

ROUND-TABLE ON 'IMPROVEMENT OF LIQUID SCINTILLATOR RESPONSE'

HOWARD H. SELIGER

National Bureau of Standards, Washington, D.C.

I feel in a rather peculiar position here, being a physicist, participating in the chemistry of the counting solution, but maybe I am a little fortunate in that I can talk physics to the chemists, and to the physicists I can say, *Phenylbiphenyloxadiazole-1,3,4*, and that might be enough.

It is rather significant that in 1895, an investigation of the luminescence process gave rise to the discovery of radioactivity. In 1903, Sir William Crookes and Elster and Geitel showed that it was possible to detect single alpha-particles using the photoluminescence of zinc sulfide. Thus scintillation counting became the first tool for the standardization of the disintegration rates of radioactive nuclides. The first application of the coincidence-counting technique was made by Geiger and Verner to determine the efficiencies of observers counting alpha-scintillations from zinc sulfide. However, with the advent of the electronic methods of detection of nuclear radiations which made it possible to detect not only individual alpha-particles, but the much less ionizing beta-particles, and at intensities tens of thousands of times greater than visual scintillation counting, the field of application of the photoluminescence counting technique lay dormant. In 1947, Kallmann showed that scintillations produced in transparent naphthalene by beta and gamma rays could be detected with an electron multiplier phototube, and is thus responsible for the re-emergence of photoluminescence as one of the most important and widely used properties for the measurement of radioactivity.

At the National Bureau of Standards, we are concerned with the preparation of disintegration-rate standards of the various radionuclides. With this in mind, we have investigated both solid and liquid scintillation counters for use as detectors and for standardization. We have, therefore, been concerned with those factors affecting the efficiency of the conversion of the kinetic energy of the incident particle into an electronic signal which can be detected. Two of the factors which will be summarized in this paper are the quenching by oxygen of, and the effect of temperature on, the light output of the liquid scintillator. In the gas counting technique, the products of ionization are separated by an electric field, and a gas discharge is initiated at the

collecting anode, producing a signal which can then be detected. In the scintillator, the energy absorbed must be converted into light, and the light must then produce photoelectrons at the photocathode of a phototube, the subsequent electron multiplication being analogous to the gas avalanche in the Geiger or proportional counter. This extra conversion process in the scintillator necessarily makes it less sensitive than the gas counter. The problem is therefore one of making the energy–light–photoelectron process as efficient as possible. In 1930, Baudoin and in 1931, Kautsky and Eberlein reported that molecular oxygen in solution in an organic, fluorescent liquid is in many instances a strong quenching agent. Kautsky showed that the quenching by oxygen of the fluorescence of the dye trypanflavine increases as the dye is dissolved in water, alcoholic and acetic solutions, corresponding to the increasing solubility of oxygen in these solvents. It was not until 1953

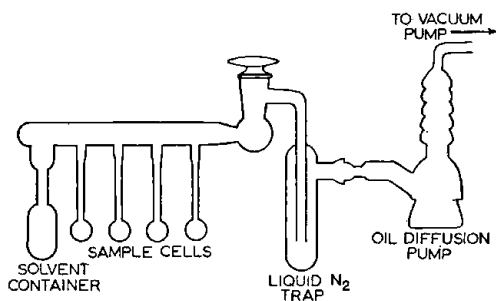


Fig. 1. Schematic view of vacuum distillation system.

that the removal of dissolved oxygen was applied to liquid scintillation counting. Similarly, while it was again well known in the field of fluorescence, that the fluorescence yield of organic fluorescent solutions was in many cases extremely temperature dependent, the application of this temperature dependence to the liquid scintillator was not made until 1956. The quenching by oxygen of the light output of the liquid scintillator appears to be a rather complicated process. Oxygen is paramagnetic and may affect the internal transition probability for de-excitation by radiation. It may form very weak bonds, which have a high probability for dissociation, or it may absorb radiation directly while forming these bonds. From several of the experiments we have performed at the National Bureau of Standards, it would appear that the quenching by oxygen is a solute effect, at least at the solute concentrations considered. This appears to be in agreement with data reported by Pringsheim (*Fluorescence and Phosphorescence*, Interscience, 1949), where the quenching constants of oxygen for various hydrocarbons dissolved in hexane are spread out over a very wide range. Figure 1 is a schematic drawing of the gas system used to prepare gas-free liquid scintillators. Carefully weighted amounts of solute to give various concentrations were placed inside

