

LIQUID SCINTILLATION COUNTING IN INDUSTRIAL RESEARCH

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It is the purpose of this paper to discuss liquid scintillation counting primarily from the point of view of its utility in tracer experimentation in industrial research. Emphasis is placed upon experience with this method gained over the past five years at the Shell Development Company laboratories in Emeryville. Special attention is devoted to the subjects of concentration sensitivity of the method, absolute counting efficiencies for different beta-emitters, fluorescence quenching, and examples of the use of the method in a number of tracer studies at Emeryville.

ADVANTAGES OF THE LIQUID SCINTILLATION METHOD

The principal advantages of the liquid scintillation (LS) method for the counting of beta-emitting radioisotopes may be summarized as follows:

- (1) freedom from limitations of self absorption,
- (2) freedom from window absorption,
- (3) simplicity of sample preparation,
- (4) short dead time, (approx. 1 μ sec),
- (5) proportional response,
- (6) ease of absolute calibration.

These various features combine, as will be shown in more detail below, in producing a method ideally suited to high efficiency detection, even in routine counting, of even extremely low concentrations of beta-emitters—down to concentrations as low as 1 disintegration/min g.

DISADVANTAGES OF THE LIQUID SCINTILLATION METHOD

No method, of course, is without its limitations or disadvantages. The principal disadvantages, or complications, connected with the LS method are summarized below:

- (1) relatively high cost of the counting apparatus,
- (2) difficulties caused by fluorescence quenching,
- (3) difficulties caused by light absorption (colored samples),
- (4) limitation to samples soluble (or readily suspended) in the liquid scintillator,

- (5) greater electronic complexity, leading to problems of drift, reliability and precision.

As will be shown below, none of these limitations is really very serious, as means of circumventing them are readily available.

TECHNIQUES FOR ATTAINING MAXIMUM RESPONSE IN LIQUID SCINTILLATION COUNTING

There are a number of well-known, and some lesser known, methods of achieving maximum efficiency in LS counting. Many of these are quite suitable for use in routine counting, but add to the expense of the counting apparatus. Others are sufficiently complicated that their use is not justified in routine counting, but only in special cases where the ultimate in counting efficiency is mandatory. The importance of some of these factors is different if one is seeking maximum counting efficiency, instead of maximum concentration sensitivity. These methods and factors are discussed below.

(1) *General factors conducive to maximum counting efficiency and low noise*

(a) *Apparatus:*

- (1) selection of photomultiplier tubes with high signal to noise ratios,
- (2) use of high-gain, low-noise, linear, non-overloading amplifiers,
- (3) magnetic shielding of photomultiplier tubes,
- (4) refrigeration of photomultiplier tubes to minimize thermal noise,
- (5) use of an efficient sample cell holder, transparent to scintillator light, coated with efficient reflector of scintillation light, and firmly coupled optically to the photomultiplier tube faces,
- (6) use of upper and lower level discriminators, so as to eliminate many small noise pulses and reject many of the larger background pulses,
- (7) use of adequate shielding around the sample to decrease the radiation background,
- (8) rigid light-tightness of the sample-photomultiplier tube assembly,
- (9) operation in single channel for maximum counting efficiency, or in dual channel coincidence if single channel noise is excessive.

(b) *Scintillator solution:*

- (1) choice of an optimum combination of solvent, scintillator, and wavelength shifter,
- (2) removal of dissolved oxygen in the scintillator solution.

(c) *Sample:*

- (1) choice of a sample which contains no substances capable of quenching the liquid scintillator fluorescence,
- (2) choice of a sample that contains no substances capable of absorbing the fluorescence light,
- (3) use of optimum volume of scintillator solution plus sample (for optimum effective geometry).

(2) *Maximum sensitivity for the detection of small amounts of beta-emitter*

In general, a given amount of beta-emitter can be detected more readily, the smaller the total sample in which it is present, i.e. the higher the specific activity. With very small samples, difficulties due to quenching and light absorption are minimized, and the radiation background is at a minimum.

(3) *Maximum sensitivity for the detection of small concentrations of beta-emitter*

To achieve maximum concentration sensitivity, one should employ as large a sample as possible, consistent with the decreasing counting efficiency with increasing dilution of liquid scintillator by sample. With the present apparatus samples as large as 40 ml can be counted, dissolved in 25 ml of scintillator. Under these conditions, C^{14} specific activities as low as 1.5 disintegrations/min ml can be determined to a standard deviation of $\pm 10\%$ in 30 min counting time, assuming an equal counting time for background (200 counts/min) measurement. A high degree of concentration sensitivity is very important for large-scale tracer studies.

