with oxygen, moisture, and carbon dioxide undoubtedly occurred during handling.

Cathodic evolution of hydrogen in small quantities decreased current efficiencies but did not preclude deposition of the metals. In ethylenediamine, hydrogen reduction is generally insignificant. Simultaneous hydrogen and metal deposition have been noted in many cases—for example from chromium and iron salts in liquid ammonia (*5*) and from rare-earth salts in absolute ethanol (*6*). Addition of up to 4 drops of water per 60 ml of solution facilitated formation of black, lustrous deposits from yttrium acetate solutions, but larger quantities gave hydrous yttrium oxide. The accelerating effects of water have been noted in other systems. Thus, copper is plated from moist copper (II) nitrate solutions in liquid ammonia but not from anhydrous solutions, presumably because of greater ease of reduction of the $[Cu(H_2O)_x]^{++}$ ion (*7*). Also, poor deposits of zinc are obtained from anhydrous acetamide solutions, but bright plates result in the presence of traces of moisture (*8*). Perhaps water converts $[Y(en)_x]^{+3}$ species to more readily reducible $[Y(H_2O)_y]^{+3}$ species.

X-ray diffraction established the fact that the deposits were not rare-earth metal compounds. Very high "d" spacings in the lattices of the yttrium deposits were noted. The neodymium deposits appeared to be on the borderline between crystallinity and the amorphous state, and the lanthanum deposits were amorphous. Initial deposition in amphorous forms have been reported in other cases (*9*).

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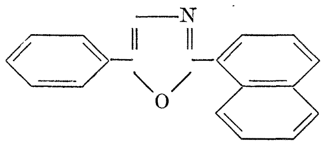
Energy Transfer in Irradiated Solutions of Mixed Phosphors

Frank E. E. Germann, Frank T. Brown, Richard Wissell, Thomas D. Waugh

University of Colorado, Boulder

The field of scintillation counting for the determination of radioactivity is rapidly expanding. One of its most interesting developments has been the replacement of organic and inorganic crystals by solutions of selected organic phosphors. The high efficiencies obtained by Hayes (*1–3*) and his coworkers and by Arnold (*4*) in counting radiations from tritium and C^{14} with a toluene solution of diphenyloxazole (DPO) and alphanaphthylphenyloxazole (ANPO) indicate that mixtures of solutes are more efficient than single solutes. Mixtures of p-terphenyl

and ANPO



have been found to be highly efficient.

In the afore-mentioned studies, solutions containing 3 to 4 g of a primary phosphor such as p-terphenyl and about 0.05 g of a secondary phospher such as ANPO in 1 lit of toluene or xylene were used. The addition of this small amount of ANPO markedly increased the efficiency of the scintillation counter. This enhancement has been ascribed to an energy transfer from the primary to the secondary phosphor. Kallmann and Furst (*5*) proposed such a transfer. Bowen and his coworkers (*6*) have reported that at concentrations in the afore-stated range the shift of energy from the primary phosphor to the secondary phosphor is almost complete and the emission of light from the primary is almost completely eliminated.

Several explanations of the course of this energy transfer have been suggested (*5–8*). They generally are based on a process of successive energy transfer from a radioactive source to a solvent, to a primary phosphor, to a secondary phosphor, and to emitted light that is directed onto the photocathode of a photomultiplier tube. It seemed that an understanding of the energy-transfer process might be facilitated by a more straightforward experimental procedure.

Harrison (*9*) has reported that fluorescence under ultraviolet excitation and scintillation under radioactive excitation are identical phenomena. Therefore it was decided to investigate these energy transfers by normal ultraviolet spectrographic procedures (*10*). Accordingly a cylindrical quartz cell 2 cm in diameter was supported so that its flat end faced the slit of a Hilger quartz spectrograph. A UA-2 mercury lamp was placed so that light from it was incident at 45° on this flat surface. The rest of the cell was effectively shielded. By this means light that fails to penetrate the cell is reflected away from the slit of the spectrograph. Only a small amount of direct light from the mercury lamp enters the spectrograph. This light causes the narrow pips on the tracing in Fig. 1. These are characteristic lines of the mercury spectrum and serve as reference points.