numbered sample cells, which were then flame-sealed on the system. The solvent was distilled into the cells using liquid nitrogen, and while the system was still under vacuum, the cells were closed by flame-sealing and removed. They were then placed with reproducible geometry in a collimated beam of gamma-rays from barium-137. The scintillations were viewed at right angles to the gamma-ray beam by a phototube, also in a fixed position relative to the cell. The measured pulse-height distribution was exponential with no photo peaks or Compton edges. In this case, the integral of the pulse-height distribution curve can be taken as an index of the light output. This has been verified by Liebson, and has also been verified at the N.B.S. in d.c. current measurements. Curves of light intensity vs. concentration curves are shown in Fig. 2. Here we have plotted the relative light outputs as functions of concentration for several scintillating solutes in xylene. The black dots are taken

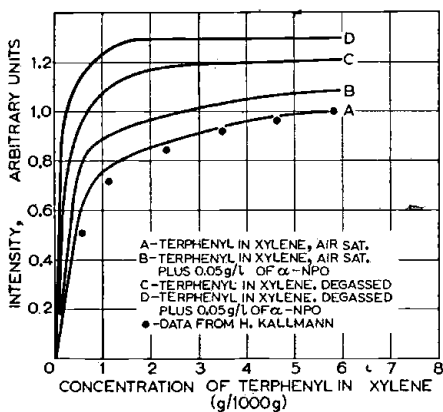


Fig. 2. Relative light output vs. concentration for various liquid scintillation solutes under air-saturated and gas-free conditions.

from the data of Kallmann, and curve *A* corresponds to our own data using integral counting rates. The agreement is quite close. Curve *A* is for air-saturated *p*-terphenyl in xylene. Curve *B* shows the effect of the addition of 0.05 g/l. of α -naphthylphenyloxazole. Now, upon removal of oxygen from the *p*-terphenyl- α -naphthylphenyloxazole combination, curve *D* was obtained. The curves show two important features: (a) the concentration at which peak light output is obtained is reduced when oxygen is removed from the system, and (b) the quenching by oxygen is dependent upon the concentration of solute. This can be seen more clearly in Fig. 3. Here the same data are plotted in terms of percentage increase due to degassing as functions of concentration. If the quenching by oxygen occurred in the solvent alone, the concentration dependence should not be present. In addition, there should be no difference between the two curves, the one for α -naphthylphenyloxazole added and the other with no α -naphthylphenyloxazole added. To investigate this point more

closely, the following experimental arrangement was devised. Figure 4 shows a black box, on one end of which we have an ultraviolet light source with sharp cutoff filters. The scintillator sits in the center, and at right angles to the

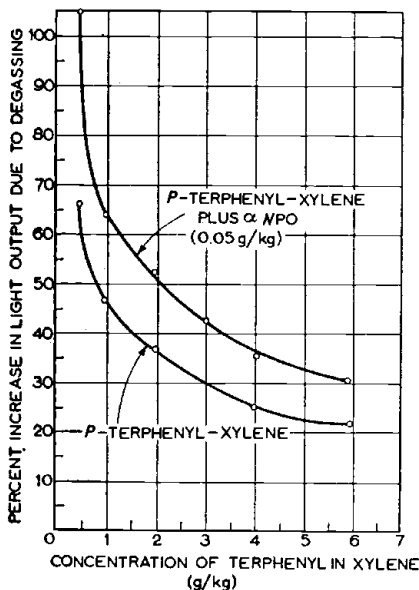


Fig. 3. Effect at 28°C on light output of degassing as function of concentration for *p*-terphenyl in xylene solutions with and without α -naphthylphenyloxazole. Circle diameters indicate precision.