COMMERCIAL LIQUID SCINTILLATION COUNTERS

Liquid scintillation counters have only been available commercially for approximately the last 4 years. At the present time there are three manufacturers of such counters: The Packard Instrument Company, Technical Measurements Corporation, and Tracerlab. All three of these companies are located in the United States. As yet, none are manufactured outside the United States. Each of these three commercial units is of the dual coincidence type, pioneered by HAYES *et al.*¹ and HIEBERT and WATTS.² Primarily because of the coincidence circuit involved, these instruments are somewhat expensive, costing in the range of \$4500–\$8000 for a complete apparatus, including scaler. Excellent refrigerated single channel liquid scintillation counters have been developed by ROSENTHAL and ANGER,³ and GORDON and HODGSON,⁴ but no commercial single channel instrument is as yet available. A commercial single channel apparatus should be considerably less expensive than the coincidence type. With the advent of improved photomultiplier tubes and low-noise, high-gain amplifiers, room temperature single channel instruments have been recently developed by PRINGLE *et al.*⁵ and by GORDON and HODGSON.⁴

PROCEDURES FOR ROUTINE LIQUID SCINTILLATION COUNTING

The work described below has been carried out with two coincidence-type liquid scintillation counters, one developed in 1953 in co-operation with Tracerlab,⁶ and the other a similar, but improved, unit—the first Tracerlab commercial model, obtained in 1954.

The instruments in each case consist of two selected Du Mont 6292 photomultiplier tubes mounted at right angles to one another, along with their respective cathode followers, inside a small sized refrigerator. The two photomultiplier tubes are each coupled with high viscosity silicone fluid to a Lucite sample cell holder (with white reflector), each tube is enclosed lengthwise with a Mu-metal magnetic shield, and the whole sample-phototube region is surrounded by 2 in. of lead shielding. Provision is made for sliding back part of the lead shield during the changing of samples. This latter operation is carried out via a gloved port located in the door of the refrigerator. With a rack of samples placed in the refrigerator, it is then possible to proceed from one sample to the next without the necessity of opening the refrigerator or of turning off the phototube high voltage. Difficulties with moisture condensation on sample bottles and on the Lucite holder faces are thus obviated. The rack holds twenty samples. The refrigerator not only serves as a cold region (-5°C), to minimize thermal noise from the phototubes and increase the fluorescence efficiency of the solution, but also as a light-tight region, since no light other than scintillator fluorescence light can be permitted to fall upon the photocathodes of the phototubes. The apparatus employs line voltage filter-stabilizers and a precision stepped high voltage supply. The focusing voltage, between the photocathode and the first dynode, is adjusted to give maximum efficiency for each phototube. An upper level discriminator is used to reject pulses too large to have possibly come from the isotope in question. This is very helpful in reducing the background in tritium counting.

Two types of sample bottles are used. One type is a standard 75 ml volume wide-mouth weighing bottle, with ground glass stopper. These are selected from a supply of the regular weighing bottles according to outside diameter. Only those fitting the Lucite cell holder with not more than a few tenths of a millimeter to spare are used. For very accurate work, especially with tritium samples, a set of calibrated cells is used (calibrated with tritium under fixed conditions). The second type of sample bottle is a precision-made bottle supplied to close tolerances by a manufacturer of scientific glassware. Both types are completely transparent to the scintillation light. No liquid coupling is used between the sample bottle and the Lucite holder.

Although many solvent-scintillator-shifter combinations have been studied, the standard ones used consist of 4 g 2,5-diphenyloxazole (PPO) and 15 mg of 1,6-diphenyl-1,3,5-hexatriene (DPH)/l., of solvent. *p*-Terphenyl is not sufficiently soluble at -5°C for efficient use as a scintillator. The solvent used is toluene for organic samples, and a mixture of 2/3 toluene and 1/3 absolute ethanol (by volume) for aqueous samples. Although slightly higher counting efficiencies can be obtained, especially for tritium, by flushing dissolved oxygen out of the scintillator solutions,⁷ this is not done in routine counting because of the time required and the possibility of lack of reproducibility if some

oxygen gets back into the solution between the time of sample preparation and counting. A half hour period is allowed for each rack of samples, after placing in the refrigerator, to provide time for decay of the short-lived phosphorescence of the liquid scintillator after exposure to room light, and for cooling of the solutions. Where a large number of samples are to be counted, additional racks of samples are pre-cooled and dark-adapted in another refrigerator and then transferred in the dark to the LS unit just before counting. With this saving of time, it is quite feasible both to prepare and count as many as 100 samples/8hr day.

