

VARIATION OF COUNTING EFFICIENCY OF TRITIUM IN LSC COCKTAILS WITH DIFFERENT COMPONENTS AND EVALUATION OF THEORETICAL CALCULATION OF TIME TRANSFER OF COCKTAILS

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ABSTRACT. Ternary mixtures comprised of a scintillator PBBO (2-[4-biphenyl]-6-phenylbenzoxazole) or PPO (2,5-diphenyloxazole), various solvents (toluene, *p*-xylene, pseudocumene, di-isopropylnaphthalene, 1-methylnaphthalene), and various surfactants (Triton X100®, Tergitol NP-9®, and di[ethylene glycol] *n*-butyl ether) were tested in terms of efficiency of detection for tritium measurement. Comparisons were performed with a theoretical model based on a kinetic approach of energy transfer using the Förster theory and Millar's equation. A non-linear relationship is observed between the kinetics of energy transfer and the efficiency of detection for tritium in a range of time depending upon the fluorescence lifetime of the solvent and the concentration of the scintillator. A new concept is introduced: the extrapolation at "zero time transfer" quantifies under the operating conditions followed by an operator, the theoretical efficiency of detection for tritium where no competing reactions take place other than the long-range dipole-dipole interaction. This limiting value takes into account only the fast energy transfer via singlet-singlet coupling and expresses what efficiency of detection should be obtained under optimal conditions. It thus becomes possible to relatively evaluate the performances of any scintillating cocktails in terms of beta efficiency by performing only a few experiments.

INTRODUCTION

Determining tritium in environmental matrices is very important for environmental surveys because this isotope is very mobile and can be concentrated in various biological species (Guenot and Belot 1984; Garland and Cox 1980; Belot et al. 1996; Lang and Mason 1960; McFarlane 1976; Couchat et al. 1983). Organically bound tritium (OBT) is a tracer of biological contamination in cases of accidental or chronic releases (Fuma and Inoue 1995; Yamada et al. 1989, 1992; Kozak 1982; Kozak et al. 1986, 1993; Kalin et al. 1995). The radioactivity in such biological samples can be as low as a few Bq per kg and requires β -scintillating mixtures with high β efficiency. Due to the low kinetic energy of the β particle emitting from the tritium atom ($E_{\beta\text{max}} = 18.6$ keV), the detection efficiency is generally low compared to that of ^{14}C or ^{90}Sr . For instance, the counting efficiency in a Packard 2900 TR using Ultima Gold LLT® as a scintillating mixture does not exceed ~25% for a ratio of sample/scintillating cocktail equal to 1. It is possible to increase the efficiency up to 45% by mixing the sample and the cocktail with a ratio of 1/19. Counting efficiency and resolution depend upon the number of photons collected. Several phenomena like chemical, color, and physical quenchings cause a reduction in the number of photons on the photomultiplier tube. The number of primary excited states produced during the interaction between the β particle and the solvent is hard to quantify and requires Monte Carlo simulation and a physical model of transfer. Therefore, we have only focused on the energy transfer after the end of the interaction of particle/solvent because the number of photons collected at the end of the energy transfer process depends on a judicious choice of the couple donor/acceptor, i.e. solvent/scintillator. Energy transfer occurs via a long-range dipole-dipole transfer as described by Förster (1949). Later, Göselle et al. (1975) took into account the diffusion and the dipolar interaction (Göselle et al. 1975), which led to an approximate solution that was found to be amazingly precise (Butler and Pilling 1979; Valeur 2002; Millar et al. 1981). Millar et al. (1981) tested this equation, originally developed for interaction in the nanosecond range down to the picosecond range (Millar et al. 1981).

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In order to create new, more efficient β -scintillating cocktails dedicated to tritium measurements, it is necessary for comparison to test the theoretical model with the counting efficiency for each mixture. External calibration is required because the model does not quantify the primary number of excited states. Moreover, an external calibration allows any laboratory to perform comparisons using their own equipment. We show that theoretical calculations can be used to assess the potential performances of scintillating mixtures by knowing only the spectroscopic properties. A comparison was performed between 2 common scintillators, 2-(4-biphenyl)-6-phenylbenzoxazole (PBBO) and 2,5-diphenyloxazole (PPO), diluted in the following solvents: toluene, *p*-xylene, 1,2,4-trimethylbenzene (pseudocumene), di-isopropylnaphthalene (DIN), and 1-methylnaphthalene. No optimization was undertaken for surfactants since we only study the energy transfer. We used Triton X100[®], Tergitol NP-9[®], and di(ethylene glycol) *n*-butyl ether as surfactants because they do not have excessive quenching properties. Performances of the mixtures in terms of counting efficiency for tritium measurement are also compared.

