

## Neutron-sensitive plastic scintillator activated by naphthalene

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In the work, liquid and plastic scintillators containing naphthalene as an activator are obtained. Their scintillation properties were studied. The possibility of creating neutron-sensitive plastic scintillators activated by naphthalene molecules was evaluated.

**Keywords:** liquid scintillator, plastic scintillator, naphthalene,  $n/\gamma$ -discrimination.

**Нейтроночутливий пластмасовий сцинтилятор, активований нафталіном.**  
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Отримано рідкі та пластмасові сцинтилятори, що містять нафталін як активатор. Вивчено їх сцинтиляційні властивості. Оцінено можливість створення нейтроночутливих пластмасових сцинтиляторів, активованих молекулами нафталіну.

Получены жидкие и пластмассовые сцинтилляторы, содержащие нафталин в качестве активатора. Изучены их сцинтилляционные свойства. Оценена возможность создания нейтрончувствительных пластмассовых сцинтилляторов, активированных молекулами нафталина.

### **1. Introduction**

The appearance of plastic scintillators (PS), capable of separating the scintillation signal from neutron and  $\gamma$ -quanta by pulse shape, was largely due to the analogy with the properties of  $n/\gamma$ -discrimination of a liquid scintillator (LS) [1, 2]. It is known that naphthalene is used as the activator in the most effective liquid scintillators with respect to the  $n/\gamma$ -discrimination parameter [3, 4]. In the neutron-sensitive PSs existing today, 2,5-diphenyloxazole-1,3 (PPO) and 2,5-diphenyloxadiazole-1,3,4 (PPD) or their derivatives are used as an activator [5, 6]. And this is largely explainable, since the possibility of  $n/\gamma$ -discrimination is directly related to delayed luminescence, the realization of which is due to the possibility of the effect of triplet-triplet annihilation (TTA).

TTA occurs due to the exchange interaction, the probability of which decreases exponentially with increasing distance between the molecules. Therefore, the closer the molecules that carry triplet excitation are located to each other, the greater the probability of their interaction, which leads to the conversion of one of the molecules to an excited singlet state. That is, to increase the efficiency of TTA, it is necessary to introduce an activator in PS in high concentrations to ensure a minimum distance between its molecules. And PPO and its derivatives have high solubility in polystyrene — up to 40 wt. %. However, today the possibilities of improving the properties of PS neutron sensitivity through the use of PPO and its derivatives are practically exhausted. Therefore, it becomes necessary to search for activator molecules capable of

improving the  $n/\gamma$ -discrimination factor of PS. Since LS with naphthalene demonstrate the best  $n/\gamma$ -discrimination parameters, the issue of the effectiveness of using naphthalene as an activator of a neutron-sensitive plastic scintillator is relevant. To date, PS with the property of  $n/\gamma$ -discrimination using naphthalene or its derivatives are not described in the literature.

The aim of this work was to evaluate the possibility of creating a neutron-sensitive PS based on naphthalene activated polystyrene.

## 2. Experimental

To obtain LS samples containing naphthalene or PPO, calculated quantities of the corresponding activator, shifter, and solvent (toluene or hexane) were placed in glass ampoules. The mixture was purged with argon for 15 min, after which the ampoules were hermetically sealed.

PS samples containing naphthalene were obtained by thermally initiated bulk polymerization. For this, the corresponding amounts of styrene, naphthalene and a luminescent additive were placed in glass ampoules. The mixture was purged with argon for 10 min, after which the ampoules were sealed. Samples were polymerized at a temperature of 140°C for 6 days. Samples were cut out of the obtained blanks in the form of cylinders with a diameter of 16 mm and a height of 10 mm, which were polished to optical transparency.

As a luminescent additive, PPO, 2-(4-biphenyl)-5-phenyloxazole (BPO) and 9,10-diphenylanthracene (DPA) were used.

## 2. Experimental

Scintillation pulses were recorded by a Hamamatsu R1307 photomultiplier tube (PMT) with an anode voltage of  $V_a = 1000$  V. To improve optical contact, the space between the sample and the PMT was filled with immersion liquid (liquid paraffin). The signal from the PMT anode was fed to the input of a RIGOL DS1302CA digital oscilloscope (300 MHz, 2 GSa/s, 8 bit) with an input resistance of  $R_{input} = 50 \Omega$ . The digitized data was processed using a computer.

### 2.1. Determination of light yield and pulse shape.

After digital processing, the shape of the pulse and the value of the pulse area ( $Q_{total}$ ) were saved in a file for each registered event. Then, the amplitude spectrum was

constructed as the distribution of the number of events over  $Q_{total}$ . The light yield of the PS was determined from the amplitude spectra from the position of the peak maximum arising from the interaction of 975 keV ( $^{207}\text{Bi}$ ) conversion electrons with the sample.