Tritium samples insoluble in either of the scintillator solutions are usually burned, the water of combustion collected quantitatively, and then counted in the toluene-ethanol scintillator solution. Insoluble C^{14} samples, on the other hand, are normally burned, the resulting CO_2 collected quantitatively, and then measured in an ionization chamber-vibrating reed electrometer apparatus. The technique of counting insoluble samples as suspension, described in the literature,⁸ is not employed.

Samples are usually counted at maximum amplifier gain and a phototube high voltage that gives the optimum sample to background counting rate ratio for the particular isotope in question. With the relatively low gain (ca. 9000) amplifiers used, H^3 , C^{14} - S^{35} and P^{32} are normally counted at 1800, 1650 and 1250 V, respectively. Background and standard solutions of the isotopes in question are counted at intervals during the course of counting a series of samples, so as to provide corrections for any apparatus drifts.

It might be mentioned that beta-gamma emitters may be counted in the same fashion as pure beta-emitters, as only a small fraction of the gamma-ray photons interact in the small volume of scintillator solution, and those are normally in coincidence with a beta particle. In studies involving beta-gamma emitters, however, it is usually simpler to count the gammas, with a NaI(Tl) scintillation counter, rather than the betas, unless gammas are emitted in only a small percentage of the disintegrations of the isotope.

EFFECTS OF FLUORESCENCE QUENCHING

It is well known that a number of types of compounds can act as quenching agents in scintillator solutions, disposing of some of the excitation energy in non-radiative processes, and thus decreasing the light output/beta-particle. In this fashion many of the light pulses resulting from beta-particles at the low end of the beta energy spectrum may be decreased to the point that they do not produce a measured count, i.e. the counting efficiency is reduced.

Since samples to be counted may contain one or more such quenching substances, at various concentrations, this can pose a troublesome problem in liquid scintillation counting. Studies in these laboratories, however, have shown that the problem of fluorescence quenching has perhaps been exaggerated in the minds of some. For example, in Fig. 1 are shown typical C^{14}

quenching curves for a variety of types of organic compounds. In each case 25 ml of toluene-PPO-DPH plus 1 ml of a standard C^{14} -benzene solution was counted, with progressively increasing amounts of the non-active compound whose quenching characteristics were under investigation. Amounts of compound of 1, 2, 5, 10, 20, 30 and 40 ml were studied. With no quenching

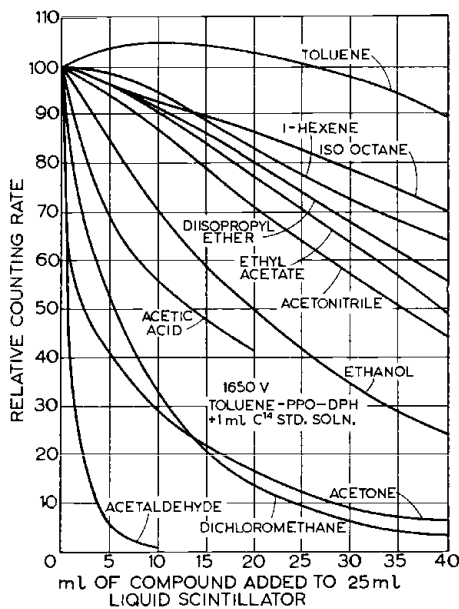


Fig. 1.

one might then expect an almost horizontal line for the plot of counting rate vs. volume of compound added. As can be seen from Fig. 1, this is approximated by the behavior of toluene. The rise to a slight maximum at about 10 ml toluene is due to the fact that the effective geometry is optimum at about 35 ml total volume. The curve for pure scintillator solution for volumes of 25–65 ml, containing the same amount of C^{14} , follows exactly the same path as that shown in Fig. 1 for toluene plus scintillator solution, showing that the dilution effect of the toluene is negligible. Other aromatic hydrocarbons, such as benzene and xylene, behave almost exactly the same as toluene.

Saturated hydrocarbons and olefins do not act as quenchers, but in very large amounts do somewhat decrease the energy transfer from solvent to scintillator. Thus, with 40 ml of added compound, these substances still give counting efficiencies from 70 to 90% of that with 40 ml of toluene. Examples of such compounds studied in this manner are *n*-heptane, *iso*-octane, methyl cyclopentane, methyl cyclohexane, 1-decene, *n*-decane, 1-hexadecene, and 1-hexene. Two representative compounds, *iso*-octane and 1-hexene, are

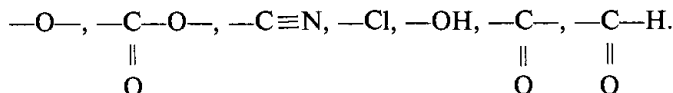
shown in Fig. 1. Ethers, esters, and nitriles are found to behave in a similar fashion, but with somewhat greater effect on counting efficiency. Thus, as shown in Fig. 1, di-*isopropyl* ether, ethyl acetate, and acetonitrile give counting efficiencies (C^{14}) respectively 62%, 54% and 49% of that obtainable with an equal volume, 40 ml, of toluene. With only 1–5 ml samples of such compounds, in 25 ml of scintillator, the counting efficiencies are only a few per cent lower than with toluene.

