

## Chapter 3

# Emission Spectra of Liquid Organic Scintillators

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### INTRODUCTION

Modern scintillation materials are of great importance in applied nuclear physics. For special purposes, the liquid organic scintillant materials exhibit remarkable properties that have also been studied in our laboratory.<sup>1-6</sup> The efficiency of a scintillation system is dependent on all the stages involved in the transfer process of the incident energy (excitation by particles or radiation) in production of light and its conversion into photoelectrons. The light yield of the scintillator is offset by competing non-radiative degradation processes, which are related to the specific energy loss processes in the scintillator. Unfortunately we are lacking a thorough understanding of all phenomena in the scintillant material up till now because the systems are very complex. One can consider three sources of experimental information in the liquid organic counting field: (1) light yield, (2) time dependence of the light pulses, (3) optical spectra. In this work, we consider the optical luminescence spectra of some common scintillation systems, comparing them when using different modes of excitation ( $\alpha$ -,  $\beta$ -,  $\gamma$ -rays and ultraviolet light). Some experiments comparing radioluminescence and photoluminescence spectra (mostly excited by  $\beta$ -rays and ultraviolet light) have already been performed, showing the identity of the spectral output in all cases,<sup>7-9</sup> but the sensitivity and resolution of the spectra were insufficient, so that new measurements with more refined experimental conditions were necessary. No detailed discussion was found hitherto concerning the independence of luminescence spectra on the kind of excitation. The study of the luminescence mechanism in detail shows that the behaviour of an excited molecule in the system is affected by local effects of the penetrating radiation (heating, dissociation, electric fields, mutual quenching by neighbouring molecules). The molecular absorption and emission characteristics may be changed therefore when using different radiation. This is plausible because: (1) the scintillation efficiency depends strongly on the type of particle, (2) the shape of a scintillation pulse is affected by the ionisation properties of the incident particle, (3) the luminescence spectra of a given molecule are dependent on the kind of solvent.

## THEORY

The solvent of a liquid scintillation system is the constituent absorbing most of the incident energy. For high-energy particles, only the organic aromatic systems are suitable for effectively converting the absorbed energy into light. In the case of scintillator molecules dissolved in a liquid organic medium there is a fundamental influence of the solvent on the spectral characteristics of these molecules. The influence of neighbouring molecules in a liquid medium has not been described in a general form. The results of many investigations are also contradictory. The model commonly utilised to represent the collective actions of the system particle + medium is the Onsager model, in which the molecules are regarded as dipoles in a dielectric medium and exposed to the influence of the internal field of the solvent.

It can be shown theoretically and experimentally that there is a red shift of the absorption and fluorescence spectra of substances in solution as compared with these spectra in the vapour phase.<sup>10-12</sup>

The interaction of the fluorescing molecule with the molecules of the solvent is described by the total energy  $U$  arising between two molecules  $f$  and  $s$  with the dipole moments  $\mu_f$  and  $\mu_s$  and the polarisabilities  $\alpha_f$  and  $\alpha_s$ :

$$U = - \frac{1}{R^6} \left[ \frac{2}{3} \frac{\mu_f^2 \mu_s^2}{kT} + \mu_f^2 \alpha_s + \mu_s^2 \alpha_f + \frac{2}{3h} \sum_{\chi, \tau} \frac{a^2 \psi_\chi a^2 \sigma_\tau}{\nu_\psi + \nu_\sigma} \right] \quad (1)$$

$\Sigma$  = sum extended over all transition frequencies  $\nu_\psi$  and  $\nu_\sigma$  of both the fluorescing molecule ( $f$ ) and one neighbouring molecule of the solvent ( $s$ ) and their corresponding moments of transition  $a_\psi$  and  $a_\sigma$ .

The ground states of both molecules are denoted by  $\psi$  and  $\sigma$ . The four terms of equation (1) mean: 1. the orientation effect, 2, 3. the induction effect, 4. the dispersion effect.

