cesium-137.

When calibrating the human counter for the measurement of radium-226 and thorium-228, it was taken into account that these isotopes are mostly deposited in the bones. Therefore, a polyethylene phantom, Fig. 2, (called Silent Sam) was used which has hollow spaces in the spinal column, arms, and legs. Into these hollow spaces glass tubes containing the isotope under consideration were inserted. Around the spaces (formed from polyethylene tubes) that contain the glass rods, distilled water was introduced to act as the body flesh.

Silent Sam has a second advantage in being hollow. When calibrating with thorotrast, the solutions could be placed at different parts of the body. The organs in which it is deposited, depending on the medical application, could be liver, spleen, kidney or neck tissue.

It was expected that from measuring these patients, the metabolism of the daughter products of thorium could be ascertained. Accordingly, a separation between the gamma rays of mesothorium and the daughter products of thorium-228 has been made, as shown in Fig. 3. Line No. 1 gives the gamma spectrum of a thorotrast solution, line No. 2 shows the gamma spectrum of thorium-228, and line No. 3 gives the difference of the two which is then the gamma spectrum of mesothorium. Taking the counting ratios of our three channels when measuring an individual who has incorporated thorotrast, the equilibrium between mesothorium and thorium-228 can be examined.

Fig. 2. "Silent Sam" the polyethylene phantom.

Fig. 3. Thorium spectra from the Landstuhl Human Radioactivity Detector

When comparing the Landstuhl results with those of Rundo (1), it is seen that the "wash-out" for the whole body is not as big as was found for separated organs. The explanation might be that part of the daughter products is washed out of the original deposits and then relocated at other parts of the body. All these measurements on thorotrast patients are part of a more extensive program which is now being conducted at the Landstuhl Human Radioactivity Detector and the Institute of Biophysics of the University of the Saar, Homburg.

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MEASUREMENTS OBTAINED WITH THE 2π LARGE VOLUME COUNTER
(GENCO) AND THEIR COMPARISON WITH THE RESULTS OBTAINED
FROM OTHER PHYSICAL OR CHEMICAL METHODS

Alexander A. Pfau and Georg Kallistratos*

External counting with large volume detectors of the liquid scintillation type offers mainly two advantages over similar devices using other detection techniques:

1. Less geometrical error introduced by the shape and the size of the object being counted, and

2. Relatively short counting times (100 sec.).

These factors are appreciated in routine as well as in diagnostic application of large volume counters.

In contrary to a so-called 4π counter now in use for several years in the U.S.A., we have a 2π counter available for our experiments. The outstanding feature of this type is its low price as compared to a 4π detector. But there is a disadvantage due to its incomplete geometry. Therefore the first topic of this report deals with geometrical problems in a 2π detector.

The second topic to be discussed is inherent in all γ ray spectroscopy. If the γ ray energies of an unknown

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mixture of radionuclides are the same or close together there is in most cases no other way for identification but conventional radiochemical procedures. By chance only a few fission products are absorbed to a broad extent by biological systems. Therefore large volume detectors of the liquid scintillation type can be used to determine the Cs-137 and K-40 content in human beings or in milk. But the Cs-137 contamination is not restricted to these objects alone. We thought it would be worthwhile to see how far a large volume liquid scintillation detector could be used for Cs-137 measurements in animal foodstuffs in which other fission products could interfere in Cs-137 and K-40 determinations.

Large volume counters were originally designed for low level counting. Therefore it is no wonder that strange effects can be observed if people contaminated with activities about 1 μ c shall be counted. From this reason the last topic of this report deals with phenomena observed if activities higher than 10^{-7} c Cs-137 were introduced in the large volume detector.

GEOMETRICAL PROBLEMS INVOLVED IN A 2π LARGE VOLUME LIQUID SCINTILLATION DETECTOR

A suggestion was made by Onstead (previous article) to introduce a calibration system for the 2π counter based on weight and height of the object being counted. The calibration curves obtained by such an ideal model of natural objects (for example human beings) should be checked for its reliability with a natural object which could be analyzed easily by other methods.

We decided to use hams for this purpose. The reason was threefold:

1. Hams have irregular external shape and enough lean meat to get sufficient counts due their K-40 content.
2. Size and weight of hams are not too great. They are easy to handle, complete ashing is no problem and the ash can be estimated conveniently for its K-content by a flame photometer.

3. If our model proved to be reliable we could compare our results with those reported by Kulwich, Feinestein and Anderson (1) who found a correlation between the fat-free lean of the ham and its K-40 content. Furthermore we could learn how far a simple calibration system would work if a 2π detector for K-40 studies on living animals should be designed.

Ten hams, five fat and five lean at random were selected. Table 1 shows the different fat hams as F-1 to F-5 and the lean ones as M-1 to M-5 and gives the approximate dimensions, the weight and the percentage of the different parts of the ham related to the total weight of each ham. The hams were counted in the middle position of the detector, then cut into 33 pieces (skin, bones, external fat and lean) and each part was counted again, and weights of these parts were determined. The internal fat of the lean meat was estimated and from this the fat-free lean was calculated. All parts were ashed at 400°C . The K content of ash of the different parts as well as the total ham ash was estimated by flame photometry. The error of the counting and the flame photometric procedures could be estimated to be not more than 5% in all measurements.

Table 2 shows the total K content and the percentage of K in different parts of the various hams obtained by flame photometric measurements. The values for the external fat seem to be relatively high. But this might be due to the fact that it is very difficult to remove all the meat from the fat.

In Table 3 the results of K obtained by external counting, using the calibration diagram (Fig. 1) for the calculations of the K content, are compared with the results obtained by flame photometry.

The values of the total K obtained by analytical method fairly agree with the values obtained by radioactivity measurements. Therefore the calibration system, by taking weight and height into consideration, is proved to be reliable. If the calibration had to be done only on the weight basis, there would be clear discrepancy between the counted and the analyzed values.

TABLE 1. DIMENSIONS, WEIGHT AND PARTS OF HAM IN PERCENT OF TOTAL WEIGHT.

Ham No.	Dimensions cm	Weight kg	Parts of Ham in % of Total Weight					
			Bones %	Skin %	int. %	Fat ext. %	total %	Lean Fat-Free %
F-1	46x29x14	9.67	10.25	5.89	5.48	31.71	37.19	46.67
F-2	40x34x15	11.64	8.97	6.62	4.28	32.75	37.03	47.37
F-3	45x27x15	9.74	9.11	4.94	3.67	39.33	43.00	42.95
F-4	51x30x18	10.18	8.84	4.36	3.97	37.51	41.48	45.33
F-5	51x32x17	10.56	9.69	6.15	2.27	37.38	39.65	44.51
M-1	45x30x16	12.11	8.09	4.95	4.85	29.95	34.80	52.18
M-2	44x27x17	11.84	8.31	4.51	5.07	35.46	40.53	46.65
M-3	49x29x18	12.94	8.66	5.12	3.95	32.92	36.87	49.74
M-4	43x26x17	10.90	6.32	4.27	2.52	35.21	37.73	51.68
M-5	45x30x18	12.47	6.39	4.57	3.43	39.19	42.62	46.42

TABLE 2. TOTAL K IN HAM AND PERCENTAGE OF K IN VARIOUS PARTS OF THE HAM
OBTAINED BY FLAME PHOTOMETRIC MEASUREMENTS.

% of K in Various Parts of the Ham							
Ham No.	Total K in Ham (analyzed) g	Bones %	Skin %	int. %	Fat ext. %	total %	Fat-Free-Lean %
F-1	17.78	3.45	1.95	2.31	13.39	15.70	78.90
F-2	20.56	3.93	2.92	1.42	15.29	16.71	76.68
F-3	18.12	3.16	1.61	1.60	16.94	18.54	76.70
F-4	18.49	2.89	1.22	1.42	13.20	14.62	81.27
F-5	17.41	3.76	2.95	1.00	16.48	17.48	75.82
M-1	22.96	2.88	1.87	1.39	8.59	9.98	85.26
M-2	20.24	3.00	1.72	1.45	10.12	11.57	83.71
M-3	24.20	2.89	1.90	1.67	13.93	15.60	79.50
M-4	22.02	2.04	1.29	0.84	11.74	12.59	84.08
M-5	23.33	2.19	1.51	1.32	15.05	16.37	80.00
Mean values		3.03	1.91	(1.44)	(13.47)	14.92	80.19

TABLE 3. TOTAL K IN HAM AND IN LEAN PORTION OF THE HAM OBTAINED BY EXTERNAL COUNTING AND BY FLAME PHOTOMETRIC MEASUREMENTS.

Ham No.	Total K in Ham		K in Lean Portion of Ham			
	analyzed g	counted g	analyzed g/kg	counted g/kg	counted single g/kg	counted together g/kg
F-1	17.78	17.49	2.86	2.91	3.05	3.27
F-2	20.56	21.48	2.88	2.87		
F-3	18.12	16.04	3.12	3.10		
F-4	18.49	17.62	3.05	3.13		
F-5	17.41	18.27	2.88	3.19		
M-1	22.96	24.06	2.88	3.29	3.14	3.29
M-2	20.24	22.88	2.82	3.29		
M-3	24.20	24.96	2.83	3.22		
M-4	22.02	22.11	3.16	3.27		
M-5	23.33	22.67	3.04	2.93		

Figure 1. Calibration diagram for K in k-40 channel. Grams of K per net counting rate against weight (density $\sim 1 \text{ g/cm}^3$) with the height of the object as parameter.

Table 4 shows a comparison between the gravimetric determinations of the fat-free lean of the hams in percent

TABLE 4. FAT-FREE LEAN OF THE HAM IN % OF THE TOTAL WEIGHT AND GRAMS OF K RELATED TO THE TOTAL WEIGHT OF THE HAM OBTAINED BY GRAVIMETRIC AND K-40 MEASUREMENTS.

Ham No.	Fat-Free Lean of Ham in % of Total Weight %	Grams of K Related to Total Weight of Ham (counted) g/kg
F-1	46.67	1.81
F-2	47.37	1.85
F-3	42.95	1.65
F-4	45.33	1.73
F-5	44.51	1.73
M-1	52.18	1.97
M-2	46.65	1.93
M-3	49.74	1.93
M-4	51.68	2.03
M-5	46.42	1.81

of the total weight and the content of K in grams as related to the total weight of the hams obtained by K-40 measurements. The values indicate a correlation for the fat-free lean and the K content related to the total weight of the hams. But the nondestructive method of the K-40 determination is too coarse to show slight variations in the fat-free lean of the hams. Even to get the radiometric results of Table 4 a counting time of 33 min. for each ham was necessary without taking into consideration that the same amount of time had to be spent on the background counts too.

Therefore in our opinion the nondestructive method of determining the lean portion of the ham by its K-40 content has no practical value because in this case the K-40 yield in ham is too small and for this reason the counting time

for significant results is too long. The situation is improved by using a whole animal instead of a single part.

In Table 5 the specific K content was calculated on the basis of our ham results for the different parts of a swine. In a rough estimation one should expect at least as many counts as necessary to operate a 2 π counter by normal counting times (100 sec.) used for measuring human beings.

TABLE 5. EXPECTED TOTAL NET COUNTING RATE FOR A 110 kg. SWINE IN A 2 π COUNTER.

Parts of Swine	Weight (mean values of 305 animals 208 days old) kg	Mean Values of K g/kg	Expected Net-Counting Rate in 2 π counter cps
Lean Port.	36.54	3.01	37
Fat	32.90	0.695	8
Bones	11.29	0.648	2
Skin	5.57	0.658	1
Other Parts	23.71	?	?
110.00 kg Total Weight		48 cps Total Net-Counting Rate	

(1 g $\cong$ 0.3 cps)

At the moment it is uncertain if this K-40 determination would be of any value to a slaughter house. We think more investigation on the biological side of the problem has to be done until this external K-40 determination as an indicator of internal lean percentage of an animal can be introduced in practice. Especially more experimental data of the K-content of the different parts of the body of the animal must be obtained and the K content as function of the age of the animal must be studied. But besides this,

the experiments done, showed the reliability of the calibration system based on weight and height of the object being counted in a 2π detector.

PROBLEMS INVOLVED IN Cs-137 MEASUREMENTS IN OTHER OBJECTS
THAN IN MAN AND MILK

The energy resolution (half-width at half-height) for the K-40 peak in a liquid scintillation detector was reported to be 30% for a 4π counter and 18% for a 2π counter (2). The equivalent value for a NaI crystal of maximum dimension is about 3-5%.

The γ ray energy discrimination for a NaI crystal still remains a problem. It becomes obviously more complicated if one uses a liquid scintillation detector. There are no difficulties if the radionuclides are known like in medical diagnosis with the human or animal bodies' natural discrimination against certain radionuclides. Therefore Cs-137 measurements in man and milk can be done without any interference of other radionuclides. But if one wants to use the same nondestructive method for other objects, for example animal foodstuff, to get experimental data for the chain of contamination--animal foodstuff—> domestic animals —> animal products —> man--one must be aware that other gamma emitting fission products are present which show higher Cs-137 or K-40 activities than is really present.