Alcohols and carboxylic acids reduce the counting efficiency still further. As shown in Fig. 1, ethanol gives a counting efficiency only 27% of that obtained with an equal volume (40 ml) of toluene. Other alcohols studied (methanol and *isopropanol*) give almost identical curves. The curve for acetic acid stops at a volume of 20 ml because of the limited solubility of acetic acid in the scintillator solution at -5°C . At this point the counting efficiency is 46% of that obtained with an equal volume (20 ml) of toluene.

Ketones are fairly severe quenching agents. Thus, as can be seen in Fig. 1, even 1 ml of acetone, added to 25 ml of scintillator solution, reduces the counting efficiency by 40%. Methyl ethyl ketone (not shown in the Fig.) is also a severe quencher, but not as severe as acetone, 1 ml of methyl ethyl ketone reducing the counting efficiency by 33%. Aldehydes are severe quenching agents. Thus (see Fig.) 1 ml of acetaldehyde lowers the counting efficiency by 62%. The aromatic aldehyde, benzaldehyde (not shown in the figure), is even more severe, even 0.1 ml lowering the efficiency by 49%.

Monochloro compounds are not severe quenchers. Thus, 40 ml of 1-chloropropane (not shown in Fig. 1) still gives a counting efficiency 32% of that obtained with 40 ml of toluene. A dichloro compound, with both chlorine atoms on the same carbon atom, is a fairly severe quencher. Thus (see Fig. 1), even 1 ml of dichloromethane lowers the counting efficiency by 20%. A similar trichloro compound, chloroform (not shown in the figure), is more severe yet: 1 ml lowers the efficiency by 42%. Carbon tetrachloride (also not shown in the figure) is even more severe: 1 ml lowers the efficiency by 99.5%.

It is evident from the above examples that fluorescence quenching in these systems is determined by the presence of functional groups. Thus, the severity of quenching increases in the sequence of functional groups,



Rigorously, such comparisons should be made at equal mole fractions, rather than equal volumes, of the compounds studied, but the sequence is unchanged if such a comparison is made. At equal mole fractions, one might then expect all monofunctional alcohols, for example, to show about the same degree of quenching. This would not be true, of course, on an equal volume fraction

basis, if one extended the comparison to the higher molecular weight alcohols. Other types of quenchers reported in the literature are nitro compounds, mercaptans, phenols, and amines.⁹

Quenching studies have also been carried out in these laboratories with the same compound studied with C^{14} , but with tritium as the beta-emitter. Tritium, of course, because of its 8-fold lower beta E_{\max} , produces much smaller liquid scintillation pulses than does C^{14} , and hence would be expected to be more sensitive to fluorescence quenching than C^{14} . Such proves to be the case. Some of the results are shown in Table I. It is seen that for each type of compound the counting efficiency for H^3 is lowered more by the addition of 40 ml of the compound than is the counting efficiency for C^{14} . On the other hand, the counting efficiencies for isotopes emitting more energetic beta-particles, e.g. Cl^{36} ($E_{\max} = 0.71$ MeV) and P^{32} ($E_{\max} = 1.71$ MeV) are much less sensitive to the effects of quenching agents than is the case for carbon-14.

TABLE I
Comparison of Quenching Effects on H^3 and C^{14}

Compound	Relative counting rate with 40 ml of compound added (100 = no quenching)	
	H^3	C^{14}
Toluene	68	91
<i>n</i> -Heptane	36	68
Ethanol	5.6	21
Acetone	0.73	6.5

In those instances in which appreciable quenching is either known or suspected to be present, the internal standard method¹⁰ is employed to correct each sample counting rate to what it would be in the absence of quenching. This procedure involves, of course, two countings of each sample, with the addition of a small, exactly measured amount of a reference solution of the same isotope added in between the two counts. From the increase in counting rate following addition of the reference solution, the degree of quenching is readily computed and the correction made. For samples giving a counting rate of more than a few thousand counts/min, a much simpler approximate method of quenching correction may be employed. This method, described more fully below, involves the calculation of the counting efficiency of the sample from the counting rates obtained in the two separate channels and in coincidence. No reference solution or calibrated standard is required, and hence no additional handling of the sample. Furthermore, this method enables one to normalize all data, with or without the presence of quenching agents

or colored substances, to a 100% efficiency basis, i.e. to a disintegrations/min, rather than merely counts/min, basis.