This equation can describe, despite the simplicity of the model used, the shift of the spectra in all cases (dipole or dipoleless molecules in a polar or a nonpolar medium). One can also show that it follows for the total amount of the shift of the spectra of solutions relative to the spectra of vapour:

$$\Delta \nu = \nu_{\text{sol}} - \nu_{\text{vap}} = \frac{1}{R^3} \left[ C_1 \frac{2\epsilon - 2}{2\epsilon + 1} + (C_2 + aC_3) \frac{2n^2 - 2}{2n^2 + 1} \right] \quad (2)$$

$R$  = radius of the molecule ( $\sim$  effective Onsager radius)

$\epsilon$  = dielectric constant } of the solvent

$n$  = index of refraction }

$a$  = oscillator strength of the electronic transition

$C_1, C_2$  = functions of the permanent dipole moment of the molecule in the lower and upper electronic states

$C_3$  = function of the frequency of the purely electronic transition

The magnitude of the red shift is of the order of 4% and can be proved experimentally.<sup>13</sup>

These considerations are valid only for photoluminescence in the first instance. When regarding the interaction with ionising radiation, one must notice the following facts: it is known that the light yield per unit energy absorbed by a liquid scintillator depends on the particle type of the penetrating radiation (for example 250 to 350 eV/photon in the case of  $\alpha$ -particles, 25 to 35 eV/photon for  $\beta$ -particles). This fact can be discussed, when regarding the strong electric fields in the neighbourhood of the incident particles, which may produce perturbation of the electronic molecular orbitals. Wright<sup>1,4</sup> attributes the existence of energy losses by radiationless transitions to these fields.

The incident particle dissipates its energy mainly in producing ionised and excited molecules of the solvent and free electrons along its path. The excited molecules are very rapidly quenched as a result of the strong local electric fields, heating and high density of excitation which exist along the incident particle track immediately after its passage.

There may be created photons in the very first step of interaction whose total number and spectral distribution depend upon the distance from the path of the particle and its velocity. These primary photons would have indeed a modified spectral intensity distribution because the dipole moments of the molecules near the particle track may be altered. Also an effect analogous to the already mentioned dispersion phenomenon is possible (see equation (1)). So one should expect a difference between radioluminescence and photoluminescence spectra if these primary photons contribute to the total luminescence. But if the spectra do not change with the mode of excitation, one has to draw the following conclusions:

- (a) Most of the primary photons are reabsorbed within the volume element in question, producing light perhaps in later stages of the process.
- (b) The main portion of fluorescent light is observed, when the strong quenching fields due to the incident radiation no longer have a considerable influence, so that no distortion of emission spectra is caused. It follows that detectable luminescence is emitted from excited neutral molecules resulting from recombination phenomena.

It is shown experimentally that the optical spectra of several luminescent organic systems are indeed independent of the mode of excitation within the experimental error.

To account for the observed differences in the light yield of  $\alpha$ - or  $\beta$ -excitation, one has to regard further the secondary processes such as intermolecular light transfer and fluorescence with their inevitable degradation and energy loss mechanisms.

The above mentioned most important primary processes are not very well understood. The excitation and ionisation densities are dependent on the velocities of the incident particles and change along their track. The ions and electrons recombine during a short time ( $10^{-11}$  to  $10^{-13}$  s).

The decay times  $\tau$  for light pulses of liquid scintillators are known to be  $10^{-8}$  to  $10^{-10}$  s.  $\tau$  consists of a fast and a slow component; the corresponding times differ by a factor of about 100. The fast component includes decaying singlet states, but the remainder also a rather large number of excited molecules in triplet states. The excited triplet state is produced mainly by recombination processes, the singlet state by direct excitation. In the case of proton- or  $\alpha$ -excitation, the density not only of excited molecules, but also of ions and dissociation products is greater than in the case of  $\beta$  or ultra-violet excitation. It follows that with greater specific ionisation more of the excited

triplet state is produced, so that the decay times of the slow pulse components will increase.<sup>15</sup> In addition, heavily ionising particles will cause intense electric quenching fields, especially near the end of the range. During this period, little light may be produced.

The strong quenching effect in the immediate vicinity of the particle track lasts for  $10^{-10}$  s, being terminated as a result of rapid migration of the excitation away from the particle track. So the ions formed along the path of the incident particle are relatively unaffected by the quenching conditions and cause a new crop of excited molecules. It follows that the light yield and emission spectrum of the slow component should be nearly independent of the mode of excitation, while the intensity of the fast component will be less in the case of alpha induced emission than for beta excitation. On the other hand, a modified fluorescence spectrum should be correlated to this fast component.

Further discussion has to regard the relative roles of excited and of ionised molecules in detail (including free radicals) and to study the slowly decaying components of the scintillation when one influences the recombination process by external fields or by electron attaching molecules.