THEORETICAL

The time required to achieve a complete energy transfer between the excited solvent and the scintillator is calculated using the equation of Gösele et al. (1975), which gives the probability for a donor to be still excited at the time t :

$$\rho(t) = \exp\left(-\frac{t}{\tau_D} - 4\pi D r_F n_A t - g \frac{4}{3} \pi^{\frac{3}{2}} n_A R_0^3 \sqrt{\frac{t}{\tau_D}}\right) \quad (1)$$

where D is the coefficient of diffusion ($D \approx 7.10^{-9} \text{ m}^2 \text{ s}^{-1}$ in aromatic solvent; Voltz et al. 1966a,b), g is a numerical factor equal to 0.845, n_A is the acceptor number density, τ_D is the fluorescence lifetime, and

$$r_F \approx 0.676 \cdot R_0 \cdot 4 \sqrt{g^2 \frac{R_0^2}{\tau_D \cdot D}}$$

is the effective trapping radius. Although this equation is an approximation, its precision is surprisingly high from a ps to ns time scale (Butler and Pilling 1979; Valeur 2002; Millar et al. 1981).

For a binary system, we can consider a single energy transfer and the de-excitation of the scintillator mainly by the fluorescence process:

Step 1: Solvent $\xrightarrow{\text{Energy transfer}}$ Scintillator;

Step 2: Scintillator $\xrightarrow{\text{Fluorescence}}$ Light emission.

Equation 1 describes the probability for any donor to be still excited. The complementary probability $1 - \rho_{step1}(t)$ represents the probability of an energy transfer by coulombic interaction with the acceptor. This probability takes into account all physical processes of de-excitation (like fluorescence, phosphorescence, intercrossing system, internal conversion, etc.) corresponding to the intrinsic characteristics of both molecules (donor and acceptor), but does not take into account all other chemical reactions leading to a quenching of the light emission. Under optimal conditions, no other energy transfer occurs (e.g. chemical quenching) for the scintillator other than its own fluorescence. Equation 1 is then reduced to the unique fluorescence:

$$\rho_{step2}(t) = \exp\left(-\frac{t}{\tau_D}\right)$$

and the complementary probability is the probability for light emission. Thus, the overall probability for light production can be described by the kinetics of energy transfer according to the equation:

$$\overline{\rho_T(t)} = [1 - \rho_{step1}(t)] \times \left(1 - \exp\left(-\frac{t}{\tau_D}\right)\right) \quad (2)$$

Scintillating cocktails generally contain more than 1 fluorescent molecule. A second fluorescent molecule, a “shifter,” is added at a low concentration in order to shift the fluorescence spectrum towards the highest sensitivity region of the photomultiplier tube. For example, all commercial scintillating mixtures dedicated to β scintillation contain 2 active fluorescent molecules. For successive energy transfers from the solvent to the primary scintillator and from the latter to the wavelength shifter, the overall probability is simply the product of all complementary probabilities. Thus, generalizing Equation 2 for any consecutive number of couples donor/acceptor gives:

$$\overline{\rho_T(t)} = \left(\prod_{i=1}^n [1 - \rho_i(t)] \right) \times \left(1 - \exp\left(-\frac{t}{\tau_n}\right)\right) \quad (3)$$

where τ_n is the fluorescence lifetime of the last acceptor emitting light, which will be detected by the photomultiplier tube. The presence of several active molecules requires taking into account all possible interaction between each couple of molecules. For instance, the Ultima Gold cocktail is a mixture of di-isopropylnaphthalene isomers (DIN), PPO, and bis-MSB. Although the main pathway for energy transfer is $\text{DIN} \rightarrow \text{PPO} \rightarrow \text{bis-MSB}$, an energy transfer between DIN and bis-MSB must be taken into account because the absorption spectrum of bis-MSB fully overlaps the fluorescent spectrum of DIN (Aupiais et al. 2003). For this case, the sum over all acceptor molecules near each molecule of the donor must be considered; therefore, for multiple energy transfers from the i^{th} donor to j acceptors, Equation 1 is modified according to the general form:

$$\rho_i(t) = \exp\left(-\frac{t}{\tau_D} - 4\pi D t \sum_j (r_{F,j} \times n_{A,j}) - g \frac{4}{3} \pi^{\frac{3}{2}} \sum_j (n_{A,j} \times R_{0,j}^3) \sqrt{\frac{t}{\tau_D}}\right) \quad (4)$$

where $r_{F,j}$ represent the effective trapping radius calculated for the donor i and the acceptor j ; $n_{A,j}$ the acceptor number density of the j^{th} acceptor; and $R_{0,j}$ the critical distance between the i^{th} donor and the j^{th} acceptor.

