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Tuning the decay time of liquid scintillators

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Abstract

The choice of an appropriate viscosity of a liquid scintillator solvent can lead to the fine tuning of its decay time. We present herein the photophysical and scintillation properties of liquid scintillators containing pyrene and 9,10-diphenylanthracene as the primary and secondary fluorophores, respectively, being dissolved either in toluene, diisopropylnaphthalene or mixtures of these two solvents. By modifying the dynamic viscosity, the photoluminescence decay time can be easily chosen in the range 40 – 120 ns. For all liquid scintillators the light yields were satisfying, and the scintillation decays were slightly different, ranging from 36 up to 125 ns.

Keywords

Liquid scintillator; Pyrene; TCSPC; Radiation detection

1. Introduction

Thanks to their carbon-based nature, organic – and in the context of this document, liquid – scintillators can be chemically fully modified, provided the fact they keep their scintillation efficiency.¹ The concept of liquid scintillator appeared in 1950 in two seminal papers that were published nearly at the same time.^{2,3} Immediate interest was granted from the community⁴ and the next decades have seen the positioning of liquid scintillators (LSs) at the central place of radiation detectors with numerous applications, from fundamental physics research (such as Borexino⁵ or SNO+⁶), metrology of the activity,⁷ dosimetry,⁸ environmental assays⁹ and various R&D activities looking at new, promising media.¹⁰ Five different advantages of LSs can be highlighted:

1. the possibility to perform pulse shape discrimination of particles displaying different dE/dx ratios,
2. the detection of beta-emitters with very low energy such as ³H,
3. the possibility to load the scintillator with various elements from the periodic table,
4. their radiochemical purity which is paramount for the detection of rare radioactive decays,

5. an outstanding access up to cubic meter volumes which is particularly suitable for large experiments where almost no other radiation detector can compete in terms of effective size.

Unfortunately, LSs do not represent the Holy Grail in terms of detectors. Since they are composed of hydrogenocarbon molecules, they are not suitable for gamma spectroscopy due to their low effective atomic number, unless they are loaded with heavy elements (although this can be advantageous when performing beta counting in the presence of high energy gamma rays). They are also tricky to handle and depending on the nature of their solvent they can be hazardous or even toxic at some point. Above all, oxygen is a very efficient quencher of the scintillation light,¹¹ which imposes to use LSs constantly degassed and maintained or encapsulated under neutral atmosphere to have the best detection efficiency.

Chemically speaking, a liquid scintillator is a formulation of one or several fluorescent molecules that are dissolved in an organic solvent. Eventually, some additives can be added such as organometallics or chelatants. All these stages have been extensively studied in the past. Since the solvent is the main component of the scintillator, several developments have been performed regarding the effect of impurities, substituting hydrogen with deuterium for neutron detection, and an important work has been performed on the quest for safer liquid scintillators so as to replace small organic molecules such as xylenes or toluene by linear alkyl benzene (LAB) or diisopropylnaphthalene (DIN). This allows scintillators with less toxicity, higher flash point and eventually biodegradability feature. The solvent is also the medium where the initial radiation/matter interaction happens, hence the start of the scintillation process. Not to reduce to a small piece their influence and the huge work on their choice and modifications, primary and secondary fluorophores have less impact on the scintillation efficiency, as they will mainly govern the photophysical properties such as emission wavelength and decay time provided the fact that their concentration is adequate in the solvent. Particularly efficient molecules are for instance 2,5-diphenyloxazole (PPO) and 1,4-bis(5-phenyl-2-oxazolyl)benzene (POPOP), which act as primary and secondary fluorophores, respectively.

Usually, the main decay time of LSs (in principle the fastest component when the decay is double- or even multi-exponentially fitted) falls within the range 1 – 10 ns.^{12,13} Such timing resolution is very fast so one has to adapt the electronics that are dedicated to the signal processing for a good digitization of the fast pulse. Various research programs were conducted to accelerate this decay time for fast timing applications, leading to ultra-fast liquids,¹⁴ but to the best of our knowledge extending the decay time to longer values has only been barely studied.¹⁵ Here in 15 all the liquid scintillators that have been tested are from Nuclear Enterprises and their formulation is proprietary. On the basis of the Authors' work, only three liquids display decay times higher than 10 ns: NE 321 (15.70 ns), NE 227 (17.02 ns) and NE 317 (20.21 ns). NE 321 is a boron-loaded LS presumably based on 4-isopropylbiphenyl but the fluorophores are not revealed,¹⁶ and the two other scintillators are still unknown to us in composition. In this context and following our preliminary studies with the extension of the decay time of plastic scintillators,¹⁷ we propose herein several new formulations or possibilities that allow tuning the decay time of scintillating liquid in a range between 36 and 125 ns.

2. Experimental

Pyrene was purchased from Sigma-Aldrich and was carefully purified by sublimation prior to use. 9,10-diphenylanthracene was purchased from Alfa AesarTM and used without purification. Spectroscopic toluene was purchased from Carlo Erba and used as received. Diisopropylnaphthalene (DIN) was purchased from Perkin-Elmer, was purified on silica gel chromatography and kept in the dark prior to

use. BC-501A was purchased from Saint-Gobain Crystals and Detectors. Prior to each experiment, the liquid scintillator was carefully saturated with argon during 8 minutes.

Fluorescence spectra were recorded at 90° angle with a Horiba Jobin Yvon Fluoromax-4P device, monitored with FluorEssence software. The photoluminescence decay characteristics of the liquid scintillators were investigated with the Time-Correlated Single Photon Counting (TCSPC) module available on the Fluoromax-4P spectrofluorometer, with an excitation provided by a laser diode operating at 274 nm which allows exciting the entire formulation of the scintillator. Another NanoLED emitting at 368 nm was also used to probe the secondary fluorophore only. Decay spectra were fitted using DAS6 software (Horiba Jobin Yvon), the quality of the fit was determined so that the χ^2 value was less than 1.30.