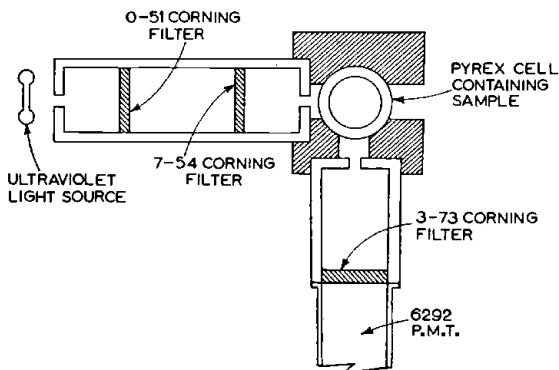


Fig. 4. Schematic drawing of light-excitation experiment.

ultraviolet source-scintillation direction we observe the light with a 6292 phototube. In these experiments diphenyloxazole and α -naphthylphenyloxazole in xylene were investigated. The solutions were made oxygen-free by the vacuum technique just described. The light filters were such that the light

incident on the solutions was confined to the long wavelength end of the solute absorption spectrum, well above the absorption spectrum of the xylene solvent. Thus, only the solute should have been excited. We believe that only the solute was excited. Similarly, the light incident on the phototube was cut off below 4000 Å, so that only the fluorescence of the solute could be seen. The spectral arrangement is shown schematically in Fig. 5. We have

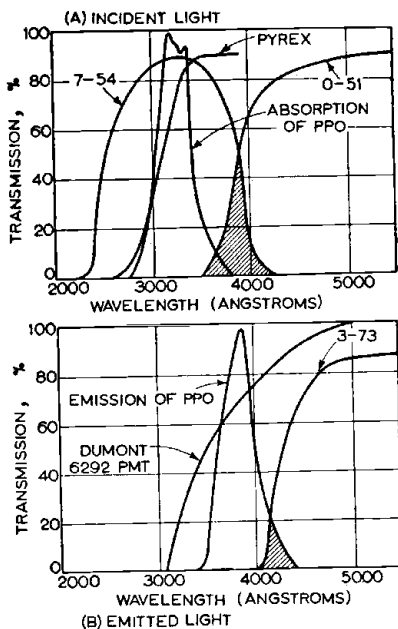


Fig. 5. Effective spectral ranges covered by the present experiments. (a) The shaded region shows the spectral range of the light exciting the solutions. (b) The shaded region shows the spectral range of the observed emission.

here the absorption spectrum of diphenyloxazole and the cutoff filter which permitted only the shaded portion of the ultraviolet spectrum to come through. The wavelength region where absorption by the diphenyloxazole could take place consisted of the little triangle below 4000 Å. Similarly the wavelength region which could be seen by the phototube consisted of the little triangle above 4000 Å on the bottom of the figure. This portion should be well above the emission spectrum of xylene. In this case the integrated current output from the phototube was taken as a measure of the light output. Similar data were obtained for excitation by gamma-rays using the integral counting technique. The results are shown in Fig. 6. The dashed curves are for oxygen-free solutions, and the smooth curves are for air-saturated solutions. Now, the important point to bring out here is that there

is a definite increase in the light output upon removal of oxygen when the solute *alone* is excited. Further, at the particular concentrations used, the ratios of the light outputs of oxygen-free to air-saturated solutions excited by gamma radiation is the same as those for the solutions excited by ultra-violet light. This appears to be further evidence that at least in the case of diphenyloxazole that oxygen quenching occurs in the solute over these concentration ranges. Similar results were found for α -naphthylphenyloxazole.

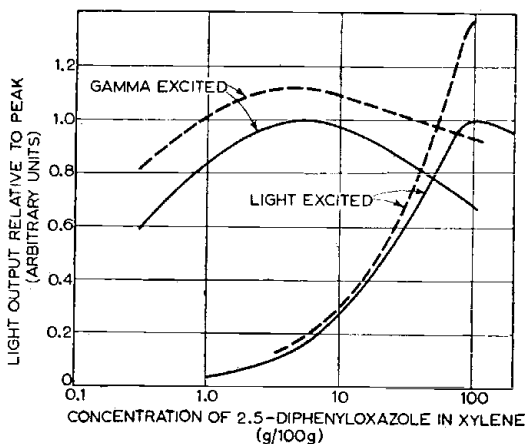


Fig. 6. Light output vs. concentration curves for air-saturated and air-free 2,5-diphenyloxazole in xylene under gamma-ray and under light-excitation. The solid lines are for air-saturated solutions and the dashed lines are for air-free solutions.