An example of $\overline{\rho_T(t)}$ variation is given in Figure 1. We used spectroscopic data available for the couple toluene–PBBO (Aupiais et al. 2003) at the concentration of $4 \text{ g}\cdot\text{dm}^{-3}$. At 99% probability, the energy transfer ends within 7.5 ns. The time for complete energy transfer is strongly dependent on the acceptor concentration. As shown in Figure 1, when PBBO concentration is set to $0.4 \text{ g}\cdot\text{dm}^{-3}$, the time of transfer increases up to 55 ns. Since the time transfer is longer, a lower counting efficiency is expected for tritium because the fast chemical reactions (like quenching by oxygen) compete with the energy transfer. We think that the time of transfer may be an interesting parameter to assess the counting efficiency of any scintillating cocktail. Indeed, we assume that as long as the coulombic interaction remains the principal physical process to transfer excitation, Equation 2 can be used to model the variation of the β counting efficiency. If this model can kinetically describe the variation of the population of singlet states, it cannot quantify the number of these singlet states. The forma-

tion of a singlet state due to interaction of a charged particle (e.g. 1 electron) with a solvent requires Monte Carlo simulation. Such tools are not easily available in a laboratory and it is not presently proven that a total simulation can replace the experimental determination of β counting efficiency. Moreover, the β counting efficiency depends upon the spectral response of the photomultiplier tube, the geometry of counting, the vial size, etc. It seems better to assess performances of scintillating mixtures by calculating the time of transfer for each experimental determination of the β counting efficiency. Thus, a relative comparison becomes possible between any scintillating cocktail, under the experimental conditions adopted by the operator. In addition, such a comparison could show that theoretical calculations of time of transfer could be used to evaluate scintillating mixtures without performing experiments.

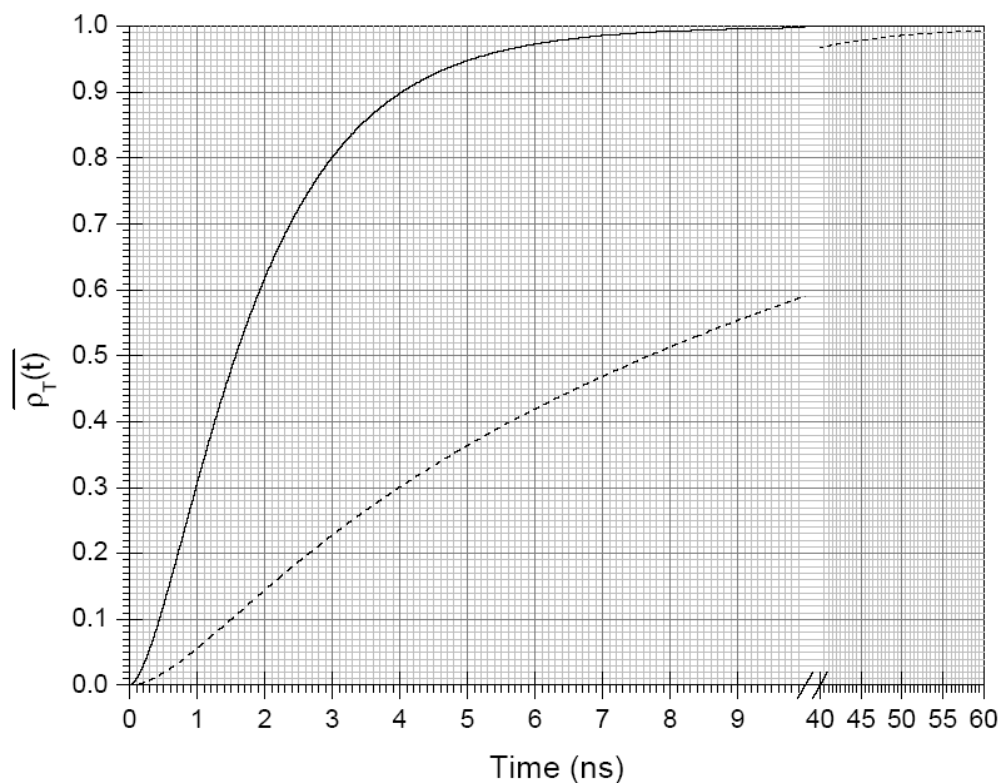


Figure 1 Variation of $\overline{\rho_T(t)}$ for the toluene–PBBO mixture, [PBBO] = 4 g.dm⁻³ (straight) and 0.4 g.dm⁻³ (dashed): τ_D , toluene = 34 ns; τ_D , PBBO = 1.2 ns; $R_0 = 3.11 \cdot 10^{-9}$ m; $n_A = 6.93 \cdot 10^{24}$ atoms/m³; $D = 7 \cdot 10^{-9}$ m²/s, and $r_F = 8.67 \cdot 10^{-10}$ m.

EXPERIMENTAL

Toluene (Aldrich, spectrophotometric grade), *p*-xylene (Merck, for synthesis), PPO, PBBO, 1,2,4-trimethylbenzene, di(ethylene glycol) *n*-butyl ether (Aldrich), Triton X100® (Prolabo), and Tergitol NP-9 (Fluka) were used as supplied. Several 1-methylnaphthalenes (purity 95–97%) presenting various colorations (from colorless to deep orange) were used either as supplied or after chromatographic purification (Goldstein and Lyon 1964) on activated alumina oxide (density 0.8 g/mL, particle size 50–200 μ m, specific surface 150 m²/g) (MP Biomedicals) and were furnished by Alfa, Aldrich, Acros Organic, Avocado, Lancaster, and Merck.