The bomb tests were stopped in autumn 1958, and in autumn 1959 we tried to measure the Cs-137 content in animal foodstuffs grown at the field station of Mariensee near Hannover, Germany, by external measurements in the 2π detector.

About three metric tons of foodstuff could easily be measured in two days. The results were reported as activities in the Cs-137 channel and as activities in the K-40 channel for the different foodstuffs (3).

The activities, especially for all products grown above the soil, turned out to be rather high in both the

Cs-137 channel and K-40 channel, and the potassium values were not in agreement with the values obtained by flame photometric measurements. Better agreement in the K values could be found for all products grown protected by outer shells like corn, rye, etc. All fruits grown underneath the soil like turnips or potatoes showed nearly the same values for both K measurements.

From this we concluded that differences between the K values from both methods could be used as an indicator for the presence of fission products other than Cs-137, but only in a very rough qualitative manner.

If one keeps in mind that the bomb tests were stopped in autumn 1958 and if it is so that radionuclides produced as induced activity during a nuclear explosion can be neglected because of abundance of total activity of other long living fission products which is 10 to 100 times more than induced activity, then there are only two fission products Zr-Nb-95 and Ru-Rh-106 which must be taken into consideration for their interference in Cs-137 and K-40 measurements with a 2π liquid scintillation counter.

That these radionuclides are really present can be seen from Figure 2 which gives a γ ray spectrum of three representative foods mentioned above. The gamma spectra were made with a NaI crystal and a 256 channel analyzer. Besides the expected energy peaks at 0.66 Mev and 1.46 Mev due to Cs-137 and K-40 there are peaks at 0.51 Mev and between 0.72 and 0.77 Mev for hay, a slight indication at 0.51 Mev for rye, but there is no additional peak for fodder beets. All three results are in agreement as predicted on the discrepancies of the K measurements.

Though an abnormally high K-yield as a result of the K-40 measurements may be used as a quantitative indicator for additional fission products contamination, from this there is only a rough estimation possible to get the true value of the Cs-137 contamination. If one looks at the decay scheme of Ru-Rh-106, there are energy peaks at 0.51 Mev with 11% gammas per disintegration, at 1.55 Mev with 3% gammas per disintegration and at 1.13 Mev with 12% gammas per disintegration, while Zr-Nb-95 has gamma energy lines at 0.75 Mev with 49% gammas per disintegration, at 0.72 Mev with 49% gammas per disintegration and at 0.77 Mev with 100% gammas per disintegration which could interfere in Cs-137 or K-40 measurements.

Figure 2. Gamma ray spectra of hay, rye and fodder beets grown 1959 at the fieldstation of Mariensee nearby Hannover, Germany

Gammas from Zr-Nb-95 do not appear in the K-40 channel of the 2π liquid scintillation counter. Therefore there is no way in estimating their contribution to the Cs-137 channel. Gammas from Ru-Rh-106 should appear in both the K-40 and the Cs-137 channel. The ratio of their appearance due to the percentage per one disintegration is expected to be about 1:4 for the ratio of K-40 to Cs-137 channel. Therefore if the ratio of the K radio-measurement and the K flame photometric determination is multiplied by 4 and then the activity of the foodstuff obtained in the Cs-137 channel is divided by this factor a better approximation for the Cs-137 activity should be obtained.

In Table 6 the Cs-137 activities in the Cs-137 channel, the K yield obtained in the K-40 channel, the Cs-137 activities found by chemical analysis and the flame photometric K estimations are listed. In the last column the estimated Cs-137 content calculated by the way described above is given.

It is true of course that in case of the foodstuffs the 2π liquid scintillation counter shows only true Cs-137 activity if by biological discrimination turnips and potatoes, in our case, have no measurable other fission products absorbed. But using a large volume counter for routine gamma ray activity determinations of foodstuffs it is worthwhile to know that the potassium value sometimes can be used, for products grown above the ground, as an indicator of additional contaminations. If by other means the presence of other long living gamma ray emitting fission products can be determined, which interfere both in Cs-137 and in K-40 channel, a rough calculation can be made by the K-ratio of the counted and analyzed values and the ratio of the contributions of the interfering radionuclides in both channels.

BEHAVIOR OF THE 2π LANDSTUHL COUNTER WITH ACTIVITIES HIGHER THAN 10^{-7} CURIES Cs-137

If activities of Cs-137 and K-40 in the Landstuhl 2π counter are not higher than 10^{-7} c the spectra of point and extended sources look like those shown in Fig. 3. It can

TABLE 6. COMPARISON OF THE Cs-137 AND K-40 RESULTS OBTAINED BY DIFFERENT METHODS.

Foodstuff From Marien- see, 1959.	Activity in Cs-137 channel 10^{-10}c /kg	K measured in K-40 channel g/kg	Radio- chemical Cs-137 Ana- lysis 10^{-10}c /kg	Flame photometric K Analysis g/kg	Approximate Cs-137 yield (calculated) 10^{-10}c /kg
Clover grass mixture (Hay)	72.7	34.6	3.45	14.8	7.2
Rye	3.94	4.08	1.23	4.24	--
Turnips (Ovana)	0.16	3.85	0.22	3.75	--

Figure 3. Gamma ray spectra of Cs-137 and K-40 from point and extended sources. For comparison purpose the normal spectra are related to the same activity. The channel width for the K-40 measurements is indicated.

clearly be seen that for some activities the maxima for point sources in comparison to extended sources are in both cases (Cs-137 and K-40) higher and shifted to higher energies. This effect must be kept in mind if a large volume counter has to be calibrated for the settings of the Cs-137 and the K-40 channel of the discriminator threshold and channel width. If the activity, for example in Fig. 3 for Cs-137, is increased using an extended source not only the maximum of the peak will be increased but also the bases of the curves. That means the spectrum is widened in such a way that it looks like a shift of the whole spectrum of Cs-137 to higher energies. The more activity is used the more counts can be observed in the K-40 channel until the complete activity due to K-40 is covered by the counts due to Cs-137 (Fig. 3).

The efficiency (cps/dps) for Cs-137 counts in the K-40 channel does not remain constant any longer. It is as one can see from Fig. 4, a function of the activity (net counting rate in Fig. 4) of the source used.

If this efficiency versus net counting rate curve, which seems to be a straight line in the range covered by Fig. 4, is watched for a few weeks it can be noticed that the calibration points fluctuate, but all points lie on straight lines (Fig. 4). Because counting rates of Cs-137 activities higher than 10^{-7} c will block the mechanical register of the scaler of the Cs-137 channel, the result of the Cs-137 measurements in the K-40 channel represented in Fig. 4 could be of help in estimating the body burden of a person who was contaminated by Cs-137 in the range of 10^{-6} c.

The person and the calibration sources were measured at the same intervals (Fig. 4). In the meantime urine and fecal excretion measurements of the same person were done. Due to the fluctuation of the calibration curve after 28 days when the second whole body counting was made the first measurement had to be corrected.

The results of all the measurements are shown on the right side of Fig. 4. From this table it can be seen that the agreement between the whole body counting and the excretion measurements is pretty good. The limiting factor using this method for higher activities is set to be the mechanical register in the scaler.

Though the effect of the shifting of the spectra of

Figure 4. Net counting rate against efficiency for Cs-137 in the K-40 channel. On the right side of the diagram the values for the whole body and excretion measurement for Cs-137 are given.

Cs-137 for higher activities is not quite clearly understood at the moment, it must be stated for future designing of large volume counters of the liquid scintillation type for measuring human bodies, to improve the electronic part of the machine in such a manner that the activity range from 10^{-10} c to 10^{-5} c can easily be covered, avoiding such effects described above.

SUMMARY

To summarize our experiments and experience with the 2π Landstuhl large volume liquid scintillation counter (abbreviated GENCO) we would say the incomplete geometry is no handicap in getting significant results if a calibration system as described by Onstead is used. The reasonable price in comparison to a 4π counter recommends the counter for routine work itself. The measurements of different objects must be of course restricted to such items from which the kind of the radionuclide to be measured is known or can be learned by other methods. In this connection it would be good to combine the 2π counter with a NaI crystal device in one unit. In doing so the vertical arrangement used in Landstuhl must be changed back to the horizontal version like in use for 4π counters.

The electronic part of the unit should by future designers be improved in such a way that the upper limit should be at least 10^{-5} c to cover the important range of clinical application of a whole body counter and to give a chance to measure human body contaminated in the level around $1 \mu\text{c}$ without any complicated calibration system as described.

Using large volume counters for lean meat determinations on the basis of K-40 measurements should be of no practical value for single parts of an animal (ham, for example) because the K-40 content is too low, and therefore the counting time too long for significant results. Things will improve if whole animals can be measured. For these studies a horizontal 2π counter or better two 2π counters which are movable against each other would be versatile

instruments. The correlation between fat-free weight and the potassium yield in ham found by other investigators could be confirmed. But to decide if this method can ever be used in practice for living animals is still a problem for biological research.

ACKNOWLEDGMENT

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Diagnostic Radio-Vitamin B₁₂-Absorption and Retention
Studies with Test-Radioactivities which are within the
Range of the Natural Radioactivity Content of the Human
Body using the Landstuhl 2 π -Whole Body Detector

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A. Introduction

The estimation of the absorption and the retention of tracer doses of ⁵⁸Co- or ⁶⁰Co-labeled vitamin B₁₂ in human beings is presently of considerable interest in the diagnosis and differential diagnosis of different haematological, neurological and gastrointestinal diseases. The application of the different radio-vitamin B₁₂-absorption-tests as routine methods in clinical diagnosis is described in detail elsewhere (HEINRICH, 1960b). Radioactive vitamin B₁₂ was also used during the last 9 years for several hundred more fundamental studies on the intestinal absorption, "in vivo"-retention, excretion and other phases of the vitamin B₁₂-metabolism in animals and human beings.

Mostly the clinical and biochemical investigations were performed with the help of "in vitro" counting arrangements measuring the γ -emissions of cobalt-labeled vitamin B₁₂ in more or less large samples of urine, faeces, blood or organs and tissues. The disadvantages of these "in vitro"-techniques for example in the analysis of the intestinal absorption and total body retention of radio-vitamin B₁₂ for diagnostic purposes are: unreliable cooperation of patients and nurses in the collection of excreta (faeces and urine), time consuming, uncovenient and unpleasant procedures in the preparation of the test samples from the collected excreta. But the most limiting factor in the broad clinical application of these tests

is the amount of radioactivity required for a reliable performance of the "in vitro" tests. The radiation hazard introduced into the patients body especially with several repeated oral radio-vitamin B₁₂-absorption-tests is not negligible, since between 0,25 and 5 µC of ⁵⁸Co- or ⁶⁰Co-labeled vitamin B₁₂ are still today routinely used in the faecal-, urinary- and blood-tests.

Through the introduction of a combined annular beaker-welltype-scintillation detector (HEINRICH u. Mitarb., 1958; PFAU u. HEINRICH, 1959) it was at least possible to operate the radio-vitamin B₁₂-absorption-faecal- and -urinary-excretion-tests with low test radioactivities like 50 nC of ⁶⁰Co-B₁₂. But all the other disadvantages of the "in vitro"-procedures for the estimation of intestinal vitamin B₁₂-absorption are still remaining.

Therefore we became interested in the development of a test which (1) does not any longer require the cooperation of patients and nurses in the collection of excreta (2) does not require inconvenient and unpleasant procedures in the counting sample preparation from the collected excreta (3) is so sensitive that test radioactivities in the range of the natural radio-activity content of the human body are sufficient and (4) permits quantitative and rapid conclusions on the degree of the intestinal absorption and whole body retention of radio-vitamin B₁₂.

A liquid scintillation whole body detector was finally found to be extremely useful for the development of a radio-vitamin B₁₂-absorption-whole body-retention-test (= Radio-B₁₂-WBRT), which fulfills all the essential requirements given above.

B. Methods

In close cooperation with Dipl.Phys. A. PFAU (Max Planck Institute for Animal Nutrition, Mariensee near Hannover), Dr. E. ANDERSON and Dr. F.N. HAYES (Biomedical Research Group, Los Alamos Scientific Laboratory/New Mexico) and Dr. Ch. ONSTEAD (US Army Medical Research Unit No. 1, US-Hospital for Europe, Landstuhl) it was possible for us to use the Landstuhl 2π-Whole Body Detector for the development of the Radio-B₁₂-WBRT. Physical and technical data for the Landstuhl-2π-Whole Body Detector - which was originally developed and

operated for the 2nd. Geneva Conference on the Peaceful Uses of Atomic Energy - are given in detail in two publications of ANDERSON et. al. (1958).

Using point sources of $^{60}\text{Co-B}_{12}$ in front of the concave scintillator tank over-all efficiencies of 48 % can be obtained if the discriminator settings include the potassium-40 and cesium-137 channels. In our studies we used the potassium 40-channel for the measurement of ^{60}Co and the ^{137}Cs -channel was useful for ^{58}Co -measurements. However a special discriminator setting (the ^{58}Co -channel) was practical for more sensitive ^{58}Co -counting and therefore used in double-labelling experiments as a third channel.