To record scintillation properties, a scintillation vial containing 15 cm³ of the fully degassed liquid sample was placed in the center of a white chamber which was connected to a Hamamatsu R6231-100 photomultiplier tube operating at +1400 V. A ¹³⁷Cs source (530 kBq, 02/15/2016) was used to excite the scintillator. Pulses coming from the PMT were sorted and treated with a CAEN DT5730B electronic board during an acquisition time of 20 minutes. The high voltage was kept constant for all tested scintillators. Determination of the Compton edge (CE) position was evaluated from the top of the Compton edge with a relative uncertainty of 5% of its channel value. The relative scintillation yield was calculated using a reference spectrum (BC-501A sample), whose scintillation yield is given as 12,000 ph/MeV.¹⁸ This comparison is possible due to the fact that the tested scintillators emit in the same wavelength range as the reference material. By rule of thumb, the light yield of the prepared plastic scintillator sample is determined using this equation:

$$R_{sample} = R_{BC-501A} \times V_{CE,sample} / V_{CE,BC-501A}$$

where R is the scintillation yield, and V is the channel of the Compton edge position. The response linearity evaluation was performed by plotting the Compton edge position against the Compton edge energy connected with the corresponding gamma ray emitter. For the energy calibration, the following gamma-emitting sources with activities were used: ²⁴¹Am (1.7 MBq, 06/13/2016), ¹³⁷Cs (530 kBq, 02/15/2016), ⁶⁰Co (101 kBq, 05/22/2018), ²²Na (1.28 MBq, 05/22/2018). The same strict experimental setup was used as for light yield evaluation.

Scintillation pulses were recorded using the above-mentioned ⁶⁰Co source which was used for the excitation, and the setup was identical as before as well, except that the CAEN digitizer was replaced by a digital oscilloscope LeCroy wavepro 7300A operating at 500 MS/s. 5,000 pulses were collected and averaged, inverted (since the pulses incoming from the photomultiplier tube are negative), and the resulting pulse was fitted with the same DAS6 software used for TCSPC.

3. Results and discussion

Photophysical properties

Decay time characterization of liquid scintillators has been the main subject of numerous publications.^{12,15,19,20} As already mentioned, having access to long-lived (*i.e.* 10 – 100 ns) photoluminescence decay times in liquid media is not straightforward. First, the choice of organic, simple molecules able to decay with lifetimes higher than 10 ns is rather narrow. In the context of our studies, naphthalene and pyrene have been chosen thanks for their decay, but also for their efficiency as scintillating molecules. A recent paper from Biller et al. introduced the use of acenaphthene as slow fluorophore in linear alkyl benzene for neutrinoless double beta decay,²¹ so this might be another molecule choice. Besides, one has to keep in mind the low cost of a new liquid scintillator, so complex

molecules are to be avoided, or at least for a first approach study. Here, naphthalene will not be presented and acenaphthene has not been tried. In the world of photoluminescence, pyrene is one of the most exciting fluorophore thanks to several of its prominent photophysical characteristics: the fluorescence spectrum strong dependence on its chemical environment,²² a long decay time and an excited pyrene emission vs. excimer emission.²³ It seems that pyrene in polystyrene appeared as early as 1953,²⁴ but J. B. Birks was the first scientist that extensively studied this molecule in the field of organic scintillation counting.²⁵ Almost sixty years later, the pyrene moiety is still under interest in the scintillation domain.²⁶

Since the mobility of pyrene can affect its decay time, we decided to check the influence of the viscosity of the solvent upon its photoluminescence. In other words, mixing a viscous, scintillation-grade solvent to another fluid, scintillating solvent would afford liquid scintillators with various decay times. Mixing at least two solvents to prepare liquid scintillators is somehow peculiar in this field. Mixed solvent such as linear alkyl benzene and pseudocumene have already been described, here to benefit from advantages of each solvent to some extent.²⁷ Although not related to the scintillation field, Wolff et al. have noticed that adding viscous solvent (which is in this case diisopropylnaphthalene – DIN) to a fluid solution containing 9,10-dimethylantracene leads to increasing its apparent decay time from 12 up to 30 ns.²⁸ Other applications have already studied the viscosity dependence on the fluorescence lifetime, such as in the field of molecular rotors,^{29,30} and protein fluorescence kinetics.³¹ Interestingly in 29 the Authors list fluorophores that are sensitive to viscosity and/or temperature. Table 1 gives an overview of various solvents that are suitable for liquid scintillation counting, along with their dynamic viscosity given at room temperature. This list is sorted from more fluid (toluene) to more viscous solvents, and the two limits thus constitute our choice in the preparation of the scintillating mixtures. Obviously more viscous solvents than DIN exist but the choice was restricted to scintillating-grade solvents only.

The abbreviation of DIN as reported in many publications may be the cause of several mistakes due to the number of isomers of diisopropylnaphthalene. Herein we talk about the DIN which is currently used in several commercial LS cocktails: it is in fact a mixture of isomers and is registered under the CAS [38640-62-9]. Its dynamic viscosity at 20 °C is equal to 12.67.³²

Table 1 Dynamic viscosities for selected scintillation-grade solvents at 25 °C (unless otherwise stated)

Solvent	Dynamic viscosity η (mPa.s)
Toluene	0.59
<i>p</i> -Xylene	0.65
Benzene	0.66
<i>o</i> -Xylene	0.81
Pseudocumene	0.9
Linear alkyl benzene	4.00
PXE	≈ 6.8
DIN	12.67 (at 20 °C)

The two viscosity limits being established, we decided to study the photoluminescence decay dependence of scintillators in this range. Pyrene and 9,10-diphenylantracene (9,10-DPA) were chosen as the fluorescent probes, since they are highly referenced in the scintillation field and they are often matched. Thus, toluene-based or DIN-based liquid scintillators were prepared from the appropriate solvent containing pyrene and 9,10-diphenylantracene. From these stock solutions, combinations were performed from 100% toluene-based LS to 100% DIN-based LS. Starting with the more fluid

solvent (toluene, $\eta = 0.59$ mPa.s at 25 °C) to the more viscous solvent (DIN, $\eta = 12.67$ mPa.s at 20 °C), the viscosity of solvents mixture is given by:

$$\text{Log}(\eta_{\text{mixture}}) = X_{\text{toluene}} \times \text{Log}(\eta_{\text{toluene}}) + X_{\text{DIN}} \times \text{Log}(\eta_{\text{DIN}})$$

where X_i is the molar fractions of molecules and η_i the dynamic viscosity of the solvent i .