Tritium stock solution at 310.7 Bq/g was furnished and certified by the primary laboratory for radioactive measurements (Laboratoire National Henri Becquerel). Tritium measurements were performed with a Tri-Carb 2900TR from Packard (Groningen, the Netherlands).

Sample vials are prepared by mixing either 1 mL of tritium stock solution with 19 mL of scintillating cocktail or 5 mL of sample with 15 mL of scintillating cocktail. The scintillating cocktails are prepared by dissolving various amounts of scintillator (PBBO or PPO) in a mixture of surfactants (Triton X100 or Tergitol NP-9 and di[ethylene glycol] *n*-butyl ether) and solvents (toluene, *p*-xylene, 1,2,4-trimethylbenzene, di-isopropyl-naphthalene or 1-methylnaphthalene). Two kinds of mixtures were prepared according to the following proportions:

- Solvent + Triton X100 42% w/w + scintillator.
- Solvent + Tergitol NP-9 30% w/w + Di(ethylene glycol) *n*-butyl ether 15% w/w + scintillator.

RESULTS AND DISCUSSION

Primary interactions between the electron and solvent are stochastic. It is therefore difficult to quantify the number of original singlet states produced during this interaction. Moreover, quantifying the number of photons emitted from the scintillating mixture is strongly dependent on the couple scintillator/detector. In order to compare different kinds of mixtures adapted to the detector, only a relative comparison is possible. We tested Equation 3 by calculating for each concentration of scintillator the corresponding time of energy transfer at an arbitrary value of $\overline{\rho_T(t)} = 0.99$. Consequently, the singlet state of the donor may be still excited with a probability of 1%. All calculations were performed by using all available spectroscopic data (Aupiais et al. 2003; Murov et al. 1993; Horrocks 1974; Berlman 1971) required in Equation 1 and gathered in Table 1. The yield of counting efficiency was determined by counting a vial containing a known activity of tritium. In Figure 2, we represent the experimental variation of the counting efficiency as a function of the time of transfer calculated for the couple 1-methylnaphthalene–PBBO. The ratio of aqueous/organic phase is 1/19, and the scintillator cocktail is a mixture of 1-methylnaphthalene + Triton X100 42% (w/w) + PBBO at 4 g/L. Each sample was counted 4 times for 15 min. We fitted experimental data as a function of the time t by one simple exponential decay of the general form:

$$R(^3H) = y_0 + A \exp\left(-\frac{t - \overline{\rho_T(t)} = 0.99}{t}\right) \quad (5)$$

where y_0 and A are 2 constants determined experimentally by the fitting procedure.

Table 1 Fluorescence quantum yields Φ_D , fluorescence lifetimes τ_D , refractive index n , and calculated critical distances R_0 .

| Donor | Φ_D | τ_D (ns) | n (20 °C) [23] | R_0 (Å) | | |
|---------------------|-----------|---------------|------------------|-----------|------|---------|
| | | | | PBBO | PPO | bis-MSB |
| Toluene | 0.14 [24] | 34 [24] | 1.4961 | 31.1 | 33.7 | 22.0 |
| <i>p</i> -xylene | 0.22 [24] | 30 [24] | 1.4958 | 33.4 | 36.3 | |
| Pseudocumene | 0.33 [25] | 27.2 [26] | 1.5048 | 36.5 | 39.5 | |
| DIN | 0.62 [21] | ? | ~1.6 | 47.7 | 40.3 | 38.8 |
| 1-methylnaphthalene | 0.21 [24] | 67 [24] | 1.6170 | 39.3 | 33.8 | |