The overall-efficiencies for the three channels and the used isotopes (^{58}Co and ^{60}Co) as point sources are given in table No. 1.

Table 1: Percentage sensitivity ($E\% = \frac{\text{cpm} \cdot 100}{\text{dpm}}$) for ^{58}Co and ^{60}Co in the three counting-channels.

(radioactive sample as point sources in the center of the detector)

Test-	^{137}Cs -channel	^{58}Co -channel	^{40}K -channel
Radioactivity	(0,65 - 1,55)	(0,75 - 2,30)	(2,25-4,05)
$^{60}\text{Co-B}_{12}$ (10,14·10 ⁻⁹ C)	12	-	33
$^{58}\text{Co-B}_{12}$ -Coenzym (24,66·10 ⁻⁹ C)	35	52	4

C. Results and Discussion

After oral uptake and the "in vivo" distribution of the radio- B_{12} in the human body the overall-efficiency depends mainly on the geometric relation between the individual (size, diameter, fat content a.o.m.) and the detector. Immediately after oral uptake the radio- B_{12} is localized in the stomach and the upper duodenum of human

beings. The overall-efficiency of the 2π -detector then is between 8 and 13 % (Table 2). Usually after one day the "in vivo" distribution of the absorbed (liver and muscle incorporated) and unabsorbed vitamin B_{12} is approaching the optimal detector sensitivity and the highest values for the overall efficiency (12-15 %; table 2) are obtained. After this time the variations of the geometry depending overall efficiencies in the 2π -detector can be considered by the use of correction factors. They are less significant if 4π -Whole Body Detectors are used.

After 2 days the decrease of the overall-efficiency is mainly caused by the faecal excretion of the small amount of unabsorbed radio-vitamin B_{12} (fig. 1). After completed faecal excretion of unabsorbed radio-vitamin B_{12} the further reduction of the overall-efficiency can be used for the calculation of the biological half life or the turnover time of the mainly in the liver and muscle incorporated radio-vitamin B_{12} . In table 2 the overall-efficiencies are given as the percentage sensitivity for three volunteers during different phases of the intestinal $^{60}\text{Co}-B_{12}$ -absorption.

For the same three volunteers the net counts in the ^{40}K -channel are given in figure 1 as cps in relation to the elapsed time and phase of intestinal radio-vitamin B_{12} -absorption. From this figure 1 and the preceeding tabulars it is possible to understand the details in the performance of the radio- B_{12} -WBRT:

1. In the first measurement before the oral application of the $^{60}\text{Co}-B_{12}$ -tracer dose the original or basal radioactivity¹² in the patient (approximately 10^{-8}C natural ^{40}K in the muscle and about 10^{-8}C ^{137}Cs from nuclear weap on fall out) is estimated in the ^{40}K - and ^{137}Cs -channels, since it has to be considered in the calculation of the results. During this measurement also other radioactive contaminations from fall out, diagnostic radioisotope application or other sources will be recognized. The first measurement like all others are done in triplicate over 100 seconds each.
2. Then between 0,10 and 1,0 μg radioactive vitamin B_{12} labeled with about 10 nC (10^{-8}C) ^{58}Co or ^{60}Co are first counted for control purposes as a point source in the 2π -Whole Body Detector and are then administered

Fig. 1. Radio-vitamin B_{12} -absorption data for 3 subjects.

Table 2: Percentage sensitivity ($E_{\%} = \frac{\text{cpm} \cdot 100}{\text{dpm}}$) for $^{60}\text{Co-B}_{12}$

"in vitro" as well as "in vivo" before, during and after intestinal absorption of the $^{60}\text{Co-B}_{12}$ (in the ^{40}K -channel)
(calculated on the theoretical basis of 100 % retention)

^{40}K -channel
(2,25 - 4,05)

Test-radioactivity "in vitro"
($10,14 \cdot 10^{-9}\text{C } ^{60}\text{Co-B}_{12}$)
as a point source in the
detector-centre

33,2

Test-radioactivity "in vivo"

volunteers

Time after oral appli- cation	phase of B_{12} -ab- sorption or excretion	σ	σ	η
		164 lbs (H)	174 lbs (K)	132 lbs (W)
5-15 min.	in the stomach be- fore absorption	11,1	8,2	13,4
8 hours	during absorption	12,3	10,5	15,0
19 "	absorption finished	13,5	12,1	15,5
32 "	" "	13,8	12,0	14,4
44 "	beginning faecal excretion of unab- sorbed B_{12}	11,3	11,2	14,8
Absorption		65 %	91 %	87 %
56 "	faecal excretion of B_{12}	8,8	10,7	13,4
95 "	faecal excretion finished	8,9	11,1	13,5

orally to the patient. Again only for control purposes it is advisable now to measure the patient who now contains all the test radioactivity - still unabsorbed - in the stomach and the upper duodenum. If the container of the test-radioactivity was washed 5-8 times with water practically no radio- B_{12} (detectable in the 2 - whole body counter) remains.¹² The washings are administered to the patients immediately after the original content of the container.

3. One day after the oral uptake of the radio- B_{12} -test-solution the patients are measured again (3×12 times for 100 seconds) since now the highest values for the overall efficiency - caused by an optimal distribution of the absorbed and the small amounts of unabsorbed radio- B_{12} within the human body - will be obtained and are representing the 100 % reference point. All total counts in the different channels have to be corrected for the ^{40}K - and ^{137}Cs -content of the individuals. Also differences in the sample-detector geometry which effect the overall-efficiency (e.g. different sizes and diameters of the patients) can be more or less easily corrected to a standard value.
4. After 7 days the (in the normal individual small) amounts of unabsorbed radioactive vitamin B_{12} are nearly completely excreted with the faeces.¹² Therefore all remaining vitamin B_{12} radioactivity now represents the absorbed radio- B_{12} which is incorporated and retained in the main B_{12} -storage organs and tissues (e.g. liver, skeletal muscle). For the calculation from the counts in the ^{40}K - or ^{137}Cs -channels the ^{40}K - and ^{137}Cs -content of the patients is subtracted and then for example the ^{60}Co - B_{12} -counts in the ^{40}K -channel or the ^{58}Co - B_{12} -counts in the ^{137}Cs -channel compared with the corresponding values for the 100 % reference point (1 day after oral B_{12} -uptake). The intestinal absorption and consequent retention of the absorbed radio- B_{12} in the whole body can be calculated in % of the oral Test radioactivity.

As shown on table 3 the results which were obtained with ^{60}Co -labeled Cyanocobamid and ^{58}Co -labeled B_{12} -Coenzym using the 2π -Whole Body Detector are in excellent agreement with the results of the radio-vitamin B_{12} -absorption-faecal-excretion-test. With both tests it is evident that the labeled vitamin B_{12} is much better absorbed than its Coenzym. This has been confirmed in the meantime also

for other organisms (rats and guinea pigs) and with "in vitro" counting-methods (HEINRICH u. Mitarb., 1960).

Table 3: Intestinal Absorption of ^{60}Co -Vitamin B_{12} and ^{58}Co -Vitamin B_{12} -Coenzym in Norman Human Beings as measured with the 2 π -Whole Body Detector and the Faecal Excretion-Test

Radio-Vitamin B_{12} - Absorptions-Test	0,50 nMol ^{60}Co -Vitamin B_{12}	0,50 nMol ^{58}Co -Vitamin B_{12} -Coenzym
Total body-retention-test (0,50 nMol ^{60}Co - B_{12} = 10 nC)	59 - 90 % (3)	51 - 54 % (3)
Faecal-excretion-test (0,50 nMol ^{60}Co - B_{12} = 100 nC)	55 - 88 % (110)	32 - 55 % (11)

The retention of the incorporated ^{60}Co - B_{12} was measured in three volunteers over a period of 12 months. From this study we know that the biological half life of vitamin B_{12} in the human body is not a constant value. From the 2nd. to the 7th. week after incorporation the biological half life is increasing from 150 to 300 days (Fig. 2). After the 8th. week the biological half life is continuing to increase till it finally approaches a value of 400 days (turnover time = 800 days). These values agree with the results of liver surface scintillation countings and excretion studies (see for references HEINRICH, 1960a). They correspond to a final vitamin B_{12} turnover rate of 0,125 % of the B_{12} -body pool/day. Since the total body content of a normal human being is at least 5 mg (see for references HEINRICH, 1960a), the turnover rate is at least 6,25 μg vitamin B_{12} /day. But the results concerning the estimation of the turnover rate of vitamin B_{12} are only of preliminary value, since we presently do not know how many different metabolic pools of the vitamin B_{12} are existing in the cell or the total body. All calculations are done on the possibly wrong assumption that there is only a single vitamin B_{12} -metabolic pool. The biological half life (400 days) or the turnover time

(800 days), which was measured in the 2π -whole body detector can easily represent just the average of several turnover times of several different vitamin B₁₂-pools, which individually can have not identical turnover rates.

Figure 2: Whole Body Retention of ^{60}Co -Vitamin B₁₂ after oral application of 0,50 nMol (= 10,14 nC) ^{60}Co -B₁₂ to normal persons as measured over 65 days with a 2π -Whole Body Detector.

(The average of the values from three volunteers is given in percent of the 24 hour-(100 %)-reference point, see text).

Much more delicate techniques are required for the solution of such a complex problem. Presently we do not know anything about the intermediar metabolism of the B₁₂-structure. But there is the possibility that the estimation of the turnover time of absorbed or injected radio-vitamin B₁₂ can be of importance in the clinical diagnosis of diseases which are connected with alterations in the turnover time of the B₁₂-vitamin.

Approximately 10 months after the body incorporation of the absorbed ^{60}Co -vitamin B₁₂ it was possible through the kindness of Dr. Marvin A. van DILLA, to measure one of the volunteers with a large (9" x 6") NaI-Crystal-Spectrometer at the Los Alamos Scientific Laboratories. The γ -spectrum obtained in a 30 min. counting period is given in fig. 3 and shows the peaks of the natural ^{40}K content, the ^{137}Cs -fall out contamination (about 14 nC ^{137}Cs) and the 1,17 MeV-peak of the incorporated ^{60}Co -B₁₂.

Fig. 3. Gamma-spektrum einer Versuchsperson (H.) 10 Monate nach oraler Verabfolgung von: 10 nC ^{60}Co -Vit- B_{12} ; gemessen m. 20 x 15 cm NaJ(Tl)-Scintillations-Spektrometer-Detektor der Los Alamos Scientific Laboratory.

The 1,33 MeV ^{60}Co -peak is overlapping with the left side of the ^{40}K -peak.

The ^{60}Co - B_{12} -retention (as well as the ^{137}Cs and ^{40}K -content) in this volunteer was estimated with three different whole body detectors: the 2π -Liquid Scintillation Detector at Landstuhl (Genco), the 4π -Liquid Scintillation Detector at Los Alamos (Humco I) and the 9"x6" NaI-Detector at Los Alamos. The values obtained with the three detectors are in reasonably good agreement.

In the diagnostic application of radioisotopes in nuclear medicine the sometimes considerable radiation burden by amounts of test-radioactivities, which are very often far away from being real tracer doses (e.g. 1-100 μC of different radioisotopes are used in many routine applications of radioisotopes in clinical diagnosis) is normally neglected. With already a single test in some cases 100 % or more of the maximum permissible incorporation radioactivity for the total body or critical organ are incorporated and the radiation burden with several repeated tests comes up to the limit or even more than the maximum permissible total body radiation burden (100 m rem/week).

Therefore it is highly desirable to use super-sensitive radiation detection equipments especially in nuclear medical diagnosis, allowing the application of test radioactivities which are so low that they do not offer any longer any radiation hazard for the patient. The utmost of course would be the use of test radioactivities which are within the range of the natural radioactivity content of the human body (10^{-8}C ^{40}K , $8 \cdot 10^{-8}\text{C}$ ^{14}C and 10^{-10}C ^{226}Ra) and the unavoidable contamination of the human being with radioactive fall out products from nuclear weapons (10^{-8}C ^{90}Sr and ^{137}Cs).

"In vitro" counting equipments offer already a certain approach to the problem, since the sensitive annular beaker arrangement of a NaI-Scintillation detector makes possible the application of only $5 \cdot 10^{-8}\text{C}$ of ^{60}Co - or ^{58}Co -labeled vitamin B_{12} in the urinary- and faecal excretion test (PFAU u. HEINRICH, 1959). By the application of 4π -liquid or plastic scintillation detectors with effective detector volumes of 1-10 liters it can be expected that even $1-2 \cdot 10^{-8}\text{C}$ of labeled vitamin B_{12} would be sufficient for a reliable test. Presently however the use of a 2- or 4π -Whole Body

Detector represents the most sensitive technique in the measurement of incorporated and retained γ -emitting radioisotopes and is by a factor of at least 5-100 more sensitive than the different conventional "in vitro" counting procedures in nuclear medical diagnosis.

In table 4 the several biological, medical and biophysical data for the five radio-vitamin B₁₂-absorption tests, their advantages and disadvantages are summarized. From this comparison it can be easily concluded that the radio-vitamin B₁₂-absorption-Total Body Retention Test is by far the most reliable, convenient and sensitive test for the estimation of intestinal absorption, total body retention and many other phases of vitamin B₁₂-absorption.