Noteworthy, the decay shape of the couple between pyrene in its excimer form and 9,10-diphenylanthracene against the viscosity of the solvent has already been studied,³³ where the two combined solvents were benzene and cyclohexanol. The dynamic viscosity of cyclohexanol is very high: 56 mPa.s at 25 °C. However, it is not a good solvent for scintillation counting.

Then the appropriate quantity of dyes giving the scintillator the best scintillation properties was determined. No optimization was performed on 9,10-DPA in this study, and a typical 0.03 wt% concentration was considered. Also, the same concentrations of dyes were used for all mixtures of solvents. Pyrene has a very strong luminescence dependence with its concentration, both in terms of intensity and emission wavelength. It is noteworthy the rather unusual, low concentration of pyrene as the primary fluorophore we have chosen. At a glance, the pyrene in its excimer form would be the best choice since its emission is centered around 480 nm, an emission wavelength which is interesting for the purpose of scintillation counting. As such, pyrene under its dimer form could be used as the only solute in a liquid scintillator, which means with no need of secondary fluorophore.³⁴ Thus, toluene containing 3 wt% of finely sublimed pyrene was tested as a binary liquid scintillator. This solution revealed good scintillating properties but a long decay time was never reached. The result of the pulse height spectrum when excited with gamma rays of ¹³⁷Cs gave a light yield of $\approx 6,500$ ph/MeV (relative to BC-501A), but the monoexponential fit of the decay time was found to be 50 ns.

So we decided to focus on the photoluminescence properties of excited pyrene in its monomer form (therefore at low concentration), and 9,10-DPA is associated to afford a ternary liquid scintillator. Figure 1 left resumes the photoluminescence spectrum of pyrene in toluene at various concentrations. As already depicted, the pyrene excimer starts to be predominant at rather low concentrations for a fluorophore usually used for scintillation. The isobestic point between the monomer and the dimer area-normalized emissions is clearly visible at 432 nm on Figure 1 left. Even if the excimer's luminescence is still visible, we decided to choose the pyrene weight concentration at 0.03 wt%, which is $1.29 \cdot 10^{-3}$ mol.L⁻¹. To get rid of all excimer emission, various pyrene concentrations are reported: from 10^{-3} mol.L⁻¹³⁵ or lower than $5 \cdot 10^{-5}$ mol.L⁻¹.³⁶ This last concentration would be too low for an appropriate use in scintillation counting. With the same excitation and emission parameters, Figure 1 right shows the resulting fluorescence integrals against the pyrene concentration. Interestingly, there is a decrease of the fluorescence intensity when the two species are present in solution, then the intensity rises, with highly diluted 0.01 wt% solution being the brightest among the others. However, we preferred to keep the concentration of pyrene at 0.03 wt%, where the integral of the monomer emission is 1.7 times higher than the excimer's. Figure 2 shows the photoluminescence difference between toluene-based and DIN-based pyrene + 9,10-DPA solutions at the same concentration. The respective emission maxima are 432 and 428 nm, a difference which is not significant for scintillation counting, given the fact that standard photomultiplier tubes have almost the same quantum efficiency for both 432 and 428 nm wavelengths. This figure also shows that the viscosity influence on the LSs decay time is not due to an increase part of excimer but a true monomolecular emission.

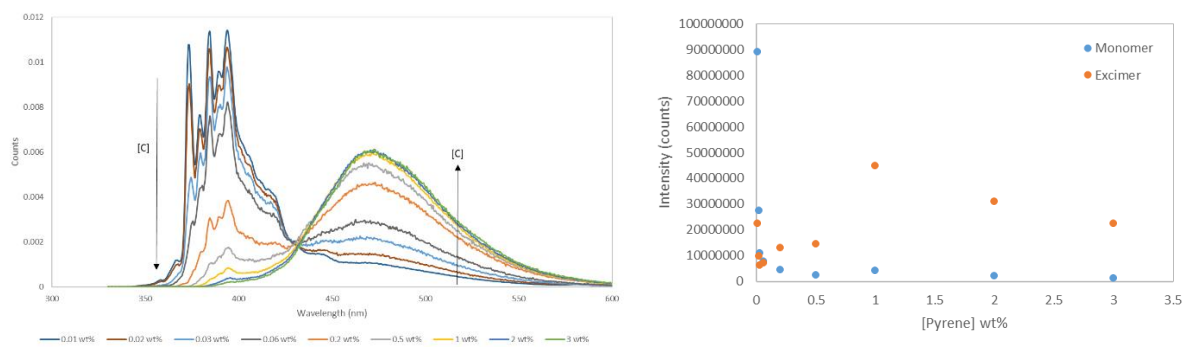


Figure 1. Left: area-normalized photoluminescence dependence of pyrene with concentration. Solvent: toluene; $\lambda_{ex} = 310$ nm, same experimental parameters for all. Right: integral of the photoluminescence curves with pyrene concentration. The delimitation to calculate monomer or excimer intensities is defined at the isobestic point.

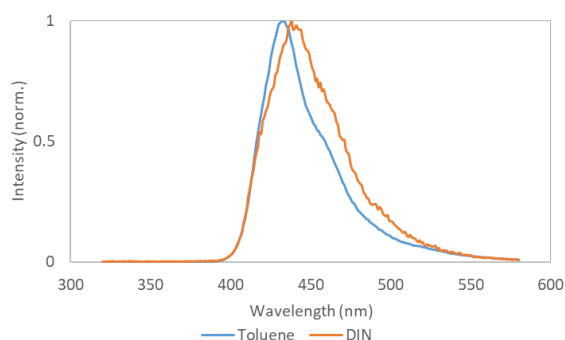


Figure 2. Normalized fluorescence spectra of toluene-based and DIN-based liquid scintillators containing pyrene and 9,10-DPA, both at concentrations 0.03 wt% ($\lambda_{ex} = 300$ nm).