Pulse rise, time measurements<sup>16</sup> as well as other experimental methods give weight to the energy exchange theory (Kallman-Furst) of liquids. Energy transfer in solutions from the lowest excited states (triplets and singlets) of donor molecules to an excited state of the acceptor solute molecules (lowest singlet or triplet) and the consequent fluorescence of these solute species should not be influenced by the strong primary quenching centers for the reason of the short time of the strong quenching effect ( $10^{-10}$  s). In references 17 to 22 reasons are discussed for identical mechanisms of energy transfer in all possible modes of excitation.

## EXPERIMENTAL

Luminescence spectra were obtained with the aid of a modified Cary 14 recording spectrophotometer (dispersion  $40 \text{ \AA}/\text{mm}$  in the visible range). The output of the multiplier phototube was fed to a d.c. amplifier (vibrating reed electrometer) and a pen recorder. It was therefore possible to measure the very small currents due to the faint light intensities (about  $2 \times 10^{-4} \text{ lm}$ ) of the liquid scintillator excited by  $\alpha$ -,  $\beta$ - or  $\gamma$ -rays. The reasons for the small light output of the liquid scintillation detector were: (1) relatively weak activity of the radioactive sources used to avoid effects of radiation damage to the organic system, (2) strong transmission losses due to the optical properties of the spectrograph (poor illumination of the slit, although a condensing lens of 5.0 cm focal length was used to increase the entrance aperture; reflection losses from surfaces and absorption within the optical elements).

The multiplier tube had to be cooled to  $-25$  or  $-80^\circ\text{C}$  to reduce the dark current (Fig. 1).

### Ultraviolet Excitation

To excite the scintillation solution with ultraviolet light, the Cary fluorescence attachment model 1412 was used. The exciting light consisted mainly of lines in the region of 2537 and 3700  $\text{\AA}$ . Rectangular cells of 0.5, 1.0 and 10 mm optical path lengths were filled with the solutions under investigation.

When the exciting light is strongly absorbed, it makes a great difference whether the

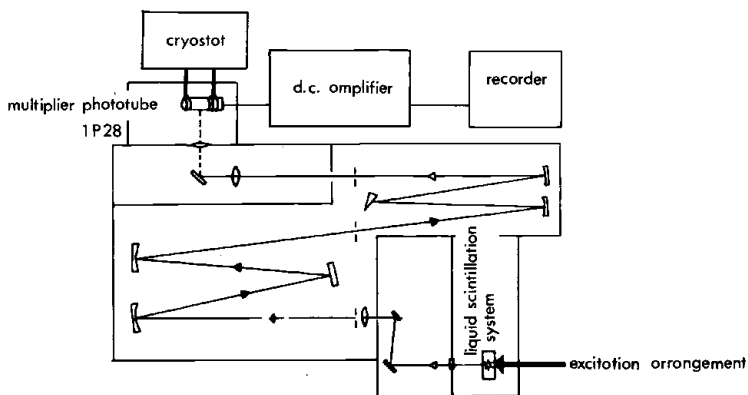


Fig. 1: Experimental arrangement.

fluorescence is observed from the front or the back of a thick liquid layer, because more or less of the shortwave part of the emitted light may be removed by reabsorption. This effect was studied by the use of different path lengths for the u.v. cells and various concentrations of solute molecules in the organic liquid. Further absorption spectra were run.

Excitation by  $\alpha$ -particles, where the penetration is small, makes front-surface observation combined with small path lengths desirable,  $\beta$ - and  $\gamma$ -ray excitation with deeper penetration will cause smaller reabsorption effects. Hence it is necessary to plan cautiously experimental conditions for comparing studies of photofluorescence and scintillation spectra by preceding studies of self-absorption effects which depend mainly on exciting radiation, physical dimensions of cells used and on the absorption spectrum of the system.

### $\alpha$ -Excitation

The  $\alpha$ -source (Fig. 2) consisted of 1 mCi americium-241 mounted on a platinum strip and plunged in the solution opposite to the entrance slit. Because of the low  $\alpha$ -range in liquids ( $5 \times 10^{-3}$  cm for 5 MeV  $\alpha$ -particles), part of the optical luminescence spectrum is modified by the reabsorption phenomena.