For the first time in the diagnostic application of radioisotopes in nuclear medicine it is now possible to work with test-radioactivities which are within the range of the natural radioactivity-content of the human body and therefore do not represent any longer any radiation hazard.

With the radio-vitamin B₁₂-absorption-Total body retention-Test the biological radiation burden from the incorporated and retained test radioactivity of 7 μC ⁶⁰Co-B₁₂ (equal to 0,07 % of the maximum permissible ⁶⁰Co-incorporation radioactivity of 10 μC) was calculated to be only 50 μ rem/week (table 4).

The natural radiation burden for the human being from exogeneous sources (cosmic rays and environmental irradiation) and endogeneous sources (⁴⁰K, ¹⁴C, ²²⁶Ra, ⁹⁰Sr and ¹³⁷Cs) is presently about 5,5 m rem/week (for details see table 5). Therefore the biological radiation burden introduced with a single radio-vitamin B₁₂-absorption-whole body retention-test into the human body (0,05 m rem/week) does not represent more than 1 % of the natural radiation burden from exogeneous and endogeneous sources which influence life already for more than several million years without demonstrated harmful effects. No more restrictions in the diagnostic application of γ -emitting radio-nuclids during pregnancy, childhood and other radiation-sensitive situations are any longer necessary, if a sensitive organic scintillation-whole body counter is available as a detector.

Table 4: Survey on different biomedical and radiobiological data for the five Radio-Vitamin B₁₂-Absorption-Tests

(All biophysical data are calculated for ⁶⁰Co; the maximal permissible incorporation-radioactivity for ⁶⁰Co is 10 μ C, which represents a total body radiation burden of 77 mrem/week (<100 mrem/week))

Radio-Vitamin B ₁₂ - Absorption-Test	<u>counting</u> <u>technique</u> <u>and</u> <u>sample</u>	<u>required</u> <u>time</u> <u>for</u> <u>assay</u> (days)	<u>quantita-</u> <u>tive check</u> <u>for</u> <u>absorption</u>	<u>possible</u> <u>errors</u> (by pa- tients, nurses, techni- cians)	<u>influence</u> <u>on assay</u> <u>by</u> <u>diseases</u> <u>of</u>
FET = Faecal-Excretion-Test	"in vitro" <u>faeces</u>	5 - 8	yes	yes (lost fae- ces)	-
UET = Urinary-Excretion-Test	"in vitro" <u>urine</u>	2 - 3	limited	yes (lost urine)	kidney
BCT = Blood-Concentration- Test	"in vitro" <u>blood</u>	0,5	no	no	-
LIT = Liver Incorporation- Test	"in vivo" <u>liver</u>	5 - 8	no	yes (reproduci- bility of geometry)	liver
WBRT = Whole-Body-Retention- Test	"in vivo" <u>total body</u>	5 - 8	yes	no	-

Table 4 (continued)

Radio- Vitamin B ₁₂ - Absorptions- Test	<u>B₁₂-metabolism</u> <u>or clinical</u> <u>situation</u> influenced by assay	<u>⁶⁰Co-B₁₂-Test-</u> <u>minimal</u> <u>Radioactivity</u> applied retained (in nC)	<u>"in vivo"-</u> <u>Retention</u> <u>in % of the</u> <u>maximal per-</u> <u>missible</u> <u>⁶⁰Co-Incorpo-</u> <u>ration-Radio-</u> <u>activity</u> (= 10 μC)	<u>biological</u> <u>Radiation Burden by</u> <u>retained ⁶⁰Co-B₁₂</u> (m rem/week)	
FET	no	50	35	0,35	0,27
UET	yes	50	20	0,2	0,15
BCT	no	1000	700	7,0	5,39
LIT	no	200	140	1,4	1,08
WBRT	no	10	7	0,07	0,05

Table 5: Comparison of the total body radiation burden from the 10 nC ^{60}Co -Vitamin B_{12} -Test-Radio-activity with the natural exogenous and endogenous radiation burdens for human beings.

Radiation Source	Total body content (nC)	Biological radiation burden (mrem/week)
=====		
<u>Exogeneous sources</u>		
Cosmic radiation	-	~ 0,67
Environmental irradiation	-	~ 2
		~ 2,7
=====		
<u>Endogeneous sources (incorporated radioisotopes)</u>		
^{40}K (1980 dpm/gK)	10	~ 0,37
^{14}C (15 dpm/g C)	80	~ 0,019
^{226}Ra ($222 \cdot 10^{10}$ dpm/gRa)	0,1	~ 1
^{222}Rn - decay products		~ 1
		~ 2,4
=====		
<u>Contamination from nuclear weapon-fall out</u>		
^{90}Sr	1 - 10	~ 0,04 - 0,4
^{137}Cs	10	~ 0,02
=====		
<u>Retention from a</u>	7	~ 0,05
<u>10 nC ^{60}Co-B_{12}-</u>		
<u>Test-Radioactivity</u>		
=====		

Only a few physical or technical problems have still to be handled to enable a more general application of organic scintillation whole body detectors in nuclear medicine. The most important problem are the poor energy resolution of organic scintillators (due to the multiple Compton scattering) for double labelling procedures and the sometimes difficult reproducibility of the counting geometry if the test samples or individuals vary in size, diameter, fat content a.o.m.

Large NaI-crystals of course offer a reasonable good energy resolution (due to the predominant photoelectric effect), which is by a factor 2-3 better than that of an organic scintillator. They are however available only with relatively small efficient detector volume sizes and do - in fact - not represent whole body detectors. Their low specific volume sensitivity ($\frac{\text{cpm}}{\text{dpm/ml}}$) has to be compensated by long counting periods (about 30 minutes), which are inconvenient for the patients and cannot be tolerated from time and capacity reasons for routine work. Only for very few applications in double labelling experiments the poor energy resolution of the organic scintillator is not sufficient and requires the use of the NaI-crystal spectrometer. For practical all single radionuclide studies the energy resolution is not a limiting factor and the 2π - or 4π -organic scintillation detectors offer the considerable advantage of their high specific volume sensitivity resulting in the required short counting periods (3-times 100 seconds) for very low activities ($3-8 \cdot 10^{-10}$ C with a statistical precision of about $\pm 3\%$) of γ -emitting radionuclides in extended samples like human beings.

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THE PERFORMANCE OF LARGE-VOLUME PLASTIC
SCINTILLATORS WITH REFERENCE TO
WHOLE BODY COUNTING

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Introduction

At the 1957 Evanston Conference, a report was given of the performance of large-volume liquid and plastic organic scintillators (1). The units tested were 20 in. long, 10 in. wide and 6½ in. thick (with semi-cylindrical ends) and scintillations were viewed by two 5 in. diameter photomultipliers mounted on one 20 in. x 10 in. face of the scintillator.

From the point of view of spectral resolution, it was found that the NE101 plastic scintillator supplied by Nuclear Enterprises (G.B.) Ltd., Edinburgh, gave a performance which was very slightly superior to the best liquid scintillator containing 3.7 g. PPO and 0.1 g POPOP per litre of oxygen-free toluene. A lead-loaded liquid scintillator was also examined, but because of excessive light attenuation by the lead compounds, the light collection efficiency at the photocathodes was very low, and gamma-ray spectra revealed neither Compton nor photo peaks.

Bearing in mind the application of these detectors to measurement of radioactivity in human beings, it was concluded that the plastic scintillators possessed the following advantages:

1. Spectral resolution slightly better than that obtained with the best liquid scintillator.
2. Freedom from fire hazards.
3. Freedom from toxicity hazards.
4. Greater ease of working. Container design and fabrication become simpler with the elimination of the problem of liquid seals.

The greater expense of the plastic scintillator constitutes an extremely small fraction of the total cost of an apparatus comprising extensive shielding and elaborate electronics.

Multiple-unit design (as opposed to a single large 2π or 4π detector) was favoured because of its greater flexibility and its adaptability for development work. Furthermore, in measuring high levels of radioactivity, overloading of amplifiers and analysers can be avoided by switching-off all units except one, and even that one can, if necessary, be positioned remotely from the source.

→ The present report describes and illustrates a number of factors relevant to the design of large plastic scintillators used for gamma-ray detection.

Factors Affecting Spectral Resolution

Table 1 illustrates the difference in spectral resolution which can arise from selected and unselected photomultipliers of the same nominal diameter.

Table 1.

RESOLUTION OF 15IN. DIAMETER X 9IN. THICK CYLINDRICAL
NE102 PLASTIC SCINTILLATOR TO K-40 GAMMA-RADIATION

Photomultipliers	Peak/Trough ratio	Half-Resolution * %
4 x EMI 9530 A (5 in. dia.)	1.75	22.5
4 x Du Mont 6364 (5 in. dia.)	1.57	25.5

* "Half-Resolution" is defined as the "half-width" of the peak on the high-energy side divided by the amplitude of the peak. See reference (1) and Fig. 3.

The EMI tubes were selected for a photocathode sensitivity of not less than 55 μ amp per lumen, the Du Mont tubes were unselected. Uniformity of photocathode response is, however, very important as will be shown later.

A series of tests was conducted using a single EMI Type 9545 photomultiplier of 12 in. nominal diameter on 15 in. diameter plastic scintillators. Some of these results are summarised in Table 2.

Table 2
RESOLUTION WITH SINGLE 12" DIA. EMI TYPE 9545 PHOTOMULTIPLIER
ON 15" DIA. CYLINDRICAL PLASTIC SCINTILLATORS

Scintillator		Radiation Source	Peak/Trough	Half-Resolution % *
Type	Thickness			
NE102	9"	K ⁴⁰ at side	1.43	32
NE101	9"	" " " K ⁴⁰ against face opposite P/M		35 22
NE 101	6" bevelled	K ⁴⁰ opposite P/M Cs ¹³⁷ " "	1.50 1.17	22 31
NE101	3" bevelled	K ⁴⁰ " " Cs ¹³⁷ " "	1.21 1.08	13 30

* The absolute values quoted for K⁴⁰ in this series are too low due to non-linearity in the pulse-amplifier.

Attention should be drawn to the following points:-

1. NE101 and NE102 scintillators gave a roughly comparable performance.
2. The shape of the spectrum obtained with the 9 in. thick scintillator was markedly dependent upon the position of the source.
3. Although the half-resolution improved when the scintillator thickness was reduced, the peak-trough ratio fell to a very low value for the 3 in. thick scintillator.

These observations indicated that the pulse-height observed for a given event depends upon the position of that event in the scintillator, and to investigate this aspect further, a collimated beam of Co^{60} gamma-rays was fired through the scintillator. The results are illustrated in Fig. 1.

When the beam is fired parallel and close to the photocathode of the large tube, the solid angle subtended by the photocathode to scintillation events is large, and the average light attenuation is low. This results in a large average pulse-height, but due to the lowered photocathode sensitivity towards the periphery, scintillation events occurring directly beneath peripheral areas of the photocathode will give a lower pulse-height than the same events occurring directly beneath the central regions of the photocathode. As the beam is moved away from the photocathode, the solid angle is decreased and light attenuation is increased. These two factors account for the reduction of the average pulse-height but because of the more uniform illumination of the photocathode surface, the same scintillation event occurring at different points along the beam will give rise to a smaller spread in pulse-height. The peak is therefore sharpened.

Fig. 1 also shows the variation in the pulse-height of the peak when the single 12 in. diameter photomultiplier is replaced by four 5 in. diameter tubes. We find now that the average solid-angle subtended by the combined photocathodes for scintillation events occurring near to the top surface is very much reduced. Consequently, the variation in light collection efficiency as the beam is moved away from the photocathode surfaces is also reduced. Indeed we observe optimum light-collection for events that take place

Fig. 1. Variation in peak amplitude with position (indicated by arrows) of collimated beam of Co-60 gamma rays 15 in. dia. x 9 in. thick NE102 plastic scintillator viewed by (i) a single 12 in. dia. photomultiplier, and (ii) four, 5 in. dia. photomultipliers. The beam was fired through the central axis of the scintillator and parallel to the surface of the photocathodes.

approximately half-way down the axis of the scintillator; there is an approximately symmetrical fall-off on either side of this point.

The non-uniformity of the photocathode response of the 12 in. photomultiplier is illustrated more directly in Fig. 2. When the collimated beam is fired along the central axis of the 3 in. thick scintillator, the ratio of large- to small-pulse events is much greater than when the beam is fired near to the edge of the scintillator.

In view of these non-uniformity factors with the single large photomultiplier, it might be expected that their effect would be diminished by the use of light guides, despite the fact that light losses would thereby be introduced. Table 3 shows that this expectation is realised.

There is a progressive improvement in spectral resolution as we proceed from no light-guide, through 3 in. to the 6 in. light-guide. Under the last condition, the single 12 in. tube (with an effective photo-cathode area of 82 in.² and a photocathode sensitivity of about 30 μ A/L) out-performs three 5 in. diameter tubes (with a combined effective photocathode area of 42 in.² and average photocathode sensitivities of about 50 μ A/L).