One problem not yet solved is that of determining the proper background counting rate to use in cases of low activity samples containing quenching agents and/or colored substances. If the sample counting rate is high, relative to the normal background counting rate, no appreciable error is introduced by using the normal background rate in subtracting from the gross counting rate to obtain the net sample counting rate. However, if the sample gives a counting rate only slightly above background, the true value of the background becomes very important. Quenching agents and colored substances also lower the background rate, but by an unknown amount. Efforts to devise empirical methods for obtaining such background corrections, by measurements with the lead shield both open and closed, and by the use of an external gamma-ray source, are in progress at the present time and will be reported upon at a later date.

EFFECTS OF COLORED SUBSTANCES

It is evident that if a sample contains one or more substances which can absorb light in the region of the spectrum in which the scintillator solution fluoresces, the counting efficiency will be reduced, just as in the case of fluorescence quenching. In tracer studies in these laboratories it is often necessary to count tritium or carbon-14 samples of various kinds or oil samples that are often yellowish in color. In such cases the same kind of internal standard correction is made as in the cases of quenching. Similarly, for more active samples, the single channel-coincidence method of correction, mentioned above in the section on quenching, is often employed.

DETERMINATION OF COUNTING EFFICIENCY

It is well known that the shapes of most beta-particle energy spectra are about the same. For example, beta-ray spectra for tritium and carbon-14, taken from the literature, are shown in Fig. 2. Although the maximum beta-particle energy of C^{14} (0.155 MeV) is about eight times that of H^3 (0.019 MeV), the shape of the curves are very similar. The distribution curves rise to a maximum at an energy at or below about 1/3 of the E_{max} , and then decline at first rapidly, and then more gradually, to zero at the E_{max} . With presently available liquid scintillators and photomultiplier tubes, the pulses produced by beta-particles having energies of more than about 20 keV are readily distinguished from phototube thermal noise pulses (including statistical broadening) purely on the basis of pulse size. For pulses arising from lower energy beta-particles it is more difficult to distinguish between beta pulses and noise pulses, because of their similarity in size, and hence the coincidence arrangement is usually employed, so as to distinguish between random noise pulses and coincident beta pulses of the same size. In principle, one should be

able to approach 100% counting efficiency for even a very weak (soft) beta-emitter, by employing sufficient electronic gain so that almost all of the beta pulses are amplified to the point that they exceed the discriminator setting of the scaler employed. In practice, however, the noise level becomes excessively high before such high counting efficiencies are reached with very soft

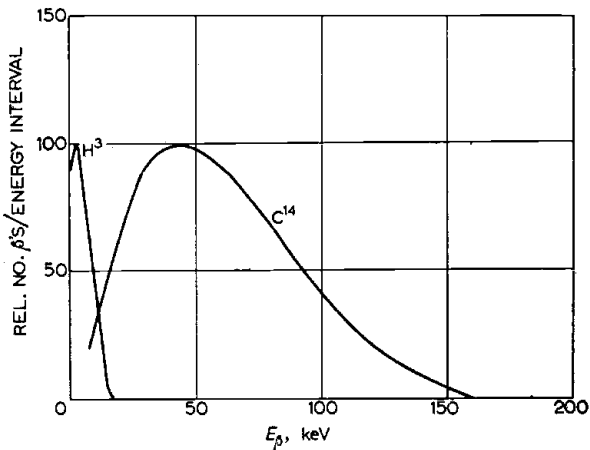


Fig. 2.

beta-emitters such as tritium. Thus, with the liquid scintillation apparatus described in this paper, the maximum efficiency attainable with tritium is about 25% ,with coincidence counting (the single channel efficiencies are thus about 50% each). This efficiency is obtained at a phototube high voltage of 1800 V. At higher voltages, although the tritium counting efficiency is higher, the noise level becomes excessive, reproducibility becomes very poor, and phototube life declines markedly. At 1800 V the noise level and radiation background (35 ml total volume) are each about 100 counts/min in coincidence. With C^{14} the maximum counting efficiency normally attained with this apparatus is about 75% in coincidence (about 85% in each channel). With very hard beta-emitter such as P^{32} the coincidence counting efficiency is about 99%.