The fluorescence spectra were recorded on Type 103-0 Kodak Spectrographic plates. Examination of the spectral images with a recording densitometer produced tracings, three of which are reproduced in Fig. 1. The number of grid spaces under a tracing appears to be an approximate factor for the comparison of the

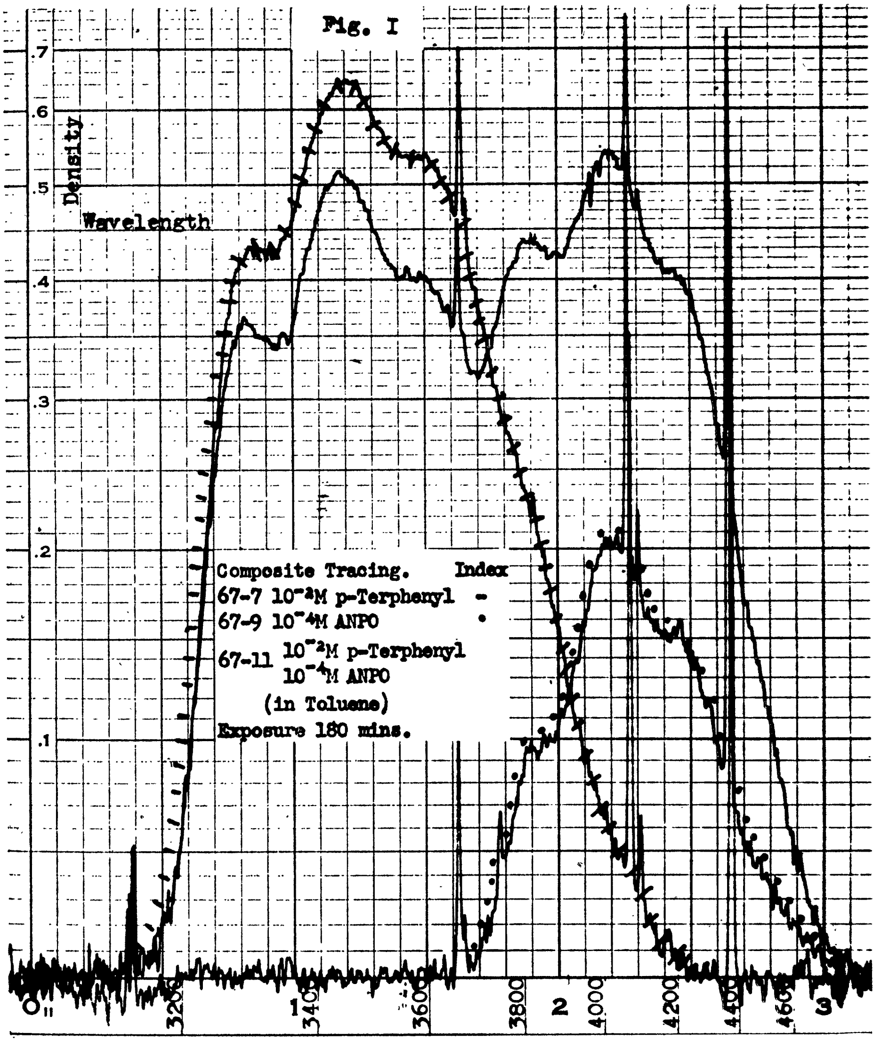


Fig. 1. Photoreproduction of a composite tracing of fluorescence spectra of (i) a solution of p-terphenyl in toluene, (ii) a solution of ANPO in toluene, and (iii) a solution of both p-terphenyl and ANPO in toluene. Indices have been added. The tracing representing the mixed phosphors shows the characteristic spectra of both phosphors. The height of the p-terphenyl peak is lowered a limited amount below that of the phosphor alone, whereas the ANPO peak is markedly enhanced.

energy of the fluorescence emitted by an irradiated solution. If one assumes that this relationship is quantitative, a count of the grid spaces under the tracings in Fig. 1 indicates that 8 percent more energy is emitted by a solution of mixed phosphors when the concentration of ANPO is $10^{-4}M$ and the p-terphenyl is $10^{-2}M$ than is emitted by these phosphors in separate solutions of these concentrations. When, however, the p-terphenyl concentration is $10^{-3}M$, the respective grid counts are about equal. When the p-terphenyl concentration is $5 \times 10^{-4}M$, the count for the combined phosphors is 22 percent less than it is when the phosphors are in separate solutions.

Although strictly quantitative comparisons have not yet been achieved, a few generalizations can be made.

1) The unique spectral characteristics of the separate phosphors persist when they are mixed.

2) The height of the ANPO peak is greatly enhanced in the mixed phosphor tracing. A slight amount of this enhancement, as well as the limiting broadening of the "shoulder" at about 3800 A, may have resulted from the overlap of the p-terphenyl and ANPO spectra. Study of many tracings reveals that the enhancement in the height of the ANPO peak is dependent on the concentrations of both phosphors.

3) The height of the p-terphenyl peak is reduced a slight amount by the addition of ANPO. This observation appears to differ radically from results reported in the literature (*5, 6*) in which it is stated that the fluorescence of the primary phosphor is largely quenched. Those reports were based on results obtained when other phosphors were excited by radiation from a radioactive source. The emissions were generally designated as scintillations. If, as was noted earlier in this paper, scintillations and fluorescence are identical phenomena, it seems that a closer agreement should be expected.

