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Comparison and improvement of the resolution of several alpha liquid scintillation spectrometers for actinide measurements

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In order to enhance the resolution in α liquid scintillation with pulse shape discrimination for the measurement of actinide at low level, a study of two scintillating cocktails (Alphaex™ and Ultima Gold LLT™) and two alpha liquid scintillation spectrometers, (PERALS™ and TRI-CARB™) was undertaken. The criteria which can be applied to improve the resolution are the use of no-water miscible cocktail, the optimisation of energy transfer through the knowledge of the spectroscopic data, the employ of P.M. with higher quantum efficiency, scintillators with low Stoke's shift and high fluorescence quantum yield and the use of vial with low optical path.

KEYWORDS: alpha liquid scintillation, energy transfer, fluorescence

I. Introduction

Many authors have demonstrated the interest of α liquid scintillation with pulse shape discrimination for the measurement of actinides in environmental samples[1-3]. Nevertheless, for a few radionuclides like ^{210}Po and ^{241}Am, there is no possibility to use isotopic dilution for a quantitative determination because this technique suffers from a lack of resolution. Moreover, isotopic ratios may be difficult to determine due to the necessary complex mathematical treatments. Indeed, the deactivation of the α emitters nuclei always occurs producing numerous sum peaks in the energy spectrum[4]. The enhancement of the resolution is a great challenge for the coming years. To extend our previous work[5], we now propose a description of energy transfer in liquid scintillation cocktails dedicated to α measurements and the relevant tools which might be used for the preparation of improved cocktails. Moreover, we highlight the possibility to improve easily the resolution by modifying the existing cocktails.

II. Theory

The light pulse emitted by the cocktail has two components[6]: a prompt signal resulting mainly from a "singlet pathway" and a delayed signal which involves triplet states. The "singlet pathway" involves spin-allowed transitions of the donor (D) and the acceptor (A) singlets

$$S_1^*(D) + S_0(A) \rightarrow S_0(D) + S_1^*(A)$$

and is well described by the Förster theory of long range Coulombic energy transfer[7] which states that the rate constant of energy transfer is proportional to the square of the dipole – dipole interaction energy. The latter is proportional to the magnitude of the dipoles and inversely proportional to the third power of the distance between both molecules.

$$k_{ET} = \frac{9000 \ln 10 \kappa^2}{128\pi^6 n^4 N \tau_D^0 R^6} \int f_D(\nu)\varepsilon_A(\nu)\frac{d\nu}{\nu^4}, \tag{1}$$

where κ is an orientation factor ($\kappa^2 = 2/3$ in the case of a random distribution), *n* the index of refraction, N the Avogadro's number, τ_D^0 the radiative lifetime of the donor and R the distance between the donor and the acceptor. The efficiency of energy transfer is measured by defining a critical distance R_0 for which energy transfer and spontaneous deactivation of the donor have equal rates:

$$R_0^6 = \frac{9000 \ln 10 \kappa^2 \phi_D}{128\pi^6 n^4 N} \int f_D(\nu)\varepsilon_A(\nu)\frac{d\nu}{\nu^4}. \tag{2}$$

A thorough reinterpretation of the Förster's theory by Millar et al[8] leads to the useful definition of the probability for a donor to be still excited at the time *t*:

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

where D the coefficient of diffusion, *g* a numerical factor equal to 0.845, n_A the acceptor number density and $r_F \approx 0.676 \cdot R_0 \cdot \sqrt[4]{g^2 \frac{R_0^2}{\tau_D \cdot D}}$, the «effective trapping radius».

The equation (3) is used to calculate the kinetics of energy transfer.

III. Results and discussion

The absorption and fluorescence spectra of the solvents and scintillators were analysed in order to investigate the efficiency of the energy transfer from the primarily excited solvent to the near-UV scintillators. This efficiency is well

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described by equation (1) which contains the overlapping integral of the fluorescence spectrum of the solvent and the absorption spectrum of PPO, PBBO or bis-MSB. According to the equation (2), the resolution can be improved by choosing molecules presenting the higher critical distance R_0, i.e. the higher overlap between the fluorescence spectrum of the donor and the absorption spectrum of the acceptor. The experimental results are given in Figures 1 and 2.