In virtually all tracer work only relative counting is needed, i.e. it is only necessary to count all samples at a constant efficiency, not necessarily at 100% counting efficiency. Similarly, in most work it is not even necessary to know the exact value of the counting efficiency, as long as it is constant. However, from the standpoint of minimizing the amount of radioisotope needed for a particular problem (important from the point of view of health physics, cost, and ease of handling) it is of value to employ a counting method of high efficiency. Furthermore, in the planning of such a tracer study at least an approximate notion of the counting efficiency is needed in order to decide how much activity is needed for the study. Thus, methods of measuring the

counting efficiency are desirable. In liquid scintillation counting the presence of variable amounts of quenching agents and/or colored substances in the samples may introduce a further complication in that the various samples in a particular study may be counted with different efficiencies, even though counted under identical conditions. Here again, some means of determining the relative or absolute counting efficiencies with which the various samples are counted is of value. The internal standard method, discussed above, serves to normalize all of the counting rates in such instances to a constant counting efficiency, but requires two handlings of each sample. If the internal standard solution has been calibrated, then it is also possible to normalize all samples to 100% counting efficiency. However, in these laboratories it has been found sufficient, and more convenient, to employ a simple approximate method, not involving the addition of an internal standard or comparison with calibrated samples, in most instances in which a determination of the absolute counting efficiency is required. This method is described below.

Under a fixed set of counting conditions, let the counting efficiencies of channels 1 and 2 be the unknown quantities e and e' , respectively. If A represents the sample activity, in disintegrations/min, then the single channel net counting rates in channels 1 and 2 will be Ae and Ae' , respectively. Similarly, the counting efficiency and counting rate in coincidence will be ee' and Aee' , respectively. Thus, the coincidence counting rate divided by the counting rate in channel 1 is equal to e' , and the coincidence rate divided by the counting rate in channel 2 is equal to e . Hence, by simply counting a sample in coincidence and in the two separate channels, one obtains the data from which each single channel efficiency and the coincidence counting efficiency may be simply computed. Of course, this method requires that one count a background sample in a similar fashion, so that net counting rates may be used.

The method, with the present apparatus, is therefore only useful with samples having a disintegration rate of the order of a few thousand disintegrations/min or higher, since the single channel noise rates are of this order in the range of voltages concerned.

This method of measuring the counting efficiency has been tested by comparison with National Bureau of Standards calibrated samples of H^3 , C^{14} and P^{32} with the results shown in Table 2. In each case 50 ml of the standard toluene-ethanol-PPO-DPH scintillator solution plus 0.2 ml of aqueous sample was employed, and maximum amplifier gains. Without the ethanol and water, of course, the counting efficiencies for H^3 would be markedly higher, and those for C^{14} somewhat higher. The agreement is seen to be fairly good, except that the computed efficiencies generally tend to be 1 or 2% higher, on an absolute scale, than the true efficiencies. It may be noted that the highest photomultiplier tube voltages reported are 1250 for P^{32} , 1650 for C^{14} , and 1800 for H^3 . The reason for this is that double pulsing begins to occur

above these voltages, with the isotopes in question (except H^3), causing erroneously high single-channel counting rates, although not affecting the coincidence counting rates. Fortunately, the computation method described gives an indication of the onset of double pulsing by showing an apparent decline in coincidence counting efficiency above a certain voltage, even though

TABLE 2
Comparison of True and Computed Liquid Scintillation Counting Efficiencies (Aqueous Samples)

Isotope	Photomultiplier tube voltage	% Counting efficiency	
		True (NBS)	Computed (coinc. method)
H^3	1500	5.7	7.3
	1600	8.3	9.6
	1700	10.7	12.8
	1800	11.8	13.4
C^{14}	1500	54.0	53.2
	1550	57.3	55.5
	1600	59.8	60.5
	1650	62.8	65.9
P^{32}	1100	84.3	88.7
	1150	86.3	89.0
	1200	88.6	89.0
	1250	90.9	90.1

the single channel and coincidence counting rates are increasing. For example, with P^{32} counted at the excessively high voltage of 1800 V, the single channels double pulse to the extent that the counting rates are 80% higher than the sample disintegration rate, but the coincidence counting rate is exactly equal to the disintegration rate—the computed coincidence efficiency is only 31%, instead of the true value of 100%. Thus, this method has served to indicate the proper region of high voltages to be used in counting the various isotopes, and to provide a means of ascertaining the approximate counting efficiency of any sample being counted, whether in the presence or absence of quenching agent or colored material, so long as the activity level of the sample is sufficient for application of the method.

CONCENTRATION SENSITIVITIES ATTAINABLE

One may define the absolute sensitivity of a counting method for a particular radioisotope as the minimum amount of that isotope (expressed, say, in terms of disintegrations/min or μc) detectable to a standard deviation of

$\pm 10\%$ in a 30 min counting time, 30 min also being devoted to background counting.¹¹ Similarly, one may define the concentration sensitivity of a counting method as the minimum concentration of the isotope in question (expressed, say, in terms of disintegrations/min/ml or $\mu\text{c/l.}$) detectable to this same accuracy in the same length of time. With these reasonably practical criteria, the thin window Geiger-Mueller (GM) counter and the coincidence liquid scintillation counter are compared below with respect to both types of sensitivity.