Then the mixtures of solvents containing 0.03 wt% of pyrene and the same concentration of 9,10-diphenylanthracene were evaluated in terms of Time-Correlated Single Photon Counting, photoluminescence spectroscopy and gamma-ray pulse height spectrum. For the TCSPC recordings, a 274 nm NanoLED from Horiba Jobin Yvon was used to excite the liquid scintillator. Figure 3 reports the mean decay values of the biexponential fits against the viscosity of the mixtures of solvents containing the two fluorophores. The mean decay values are calculated according to: $\langle \tau \rangle = \tau_{fast} \times \%_{fast} + \tau_{slow} \times \%_{slow}$. Table 2 gives the full details of the decay fitting. A linear dependence of the mean decay time on the viscosity of the solvent combination can be observed. BC-501A is added on the last line of Table 2 for comparison sake: it is a reference liquid scintillator from Saint-Gobain Crystals and Detectors. Its data has been added since it will be useful later on for the scintillation performance characterization. Here as well, a biexponential fitting is privileged, with the values which are of the same order as previously reported.³⁷

Table 2 Full data of the biexponential fits of the decays for various formulations. BC-501A is added. $\lambda_{ex} = 274$ nm, $\tau_{obs} = 430$ nm. The decay times given in the table are governed by pyrene only.

Solvent mixture (%) + pyrene & DPA at 0.03 wt%	Viscosity η (mPa.s)	Biexponential fitting $\tau_{fast} (\%_{fast}) + \tau_{slow} (\%_{slow})$	Mean value $\langle \tau \rangle$ (ns)	χ^2
PhMe 100 – DIN 0	0.59	16.1 (16.8) + 45.2 (83.2)	40.3	1.18
PhMe 90 – DIN 10	0.82	40.1 (88.8) + 105.9 (11.2)	47.5	1.21
PhMe 80 – DIN 20	1.14	37.0 (86.5) + 95.1 (13.5)	44.8	1.29
PhMe 70 – DIN 30	1.58	25.4 (21.4) + 63.5 (78.6)	55.3	1.09
PhMe 60 – DIN 40	2.16	22.8 (18.8) + 64.8 (81.2)	56.9	1.08

PhMe 50 – DIN 50	2.95	24.3 (20.0) + 78.5 (80.0)	67.7	1.19
PhMe 40 – DIN 60	3.99	21.1 (16.8) + 87.6 (83.2)	76.5	1.19
PhMe 30 – DIN 70	5.37	19.6 (14.2) + 87.5 (85.8)	77.9	1.19
PhMe 20 – DIN 80	7.19	18.4 (13.4) + 114.4 (86.6)	101.5	1.05
PhMe 10 – DIN 90	9.57	17.1 (12.2) + 120.9 (87.8)	108.2	1.06
PhMe 0 – DIN 100	12.67	18.5 (21.6) + 144.6 (78.4)	117.4	1.20
BC-501A	n.d.	2.72 (87.3) + 23.7 (12.7)	5.4	1.16

n.d.: not determined.

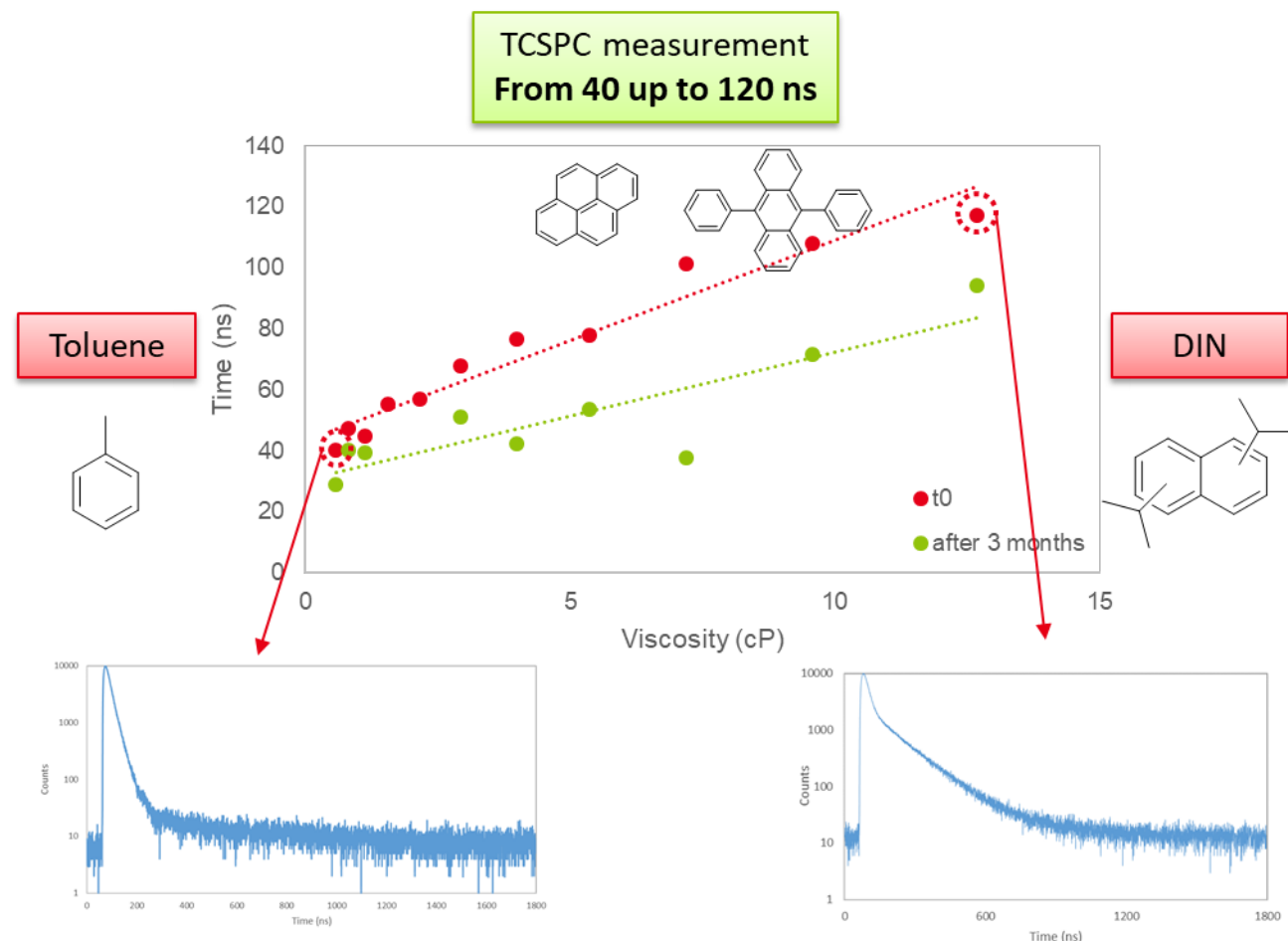


Figure 3. Mean decay value of pyrene and 9,10-DPA in mixtures of solvents, according to the viscosity. $\lambda_{ex} = 274 \text{ nm}$; $\lambda_{obs} = 430 \text{ nm}$. Time evolution at 3 months of PhMe 70 – DIN 30 and PhMe 60 – DIN 40 were not recorded.