None of the results obtained with 15 in. diameter cylindrical blocks rival the best obtained with the original 20 in. x 10 in. x 6½ in. NE101 block. However the results reported originally with this scintillator were too optimistic due to some non-linearity in the pulse-amplifier, kicksorter combination and the half-resolution reported (1) as 14.5% should in fact have been about 17.5%

Several photomultiplier types have now been tested on this scintillator and the results are shown in Table 4.

The best results obtained so far have been given by Twentieth Century 7 in. diameter photomultipliers, without light guides. In this case, the use of a 3 in. thick truncated-cone light guide worsens the performance, indicating that any gain in uniformity of illumination is more than offset by light losses. Spectra obtained with this combination are shown in Fig. 3.

Fig. 2. Spectra from collimated beam of Co^{60} gamma rays fired (a) along the central axis of the scintillator, and (b) parallel to the central axis, but 1 in. from the edge. 15 in. dia. x 3 in. thick NE101 plastic scintillator, 12 in. dia. EMI type 9545 photomultiplier.

Table 3.

EFFECT OF LIGHT GUIDES ON PERFORMANCE OF CYLINDRICAL NE101

PLASTIC SCINTILLATOR 15" DIA. X 6" THICK

Light Guide	Photomultiplier(s)	Gamma-ray Source	Peak/ Trough	Half - Resolution %
None	One EMI 12" dia. Type 9545	K^{40} Cs^{137}	1.3	31 34
3" Truncat- ed Cone	"	K^{40} Cs^{137}	- 1.15	27 30
6" Truncat- ed Cone	"	K^{40} Cs^{137}	1.5 1.3	21 30
" "	One EMI 5" dia. Type 6009	K^{40} Cs^{137}	1.02 1.04	29 39
" "	Three 5" dia.	K^{40} Cs^{137}	1.35 1.13	25.6 34.7

Table 4

RESOLUTION OF 20" x 10" x 6½" THICK, OVAL NE101 PLASTIC

SCINTILLATOR

Photomultipliers and Light Guides	Gamma-Ray Source	Peak/Trough	Half-Resolution %
2 x EMI 6009A 5" dia.	K ⁴⁰ Cs ¹³⁷	1.75 1.24	18.5 31.2
2 x EMI 9530A 5" dia.	K ⁴⁰ Cs ¹³⁷ Th (2.62 Mev)	1.91 1.46 -	17.4 26 13.4
2 x EMI 10" dia. exptl. with app. 3" Light Guides	K ⁴⁰ Cs ¹³⁷ Th (2.62 Mev)	1.80 1.40 1.79	17.3 32.3 16.9
2 x Twentieth Century 7" dia. 3" Light Guides	K ⁴⁰ Cs ¹³⁷ Th (2.62 Mev)	1.90 1.36 1.93	15.6 28.1 11.8
2 x Twentieth Century 7" dia. no Light Guides	K ⁴⁰ Cs ¹³⁷ Th (2.62 Mev)	2.13 1.56 2.12	13.1 28.2 10.4

Fig. 3. Gamma ray spectra obtained with NE101, 20 in. x 10 in. x 6-1/2 in. plastic scintillator, viewed by two Twentieth Century 7 in. dia. photomultipliers.

Conclusions Regarding Spectral Resolution.

Apart from obvious factors such as photocathode sensitivity and the ratio of photocathode area to the surface area of the scintillator, the resolution of large volume units depends on geometrical factors arising from two distinct causes, (a) macroscopic non-uniformities in the photocathode response and (b) light-transmission losses within the scintillator itself. (Since in all these experiments either heavily smoked magnesium oxide or packed magnesium carbonate reflectors were used, light was lost mainly through internal absorption in the scintillator.)

When the sensitivity of the peripheral area of the photocathode is appreciably lower than that of the central area, light guides improve the performance, but when such differential sensitivity is less marked, light guides produce deterioration because any gain in the uniformity of illumination of the photocathode is more than offset by light losses. From our experience with existing photomultipliers it seems likely that light guides will be advantageous only when the photocathode diameter is somewhat greater than 7 inches.

Because of light transmission losses, thick scintillators of a given cross-section give a poorer half-resolution than thin scintillators of the same cross-section. Thin scintillators suffer, however, from a double disadvantage. Firstly, fewer gamma-rays will be detected and secondly, the peak/trough ratio is poor. Part of the second disadvantage arises from non-uniformities in the photo-cathode response, but another factor is the decrease of multiple Compton interactions between scattered gamma-rays and the scintillator. (If a mono-energetic gamma-ray source was completely surrounded by a very thick spherical shell scintillator, the energy from every gamma-ray would be totally absorbed, and if perfect light-collection could be attained, a nearly monochromatic spectrum - with an infinite peak/trough ratio - would be recorded.)

There is a conflict of requirements therefore, and until perfectly transparent and uniform scintillators, perfect reflectors, and perfectly uniform photocathodes become available, some kind of compromise has to be made. The best compromise unit we have found for our requirements is based on the 20 in. x 10 in. x 6½ in. NE101 scintillator

with two 7 in. diameter Twentieth Century photomultipliers and no light guides.

Counting Statistics with A 3-Unit Apparatus.

A three-unit (20 in. x 10 in. x 6½ in.) apparatus will shortly be installed in a new shield. Some preliminary results have been obtained in the original steel room (1). Two units are located at the back of the seated patient; the third, adjustable and pivoted from the floor, is placed opposite the chest (Fig. 4). So far only one unit has been fitted with 7 in. diameter photomultipliers, the other two having 5 in. diameter tubes; the counting statistics obtained with this arrangement are set out in Table 5.

Table 5

WHOLE BODY GAMMA-RAY COUNTING STATISTICS WITH
3-UNIT (20 IN. X 10 IN. X 6½ IN. NE101) PLASTIC
SCINTILLATOR APPARATUS. PRELIMINARY RESULTS.

Radiation Source	Typical Count-Rate Counts/Sec.
150 g Potassium) in K^{40} in body) region" *	20
Background)	36
10^{-9} c Cs ^{137} in) body) in "Cs ^{137}) region" + Background)	2
	70
Contribution in "Cs ^{137} region" from 150 g potassium.	15

* From 0.8 to 1.8 Mev (K^{40} Compton edge at 1.24 Mev).

+ From 0.25 to 0.73 Mev (Cs ^{137} Compton edge at 0.48).

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Fig. 4. Arrangement of three 20 x 10 x 6-1/2 in. plastic scintillator units with respect to seated patient.

From the above table it can be deduced that the counting statistics of a natural potassium determination consisting of one 15 min. patient measurement sandwiched between two 15 min. background observations, will give a standard error of just over $\pm 1\%$. Alternatively if a fairly stable and frequently determined background can be assumed, the corresponding standard error for a 200 sec. determination of natural body potassium will be ± 3 to 4% . These statistical errors are only slightly inferior to those ($\pm 3\%$ in 2 min.) given by the much larger (nearly 4%) Los Alamos liquid scintillator human counter (2).

For a 15 min. determination of the Cs^{137} content of the body, the counting statistics component of the standard error will be equivalent to approximately $\pm (2 \times 10^{-10})\text{c}$; errors of interpretation will however generally be larger than this.

Acknowledgments.

I am indebted to my colleagues, and in particular to Mr. D. B. Appleby and Dr. D. Hughes for assistance with these observations.

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THE NEW LOS ALAMOS HUMAN COUNTER: HUMCO II*

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INTRODUCTION

A new well-type liquid scintillation gamma counter, large enough to provide 4π steradian counting geometry for the human body and for samples up to several hundreds of kilograms in weight, has recently been placed in operation at the Los Alamos Scientific Laboratory. Called Humco II (short for Human Counter), this counter is the sixth in a developmental sequence of large liquid scintillation counters constructed for biological purposes. Its predecessors are shown in Table 1.

The major objectives in the design of Humco II were increased energy resolution in terms of both peak widths and peak-to-valley ratios, increased useful energy range to include the efficient counting of bremsstrahlung from hard betas (especially Sr-90 and P-32), and electronic improvements including transistorization and automatic data recording and processing with punched cards.

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*Work performed under the auspices of the U. S. Atomic Energy Commission.

TABLE 1. PREDECESSORS OF HUMCO II

Name	Volume (liters)	Scintillator Thickness (in.)	Composition	Sample Well Dimensions (in.)	Multiplier (No.)	Phototubes Dia. Size (in.)	Ref- erences
"Herr Auge"	200	5	Terphenyl plus NPO in toluene	20 (dia.) x 30	45	2	(1)
K-9	75	4	PPO plus NPO in tri- ethylbenzene	9 (dia.) x 28	8	2	(2)
Humco I	530	6	Terphenyl plus POPOP in toluene	18 (dia.) x 72	108	2	(3,4)
WRAIR Counter	600	6	Terphenyl plus POPOP in toluene	20 (dia.) x 72	30	5	(5)
Genco	280	6	Terphenyl plus POPOP in triethyl- benzene	18 (dia.) x 72 (semi- cylinder, 20)	6	16	(6,7)

DESCRIPTION

An artist's sketch of Humco II is shown in Fig. 1. The sample is introduced into the well by the usual trough and sling arrangement (3,4). Shielding is provided by 7-1/2 in. thick naval armorplate in the form of a room with inside dimensions 8 x 10 x 7 feet high. Use of room-type shielding provides easy access to the counter for installation and maintenance. The tank, which has a volume of 1600 liters, is 72 in. long and provides a minimum scintillator thickness of 12 in. around the 18 in. diameter well. Previous counters have not exceeded 6 in. in thickness. It was hoped that the extra thickness would increase the probability of multiple Compton scattering and would thereby enhance the Compton peak relative to the continuum at low energies.

Scintillation light is collected by 24 multiplier phototubes (DuMont No. K-1328) with nominal 14-1/2 in. diameter photocathodes. Thus, 24 per cent of the total wall area is photosensitive compared with 18 per cent in Genco. This fraction is a measure of primary light collection efficiency. Because of the comparatively poor reflectance of all reflectors when wet and the difficulty of obtaining long optical mean free paths (several meters) in the scintillator, rapid collection of the scintillation light is essential.

Phototubes are balanced individually through the use of a small test tank of 40 liter capacity (16 in. diameter x 12 in. deep). Balancing potentiometers in series with the dynode resistors are adjusted to give the same peak pulse height for each tube when tested with a K-40 source and a supply voltage of 1500.

During most of the testing period, the counter has been filled with a conventional scintillation solution consisting of 4 g/l terphenyl and 0.05 g/l POPOP in toluene. For routine operations, this will be replaced with a solution of low volatility described later.

Figure 2 is a photograph of the partially assembled tank showing the arrangement of the phototubes and the extent of photocathode coverage. The outer wall of the tank is hexagonal in cross section to provide flat surfaces on which to mount the tubes. No windows are used, the phototube being in direct contact with the liquid. Because of the curvature of the glass faceplate and the desirability of providing optical coupling to the scintillator, use of

Fig. 1. Artist's sketch of Humco II.

Fig. 2. Photograph of Humco II tank.

windows would be quite complicated. Failure of a photomultiplier is a sufficiently rare event that the necessity for draining the tank to replace tubes is not a serious drawback.

Liquid-tight seals between phototube and tank are provided by cementing the tube to a steel ring with an epoxide adhesive. A silicone-rubber O-ring makes the seal between the ring and flat machined surface on the tank. The ring is clamped by 16 studs welded to the tank; a torque wrench set at 16 in. pound ensures uniform tension. It is very important that the surface of the tank to which the O-ring seals are made should be flat to a tolerance of ± 0.005 in. Deviations larger than this will cause strains in the phototube faceplate, which may result in cracking of the glass-metal seal. A simple method of obtaining such a flat surface is to cement to the roughly machined tank a flat aluminum ring using Rezolin Epoxy Resin F.* Successful liquid-tight seals have also been made using special silicone-rubber gaskets between the ring and the phototube envelope. This method further reduces the possibility of straining the phototube, but is considerably more complicated than the epoxide cement method.

Figure 3 shows the transistorized electronics for the counter. The chassis in the relay rack, reading up from the bottom, are the pulse height analyzer consisting of 6 plug-in type single channel units, the amplifier, the punch control unit, a data input chassis which permits sample identification information to be entered, a preset timing unit, 3 double-scaler chassis, a digital master clock, and a slave clock which provides the time of day output. At the completion of each count, all data are entered on an 80 column decimal punched card by the IBM 526 punch. Auxiliary typewriter input permits additional information to be entered manually in the last 8 columns of the card. (Alphabetic information can be entered only in these columns.) An IBM 704 computer will perform all data processing, including averaging of replicate runs on a single sample, subtraction of appropriate backgrounds, calculation of calibration runs, and solution of simultaneous equations for the amounts of various selected nuclides (up to 6) present in the sample. A multichannel analyzer is used for energy calibration and for spectral analysis of unknown activities. As will be seen later, the ability of the liquid scintillator to resolve complex mixtures

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* Rezolin Inc., Santa Monica, California.

Fig. 3. Transistorized electronics for Humco II.

is limited; however, spectral identification is possible for the components of several simple mixtures which are commonly encountered.