4) The decrease of the height of the p-terphenyl tracing is a function of the ANPO concentration. In a number of toluene solutions whose ANPO concentration was $10^{-4}M$, and whose p-terphenyl concentration varied from $10^{-2}M$ to $10^{-5}M$, the decrease in the

height of the p-terphenyl peak was about 0.13 scale units in every case.

5) Evidence has been produced that shows that certain pairs of phosphors in some solvents at certain concentrations emit more fluorescent energy in mixed solutions than they do when each phosphor is alone in the solvent (at the same concentration as was used in the mixture).

6) A purely spectrographic method has been devised for the study of the fate of the energy that is involved in the fluorescence of liquid scintillation phosphors. This avoids the complexities introduced by energy transfer from radioactive emanations to the solutions and by the variable response of photomultiplier tubes.

Studies of these and other primary phosphors and "bandshifters" in a variety of solvents and plastics are being continued. The use of filters to allow only portions of the mercury spectrum to enter the solutions is proving most fruitful. Detailed reports of the various facets of these investigations are in preparation.

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Continuous-Flow Operation of Electroconvection Cells

Samuel Raymond

College of Physicians and Surgeons,
Columbia University, New York

Electroconvective separation and purification of proteins is becoming more useful as a result of the availability of practical and efficient apparatus for this purpose. Recently two papers have appeared (*1, 2*) describing continuous-flow electroconvection for the fractionation of protein solutions. (Continuous-flow has also been practiced industrially for many years, chiefly for the purification of rubber latex (*3–6*).) Contrary to expectation, continuous-flow electroconvection is theoretically much slower and much less efficient than batch operation; this has also been confirmed experimentally.

Consider the batch operation in which V (ml) of solution containing C_A (g/ml) of A (at its isoelectric point) and C_B of B is placed in each reservoir. After a period t (hr) of electroconvection the upper reservoir still contains the original concentration of the isoelectric A, but the concentration of B has been reduced to yC_B in the upper reservoir and increased to $(2-y)C_B$ in the lower reservoir, where y is a fraction determined from the equation

$$t = 1.9\theta \int_0^{1-y} [(1-y)^{-3/5} - (1+y)^{-3/5}]^{5/4} dy; \qquad (1)$$

θ is the experimental transport constant as defined by Brown *et al.* (*7*). If y is taken as 0.001, $t = 5\theta$, so that for a batch operation the average rate of purification VC_A/t is $0.2VC_A/\theta$.

If now we begin to force buffer up through the bottom reservoir and channel at such a rate that the upward transport of B owing to buffer flow is just equal to the downward transport of B owing to electroconvection, the conditions at the top of the channel remain essentially constant insofar as B is concerned; A, however, is carried upward by the buffer stream and out the top of the cell, carrying with it the steady-state concentration yC_B of the B-component. For a buffer flow rate F (ml/hr), the upward buffer-flow transport of B is $2C_BF$ (g/hr) when y is a small fraction. This must not exceed the downward electroconvective transport $VC_B dy/dt$. The derivative dy/dt from Eq. 1 reduces to $0.53y^{3/4}/\theta$ when y is a small fraction; hence, the maximum F is given by

$$F = 0.26Vy^{3/4}/\theta. \qquad (2)$$

For a typical system, if $y = 0.001$, the theoretical rate of purification in continuous-flow operation approximates $0.005\ VC_A/\theta$. The average batch rate is 40 times this rate.

For an amount A_t of the immobile component recovered in the effluent, conservation of mass gives

$$A_t = A_0(1 - e^{-Ft/V}), \qquad (3)$$

where A_0 is the amount initially present in the bottom reservoir and Ft is the total volume of buffer passed through the cell.

The foregoing equations are derived on the assumptions of the Kirkwood theory (*8*), specifically that of complete mixing in the reservoirs. In practice, mixing is far from complete; how far may be seen by comparing the foregoing equations with the experimental results obtained by Timasheff *et al.* (*2*). In their report 94 percent of BGG was recovered from a volume of 50 ml by passing 930 ml of buffer. The theoretical volume required is 140 ml; thus the mixing of the buffer stream with the reservoir contents was only 15 percent efficient.

The analysis of mixing in the bottom reservoir is further complicated by the fact that, although the concentration of the immobile component A remains uniform throughout the reservoir, the mobile component B concentrates as a result of electroconvection in a layer on the bottom of the reservoir, whereas the buffer stream, since it is less dense than the reservoir contents, tends to form a layer at the top of the reservoir. If the degree of mixing between these two layers is very small, as would be expected, the buffer entering the channel will not carry $2C_BF$ (g/hr) of the mobile component but a small fraction k of this amount. The