The observed decay times given in Table 2 point at a dual emissive system. As the primary fluorophore (pyrene) and secondary fluorophore (DPA) are present at almost the same concentrations, two emission pathways should be considered. The direct excitation of DPA gives the fast components and the classic cascade of pyrene toward DPA energy transfer gives the slow component. The decay time variation shows steady fast component which makes the slow component the only responsible for the decay tuning. This excludes non-specific quenching, which should have an effect on all the components. It implies that either, specific molecular quenching, pyrene exciton dynamics and/or pyrene to DPA energy transfers are the sources of the decay variation. A preliminary conclusion is that the variation is governed only by the pyrene behavior in a solvent with changing viscosity.

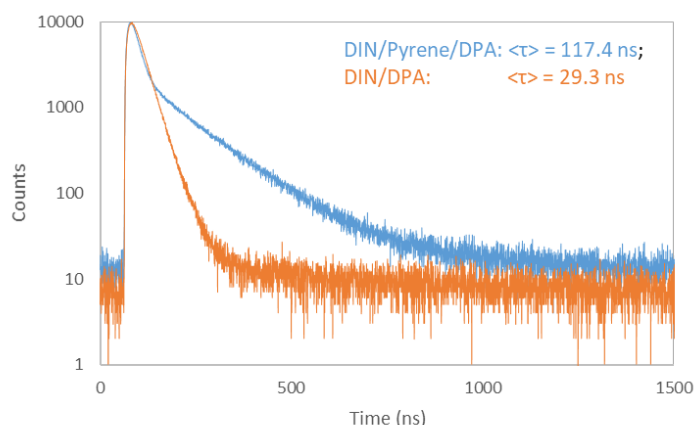


Figure 4. TCSPC of DIN-based liquid scintillator including either pyrene and DPA (blue) or DPA only (orange). $\lambda_{ex} = 274 \text{ nm}$, $\lambda_{obs} = 430 \text{ nm}$.

It is also noteworthy that our values do not correspond to the reported decay value of excited pyrene monomer in organic solvent at room temperature. In a binary mixture of pyrene in DIN, a 282 ns decay time was observed, in agreement with literature, so adding DPA to the solution prevents keeping this decay time.³⁸ Also, this decay is highly sensitive to oxygen quenching and might be an issue for our scintillators. Here the purpose of our work is to prepare liquid scintillator cocktails having in mind these formulations could be prepared by nuclear physicists, so without easy access to chemical facilities allowing low oxygen content within the scintillator. Table 3 shows two things. First is the reproducibility of the bubbling procedure. It is clearly seen the possibility to reuse the same scintillating solution after a while, simply by bubbling once again with neutral gas. However, the same (slowest) scintillator gives mean decay fittings with a pretty wide variation: from 102 ns up to 142 ns, related with the “quality” of the bubbling step. Second is the evolution of the TCSPC with time for the fastest and the slowest formulations and Table 3 gives the complete dataset. At t_0 both scintillators were carefully saturated with neutral gas, the scintillator vial was sealed with Parafilm® then the decay values were recorded from time to time. For the DIN-based liquid scintillator, a TCSPC recording was performed each minute during the first twenty minutes and virtually no variation was observed. After four days, the decay was decreased to about 30 % the initial value, but this (small) decrease leads way enough time for radioactive assays. The results we show herein are also the most penalizing ones, since on another try performed on a 100 days’ timeline, the decrease of the decay was 34 % only (94 ns instead of 142 ns – bubbling #2). The results of decay time evolution after 100 days for almost all scintillators is shown in Figure 3. All the scintillators’ decay decrease, but the slope is not the same as for the neat materials. Scintillators with fastest decays are less affected than slowest.

Table 3 Evolution of the decay time of two liquid scintillators with time. $\lambda_{ex} = 274 \text{ nm}$, $\lambda_{obs} = 430 \text{ nm}$.

Solvent mixture (%) + pyrene & DPA at 0.03 wt%	Time of recording	Biexponential fitting $\tau_{fast} (\%_{fast}) + \tau_{slow} (\%_{slow})$	Mean value $\langle \tau \rangle$ (ns)	χ^2
PhMe 100 – DIN 0	t_0	16.1 (16.8) + 45.2 (83.2)	40.3	1.18
	$t_0 + 1 \text{ day}$	16.7 (31.1) + 40.1 (68.9)	32.8	1.15
PhMe 0 – DIN 100	Bubbling #1	18.3 (25.9) + 131.6 (74.1)	102.3	1.14
	Bubbling #2	19.4 (17.8) + 169.3 (82.2)	142.6	1.14
	Bubbling #3	18.5 (21.6) + 144.6 (78.4)	117.4	1.20
	Bubbling #4	17.8 (22.4) + 132.2 (77.6)	106.6	1.19
	Bubbling #5 – t_0	18.1 (23.3) + 136.6 (76.7)	108.9	1.16

$t_0 + 20 \text{ min}$	18.1 (23.4) + 135.3 (76.6)	107.8	1.14
$t_0 + 2 \text{ hours}$	17.9 (24.5) + 123.7 (75.5)	97.8	1.20
$t_0 + 1 \text{ day}$	15.1 (30.9) + 95.5 (69.1)	70.7	1.23
$t_0 + 2 \text{ days}$	16.2 (29.4) + 92.9 (70.6)	70.3	1.11
$t_0 + 3 \text{ days}$	16.2 (31.4) + 90.2 (68.6)	67.0	1.13
$t_0 + 4 \text{ days}$	16.2 (27.9) + 93.7 (72.1)	72.0	1.21