Besides the bubbling technique generally used, and the vacuum distillation technique described here for producing oxygen-free liquid scintillators, Schleck and Ziegler have developed a degassing technique using ultrasonic agitation, but they will report on this tomorrow. The data contained in Pringsheim's book is a veritable gold mine for the researcher desiring to find 'new' effects for application in scintillation counting. One of the important effects discussed is the relatively large increase in fluorescence yield for some organic dyes upon reduction of temperature. Following this lead, the effects of reduction of temperature on several liquid scintillators were examined: diphenyloxazole, phenylbiphenyloxadiazole-1,3,4 and α -naphthylphenyloxazole, at 4 g/l., 8 g/l. and 3.2 g/l. in *m*-xylene respectively, were examined. These are approximately the peak concentrations at room temperature, as reported by Hayes *et al.* The freezing point of *m*-xylene is -48°C . The lowest temperature recorded in these measurements was -36°C . The same vacuum distillation technique was used to prepare oxygen-free solutions at each concentration. At each concentration two cells were prepared. In one cell, along with the solute, was placed a gold trident on one spear of which was

plated sufficient polonium to give approximately 2000 alpha-counts/sec. This trident was placed inside the cell before the cell was sealed on to the system. The second cell had no trident. In the measurements the light output was assumed proportional to the peak-position of the alpha pulse-height distribution curve. The 'sister' cell, without a trident, was placed in the path of a collimated gamma-ray beam, and the light output was assumed proportional to the measured integrated phototube current. The results obtained are shown in Fig. 7. The dashed curves represent data obtained for alpha excitation and the solid curves represent the data for gamma excitation. In

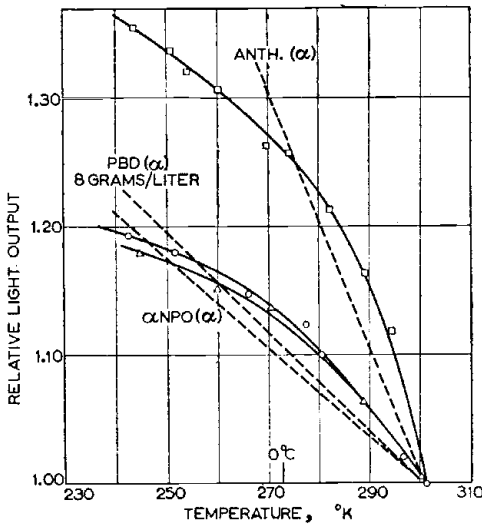


Fig. 7. Relative light outputs vs. temperature for gas-free liquid scintillators. The dashed curves represent data for alpha excitation. The solid curves represent the data for gamma excitation.

□, Anthracene 1 g/l.; ○, PBD 10 g/l. + POPOP 2 g/l.; △, α -NPO-3, 2 g/l.

the alpha-particle case the points plotted are the relative peak position as a function of temperature. We see that as the temperature is reduced the peak position moves to higher pulse height readings, indicating an increase in the light output of the liquid scintillator. The gamma-ray data show approximately the same increase. However the shapes of the curves are slightly different, rising more steeply at the onset and tapering off and then crossing over the alpha curves. The reason for this difference in shape is not clear, although the magnitudes of the increases are quite similar. There are several possible explanations for the increase in the light output upon reduction of temperature:

- (a) There is a reduction of internal quenching.

- (b) There is a reduction of self-quenching. This is a property of the concentration of the solute.
- (c) The increase in viscosity could make for much better energy transfer.
- (d) There could be a change in the spectral emission of the solute to match even better the photocathode sensitivity.

At the present time, we do not have sufficient experimental data to decide between these hypotheses.