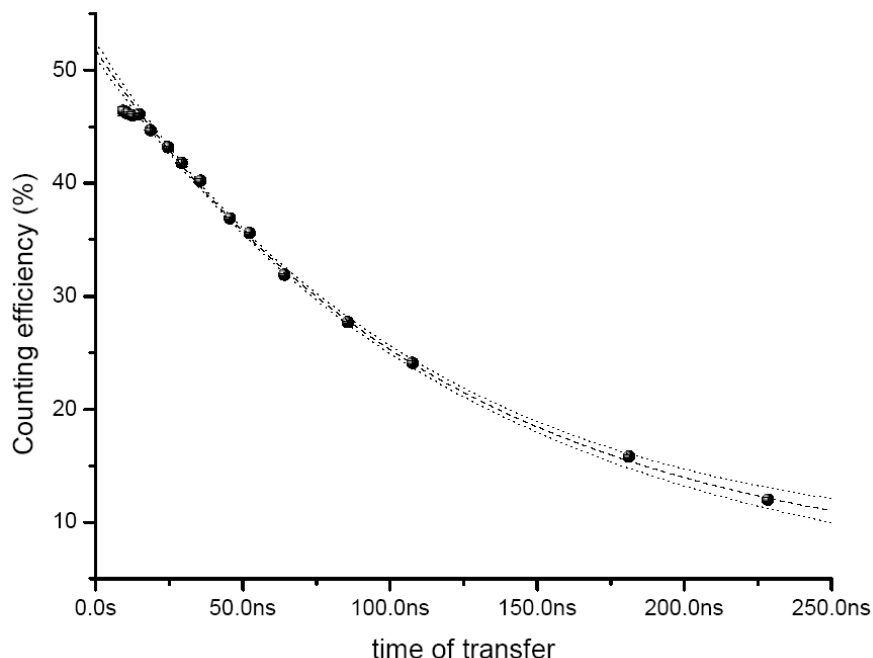


Figure 2 Experimental variation of the counting efficiency for ^3H measurement as a function of the time transfer calculated for each experiment according to data in Table 1. Ratio of aqueous solution of ^3H / organic scintillating mixture = 1/19; acquisition window 0–18 keV. Extrapolating function: $y = A \exp\left(-\frac{x}{y}\right) + y_0$; coefficient of correlation $r = 0.9995$.

The coefficient of correlation is equal to 0.9995. In fact, we expect that such a correlation is due to the following: a) kinetics of energy transfer is precisely described by theory; b) counting statistics are high due to the high activity measured ($A \approx 300 \text{ Bq/g}$); c) 1-methylnaphtahlene is weakly volatile and no loss is observed during the elaboration of the scintillating mixtures; and d) all compounds were weighed. Extrapolation at a null time gives the maximum counting efficiency observed under ideal but hypothetical conditions, i.e. where coulombic interaction is the only mechanism for the energy transfer and where the excited molecule of solvent is entirely surrounded by the scintillator $R_0 = 51.8 \pm 1.4\%$. This limiting value might be an interesting concept for a relative comparison between scintillating mixtures because it only compares the efficiency of energy transfer, disregarding other competing processes such as dimerization of the solvent and all sorts of quenching. The high precision of the model requires only a few experiments to get external calibration and to determine the counting efficiency for any concentration of scintillator. The modelling of counting efficiency versus concentration of PBBO was performed in 2 steps. The first step requires calculating the time of transfer at 99% probability for a given concentration of scintillator. This step does not require an experiment since calculation is performed by only taking into account spectroscopic data, i.e. fluorescence and absorption spectra, fluorescence quantum yield of the donor and its refractive index. The second step consists of calculating the counting efficiency by applying Equation 5. The theoretical calibration results of the time transfer and the counting efficiency of tritium are given in Figure 3. This figure shows that deviation from the experiments does not exceed $\pm 1\%$ as long as no other competing reactions occur, especially at a high concentration of scintillator. The upper limit of Equation 3 corresponds to an infinite concentration of acceptors, which has no physical sense. The limiting value introduced as the theoretical maximum counting efficiency must be understood in the

same fashion as the definition of the stability constant extrapolated at zero ionic strength in thermodynamics. Although the limiting value characterizes a system under hypothetical conditions, this value is necessary to extrapolate the performances of LSC cocktails under real conditions. The lower limit corresponds to the simple product of complementary probabilities involving only fluorescence decay of all molecules present in the mixture. This value is out of the model's range since it can be applied only if diffusion is significant (Valeur 2002). For example, in Figure 3 the lower limit for the couple 1-methylnaphthalene–PBBO is equal to 8% instead of 0% at an infinite dilution of PBBO. In practice, Equation 3 is valid and precise for a time of transfer below ~50–60 ns.

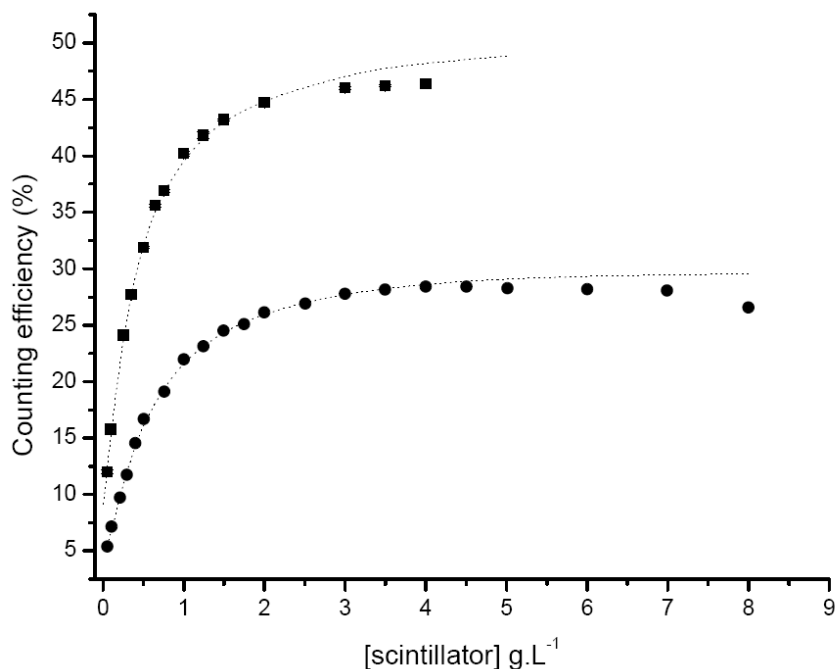


Figure 3 Variation of counting efficiency for 2 couples of donors/acceptors. Black squares: 1-methylnaphthalene/PBBO, black circles: 1-methylnaphthalene/PPO; ratio aqueous/organic phase = 1/19; scintillators [PBBO] = 0–4 g/L; [PPO] = 0–8 g/L; Triton X100 42% w/w. Small dots are theoretical calculations using external calibration for quantification. The precision of the model does not exceed $\pm 1\%$.