Figure 5 shows the impact of temperature on the decay time of the longest-decaying liquid mixture, with temperatures ranging from 8 up to 42 °C. Since the fitting of the TCSPC curves is biexponential, it is represented in Figure 5 with fast component (blue), slow component (orange) and the mean value τ_{mean} (grey). The mean component is based on the relative weight of each components. By changing the temperature in this range, the mean value of the decay time spans from 163.6 ns down to 69.2 ns, so almost 100 ns can be covered just by adjusting the temperature of the sample. It is interesting to see that only the slow component of the photoluminescence is actually influenced by the temperature variation. Considering the whole dataset, when the mean value of τ_{fast} is 18.2 ns with a standard deviation of 1.2 ns, the mean value of τ_{slow} is 133.6 ns with a standard deviation of 31.0 ns. This information is critical for the detection of radionuclides, especially for choosing the best coincidence parameters or to insert it in a physical model. This difference of behavior of the slow and fast components fit with the explanation of the fast components coming from the direct excitation of the DPA and the slow components from the pyrene + DPA system. The strong variation of the slow components suggest that the pyrene is the one being the most influenced by the temperature changes. Several hypotheses can be made on the cause of this temperature dependence and we will try to narrow it down. Figure 5 bottom shows that the relative weight of the slow and fast components are behaving as expected, meaning the higher the temperature the more fast transition you get. However going in the right direction the range of this phenomenon variation is not enough to explain the 100 ns difference between high and low temperature decay time. An explanation based only on molecule specific quenching is thus impossible and other effect must be considered. Hence, our hypothesis is that the majority of this decay change is due to a dual effect. An indirect one is the influence of the temperature on the viscosity, and a direct one is the efficiency of the pyrene transition, as specific or non-specific quenching are not enough to explain the overall trend. This will require further study; as such a strong dependence on temperature ($\pm 40^\circ\text{C} \rightarrow \pm 100 \text{ ns}$) can be a crucial parameter in the many precise application of liquid scintillators. As a conclusion, it is another possibility to tune the decay time of the liquid scintillator, not by changing the formulation but the experimental temperature.

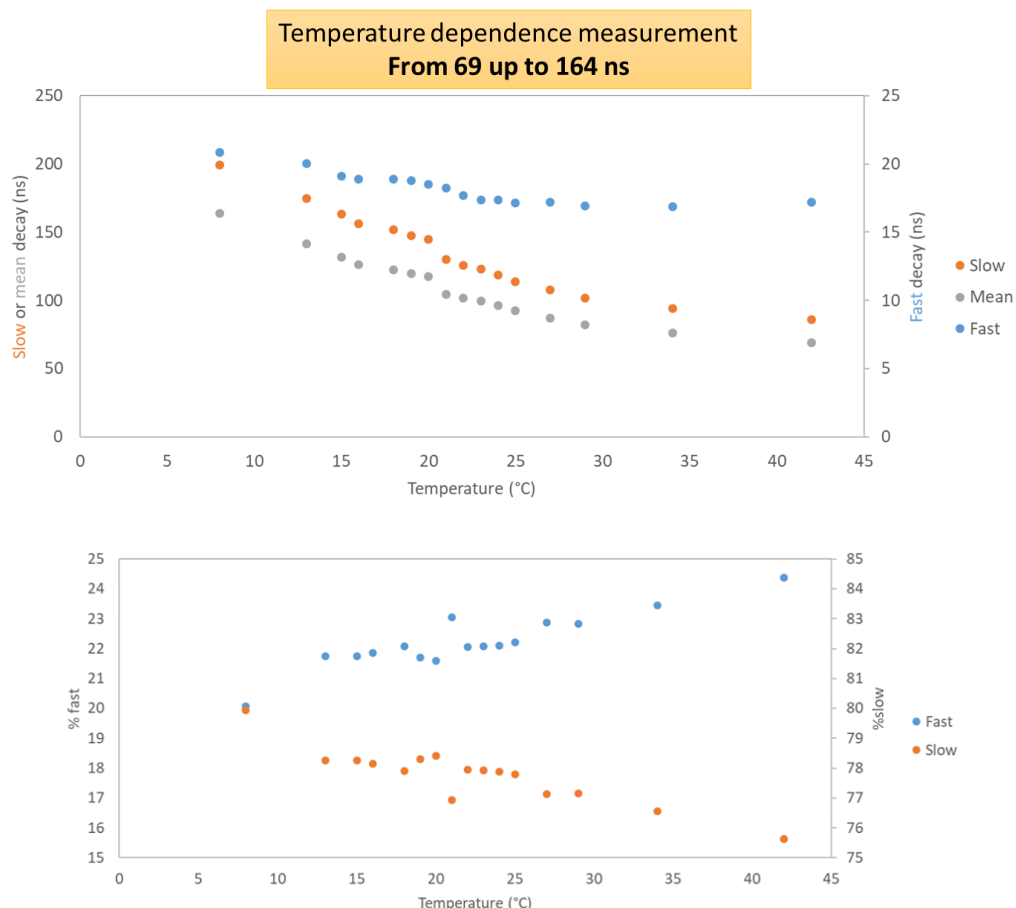
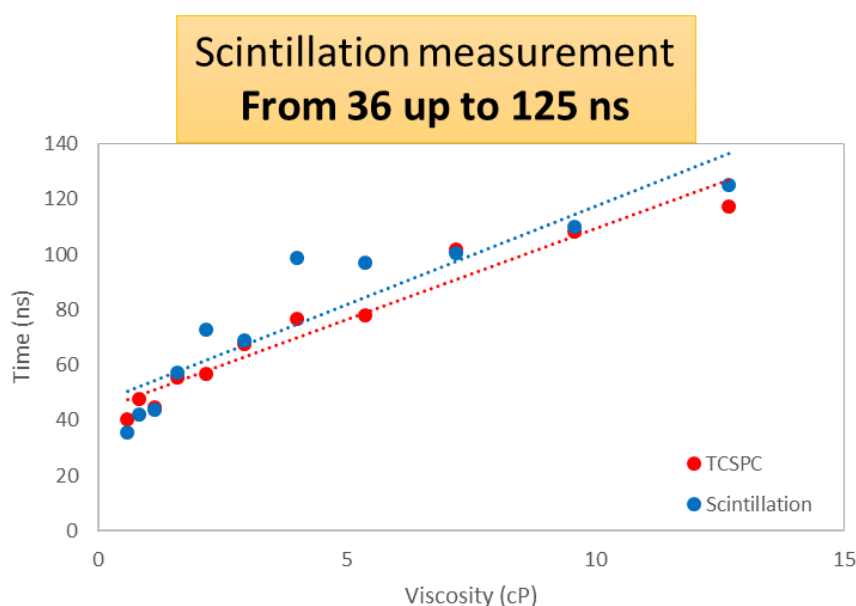