Since the glass case in which the LS was located completely absorbed the conversion electrons, the light yield of the LS was determined from the amplitude spectra at half maximum of the Compton scattering decay curves arising from the interaction of gamma quanta with an energy of 1.064 MeV ( $^{207}\text{Bi}$ ) with the sample.

### 2.2. Determination of $n/\gamma$ -discrimination by pulse shape.

In the measurements, the LS and PS were irradiated with fast neutrons and  $\gamma$ -quanta from a plutonium-beryllium source ( $^{239}\text{Pu}-\text{Be}$ ) through a lead plate 20 mm thick. After digital processing, the shape of the pulse and the area of the slow component ( $Q_{slow}$ ) in the range from 50–70 ns to 200 ns and the entire pulse ( $Q_{total}$ ) were stored in the source file for each detected pulse. The choice of the initial integration time point for  $Q_{slow}$  calculation was selected individually for each sample. Then, for each event, the ratio  $D = Q_{slow}/Q_{total}$  was calculated and the distribution of the number of events over  $D$  was built, from which the FOM was determined.

## 3. Results and discussion

The most widely used scintillation base of a liquid scintillator is toluene. From the point of view of the spectral-luminescent properties of naphthalene molecules, they are not optimally consistent with the spectral-luminescent properties of toluene. And therefore, the light yield of a liquid scintillator using naphthalene is significantly inferior to the light yield of a LS activated by, for example, PPO molecules, which are more fully consistent with toluene in spectral-luminescent characteristics (Fig. 1).

It is known that standard LS does not allow efficiently discriminate neutrons and  $\gamma$ -quanta by the form of a scintillation pulse. To carry out such discrimination, naphthalene molecules are added to the composition of the LS. This is due to the fact that TTA requires molecules with long-lived triplet states. The lifetimes of the triplet states of naphthalene significantly exceed the similar lifetimes of benzene molecules [7]. Therefore, when creating LSs

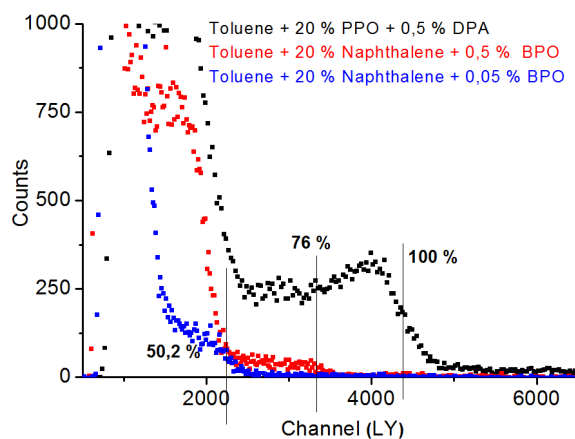


Fig. 1. Scintillation amplitude spectra of LSs (radionuclide  $^{207}\text{Bi}$ ).

capable of efficiently performing  $n/\gamma$ -discrimination, an efficient energy collection of triplet states by activator molecules is necessary.

From the data given in Table 1, Fig. 1 and Fig. 2, it is seen that the maximum light yield of the LS based on toluene is achieved at a content of 20 wt. % of naphthalene and 0.5 wt. % of BPO. In this case, the maximum  $n/\gamma$ -discrimination parameter is achieved with a content of 20 wt. % of naphthalene and 0.05 wt. % of BPO. Thus, a decrease by an order of magnitude of the concentration of the shifter in the composition of the LS, although it slightly reduces the light yield (LY), it leads to a significant increase in the  $n/\gamma$ -discrimination parameter FOM (Table 1, Fig. 1, and Fig. 2).

Thus, it is seen that the conditions for obtaining the maximum light yield of the LS and the most efficient  $n/\gamma$ -discrimination are somewhat different. This is due to the fact that, at a certain concentration, the shifter molecules (BPO) are already beginning to collect the energy of triplet excitation from the activator molecules (naphthalene). But at the same time, the concentration of the shifter molecules is insufficient so that they themselves realize the effect of

Table 1. Scintillation properties of LSs

Composition PS, wt. %	LY, %	FOM
Toluene + 20 % PPO + 0.5 % DPA	100	1.49
Toluene + 20 % naphthalene + 0.5 % BPO	76	1.8
Toluene + 20 % naphthalene + 0.05 % BPO	50.2	2.86