Other solvents at the same concentration of PBBO and Triton X100 were tested. Results are reported in Figure 4 and the maximum counting efficiency is given in Table 2. Two classes of scintillating mixtures can be observed, one with PBBO and the second one with PPO. We must emphasize that both categories cannot be compared because the whole system is only calibrated under specific conditions adopted by the operator. Indeed, PPO and PBBO do not have the same fluorescence spectra, and the spectrum of PBBO better matches the spectral response of the photomultiplier tube used in the Packard 2900. Nevertheless, for 1 scintillator comparisons are possible. Thus, similar performances are observed in both classes whatever the solvent, within the experimental uncertainties. A careful examination shows, however, that the couple 1-methylnaphthalene or toluene–PBBO present higher efficiency, ~5%, than in other ones. It is not surprising to observe such behavior in practice; these solvents have been studied for many years and do not present particular performances. The theoretical calculation results are given in Table 3. No major difference in the time of

transfer is observed at a constant concentration of PBBO. Note that the time of transfer is very similar, between 8 and 14 ns. The transfer is very fast, leading to a predictably similar behavior because a few nanoseconds of difference is too short for observing the effect of competing reactions (quenching), which hinder the energy transfer.

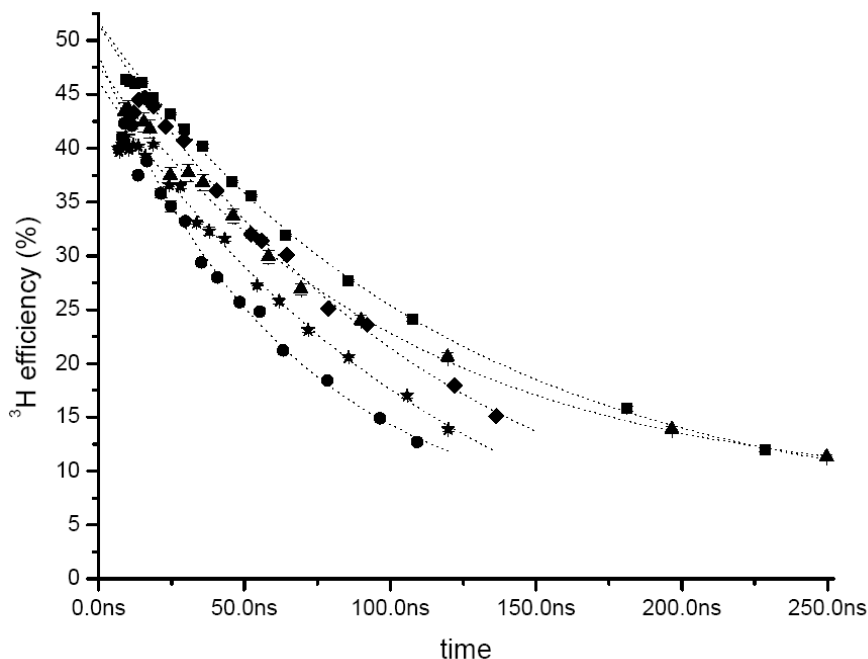


Figure 4 Variation of counting efficiency for ^3H measurement as a function of the time of transfer. Ratio aqueous/organic phase = 1/19, scintillator PBBO from 0 to 4 g/L, Triton X100 42% w/w, solvents: pseudocumene - circles; di-isopropylnaphthalene - triangles; toluene - diamonds; *p*-xylene - stars; 1-methylnaphthalene - squares.

Table 2 Theoretical maximum counting efficiency, confidence interval 95%.

| Solvent | Scintillator | $R(^3\text{H})$ (%) |
|---------------------|---------------|---------------------|
| Pseudocumene | PBBO | 48.6 ± 1.4 |
| DIN | PBBO | 47.8 ± 2.2 |
| Toluene | PBBO | 51.7 ± 3.2 |
| <i>p</i> -xylene | PBBO | 46.2 ± 3.6 |
| 1-methylnaphthalene | PBBO | 51.8 ± 1.4 |
| 1-methylnaphthalene | PPO | 31.8 ± 1.1 |
| DIN | PPO + bis-MSB | 32.1 ± 0.6 |

A comparison between scintillators is only possible if their fluorescence spectra are similar in terms of maximum wavelength and frequency extension. For example, although the fluorescence spectra of PBBO and PPO are different, PBBO and PPO + bis-MSB can be compared. Indeed, a calculation applying Equations 3 and 4 shows that the system DIN–PPO–bis-MSB can be kinetically reduced to the system DIN–PPO but with the fluorescence spectrum of bis-MSB (Aupiais et al. 2003). The calculation shows that the contribution of the energy transfer between PPO and bis-MSB is negligible. Fluorescence spectra of PBBO and bis-MSB are very similar; therefore, a small difference is expected in the determination of counting efficiency.