As far as absolute sensitivity is concerned, the method having the higher absolute counting efficiency and the lower background is at an advantage. For the GM method, one may reasonably assume a shielded background (2 in. of lead) of 20 counts/min, a 50% geometry, negligible window or air absorption, negligible backscattering, and a 100% counting efficiency for beta-particles entering the counter, independent of the beta energy. For tritium, one may assume an infinitely thin window, i.e. a windowless flow counter. With these assumptions, one may compute that the minimum amount of beta-emitter detectable is $1.2 \times 10^{-5} \mu\text{c}$, i.e. 27 disintegrations/min. For the coincidence liquid scintillation method both the counting efficiency and the background counting rate depend upon the isotope used. The background is different for the different isotopes because of the fact that a higher overall gain is needed for the lower energy beta-emitters, such as tritium, thus resulting in a higher background. Assuming that 35 ml of scintillator is used in each case, and 2 in. of lead shielding, the coincidence backgrounds and counting efficiencies for H^3 , C^{14} , S^{35} , Cl^{36} and P^{32} would be as shown in Table 3. Computed absolute sensitivities, based upon these

TABLE 3

Liquid Scintillation Counting Efficiencies and Backgrounds for Several Beta-emitters (35 ml Total Volume)

Isotope	Efficiency, %	BG, counts/min
H^3	25	200
C^{14} , S^{35}	75	150
Cl^{36}	85	125
P^{32}	95	100

numbers, are shown in Table 4. As can be seen, the liquid scintillation method will detect almost as small an amount of isotope as the GM method. The 4π counter and the gas counter are also very good, from the standpoint of absolute sensitivity.

It is in the realm of concentration sensitivity, however, that the principal advantage of the LS method is evident, that of utilization of large samples

TABLE 4
Liquid Scintillation Counting Absolute Sensitivities

Isotope	Minimum amount detectable	
	disintegrations/min	μc
H ³	153	6.9×10^{-6}
C ¹⁴ , S ³⁵	44	2.0×10^{-6}
Cl ³⁶	36	1.6×10^{-6}
P ³²	29	1.3×10^{-6}

without self absorption limitations. Thus, with 40 ml of sample, plus 25 ml of liquid scintillator, the counting efficiencies, backgrounds, and concentration sensitivities shown in Table 5 are obtained. For the GM method, assuming infinitely thick samples, with 88% self absorption in the infinite thickness

TABLE 5
Liquid Scintillation Counting Concentration Sensitivities (40 ml Samples)

Isotope	Efficiency, (%)	BG, (counts/min)	Minimum concentration detectable	
			disintegrations/min ml	$\mu\text{c/ml}$
H ³	15	250	7.1	3.2×10^{-6}
C ¹⁴ , S ³⁵	65	200	1.5	0.68×10^{-6}
Cl ³⁶	80	175	1.1	0.50×10^{-6}
P ³²	90	150	0.93	0.42×10^{-6}

layer, and a 5 cm² sample area, one obtains the values shown in Table 6 for the concentration sensitivities of the GM method for these beta-emitters. The LS method is thus seen to be, respectively, 7800, 1000, 870, 156 and 60 times more sensitive than the GM method for H³, C¹⁴, S³⁵, Cl³⁶ and P³².

TABLE 6
Thin Window Geiger Counter Concentration Sensitivities

Isotope	Minimum concentration detectable	
	disintegrations/ min ml	$\mu\text{c/ml}$
H ³	55,400	2.5×10^{-2}
C ¹⁴	1480	6.7×10^{-4}
S ³⁵	1310	5.9×10^{-4}
Cl ³⁶	174	7.8×10^{-5}
P ³²	56	2.5×10^{-5}

The GM calculations assume samples of unit density and ranges of 0.0008, 0.030, 0.034, 0.25 and 0.79 cm in such a medium for the E_{\max} betas of H^3 , C^{14} , S^{35} , C^{136} , and P^{32} , respectively. The LS calculations utilize counting efficiencies and backgrounds obtained with 40 ml non-quenching organic samples. With aqueous samples the minimum detectable concentrations are at least 40 times larger, since one is then restricted to a maximum sample size of about 1 ml, instead of 40 ml. Also, the H^3 and C^{14} counting efficiencies then decrease to about 10% and 60%, respectively, because of the less efficient scintillator solution used.