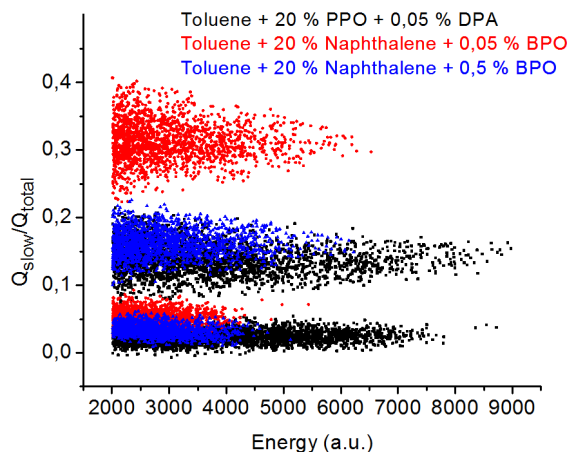


Fig. 2. The effectiveness of  $n/\gamma$ -discrimination of various compositions LSs.

triplet-triplet annihilation. The efficiency of the collection of excitation energy from the base of the liquid matrix (toluene) is primarily determined by the ability of their diffusion in solution. It is known that the diffusion coefficient of molecules in a liquid is about  $10^{-5} \text{ cm}^2 \cdot \text{s}^{-1}$ . Therefore, during the lifetime of the excited triplet state (hundreds of nanoseconds), it can easily be transferred to activator molecules, the average distance between which at a concentration of 20 wt. % is about 1 nm. It is the efficiency of collecting the energy of triplet excitation by naphthalene molecules from toluene molecules that determines such a significant efficiency of  $n/\gamma$ -discrimination. It should be noted that the  $n/\gamma$ -discrimination parameter of LSs based on PPO molecules is almost two times lower than the similar parameter for the discrimination of LSs activated by naphthalene molecules (Fig. 2), although its light yield significantly exceeds the light yield of LSs with naphthalene.

We obtained and studied polystyrene PS with the content of luminescent additives similar to LS with a maximum  $n/\gamma$ -discrimination, containing 20 wt. % of naphthalene and 0.05 wt. % of BPO. The obtained PS showed a relatively low light yield  $\sim 53$  % with respect to the standard type PS UPS-923A [8] (Fig. 3). And this is understandable, since the ratio of the spectral-luminescent properties of the polymer base and naphthalene molecules from the point of view of non-radiative transfer is not entirely optimal. At the same time, the obtained PS does not demonstrate any distinguishable  $n/\gamma$ -discrimination (Fig. 4).

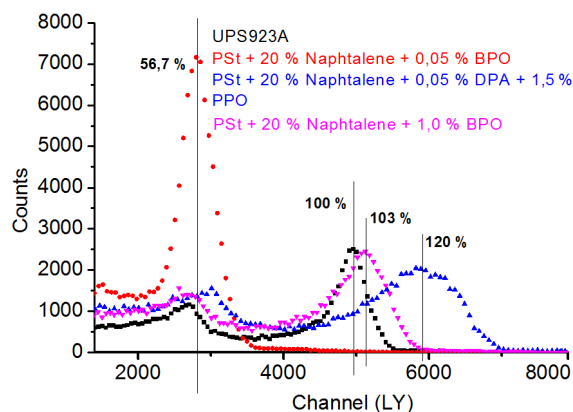


Fig. 3. Scintillation amplitude spectra of PSs (radionuclide  $^{207}\text{Bi}$ ).

Analyzing the evolution of the scintillation pulse of such a PS over time (Fig. 5), we can see that its decay time practically coincides with the decay time of naphthalene molecules and is about 100 ns. This time significantly exceeds the integration time of the output RC-chain of PMT, which in our experiments was about 30 ns. This character of the temporal evolution of the scintillation pulse differs significantly from the character of the scintillation pulse in the LS activated by naphthalene molecules (Fig. 5). In the LS, the scintillation pulse is significantly quenched, and its decay time practically coincides with the time instrumental function of the PMT. In PS based on polystyrene, containing 20 wt. % of naphthalene and 0.05 wt. % of BPO, quenching of activator molecules is completely absent. In a liquid scintillator, quenching of an activator is possible only by transferring energy between the activator molecules and the shifter molecules. The collision frequency of molecules in the diffuse quenching approximation is determined by the expression:

$$J = 4\pi R^2 D \left( \frac{\partial c}{\partial r} \right)_{r=R} = 4\pi R D c_0 \left( 1 + \frac{R}{\sqrt{\pi D t}} \right),$$

where  $R$  is the radius of the "black sphere",  $D$  is the diffusion coefficient,  $c_0$  is the initial concentration of excited activator molecules.

If we take  $\sim 1$  nm as the estimated parameters, and the number of excited naphthalene molecules is only 10 % of the total number of excited molecules, then in this case the collision frequency will be about  $10^9 \text{ s}^{-1}$ . In a plastic scintillator, the mechanism of energy transfer due to the collision of molecules is completely absent. The

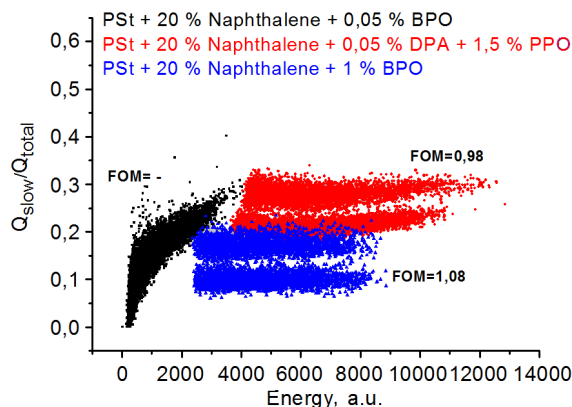


Fig. 4. The  $n/\gamma$ -discrimination efficiency of naphthalene activated PSs.