Table 3 Theoretical calculations of time transfer at $\overline{\rho_T(t)} = 0.99$ for several couples solvent – PBBO or PPO at the concentration of $1.15 \cdot 10^{-2}$ M, e.g. PBBO 4 g/L and PPO 2.5 g/L.

| Solvent | Scintillator | $\overline{\rho_T(t)} = 0.99$ (ns) |
|---------------------|---------------|------------------------------------|
| Pseudocumene | PBBO | 8.8 |
| DIN | PBBO | 8.5 |
| Toluene | PBBO | 12.2 |
| <i>p</i> -xylene | PBBO | 10.3 |
| 1-methylnaphthalene | PBBO | 9.4 |
| 1-methylnaphthalene | PPO | 13.9 |
| DIN | PPO | 11.6 |
| DIN ^a | PPO + bis MSB | 6.7 [21] |
| DIN ^b | PPO + bis MSB | 7.8 |

^aPPO 5.7 g/L, bis-MSB 0.5 g/L.

^bPPO 4 g/L, bis-MSB 0.4 g/L.

According to the theoretical maximum efficiency given in Table 2, it seems that the performance of the couple 1-methylnaphthalene–PBBO is better than that obtained for the couple DIN–PPO + bis-MSB. This result shows that higher sensitivity is expected in the former composition. Nevertheless, the former does not represent the composition of the commercial cocktail dedicated to β scintillation, nor is it practical use when a larger volume or aqueous phase is mixed with the scintillating cocktail. We have therefore attempted to assess the potentiality of the 1-methylnaphthalene–PBBO couple for practical tritium measurement, i.e. by incorporating surfactants into the scintillating mixture. The Ultima Gold cocktail is a registered product and its chemical composition is not precisely known as well as concentrations of all present molecules. In order to evaluate a new composition, it is essential to compare comparable objects. We have consequently elaborated the composition containing either the couple donor/acceptor(s) 1-methylnaphthalene–PBBO or DIN–PPO + bis-MSB and the same surfactant for both scintillating mixtures, either Triton X100 or a mixture Tergitol NP-9 + di(ethylene glycol) *n*-butyl ether. Proportions of surfactants were previously optimized in terms of quenching and the proportion of water that can be mixed. The optimized amount of Triton X100 is 42% w/w and 30/15% w/w for the mixture Tergitol NP-9 + di(ethylene glycol) *n*-butyl ether. Ultima Gold was only used as a reference cocktail since its composition is not precisely known. We have noticed various coloration of 1-methylnaphthalene, from a near colorless product up to a deep orange color, depending on the manufacturer and also the lot number. Two preliminary experiments were performed. One sample was colored orange, and the second one was slightly yellow. Experimental counting efficiencies were equal to 7% and 28%, respectively. An obvious relationship was observed with respect of the absorbance at 400 nm and the total efficiency. This behavior is expected since the yellow coloration demonstrates an absorption in the blue region corresponding to the fluorescence of the scintillator. Purification of this solvent is therefore necessary and we have applied a procedure detailed by Goldstein and Lyon (1964) in which activated acid alumina is used in a chromatographic separation column. The chromatographic characteristic of the column was determined. It seems that several colored species are present in the product because we have observed several colored bands along the chromatographic column. Therefore, we determined the coefficient of distribution of the less-adsorbed species. We found $D_g = 0.28 \pm 0.02$ mL/g, which represents a theoretical plate height of 0.82 ± 0.06 cm and a plate number of 122 ± 11 plates/m. Stability was studied by

absorbance measurement at 400 nm over 3 months in the presence of light. A slight degradation is observed, and it is recommended to keep the purified solvent away from direct sunlight.