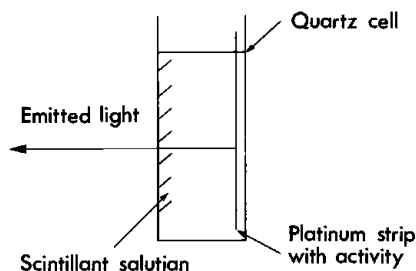


Fig. 2:  $\alpha$ -Excitation.

### $\beta$ -Excitation

For the purpose of  $\beta$ -excitation of the scintillator, 0.5 mCi promethium-147 was used in the same manner as in the case of  $\alpha$ -excitation. But now, self-absorption effects are smaller, because the  $\beta$ -range is larger (0.1 mm for 0.2 MeV  $\beta$ -particles).

### $\gamma$ -Excitation

A 2 Ci iridium-192 source was applied for excitation of the scintillant material with  $\gamma$ -rays. Self absorption of the obtained spectra is still smaller than in the two cases above, because contrary to  $\alpha$ - or  $\beta$ -excitation, each volume element of the scintillator is emitting luminescence radiation when excited in this way.

The following parameters may influence the shape of the technical fluorescence spectrum:

(a) Re-absorption of the emitted photons, secondary fluorescence. (b) Concentration of the scintillant molecules. (c) Formation of dimers. (d) Impurities in the system, quenching agents. (e) Temperature. (f) Over-all spectral sensitivity of the spectrograph.

(a) This important point has already been discussed. If the optical path lengths of the cells are carefully selected and the concentrations of the solutes are rather low, only the short wavelength-part of the emission spectra obtained may be altered so that corresponding differences in peak-height when changing the type of exciting radiation will not be regarded as fundamental for the scintillation mechanism.

(b), (c) Concentration of the scintillant solutes was changed in all modes of excitation systematically to investigate the amount of re-absorption of a given system. When discussing the structure of the spectra from different modes of excitation, the influence of the slit width setting of the spectrophotometer on the resolution of the spectra was taken into consideration.

The usual emission spectrum, characteristic of the monomeric electronic  $\pi$ -singlet states is absent under intense electron bombardment. Under these conditions the structureless emission observed is due to excimers, resulting from ion recombination processes. Intensities of the exciting radiation used in our work were too small to cause strong monomer quenching, so we could neglect the influence of dimers.

(d), (e) An influence of additional impurities in the scintillant solutions was not found to modify seriously the spectral intensity distribution. The systems were free of oxygen, which causes only diminution of the light yield, not a distortion of the spectral emission characteristics.

(e) It can be shown<sup>23</sup> that temperature effects may be ignored in our case.

(f) The spectral sensitivity of the dispersing system, especially the response curve of the photomultiplier 1 P 28 was determined and compared with data of the manufacturer (RCA). This was realised by application of a fluorescent solution as a quantum counter.<sup>24</sup> In the wavelength region of about 2000 to 3500 Å, a  $10^{-2}$  M solution of 1-dimethyl-aminonaphthalene-7-sodium-sulphonate in water was used. For 3500 to 5900 Å a  $1.25 \times 10^{-2}$  M solution of Rhodamine B in ethylene glycol was used.

With complete absorption of the exciting light at all wavelengths  $\lambda$ , the observed fluorescence intensity is independent of  $\lambda$  (if the fluorescence efficiency is constant), of concentration and of the extinction coefficient.

The spectral response  $\eta(\lambda)$  of the multiplier phototube is calculated from

$$\eta(\lambda) = k \times \frac{I(\lambda)}{I_0(\lambda)} \quad (3)$$

$I(\lambda)$  multiplier phototube output without the quantum counter

$\frac{I_0(\lambda)}{k}$  multiplier phototube current when the fluorescing solution is used

$k$  normalised to  $\eta_{\max} = 1$

The observed variation of  $\eta$  with  $\lambda$  agrees closely with the RCA data of the S-5 spectral response characteristics ( $\eta_{\max}$  at 3400 Å, see Table 1).

Cooling of the tube did not affect its response curve,<sup>2,5</sup> but when using  $\gamma$ -radiation in our experiments, the tube had to be carefully shielded and only cooled to  $-30^\circ\text{C}$ , as scintillation of the quartz window of the photomultiplier due to penetrating  $\gamma$ -rays decreased when cooling was reduced.