ENERGY CALIBRATION

It is difficult to measure directly the energy actually deposited in a large organic scintillator. As a result of the low atomic number of the material, total absorption of gamma ray energy by the photoelectric process is not an important primary process. The principal interaction over the range of gamma energies of interest is by Compton scattering, in which any amount of energy can be transferred from the incident gamma ray to the recoil electron up to a maximum amount,

$$T_{\max} = \frac{2\alpha_0}{1 + 2\alpha_0} E_{\gamma},$$

where α_0 is the gamma energy in units of m_0c^2 , the characteristic rest mass energy of electrons. E_{γ} is also the initial gamma ray energy, in whatever units are desired for $T_{\max}$ (8).

A moderately sharp energy peak results from this process, but the actual peak energy is subject to change by multiple scattering, introducing a corresponding uncertainty in the calibration. Sources of alpha rays or conversion electrons cannot be used for calibration outside the tank, and internal sources of these activities would, if dissolved, contaminate a large and expensive volume of scintillator. If used as encapsulated local sources, it is necessary to move them throughout the tank to obtain a proper space average of the resultant pulse heights. An attempt will be made to perform the latter experiment both for calibration purposes and for measurement of variations in light collection efficiency over the scintillator volume.

It is, however, possible to determine the energy deposition and to estimate the relative importance of multiple Compton scatter. The method is based on the fact that a plot of maximum Compton energy against incident gamma energy is very nearly linear above a few tenths Mev, as indicated in Fig. 4. The intercept of the extrapolated line with the abscissa varies only slightly with the energy range used. Extrapolating the theoretical curve from the range 0.66 to 1.45 Mev gives an intercept of 170 kev. Using 0.66 to 3.0 Mev, the intercept rises to about 200 kev; using 0.4 to 1.56 Mev,

Fig. 4. Calculated maximum Compton energy from single scattering versus gamma energy.

falls to 150 kev. For small detectors, the plot of observed pulse height of the Compton peak versus full gamma energy should show a similar intercept. This may be the case for the counter whose calibration is given in Fig. 5, a 40 liter test tank 16 in. in diameter by 12 in. deep, viewed with a single 16 in. multiplier phototube. The observed pulse heights from 6 gamma rays 0.51 to 1.46 Mev are plotted against full gamma energy in the lower curve. The intercept is 200 to 220 kev, which is 40 to 50 kev higher than the calculated value. The discrepancy may be real and may be due to an inherent nonlinearity in the scintillator response, possibly due to the deposition of some of the energy at high specific ionization near the end of recoil electron ranges. Anthracene crystals show a similar nonlinearity amounting to 22 to 25 kev (9,10).

If observed pulse heights are plotted against maximum Compton energy instead of against full gamma energy, one would expect a positive intercept of a few tens of kev if single Compton scatter predominates, and a negative intercept if there is much multiple scatter. The upper line of Fig. 5 shows that the former case is again indicated. The energy calibration of the 280 liter Geneva Counter is shown in Fig. 6. The scintillation tank, in this case, is hemicylindrical with a detector thickness of 6 in. so that multiple scatter is unlikely. Relative pulse height plotted against calculated maximum Compton energy yields a straight line with an intercept of 30 to 40 kev.

Figure 7 presents the similar calibration of the new counter, Humco II. Not only is total scintillator volume now much larger (1600 liters), but as a result of the 4π geometry the backscattered photons from a maximum Compton recoil now must traverse the scintillator on the opposite side of the well (the calibration source, of course, being in the sample well). The expectation of increased probability of multiple scatter is confirmed by the calibration curves. When pulse height is plotted against energy deposited by single maximum Compton collision, the line shows a negative energy intercept of 40 kev. When plotted against full gamma energy, the intercept is 120 kev. Plotting against the energy transferred by two successive 180° collisions gives the middle line, which shows the most reasonable intercept of 20 kev. A summary of the evidence regarding multiplicity of Compton scattering in detectors of various sizes is given in Table 2.

It is of interest to consider the apparent pulse heights

Fig. 5. Test tank energy calibration.

Fig. 6. Energy calibration of Genco.

Fig. 7. Energy calibration of Humco II.

TABLE 2. MULTIPLICITY OF COMPTON SCATTERING IN DETECTORS OF VARIOUS SIZES

Detector	Shape	Volume (liters)	Scintillator Thickness (cm)	Zero Pulse Height Intercept (kev)	
				Single Compton E	Total Gamma E
Test Tank	right cylinder	40	30	+20	+200
Genco	2 π well	300	15	+30	+170
Humco II	4 π well	1600	30	-30	+80
Calculated for single Compton scattering				+24 [*]	+185 ^{**}

^{*} Observed value for electrons on anthracene.

^{**} Including 25 kev for inherent scintillator nonlinearity.

of compound events occurring when cascade gamma rays are absorbed. Figure 8 is an extended graph of the energy calibration of Humco II, including the peaks resulting from Co-60 and Th-228. The points are plotted against the energy absorption calculated on the assumption of double Compton scatter. The two Co-60 gammas (1.17 and 1.33 Mev) are not resolved but appear as a single peak of height 68. This is significantly off the curve to an extent suggesting that in addition to double scattering of one of the photons, some energy absorption from the other photon has also occurred. The Co-60 sum peak at pulse height 123 also lies off the curve if it is assumed that only one gamma ray suffers double scattering (point marked "either"). If double scattering of both gammas is assumed (point marked "both"), good agreement with the calibration line is obtained.

The case of Th-228 is more complicated. The coincidence involved is that between the 100 per cent 2.615 Mev gamma and the 88 per cent 0.58 Mev gamma of Tl-208, namely ThC'' (11). Only one peak is observed above 2 Mev, and it appears to correspond best with the energy transferred by double scattering of both gamma rays.

A Monte Carlo computation of the actual energy deposition in large organic scintillators is now under way by M. A. Van Dilla of the Los Alamos Scientific Laboratory using a program written by Zerby and Moran (12) of the Oak Ridge National Laboratory. These results will not only provide further evidence on energy absorption, but will also indicate the extent to which resolution is limited by the absorption process.

ENERGY RESOLUTION

Energy resolution obtained with Humco II using a conventional toluene-terphenyl-POPOP scintillator is shown in Fig. 9. The plot is the usual Δ^2 versus $1/E$ (13), except that because of the asymmetry of the Compton peaks, the half-resolution has been used instead of the full width. The energies used are the values calculated for double Compton scatter as in Fig. 8. The half-resolution varies from 17 per cent at K-40 (1.36 Mev) to 25 per cent at Cs-137 (0.56 Mev). The results would appear to be explicable on the basis of two resolution terms, one energy independent with a half-width of 10 per cent and the square of the other varying as the reciprocal of the energy and having the value of 14 per cent at 1.36 Mev. The factors limiting the

Fig. 8. Extended energy calibration of Humco II.

Fig. 9. Energy resolution of Humco II.

obtainable resolution which might explain Fig. 9 are as follows:

1. Inherent scintillator resolution, i.e., variations in the total scintillation light emitted for events of equal energy deposition.

2. Statistical fluctuations both in number of photons emitted by the scintillator and in the photoelectron emission and amplification factor of the multiplier phototube. Since the photocathode efficiency is of the order of 10 per cent, scintillator statistics will be negligible compared with phototube statistics.

3. Variations in the amount of energy deposited in the scintillator by gamma rays of the same energy. This includes escape of scattered photons or of bremsstrahlung, and in the case of organic scintillators the shape of the Compton recoil spectrum as modified by multiple scattering.

4. Variations in the efficiency with which light is collected from various locations in the scintillator.

5. Nonuniformity in the photosensitivity of the cathodes of the multiplier phototubes.

While it is not possible at present to decide quantitatively on the relative contributions of the above effects, some of the factors can be eliminated.

The inherent resolution of organic scintillators is not greatly inferior to that of NaI (Tl). Figure 10 shows the resolution obtained by exciting a small volume of liquid scintillator (terphenyl plus POPOP in toluene) with Cs-137 conversion electrons under conditions of optimum light collection efficiency and photocathode uniformity. The full width at half-height is 11 per cent. Taylor et al. (9) obtained 12 per cent for a small anthracene crystal under similar conditions. At this energy, the resolution of a typical sodium iodide crystal would be 7.7 per cent with an inherent width of 6.5 per cent and a 4 per cent contribution from multiplier statistics (13). If the liquid scintillator light output is about 1/4 that of NaI, then the multiplier contribution would be about 8 per cent and the intrinsic scintillator resolution is 7.5 per cent full width. This effect is small compared with both the width of the K-40 line and the intercept of the extrapolated line in Fig. 9.

Fig. 10. Cesium¹³⁷ conversion electron spectrum in liquid scintillator.

Multiplier statistics also seem unlikely as the principal source of the observed peak widths. The half width of the Cs-137 line in Humco II is 25 per cent, or 22 per cent if one considers only the portion which has a $1/\sqrt{E}$ dependence. This corresponds to a standard deviation of + 19 per cent, requiring approximately 25 photoelectrons. Multiplier statistics contributed an estimated 8 per cent to the small volume full width for the conversion electron line, indicating about 850 photoelectrons for 630 kev (740 ev per electron). With equal light collection and photocathode efficiency, one would expect 750 photoelectrons for the Cs-137 gamma ray. The 25 electrons calculated on the assumption that the entire line width was due to multiplier statistics, therefore, implies an efficiency of 3 per cent relative to the small volume, or 6 per cent if the cathode efficiency of the large phototube is half that of the small tube. Since Humco II has 24 per cent photocathode area, an optical mean free path of 10 meters and a wall reflectivity of better than 90 per cent, one would expect at least 50 per cent efficiency.

The third effect, shape of the Compton recoil spectrum, is certainly an important contributor to peak width. Figure 11 gives the calculated spectrum (8) for a 600 kev gamma ray assuming single scattering only. The 18 per cent full width is certainly an underestimate, since the actual peak height will be less than that of the sharp edge given by theory. The effect of multiple scattering may also operate to broaden the distribution. The Monte Carlo calculations mentioned above will give a quantitative measure of the contribution and its dependence on gamma energy.

The last two factors also contribute to an unknown degree. Both experimental and theoretical study of their importance is planned. Geometrical variations in light collection efficiency would be expected to give a constant η^2 independent of the energy of the event and might contribute to the intercept. The effect of variation in photocathode sensitivity will depend on the averaging effect of random incidence of the photons on the cathode. The efficiency of this averaging process will depend on the number of photons involved, and hence broadening by this effect could be energy dependent.

Figure 12 shows the spectra obtained with Humco II for Cs-137, Zn-65, and K-40. The latter pair could be determined simultaneously, but closer gamma rays could not.

Fig. 11. Calculated shape of single Compton spectrum (600 kev).

ENERGY SPECTRA-HUMCO II, TOLUENE

Fig. 12. Humco II spectra.

ENERGY RANGE

Because of the desirability of efficient bremsstrahlung counting (e.g., for tracer use of P-32, monitoring industrial exposure to intake of Sr-90, etc.), an important parameter of counter performance is the apparent energy at which phototube noise causes a significant increase in background. The onset of tube noise is evidenced by a sharp change of slope in the plot of background against energy on a log-log scale, and a quantitative measure of the energy at which tube noise makes a significant contribution to background is obtained from the intersection of the extrapolated linear portions of the background curves.

Figure 13 is such a graph for the Geneva Counter [triethylbenzene filling (6)] and for Humco II operated as a 2π and as a 4π system (toluene filling). For the 2π operation, the Humco II tank was filled half full of scintillator, bringing the liquid level up to the middle of the side rows of phototubes. The lower four rows of 16 phototubes were in place, and the upper two rows of 8 were replaced with aluminum foil reflectors. Only 14 of the 16 tubes were operational, the second tube in one of the bottom rows having gone dead and the second tube in the adjacent side row having become excessively noisy. These tubes were in place mechanically but were out of the circuits electrically.

During 4π operation, Humco II was completely filled with a toluene-terphenyl-POPOP solution. Twenty-three tubes were in place, the remaining position having an aluminum foil reflector. Of these tubes, 5 showed noise levels above 90 kev when tested individually in a 40 liter test tank. Substitution of better quality tubes should improve performance.

Noise levels, as defined above, for the three systems were 60 kev for Genco, 60 kev for Humco II 2π , and 100 kev for Humco II 4π . All energies are given in terms of energy deposition in the system by single Compton scattering. A deposited energy of 60 kev corresponds to an initial gamma energy of 160 kev. Measurement of Sr-90 bremsstrahlung down to this energy should give a detection sensitivity of 0.1 μ c or better, or about 5 per cent of the maximum permissible body burden for workers.

Fig. 13. Background versus efficiency (Genco and Humco II).

LOW-VOLATILITY SCINTILLATOR

While the use of toluene as a solvent has the advantage of combining economy with near maximal pulse height, it has the serious disadvantage of flammability and toxicity. Considerable effort has been devoted to development of a solvent of comparable pulse height and reduced volatility. These requirements have been met, for example by triethylbenzene (6), but only with greatly increased cost, limited availability, and difficult purification requirements. We wish to report a new solvent of low volatility which is free from these objections. The solvent, TS-28M, is available from Shell Oil Company, by whom it is sold as a paint thinner and general-purpose solvent. The composition, according to company literature, is as follows: 12 per cent paraffins, 1 per cent olefins, 25 per cent naphthenes (cycloparaffins, derivatives of cyclopentane and cyclohexane), and 62 per cent aromatics. It has a flash point of 120°F (49°C) and a boiling range of 321 to 398°F (161 to 203°C).