After purification on activated acidic alumina, several mixtures were tested and compared in terms of the nature of surfactants and the volume ratio of the aqueous phase/organic scintillating mixture. Results are given in Table 4. Better performance was obtained for the mixture containing PBBO at 4 g/L with 1-methylnaphthalene as solvent and a mixture of surfactants Tergitol NP-9 30% + di(ethylene glycol) *n*-butyl ether 15% w/w. The efficiency yield is $28.6 \pm 0.14\%$ for a ratio of aqueous solution/organic phase equal to 5/15. This value is about 26% higher than the cocktail based on a mixture of DIN–PPO–bis-MSB and surfactants at the same concentration. Counting was performed by liquid scintillation counter (Tri-Carb 2900TR) optimized for the couple PPO–bis-MSB, but it appears that the 1-methylnaphthalene–PBBO couple gives better results. The better result is not due to the fluorescence spectrum of PBBO because its maximum of fluorescence as well as its spectral extension is not too different from the fluorescence spectra of bis-MSB (Aupiais et al. 2002). As shown in Table 3, the kinetics of energy transfer for the couple 1-methylnaphthalene–PBBO was ~24% faster than that of DIN–PPO–bis-MSB using the same concentration of scintillator. A relationship between counting efficiency and kinetics of energy transfer is thus demonstrated. We noticed that the presence of bis-MSB does not modify the total time of transfer due to a very strong coupling (i.e. a very high overlap) between PPO and bis-MSB. The kinetically limiting step is the energy transfer between DIN and PPO. The similar value obtained for the improvement of the counting efficiency (+26%) and the decrease of time of transfer (–24%) is fortuitous because in the region where time transfer lies, between 0–50 ns, the variation of counting efficiency sharply decreases with increasing time transfer (Figures 2 and 4). The well-known consequence of Equation 3 is the considerable increase expected by increasing the concentration of the acceptor. Unfortunately, amplitude is only limited by solubility of the acceptor and its capability of no dimmer association. Thus, PPO is highly soluble in DIN (Thomson 1991) and allows for an increase of the counting efficiency up to ~31% when concentration increases from 2.5–6 g/L. The corresponding ratio of aqueous/organic phase is equal to 5/15 under experimental conditions taken for comparison and justified by the impossibility in mixing both phases higher than 5/15. Ultima Gold exhibits better miscibility. We speculate that possible improvement could be achieved for the couple 1-methylnaphthalene–PBBO by using the same product contained in Ultima Gold. In addition, we are unsure if better performances compared to that of Ultima Gold could be obtained because solubility of PBBO is lower in methylnaphthalene than that of PPO in DIN, while self-quenching occurs above a concentration of 4 g/L (or 1.15×10^{-2} M) instead of ~6 g/L for PPO in DIN (3×10^{-2} M). As a result, although the value obtained for the couple 1-methylnaphthalene–PBBO is probably the optimal value, it was significantly different from the efficiency found in the first set of experiments (see Table 2). Indeed, the theoretical maximum efficiency should have been higher than 50%. We were not able to reproduce the first experiments using other lots and manufacturers. On the other hand, results for Ultima Gold are identical, which exclude the reference solution of tritium as the source of the non-reproducibility for determining the counting efficiency. Due to the impossibility in obtaining the same lot, it was not possible to investigate the exact composition of minor compounds in the solvent that were present in the lot used during the first set of experiments.

CONCLUSION

Long-range dipole-dipole interaction, including the kinetics approach of Gösele et al. (1975), describes with a high precision the performances in terms of β counting efficiency for measuring tritium after external calibration and under conditions of concentration typically found in scintillator mixtures. The theoretical calculation model is precise for a time of transfer from 0 to 50 ns. This

Table 4 Counting efficiency for ^3H tritium measurements. 1-methylnaphthalene is purified on activated acidic alumina before use. Ultima Gold is used as the reference cocktail.

| Solvent/Surfactant | Scintillator | Volume ratio: aqueous/ organic | ^3H efficiency (%) |
|--|--------------------------------|--------------------------------------|-----------------------------|
| $\text{CH}_3\text{-C}_{10}\text{H}_7$ 55% / Tergitol NP-9 30% + Di(ethylene glycol) <i>n</i> -butyl ether 15% | PBBO 4 g/L | 5/15 | 28.60 ± 0.07 |
| | | | 28.70 ± 0.15 |
| | | | 28.50 ± 0.07 |
| | | | Mean: 28.60 ± 0.14 |
| $\text{CH}_3\text{-C}_{10}\text{H}_7$ 58%/Tergitol NP-9 42% | PBBO 4 g/L | 1/19 | 27.80 ± 0.15 |
| | | | 27.80 ± 0.15 |
| | | | 28.50 ± 0.15 |
| | | | Mean: 28.0 ± 0.14 |
| $\text{CH}_3\text{-C}_{10}\text{H}_7$ 58%/Tergitol NP-9 42% | PBBO 4 g/L | 5/15 | 12.60 ± 0.04 |
| | | | 12.30 ± 0.04 |
| | | | 12.60 ± 0.04 |
| | | | Mean: 12.50 ± 0.24 |
| | PBBO 4 g/L | 1/19 | 27.90 ± 0.15 |
| | | | 28.90 ± 0.15 |
| | | | 28.20 ± 0.15 |
| | | | Mean: 28.30 ± 0.14 |
| DIN 55% / Tergitol NP-9 30% + Di(ethylene glycol) <i>n</i> -butyl ether 15% Ultima Gold ^a | PPO 4 g/L + bis-MSB 0.4 g/L | 5/15 | 22.70 ± 0.06 |
| | PPO 0–1% + bis-MSB 0–1% | 5/15 | 30.8 ± 0.07 |

^aCommercial product.

approach allows, under the same experimental conditions, a comparison of various scintillating mixtures. A limiting value, the maximum theoretical yield for β counting, is introduced for direct comparison of the performances in terms of energy transfer. Kinetics is the key parameter for high efficiency and can now be relatively quantified by measuring the tritium standard source. A theoretical calculation of kinetics using available spectroscopic data may also be used to coarsely assess the potential interest of a scintillating mixture.

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