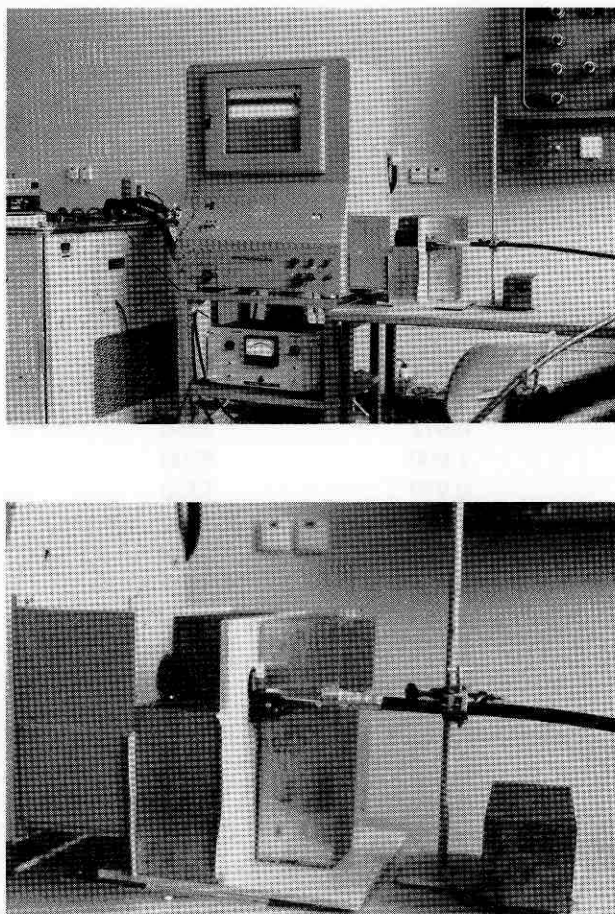


Fig. 3: Experimental arrangement for the  $\gamma$ -excitation experiment.

Table 1. Spectral Sensitivity  $\eta(\lambda)$  of the Multiplier Phototube 1P28 (RCA)

$\lambda(\text{\AA})$	$\eta(\lambda)$	$\lambda(\text{\AA})$	$\eta(\lambda)$
2100	0.377	4050	0.828
2200	0.420	4100	0.820
2250	0.438	4150	0.811
2300	0.447	4200	0.811
2350	0.605	4250	0.786
2400	0.532	4300	0.794
2450	0.589	4350	0.780
2500	0.645	4400	0.777
2550	0.802	4450	0.721
2600	0.831	4500	0.698
2650	0.756	4550	0.698
2700	0.780	4600	0.721
2750	0.744	4650	0.693
2800	0.919	4700	0.681
2850	0.843	4750	0.648
2900	0.905	4800	0.623
2950	0.936	4850	0.597
3000	0.839	4900	0.572
3050	0.834	4950	0.552
3100	0.878	5000	0.516
3150	0.886	5050	0.488
3200	0.894	5100	0.462
3250	0.981	5150	0.425
3300	0.959	5200	0.404
3350	0.971	5250	0.376
3400	1.000	5300	0.356
3450	0.977	5350	0.328
3500	0.991	5400	0.296
3550	0.967	5450	0.266
3600	0.946	5500	0.238
3650	0.955	5550	0.212
3700	0.972	5600	0.191
3750	0.910	5650	0.181
3800	0.884	5700	0.178
3850	0.878	5750	0.168
3900	0.845	5800	0.157
3950	0.839	5850	0.141
4000	0.839	5900	0.117
		5950	0.099

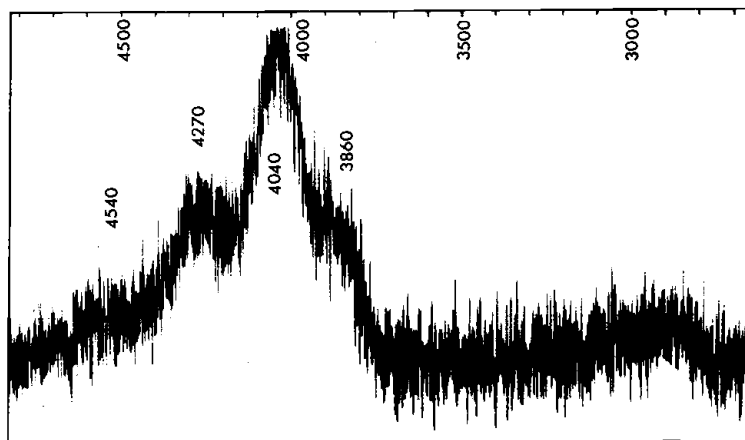
## RESULTS

The emission spectrum of a specimen is a plot of luminescence intensity (quanta per unit wavelength interval) against wavelength. This apparent spectrum may be corrected with three wavelength dependent factors: quantum efficiency of the photomultiplier, band width and transmission factor of the monochromator.