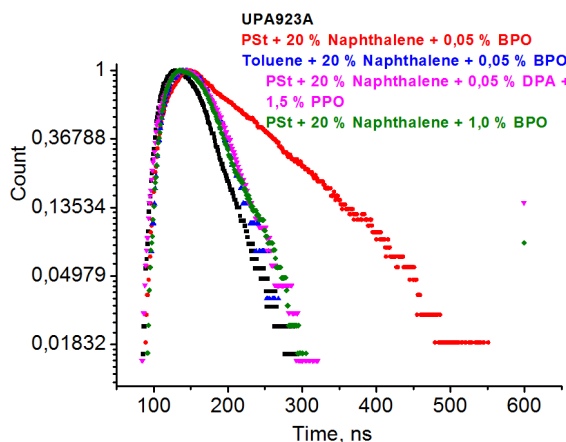


Fig. 5. The curves of temporal evolution of the scintillation pulse of various compositions PSs.

transfer of excitation energy is possible only due to the induction-resonance mechanism, which depends on the distance proportionally. When the concentration level of BPO is 0.05 wt. % such energy transfer is almost imperceptible (Fig. 5).

The realization of the TTA effect is possible only as a result of the exchange interaction of two excited molecules in the triplet state with subsequent localization of all the excitation energy on one molecule with its further conversion to the singlet state. Moreover, the intensity of delayed luminescence is very low, at a level of  $10^{-3}$  from the intensity of the main luminescence. Therefore, we can assume two options for explaining the absence of discrimination in PS with 20 wt. % of naphthalene and 0.05 wt. % of BPO molecules. Firstly, this is the absence of the effect of triplet-triplet annihilation on naphthalene molecules. Secondly, due to the long lifetime of the excited state of naphthalene molecules (of the

Table 2. Scintillation properties of PSs

Composition PS, wt. %	LY, %	FOM
UPS-923A	100	–
PSt + 20 % naphthalene + 0.05 % BPO	56.6	–
PSt + 20 % naphthalene + 1.0 % BPO	120	1,08
PSt + 20 % naphthalene + 1.5 % PPO + 0.05 % DPA	103	0.98

order of 100 ns), their main luminescence can overlap delayed luminescence. To verify these assumptions, a PS containing 20 wt. % of naphthalene and 1.0 wt. % of BPO was obtained. At such concentrations of luminescent additives, the distance between the donor molecules (naphthalene) and the acceptor molecules (BPO) of the excitation energy is set sufficiently small and allows for non-radiative transfer of excitation energy. And, indeed, the nature temporal evolution of the scintillation pulse of such PS has qualitatively changed; its attenuation time was much shorter than the initial 100 ns (Fig. 5). And such an increase in the concentration of BPO molecules immediately led to the possibility of pulse shape discrimination with the parameter  $FOM = 1.08$ . These facts confirm the assumption that delayed luminescence was indistinguishable against the background of the main luminescence of naphthalene. In addition, the light yield of this plastic scintillator was almost 20 % higher than the light yield of the standard PS UPS-923A. A similar result in  $n/\gamma$ -discrimination was achieved by quenching the activator with PPO molecules, which can also efficiently collect excitation energy from naphthalene molecules (Fig. 4 and Fig. 5, Table 2).

Thus, even with the content of naphthalene in the polystyrene matrix at the level of 20 wt. % managed to achieve a notice-

able  $n/\gamma$ -discrimination. To increase the efficiency of  $n/\gamma$ -discrimination, it is necessary to facilitate TTA by increasing the concentration of the additive. However, the limited solubility of naphthalene in PS does not allow obtaining transparent samples with a higher activator concentration. Therefore, in the future, it is of interest to use derivatives of naphthalene with increased solubility in a polystyrene matrix.

#### 4. Conclusions

The prospect of creating neutron-sensitive plastic scintillators activated by naphthalene molecules is analyzed. Using 20 wt. % of naphthalene was obtained PS with a high light yield (120 %) and an  $n/\gamma$ -discrimination parameter  $FOM = 1.08$ . This result allows us to expect that when using naphthalene derivatives with higher solubility in the polystyrene base as PS activators, it is possible to obtain PS with a high  $n/\gamma$ -discrimination factor.

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