The material was obtained by this Laboratory in our own stainless steel drums, directly from the still at the Martinez, California, refinery. As received, it had a decided yellow cast when viewed through a large thickness. Purification was carried out by absorption of the impurities upon columns of activated alumina. Three polyethylene columns, each 8 feet x 5-1/2 in. in diameter, were packed with 50 pounds each of activated alumina (Alcoa, grade F-20, 80 to 200 mesh) to an effective height of about 80 in. The solvent traveled down the column at a rate of from 1.2 to 1.5 in. per minute, and the output was 100 to 120 ml per minute depending upon the column. These rates were self-determining. The effluent was monitored regularly for transparency and from first to last, all treated solvent was as transparent as or slightly better than reagent-grade toluene from 500 down to 390 mμ. Below 390 mμ, the transparency dropped off rapidly. No saturation of the column by the impurities was noticed, although a through-put of an individual column was up to 180 gallons.

The solubility of terphenyl in TS-28 is limited, a saturated solution at 21°C containing only 3.5 g/l. The solution used to fill Humco II, therefore, contained only 3 g/l terphenyl and 0.04 g/l POPOP to prevent possible precipitation of solute by temperature changes. At these low solute concentrations, the pulse height is reduced significantly below the optimum. Substitution of PPO as the primary solute is, therefore, recommended. Use of methyl-substituted quaterphenyl (14) would also be advantageous.

Measurements of the pulse heights of air-saturated solutions in very small volumes relative to the standard reference solution (15,16) of 3 g/l PPO in toluene gave 1.16 for the toluene filling (4 g/l terphenyl and 0.05 g/l POPOP) and 0.53 for TS-28M filling (3 g/l terphenyl and 0.04 g/l POPOP). The ratio of the relative pulse heights of the two fillings is, therefore, 0.46 in a small-volume system. In Humco II, the ratio (air-saturated) was 0.47, indicating equal transparency for the TS-28M solution. Because of the greater sensitivity of the TS-28M solution to oxygen quenching, the Humco II pulse height ratio of the deoxygenated solutions was somewhat improved to 0.55. The toluene solution pulse height rose by a factor of 1.30, and the TS-28M solution rose by 1.50 following purging of the system with argon gas for 24 hours.

Small-volume tests were performed on the Humco II TS-28M solution to which 3 g/l PPO was added. The air-saturated pulse height rose to 0.98 of the toluene-PPO reference solution, or 0.85 of the toluene-terphenyl-POPOP filling used in Humco II. Assuming equal oxygen quenching factors, one can expect the same pulse height ratio of 0.85 to hold in Humco II. A tube noise level of 70 kev is, therefore, predicted for Humco II using a TS-28M solution of 3 g/l terphenyl, 3 g/l PPO, 0.04 g/l POPOP (deoxygenated), if the complete tube complement is as good as the 14 tubes used in the 2π configuration.

SUMMARY

A new 4π liquid scintillation counter for the measurement of low-level gamma activity in human subjects has been constructed. A counting well 18 in. in diameter by 6 feet long is surrounded by a layer of liquid scintillator 12 in. thick. Scintillator volume is 450 gallons; 24 multiplier phototubes with nominal 14-1/2 in. diameter cathodes provide a cathode-to-total-wall-area ratio of 0.24. Six single channel analyzers cover the energy range 0.1 to 3 Mev. Electronic circuits are completely transistorized, and all data are automatically transcribed onto punched cards. A non-volatile solvent will be used to eliminate fire hazards. Operating characteristics, including energy resolution and sensitivity, are reported.

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RECENT SCINTILLATION CHAMBER RESEARCH

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This discussion will represent an attempt to bring up to date recent reports (1,2) concerning the development of the technique of the scintillation chamber. It will be based on the following outline:

1. Brief review.
2. Image intensifier developments.
3. Studies of filament scintillators.
4. Scintillation tracks of $\pi^{\pm}$ mesons.

Scintillation track imaging has been successfully accomplished in the past few years in solid crystals (NaI (Tl)) as well as organic plastic filaments. The work of the Princeton group has been in the latter area as is this conference, so that attention will be restricted to this in the present discussion. When a charged particle at minimum ionization crosses a 1 mm. diameter filament, about 20 per cent of the light emitted can be "piped" by internal reflection to the end of the filament. Aside from attenuation losses, this will result in approximately 200 photons arriving at the end of the 1-mm. filament or 100 photons at the end of a 0.5-mm. filament, etc. It is this number of photons that one has to deal with in track imaging. The attenuation effects have been recently investigated by the Princeton group (3) and will be discussed later.

The principle of the method and the means by which stereoscopic viewing can be achieved are shown in Fig. 1. The number and intensity of available photons described above is about 10^{-5} of that necessary to record on photographic film. Thus, collection and intensification become important. If one considers collection by fast lenses, then depth of focus becomes critical and the removal of this problem by virtue of the presence of the light in the plane of the ends of the filaments is an obvious advantage. Further advantages result as will become apparent in the discussion of alternate collection methods.

The need for light intensification leads to interest in image intensifier tubes. Recent developments have been significant and will be summarized now. The principle of the image intensifier is illustrated by the three-stage electrostatic type shown in Fig. 2. Considering the action of one stage, photons incident on the cathode release photoelectrons with a quantum efficiency of about 10 per cent. These electrons are accelerated by 10,000 volts by an electrostatic lens system and focused on a phosphor screen which converts their energy into light with an efficiency of approximately 10 per cent. Taking three volts as the energy of the emerging light, the number of quanta emitted for each quantum incident is given by

$$G = \frac{0.1 \times 10^4 \times 0.1}{3} \approx 30$$

which is the theoretical gain of the stage. For single-stage tubes, lens coupling would represent a loss of a factor of approximately 10, so that multistage tubes are an obvious advantage. R. G. Stoudenheimer of RCA Lancaster has succeeded in providing two-stage tubes with gains of ~ 1000 , and three-stage tubes with gains even higher. These tubes have been able to resolve ~ 12 line pairs/mm. at the center of their 1 in. sensitive diameter and ~ 6 line pairs/mm. at the edge. Two-stage tubes with 2 in. diameter cathodes have also been provided. These tubes have had cathode window thicknesses of 0.025 in. so that filaments can be directly butted against them and satisfactory resolution achieved. An interesting development is underway at RCA Lancaster to make a single stage tube of 8 in. sensitive diameter demagnifying to a 1 in. output phosphor. It has been found possible to make the front glass 0.04 in. thick so that filaments can be joined directly with fairly good resolution.

Fig. 1. A 3-in. cube array of filaments demonstrating the light piping and stereo-viewing principles. A negative of a stereo-view of a fictitious event is illuminated on the back face of the chamber and the light is piped to the front face with some attenuation but no serious cross-talk.

THREE STAGE CASCADED IMAGE
CONVERTER

Fig. 2. A 3-stage electrostatic focus type image intensifier (RCA).

A more sophisticated approach has led to some encouraging results at Westinghouse Laboratories, Elmira, where a light pipe end window is placed on a 5-in. single-stage tube. This glass light pipe window is obtained from Mosaic Fabrications and is capable of resolving ~ 14 line pairs/mm. The quantum gain of the tube is expected to be ~ 20 and the 1-in. output can also be provided with a light pipe window to allow joining with similarly faced following stages. Prototype models have shown promising results.

Magnetically focussed tubes are also being developed and first efforts indicate very promising resolution properties. On some low gain models, 18 line pairs/mm. were resolved.

A different principle has led to recent successes both by Wilcock at Imperial College, London, and the group at the Westinghouse Laboratories, Pittsburgh. This is based on the transmission secondary electron principle used by the Russians in their early successful efforts. The method is illustrated in Fig. 3. Electrons are focused by an axial magnetic field of a few hundred gauss. Tubes built by Wilcock at Imperial College, London, are now prepared commercially by 20th Century Electronics Ltd. and those of Westinghouse, Pittsburgh (4) by Westinghouse, Elmira. At interstage voltages of approximately 4 kv, 5-stage tube gains of 50,000 and 4-stage tube gains of 10,000 have been achieved. The secondary emission material has been KCl or BaF₂ supported on thin (~ 300 Å) aluminum membranes. The low gains so far achieved have been due to relatively inefficient cathodes. Several of the tubes have achieved photographs of single electrons from the cathode. In Wilcock's tube, the spot size of a single electron was about 30 μ . Tube diameters have been approximately 1 in. The background appears low, corresponding to emission of thermal electrons from the cathode at a rate of $\sim 3000/\text{cm}^2/\text{sec}$.

A further type of intensifier is the channeled secondary emission type shown in Fig. 4. Here there is no magnetic field. The work, under way at Chicago Midway Laboratory, has not yet led to a sealed-off device, but has indicated that net gains of 2 per stage are to be expected. Thus, a 10-stage tube with a 10 per cent cathode efficiency and a post acceleration to the phosphor of 15 kv should yield a gain of 4×10^4 . The anticipated advantage is that the dynode structure can have a large lateral extent and offer good mechanical support for thin cathode windows. However, these tubes are not currently available.

The Princeton group, after some early film recording of

Fig. 3. The transmission secondary electron intensifier.

Fig. 4. The channeled secondary electron intensifier.

tracks, has gone over to closed circuit TV recording. The reasons for this have included the expected advantages to be gained in the video amplifier stage (approximately 100), contrast variation by blanking control, digitized nature of the output that would be particularly advantageous in a satellite-borne device, etc. The method has worked very well; the major difficulty being encountered is resolution, which has recently been improved by the use of thin MgO targets in the orthicon. Figure 5 shows a two-stage intensifier orthicon made available through the courtesy of G. A. Morton and J. E. Ruedy of RCA, Princeton. Tests indicate that this particular tube in a TV system was capable of providing effective gains of the order of 2×10^4 , and in fact it was found necessary to provide an additional net gain of only 10 in order to record minimum ionizing tracks, in agreement with estimates made earlier. Recently RCA, Lancaster, has begun to produce improved single-stage intensifier tubes that perform very well on the basis of lines resolved per foot candle, the usual criterion used in describing their performance.

A system incorporating the RCA two-stage tube, an f/1.9 lens, and the two-stage image intensifier is shown in Fig. 6. The filament chamber is butted directly against the end window of the first stage. In the present system, the window is 0.04 in. thick and limits the resolution of the system. All tracks to be shown later were obtained with this limitation. (A tube has just been obtained with a front window thickness of 0.025 in.). In operation, the first stage is normally on and the second stage off. After the scintillation counter selection system (which, in general, includes the chamber viewed from the opposite end by a photomultiplier as one of the counters) indicates an event of interest has occurred, the first stage is gated off and the second stage on for a period long enough for the information to be read off the first phosphor. In the present system, the first phosphor is P 11, so that the gate time is several hundred microseconds. Other tubes have been made with the lower efficiency P 15, allowing gate times of the order of several microseconds. In addition, the kinescope is pulsed for one frame (30 milliseconds).

Since this system is one-directional, it does not permit stereo-viewing so the chamber used was also one-directional. The chamber used to obtain the tracks to be shown is given in Fig. 7. It is 1 in. in diameter and 3 in. long. The filaments are 0.7 mm. in diameter and are individually supported by thin (0.003 in. diameter) nylon threads at each end. This same method has been used to prepare a 3-in. tube, two-directional

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Fig. 5. A two-stage intensifier orthicon.

Fig. 6. The Princeton scintillation chamber system.

Fig. 7. One-directional scintillation chamber.

array. Examples of minimum ionizing μ meson tracks obtained with this chamber are shown in Fig. 8, and slow meson tracks in Fig. 9. In the latter, the decay electrons are observable.

This system was used to investigate the effects of attenuation of the light in being piped from the point of origin to the end of the filament. Free filament measurements indicate that attenuation to one-half intensity occurs in 12 to 15 cm. Early chambers made with close packed filament arrays showed a more severe attenuation so the present chamber was made of individually supported filaments and its attenuation observed by the character of the tracks (3), in order to have a realistic evaluation of the effects. Tracks were photographed and their characteristics measured as a function of their distance from image tube face. The position of the track was determined to $\pm 1/4$ in. by means of triggering on small scintillator telescope moved to various positions along the chamber. Two effects showed up that agreed with the conclusion that attenuation produces significant effects but does not seriously limit the effect of the device. The first of these effects concerns the fact that since the attenuation appears to be predominantly a surface effect of internal reflection, those rays that are at the smallest angles of incidence are reflected the largest number of times and are, therefore, attenuated the most. The effect of this is to make the light coming out of the end of the filaments directed more forward for tracks deep in the chamber (i.e., those farthest from the image tube) than it is for the tracks found near the image tube. Since the light spreads in passing through the glass window, tracks originating deep in the chamber will be narrower than those occurring near the image tube. The effect is indicated by measuring the width of the tracks. The results are shown in Fig. 10. Track width was determined visually and is, therefore, a poorly defined quantity but appears to have some significance. A feeling for the number of reflections involved before attenuation becomes serious can be obtained as follows. Let $n(x, \theta)$ be the number of reflections a light ray experiences when emitted at an angle θ from a point on the axis a distance x from the end of a filament. Let d be the diameter of the filament, t the thickness of the image tube glass window, and T the track width. (The index of refraction of filament and glass are considered to be the same. This is not a serious assumption for the purpose.)

$$\text{Then: } n(x, \theta) = \frac{x}{d \cot \theta}$$

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Fig. 8. Minimum-ionizing μ meson tracks.