The spectra shown in the Figs. 4 to 12 are not corrected, as variation of the spectral sensitivity in the wavelength region of interest is only  $\leq 15\%$ . Further, the obtained spectra are indeed directly comparable because the same experimental conditions were chosen for a set of spectral intensity curves of a system. The obtained emission spectra of various liquid solutions show a spectral distribution of the luminescence produced independent of any particular method of excitation. However, under radioactive excitation of a liquid system a complete shift of its original spectrum on addition of a second phosphor with an emission spectrum of longer wavelengths is observed; in ultraviolet irradiation all compounds will fluoresce. This may be explained because in the latter case the solute molecules are directly excited, as the ultraviolet excitation energy is not very different from optical molecular levels. When using high energy particles direct excitation is not possible, but there is successive energy transfer from the solvent to the solute molecules fluorescing in the longest wavelength bands.

On the other hand the ratio of fluorescence intensity of the solvent and solute molecules depends on the respective ratio of their concentrations; this ratio is not affected by the mode of excitation.

When comparing the spectra, we ignore their spectral region subject to self-absorption.



*Fig. 4:* Anthracene in toluene, excited by  $\gamma$ -radiation.

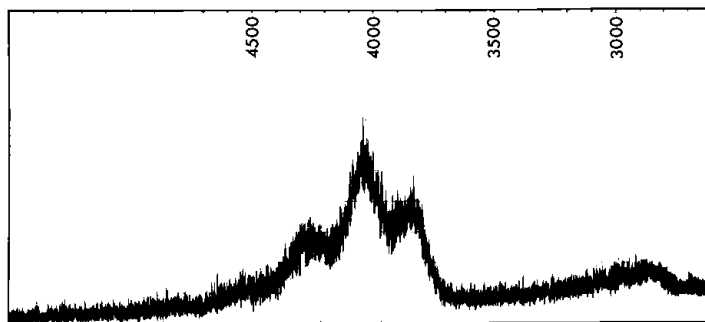


Fig. 5: Anthracene in toluene, excited by  $\beta$ -radiation.

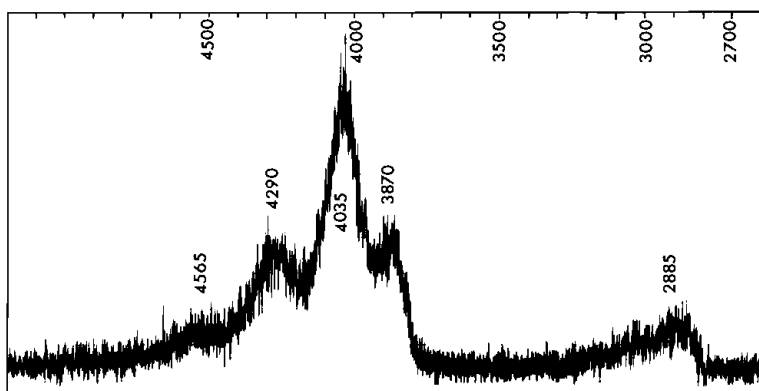


Fig. 6: Anthracene in toluene, excited by  $\alpha$ -radiation, effect of self-absorption.