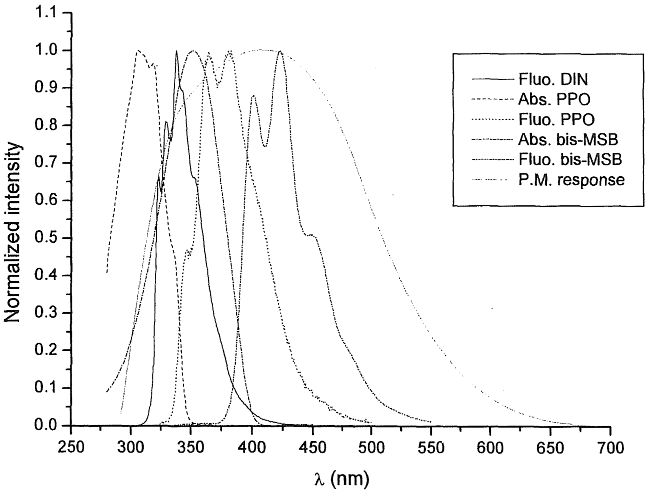

Fig.1 Normalised fluorescence and absorption spectra of the molecules present in the Ultima Gold LLT cocktail: di-isopropylnaphthalene (solvent), PPO (2.5 10^{-2} M) and bis-MSB (1.5 10^{-3} M)

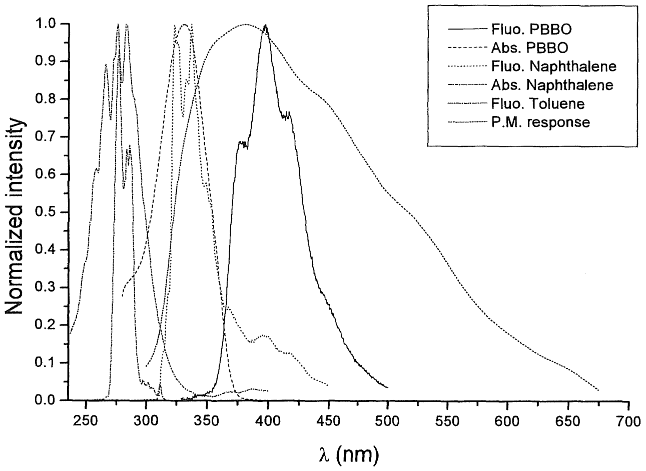

Fig.2 Normalised fluorescence and absorption spectra of the molecules present in the Alphaex cocktail: toluene (solvent), naphthalene (1.5 M) and PBBO (10^{-2} M)

As seen in the Figures 1 and 2, the overlaps seem to be nearly optimal and mean that the efficiency in the energy transfer is good. But, we can see in Figure 2 that improvement could be considered for the Alphaex cocktail because the overlap between the fluorescence spectrum of the toluene and the absorption spectrum of the naphthalene is not sufficient. On the contrary, the overlap related to the couple naphthalene-PBBO is optimal. Studies are under progress to elaborate new more efficient cocktails. According to the data in Table 1, the cocktail Ultima Gold has better overlap than that of Alphaex but we do not observe a better resolution whatever the spectrometer. This result is mainly due to a lower quantum efficiency of the P.M. used in the TRICARB (Q.E. = 0.25) in comparison with that of PERALS one (Q.E. = 0.35). Theoretical calculations have been done for each spectrometer taking into account the fluorescence spectrum of the scintillator and the quantum efficiency of the photomultiplier tube. The results show a good agreement between theoretical calculations and experimental determinations of the separation factor R_S between 2 adjacent peaks:

$$R_S = \frac{E_\alpha(\text{nuclide2}) - E_\alpha(\text{nuclide1})}{\frac{1}{2}\left(\text{FWHM(nuclide1)} + \text{FWHM(nuclide2)}\right)}. \qquad (4)$$

The experimentally observed R_S value for TRICARB – Ultima Gold is 21.6 % and PERALS – Alphaex is 25.9 %, respectively. Those R_s values coincide well with those of calculated values, 19.0 % and 21.4 %, respectively.