Fig. 9. Slow μ meson tracks showing decay electrons.

Fig. 10. Mean track width as a function of depth in the chamber.

$$T = 2 t \tan \theta + d = \frac{2 t n d}{x} + d \quad (\text{Eq. 1})$$

This relationship is plotted as the dotted line of Fig. 10 with n taken as 30, indicating that for more than this number of reflections attenuation becomes serious. Direct attenuation measurements indicate that this figure is more like 40 and also the general form of the fit is not good for shallow depth. It is probable that the crude width measurement and oversimplifications in deriving Eq. 1 have combined to render the comparison of little value except for qualitative considerations. The nature of the effect can be demonstrated with reference to Fig. 11. On the left, a slit (above) and entire filament system is photographed from the output of a two-stage tube (gain ~ 1000) illuminated from a source 24 in. away. On the right, the same pattern is seen illuminated with the source 1/2 in. behind the filaments. The effect of forward peaking in preserving resolution through the front face is apparent.

Of more interest is a consideration of chamber characteristics by means of chamber efficiency studies. A simple criterion of the number of times a track is seen, compared to the number of times the counter system indicates a track should be seen, comes to a decision as to what constitutes a track. We believe that minimum ionizing particles anywhere in the chamber are detectable. However, there is a variation of the character of the track with position. This variation occurs in the gap structure of the track, and the comparison between the length of track seen and the potential length in the chamber. Generally speaking, the observed length of track is ΔL units less than the potential length of track L due to edge effects. These edge effects are reasonable in view of the distortion and poorer resolution intrinsic to the edges of the image tube field of view, and of the reduced transmission of the coupling lens near the edge. The effect on ΔL of increasing depth within the chamber is illustrated in Fig. 12. The resemblance of Fig. 12 to Fig. 10 is apparent.

In addition to the effect of shortened tracks, there is a gap structure within the track. Some consideration has been given to the effect of the structure of the filament array along the path of the particle. When one considers the variation of path lengths of the particle in various filaments, the small number of photons involved and the consequences of

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Fig. 11. Effect of collimation of light on resolution.

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Fig. 12. ΔL as a function of depth of track.

the low cathode efficiencies (~ 10 per cent) dictated by the Poisson statistics, the ΔL and gap observations seem reasonable (3) and emphasize the need for improved first cathode efficiencies even in systems with apparently comfortable overall gains.

The system being described was placed in 90 Mev π^+ and 90 Mev π^- beams through the courtesy and cooperation of the Nevis Cyclotron group. The results were very informative and are in process of publication. Some examples are given here to illustrate the sorts of tracks obtained in high flux beams under pulsed conditions. The machine background was found to give no difficulty, even at peak current, corresponding to > 200 particles/second through the chamber. The magnetic fields were successfully shielded against. The effect of pulsing is seen in Fig. 13. In Fig. 14, the upper track is a π^+ decay (μ link not resolved) contrasted with the lower track given by a stopping π^- . Other examples of π^- stops are shown in Fig. 15 and some scatter events in Fig. 16. In general, the incident π^+ is not seen in these scatter events, due to contrast effects and a poor cathode spot. In all cases, counter selection schemes designed to trigger on the event of interest were used.

It is observed that the track quality in these figures is inferior to those previously obtained. This is due to the fact that various focussing and exposure conditions were tried. A motion picture of the kinescope face was taken, showing tracks through a continuously "open" system under varying beam intensities and gain conditions. In general, these tracks were superior to the still picture records of the kinescope. It is possible that the lower contrast film used in the motion picture is partially responsible for this.

Fig. 13. π meson tracks; upper: unpulsed; lower: pulsed operation.

Fig. 14. Upper: π^+ decay; lower: π^- stop with 35 Mev proton.

Fig. 15. π^- stops.

Fig. 16. π^+ scatters.

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APPLICATIONS OF GIANT SCINTILLATION DETECTORS*

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INTRODUCTION

In this talk, I will describe some developments of the past few years relative to the use in physical research of the very large scintillation detectors. If I may remind you, the large detector -- except for size -- operates in much the same way as a small one. The effect of size is to increase the sensitive mass and hence absorption of the system, be it for neutrons, gamma rays, charged particles, or neutrinos. Along with size come increased demands on transparency to the scintillation light, reflective coatings, the use of many photomultiplier tubes, and the trappings associated with sheer mass. I will not dwell on these design problems, but consideration of them is the day to day concern of the experimentalist and any advance, such as the discovery of a cheaper or more efficient scintillator, has an important effect on the research that can reasonably be contemplated.

PLANNED USES

Conservation of Heavy Particles

The principle of heavy particle conservation, called conservation of baryons, which implies that the number of nucleons

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*Work done under the auspices of the U. S. Atomic Energy Commission.

(reckoned algebraically) is constant, is one of the fundamental assumptions of physics. According to this principle, for example, free protons should not be expected to exhibit any radioactivity. Ordinary decay of the neutron is consistent with the principle because the products include a heavy particle, i.e., a proton. As reported in the 1957 Liquid Scintillation Counting Conference, the stability of nucleons had been checked by a Los Alamos group using large liquid scintillators with the resultant lower limit of 10^{22} years. This limit was raised by Los Alamos to 4×10^{23} years in 1958 and to 10^{26} years by a group at CERN in 1959 (1).

Equipment is now being constructed at Case Institute by C. Giamati and myself, which should enable this limit to be raised significantly. The idea of the Case experiment is to shield a relatively small (200 liter) detector from cosmic rays by going into a deep salt mine and using a large anti-coincidence detector. Figure 1 shows a schematic of the experiment. Any proton decay (either bound or unbound proton) will give rise to energetic charged lighter particles, e.g., mesons, electrons. A decay in the scintillator will, therefore, produce a pulse. To prevent such an event from also triggering the cosmic ray anticoincidence, an iron isolation shield is placed between the two detectors. It is estimated from cosmic ray measurements made in the Morton Company salt mine, which will be used for this experiment, that the anti-coincidence will be required to reduce the cosmic rays by a factor of only 10^3 to enable a lifetime of $\sim 10^{27}$ years to be detected.

Further Reactor Antineutrino Studies (2)

Thus far we have seen the interaction of free antineutrino with matter via the reaction

As described in the 1957 conference, this series of investigations was intimately related to the Los Alamos development of large scintillation systems. In those experiments we succeeded in measuring the interaction cross section to within + 23 per cent $[\sigma = (1.10 \pm 0.25) \times 10^{-43} \text{ cm}^2/\text{fission } \bar{\nu}]$, and in obtaining a very crude but reasonably direct measure of the fission antineutrino spectrum. It is a matter of some interest to measure this fundamental interaction cross section and the antineutrino spectrum with better precision, and this is one of the

Fig. 1. Schematic of nucleon stability experiment.

objects which has led to the design of the equipment shown schematically in Fig. 2. Figure 3 is a picture of the detector shell prior to the addition of the tubes, circuitry, etc. When it is outfitted, this 2000 liter vessel will have a complement of 132 5-in. photomultipliers. The sequence of events is as follows: an antineutrino transmutes a proton in the inner sphere producing a neutron and positron, which are captured and annihilate within the sphere. The essential features of this detector are that it makes a well defined target with minimal edge effects and a much higher cadmium concentration than in the past. Consideration of the characteristics of such a detector indicates significant reduction in backgrounds, both accidental and those associated with cosmic rays, a high and well determined efficiency for antineutrino-induced events, and improved energy resolution. A signal rate of 30 hr⁻¹ is anticipated.

The same detector, except for a change in the contents of the inner sphere, is being considered for use in observing the reaction

The change will consist of substituting a mixture of deuterated and regular scintillator for the regular scintillation with which reaction (1) will be studied. The deuteron reaction has a cross section which is an order of magnitude smaller than the proton reaction. However, it is hoped that the more distinctive nature of the event which is marked by two neutrons will aid in discriminating further against the background.

High Energy Neutrinos

Within the past year Pontecorvo, Schwartz, Lee, and Yang have suggested that high energy machines capable of producing observable quantities of neutrinos were now a real possibility. In the same period, two such machines -- the colossal CERN and Brookhaven AGS accelerators -- have been brought into operation. Interest in this possibility is due to the fact that the weak interaction has thus far been studied at low energies which do not reveal its structure. High energies, on the other hand, are in principle capable of asking such detailed questions. By way of orientation, it will be recalled that the wavelength of a particle, λ , which measures its size, decreases with increasing particle energy and that such reasoning led to the electron scattering experiments of

Fig. 2. Schematic of antineutrino detector.

Fig. 3. Shell of antineutrino detector.

Hofstadter and collaborators at Stanford in which the structures of the proton and deuteron were studied. Other questions which may now be subject to experimental check include: Is the β^- decay ν the same as the ν associated with meson decay?

A schematic of a high energy ν facility is shown in Fig. 4. Protons strike a target producing, among other particles, Π mesons which decay in flight giving ν 's. The high energy of the parent proton is reflected in a generally forward motion of the decay products. A massive shield removes all particles but the ν (and $\bar{\nu}$), which then enter the experimental area.

Analysis of the details shows that for ten 25 bev protons per pulse and 10^3 pulses/hr (as at CERN), we can expect to obtain 1 event/hr in a 50-metric ton mass of H_2O . This is a conservative estimate. $\lambda_1 \sim \lambda_2 \sim \lambda_3 \sim 20$ meters, which indicates the need for large detectors. Consideration of the cosmic ray background during the machine pulses shows that anticoincidence detectors are required for counting experiments.

The anticoincidence requirements are truly impressive, and measures contemplated at the ZGS machine under construction at the Argonne National Laboratory stagger the imagination -- the entire experimental set-up may be enclosed in an anticoincidence detector. This would require at least several tens of square meters of detector! There is, however, no technical reason why such a jumbo-sized anticoincidence shield cannot be constructed.

(This large area detector calls to mind the extensive cosmic ray shower detector array set up by Rossi's M. I. T. group at Volcano Ranch, near here.)

Let us consider for a moment the nature of the ν event so as to understand the ν detector needs. Reaction (1) for high energies might be generalized to read,

$$\bar{\nu} + p \rightarrow \beta^+ + n + \alpha \Pi \quad (\text{Eq. 3})$$

where α is the multiplicity of pions produced. If $\bar{\nu}$ has an energy of 500 Mev, $\alpha \lesssim 2$ and the β^+ and n have energies $\gtrsim 100$ Mev. The occurrence of this reaction would prove the identity of neutrinos from Π , μ , and β decay. Such high energies make possible the use of Cerenkov detectors, but the cost in photomultiplier tubes and the insensitivity of

Fig. 4. Schematic of an experimental arrangement for high energy neutrino experiments.

Cerenkov effect to lower energies favor scintillation detectors, especially since the recent Los Alamos find of a low cost scintillator solvent.

Cosmic and Cosmic Ray Neutrinos - High Energy

In concluding, I would like to pose the question: Is there any hope of seeing high energy neutrinos from the cosmos (cosmic) or in a less ambitious vein, neutrinos secondary to cosmic ray primaries which strike the earth's atmosphere (cosmic ray)?

Because of the high energies involved, natural radioactivity poses no problem, and we must contend only with the other particles in the cosmic radiation -- specifically, muons and their secondaries. Since the best way to contend with muons is to avoid them, a deep underground (or water) location is indicated. However, we cannot hope to go deeply enough and so an anticoincidence is necessary. A reduction of $\sim 10^6$ can be achieved by using existing salt mines; an anticoincidence could give another 10^3 or so.

The signal rate from the cosmic ray ν 's is very dependent on the theoretical assumptions but conservatively estimated might be $\sim 1 \text{ day}^{-1}$ in 5000 m^3 .

Assuming such a behemoth could be built, one might hope to achieve a signal to background of 10^{-3} . Some additional discrimination can be achieved on an energy basis, since the cosmic rays are mostly of very high energy.

It is just becoming possible to speak of these experiments. At Case we are beginning to study these questions in some relatively small-scale experiments underground.

CONCLUSION

In this talk I have touched on some of the more exotic uses and possibilities of very large scintillating systems. I have mentioned low energy γ studies, high energy physics, further cosmic ray questions, and anticoincidence applications on a large scale.

In the past few years, experimentalists have grown

accustomed to the complexities associated with high energy physics in particular, so that thoughts of hundreds of photomultipliers and thousands of gallons of scintillator are not quite as frightening as they once were. Meanwhile, it appears that the unique characteristics of large scintillation detectors will continue to make interesting new applications possible.

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