USE IN MULTIPLE TAGGING STUDIES

As mentioned earlier, the proportional nature of the LS counter enables one to distinguish between pulses arising from beta-particles of different energies. Thus, in work in these laboratories ternary mixtures of H^3 , C^{14} , P^{32} , and H^3 , C^{14} , C^{136} have been successfully counted with resolution into the independent counting rates of each isotope. Presumably, S^{35} could be

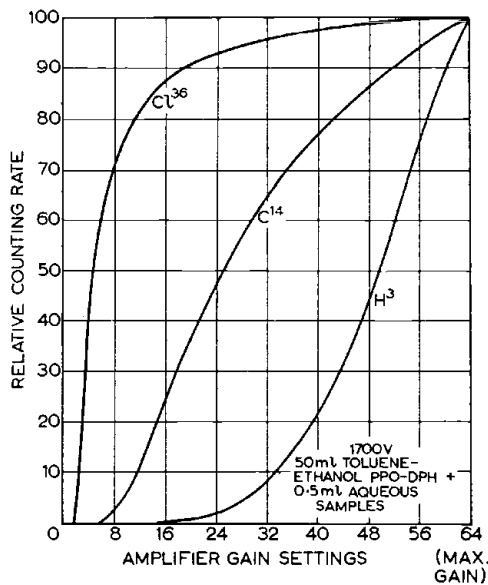


Fig. 3.

replaced for C^{14} in each of these triads with equally successful results. In fact, any three of these isotopes can be counted successfully in the presence of one another, provided that C^{14} and S^{35} are not both present simultaneously. These two have beta energies too closely alike to allow accurate resolution (E_{\max} values of 0.155 and 0.167 MeV, respectively).

There are two principal ways in which one can distinguish among the contributions of each of the two or more beta-emitters present in a LS sample. One is to count the sample at two or more different overall gains, varying either the amplifier gains or the photomultiplier high voltages. The other is to sort the output pulses by means of a pulse height analyzer. In these laboratories both methods have been used, but the gain method is used more often. An example, involving the counting of aqueous samples of H^3 , C^{14} and Cl^{36} , is shown in Fig. 3. The curves show the calibration data for separate aqueous samples of the three isotopes, plotted as relative counting rate vs. amplifier gain settings, with the counting rate at maximum gain taken as 100. If, then, an aqueous sample containing unknown amounts of these three isotopes is counted under the same conditions, but at just the three amplifier gain settings of 64 (maximum gain, corresponding to an actual amplifier gain of 9000), 16 and 6, the three contributions to the total counting rate at maximum gain may be computed. At gain setting 64, all three are contributing their maximum counts/min. At gain setting 16, tritium no longer contributes any counts, and the C^{14} contribution is reduced to 24% of its value at maximum gain, while the Cl^{36} contribution is only reduced to 88% of its value at maximum gain. At gain setting 6, neither H^3 nor C^{14} contribute any counts, whereas the Cl^{36} present is still contributing 60% as many counts as it does at maximum gain.

EXAMPLES OF USE OF LIQUID SCINTILLATION COUNTING IN INDUSTRIAL RESEARCH

In preceding sections of this paper an effort has been made to show the principal advantages of the LS counting method, particularly from the standpoint of routine counting. The advantages in speed, concentration sensitivity, short dead time, and proportional response, all of which are of importance in industrial research, have been discussed. Similarly, certain difficulties, such as those of quenching, colored samples, and sample insolubility, have been discussed. In this final section a short summary of some of the types of tracer studies carried out in these laboratories during the past four years, using the coincidence LS counter method, is presented.

H^3

- (1) The rate of combustion of lubricating oil in operating engines has been followed by means of tritium-labeled lube oil and tritium-counting of samples of exhaust water. Thousands of samples have been counted in this study.
- (2) Activity coefficients at infinite dilution have been determined directly by use of very dilute solutions of a tritium-tagged solute, employing LS counting of the equilibrium liquid and vapor phase samples.

- (3) Liquid distribution patterns in chemical engineering test trickle phase reactor units have been studied using tritium-tagged liquids and LS counting.
- (4) Exchangeable hydrogen atoms in various compounds have been determined by exchange with tritium water, followed by LS counting and correction for isotope effects.

C¹⁴

- (1) Organic reaction mechanisms, employing various C¹⁴-labeled compounds, have been studied, with LS counting.
- (2) The stability of a fuel oil additive in long term storage has been studied, with C¹⁴-tagged additive and LS counting.

S³⁵

The exchange of S³⁵-labeled H₂S with sulfur atoms in metal sulfide catalysts has been studied with LS counting of H₂S.

P³²

Entrainment in aqueous large-scale distillation columns has been studied with P³²-labeled phosphoric acid as the non-volatile tracer and LS counting of aqueous samples of overhead and bottoms.

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PART V
SPECIFIC APPLICATIONS