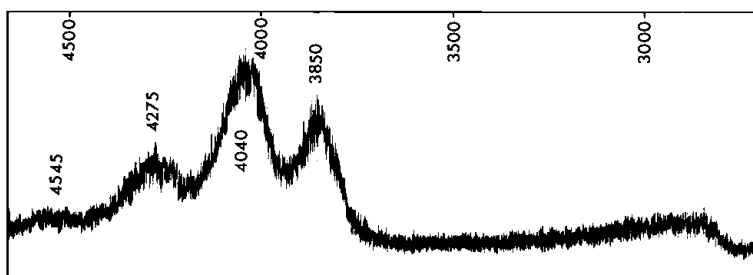
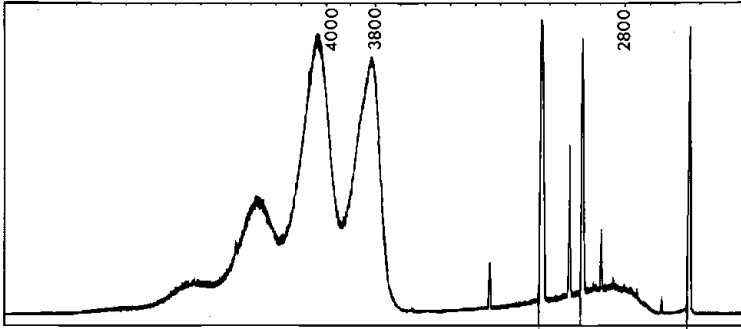
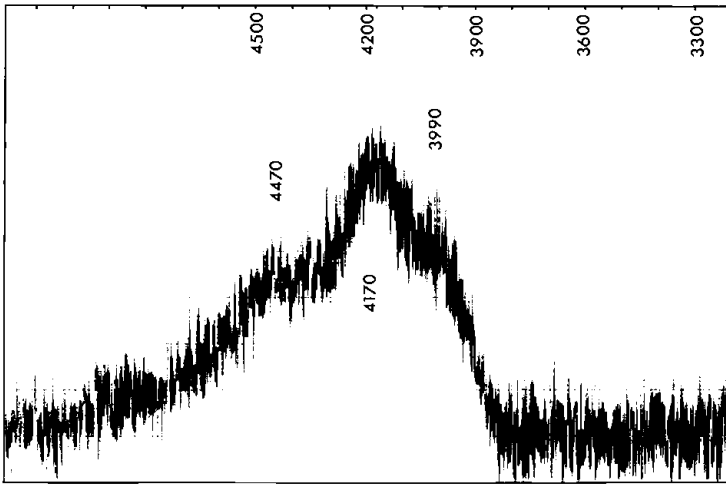


Fig. 7: Anthracene in toluene, excited by  $\alpha$ -radiation.

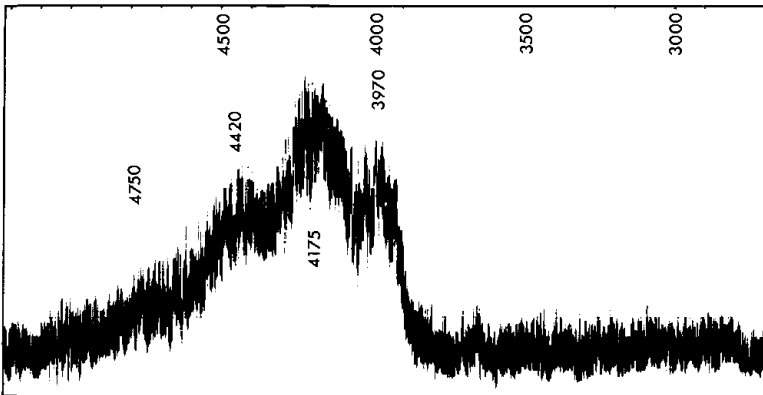
*Emission Spectra of Liquid Organic Scintillators*



*Fig. 8:* Anthracene in toluene, excited by ultraviolet light.



*Fig. 9:* POPOP in toluene, excited by  $\gamma$ -radiation.



*Fig. 10:* POPOP in toluene, excited by  $\beta$ -radiation.

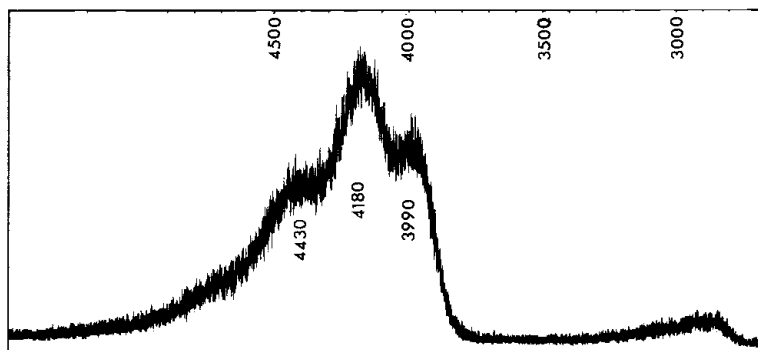


Fig. 11: POPOP in toluene, excited by  $\alpha$ -radiation.