Figure 5. Top) Time-Correlated Single Photon Counting of a liquid scintillator composed of 0.03 wt% of pyrene, 0.03 wt% of 9,10-DPA in DIN as a function of temperature. $\lambda_{ex} = 274$ nm; $\lambda_{obs} = 430$ nm. Note the vertical axis which is the same for slow and mean decay values (left) and fast decay value (right). Bottom) Evolution of the relative weight of fast and slow components as a function of the temperature.

Scintillation properties

After having determined the photophysical parameters, the as-prepared liquid mixtures were assessed in terms of scintillation efficiency. All the previous decay data were collected on TCSPC, that is to say under 274-nm UV excitation. This wavelength is suitable for excitation of the solvents mixture, but the complex scintillation mechanism may not be fully represented from these TCSPC measurements. Therefore, the next set of experiments consisted in recording the scintillation pulse of each liquid scintillator combination. TCSPC using radioactive sources is possible but is not straightforward since it usually requires very strict experimental conditions and days or even weeks of continuous recordings.³⁹ This timescale is higher than the potential stability of our materials. Thus, we decided to use the simplest method, which is recording thousand pulses and measure the time profile of the pulse. The average of 5,000 pulses obtained after excitation of the liquid scintillator with a gamma-ray emitting ^{60}Co source was processed using the same software we used to fit the data obtained from TCSPC measurements, so the comparison is easier. Figure 6 summarizes the values observed from TCSPC and from scintillation measurements. As one can see, a global trend between the two experiments is respected. This undoubtedly confirms the possibility to calculate the decay time of a liquid scintillator from a UV excitation, at least for this range of decay times, TCSPC with UV being much more of practical use than scintillation decay times.

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325 *Figure 6. Decay times obtained from TCSPC (red) or scintillation (blue) measurements. The dashed lines are drawn to guide*
 326 *the eye.*

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328 The two scintillators that have the decay time limits were also checked for pulse shape variations
 329 within a given time. Thus, the scintillators were flushed with argon and the pulses were recorded from
 330 time to time within a ≈ 100 minutes range, then approximately 18 hours in closed scintillation vial. The
 331 results are given Figure 7. Linear decrease of the mean decay time is observed for both scintillators,
 332 but with different kinetics. The slowest scintillator displays outstanding stability over these 100
 333 minutes, with a decrease of 0.02 ns/min. The fastest scintillator decay decreases more rapidly with a
 334 decrease of 0.10 ns/min. These values are stable enough for radionuclide assay experiments with such
 335 scintillators. After 18 hours, the mean decay values are 51.6 ns and 94.0 ns for these two liquid
 336 scintillators. To confirm the slow diffusion of air into the liquid leading to the quenching of the
 337 scintillation, these two scintillators were stirred in open flask for 30 minutes, then another run of
 338 experiment was performed. The corresponding decay times are still different, with τ_{mean} of 16.1 ns and
 339 62.0 ns for the fastest and slowest scintillators, respectively.

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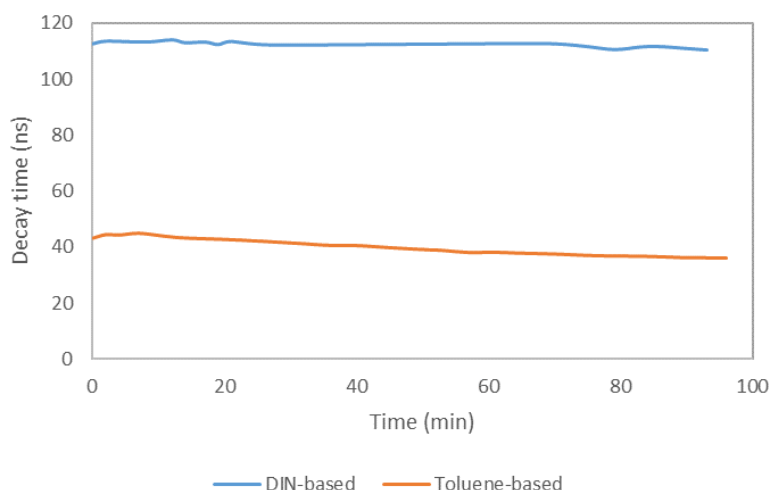


Figure 7. Mean scintillation decay time over time.

Another important factor is to keep the scintillation yield as high as possible for all mixtures, which cannot be predicted *a priori*. Among other parameters, the concentration of pyrene (0.03 wt%) is very low regarding the typical concentration one can find for all other regular primary fluorophores (typically 1 – 3 wt%). All scintillators were thus exposed to a gamma-ray emitting ^{137}Cs radioactive source and the pulse shape spectra were recorded. A commercial liquid scintillator, namely BC-501A was used as the reference. This scintillator is known to display 12,000 ph/MeV (78 % of anthracene single crystal).⁴⁰ The results are given Figure 8. Interestingly, the observed light yields were better than expected due to the low content of pyrene and fall in the range 7,000 – 9,900 ph/MeV, with the worst values observed for the 100 % toluene-based scintillator.

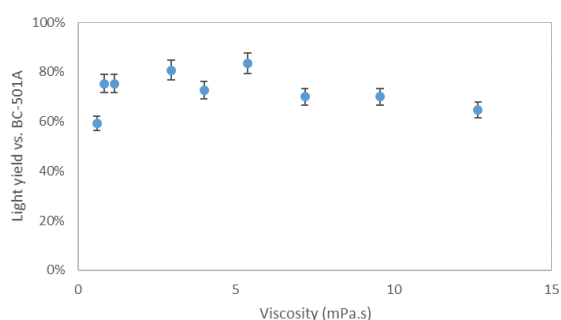


Figure 8. Relative ^{137}Cs gamma light yield against BC-501A reference as a function of viscosity. The vertical uncertainties are given at 5 % of the value.

The last experiment was performed with the slowest decaying liquid scintillator only. Most of organic and inorganic scintillators are known to feature non-linear response towards the impinging energy. Especially, gamma rays with energy below 100 keV do not fall within the same slope as for $E_\gamma > 100$ keV. Thus, the DIN-based liquid was exposed to four gamma sources with various energies, ranging from ^{241}Am ($E_\gamma = 59$ keV) to ^{22}Na ($E_\gamma = 1274$ keV, accompanied by an electron/positron annihilation of 511 keV). Backscattered Compton electrons from gamma interactions within the scintillator with a maximum energy is given by the following formula:

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$$E_{CE} = \frac{2E_{\gamma}^2}{m_e c^2 + 2E_{\gamma}}$$

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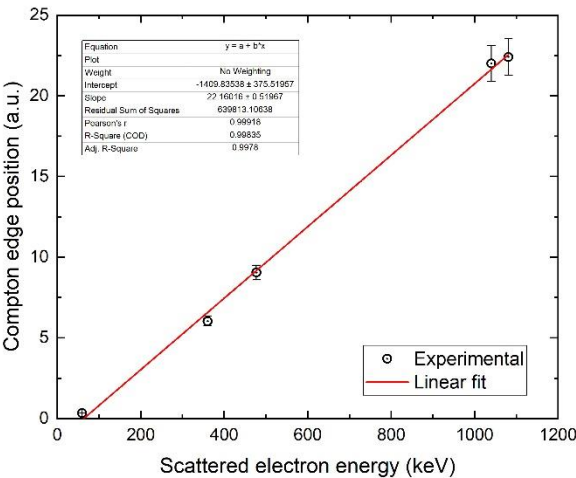
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Figure 9. Energy response against the Compton edge position of four gamma sources. The line is drawn to guide the eye.

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Along with the decay time stability, the light yield evolution with time is a key-parameter. Once again for the slowest scintillator, ^{137}Cs pulse height spectra were performed from time to time on the same DIN-based scintillator that was saturated with argon at the beginning of the experiment (Figure 10). The light yield falls quite rapidly over the first ten hours, with 91 % of the initial light output 2 hours after bubbling. This fast decrease, probably due to oxygen diffusion, may be one of the main drawbacks of the slowest formulation. After one day it seems to stabilize in the range 70 – 79 % of the maximum value obtained at t_0 .

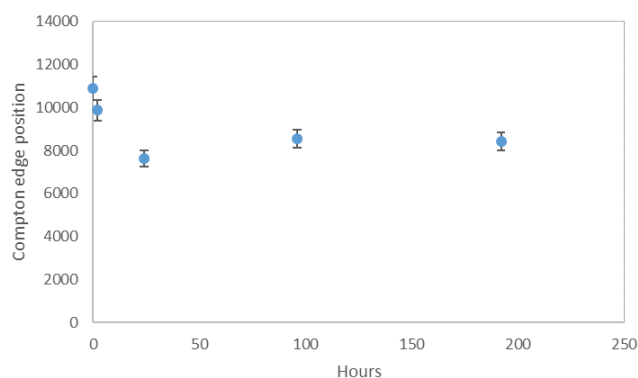


Figure 10. ^{137}Cs Compton edge position with time. The uncertainty is set at 5 % of the position of the Compton edge position.

4. Conclusion

In the prolongation of the tuning of the decay time of plastic scintillators,¹⁷ we present herein a modulation of the decay time for liquid scintillators. Compared with plastics, another strategy was developed based on varying the viscosity of the solvent used for preparing the scintillator. Thus, pyrene and 9,10-DPA were chosen as primary and secondary fluorophores thanks to their apparent long decay time when oxygen is removed efficiently and a 430 nm-centered desired emission wavelength. The concentration of pyrene was reduced to an unusual rate for a primary fluorophore so that mainly the monomer species is able to emit light.

Then various mixtures of toluene-based and DIN-based liquid scintillators containing the same molar concentrations of pyrene and 9,10-DPA were prepared. A linear dependence of the decay time was observed with the viscosity of the solvent mixture. The decay times observed by TCSPC fall in the range 40 ns – 120 ns for the less and the most viscous solutions, respectively. The quality of the bubbling procedure (or in other words, the remaining diluted oxygen in the solution) may affect the decay time, more particularly for the slowest materials.

All scintillators displayed good ^{137}Cs gamma detection properties, with relative light yields in the range 7,000 – 9,900 ph/MeV. TCSPC measurements were then compared with scintillation decays and the results were satisfactory. All scintillators decay times are within the range 36 – 125 ns. An in-depth study performed on the slowest scintillator revealed a minor drawback with a light output decrease within the first two hours. However, one should consider this 36 – 125 ns range as *ideal*. Degrading slopes of not more than 0.10 ns/min after bubbling with argon should be taken into account for the nuclear physicist, so that they would narrow this range. No obvious energy non-linearity was observed, however within a limited energy range.

An obvious criticism of such method could be the relationship of the viscosity of a solvent with temperature⁴¹. The literature example of toluene gives a 34 % variation of its viscosity in the range 293 – 333 K (thus a 40 °C range). In our case, the time-response of liquid scintillators versus temperature can represent another possibility to perform an efficient and accurate tuning of the decay time, as was exemplified with DIN-based liquid scintillator. Its decay time varied from 163 ns down to 69 ns when increasing the temperature in the range 8 – 42 °C. Interestingly, only the slow component of the biexponential fit is affected by temperature variations. So this drawback could be seen as a strength if the scintillator is carefully thermalized while in use. This 36 to 125 ns range could thus be widely extended thanks to temperature adjustments of the LS. Considering regular, fast formulations, one can have now in hands all the possibilities from ultra-fast liquids up to 163 ns.

The next step will be to evaluate these new scintillators as liquid scintillation cocktails. Various radioactive sources will be evaluated for environmental assays.

Conflict of interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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