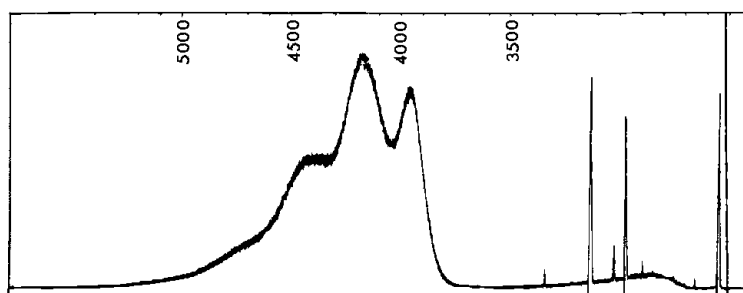


Fig. 12: POPOP in toluene, excited by ultraviolet light.

Emission spectra of the following systems were obtained:

(a) Anthracene in toluene (Figs. 4 to 8) rel. intensities:  
 emission bands: 3815, 4035, 4270, 4520, 4860 Å (0.91:1.0:0.41:0.11:0.04).  
 absorption bands: 3135, 3265, 3418, 3595, 3790 Å.  
 concentrations: 0.334 mg/ml, 0.073 mg/ml.

(b) 1.4-di-[2-(5-phenyloxazolyl)] benzene (POPOP) (Figs. 9 to 12) in toluene  
 emission: 3960, 4180, 4415, 4750 Å (0.875:1.0:0.58:0.2).  
 absorption: 3500, 3628, 3810 Å.  
 concentrations: 0.207 mg/ml, 12 mg/ml.

(c) 2-phenyl-5(4-biphenyl)-1,3-oxazole (PBO) in toluene  
 emission: 3440, 3610, 3780 Å (0.71:1.0:0.8).  
 absorption: 3060 Å.  
 concentrations: 0.075 mg/ml, 0.019 mg/ml, 0.1 mg/ml.

(d) *p*-terphenyl in toluene  
 emission: 3280, 3425, 3560, 3765 Å (0.84:1.0:0.65:0.27).  
 absorption: 2826 Å.  
 concentrations: 0.065 mg/ml, 0.255 mg/ml, 0.02 mg/ml.

(e) *p*-quaterphenyl in toluene  
emission: 3540, 3710, 3885 Å (0.97:1.0:0.63).  
absorption: 3000 Å.  
concentrations: 0.077 mg/ml.

(f) 0.7% PPO, 10% naphthalene in dioxane  
PPO = 2,5-diphenyl-1,3 oxazole  
emission: 3460, 3630, 3780 Å.  
absorption: complex.

Experimental comparison of radioluminescence and photoluminescence indicates the identity of the corresponding emission spectra relative to the spectral intensity of the bands as well as to their spectral position. The estimated tolerances are 7% for intensity and 1% for the wavelength position.

When comparing the emission spectra of the pure solvents, a red shift in the intensity maximum of about 50 Å was observed when changing from ultraviolet-excitation to excitation with  $\gamma$ -rays. This effect of the order of 1% may be explained with self-absorption phenomena.

The independence of the luminescence spectra from the mode of excitation confirms the importance of recombination phenomena in liquids interacting with high energy particles. Detailed information about the phenomena involved is difficult to derive, because complete analysis of all processes cannot be obtained by mere investigations of the optical properties of liquids.

## ACKNOWLEDGEMENT

The author wishes to thank Dr. H. Ihle for his devoted help throughout the whole work.

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## DISCUSSION

**J. B. Birks:** Christophorou (Oak Ridge) and Joneleit (Giessen) have observed that liquid benzene and toluene excited by intense electron beams have luminescence spectra differing from the photo-excited spectra. It would be of interest to study whether similar differences occur with  $\alpha$ -particle excitation. The reason for the difference has been discussed elsewhere. (J. B. Birks, *Chem. Phys. Lett.* 1970).

**E. Langenscheidt:** In our case of the application of radio nuclides the spectra of the pure solvents seem to be independent of the mode of excitation; but the pure liquids were not studied when excited by very intense  $\alpha$  or  $\beta$  radiation.

**D. A. Kalbhen:** What is the spectrum produced by the Cerenkov effect of higher energy  $\beta$ -particles in water like? Is it well-defined or diffuse?

**E. Langenscheidt:** The Cerenkov effect spectrum is diffuse, but this problem has not been studied here.