Table 1 Overlap calculations (in m^6) related to energy transfer between a donor and an acceptor: step 1=solvent→interm. molec., step 2= interm. molec.→scintillator

Process	Alphaex	Ultima Gold LLT
Step 1	1.45 10^{-25}	2.44 10^{-25}
Step 2	6.58 10^{-25}	10.7 10^{-25}

From the kinetic point of view, both cocktails have similar response. The energy transfer through the step 1 and the step 2 (see Table 1) lasts about 3 ns as calculated according to the equation (3). The temporal variation of the last scintillator, i.e. PBBO for Alphaex and bis-MSB for Ultima Gold LLT is given in Figure 3.

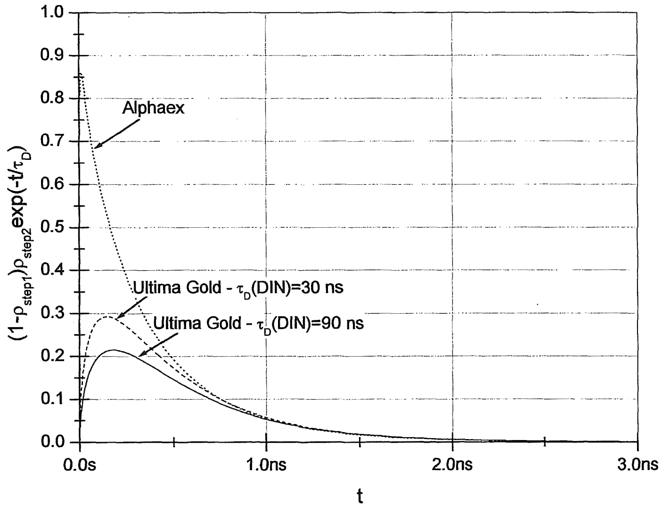

Fig.3 Decay of excited singlet states of the last scintillator in Alphaex and Ultima Gold cocktails. The isomer fluorescence decays are not known for the DIN. Based upon similar behaviour with several derivative naphthalene compounds, two extreme values have been chosen.

Since overlaps are optimal for these cocktails, the resolution can be still enhanced by limiting all phenomena decreasing the number of photons, i.e. the quenching by water molecules and the self-absorption inside the cocktail. The quenching by water has a major effect since a part of the kinetic energy of α particle is lost inside the drop of water instead of to be deposited in the scintillating cocktail. We have removed detergents in the Ultima Gold LLT and an increase of 54 % has been observed from Figure 4 to Figure 5.

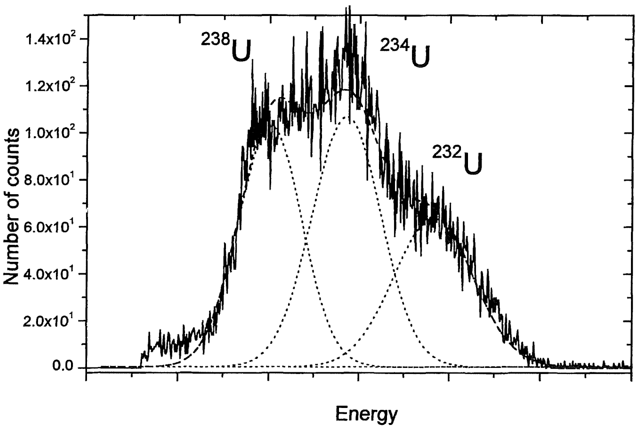

Fig.4 Scintillation spectrum of uranium isotopes with Ultima Gold LLT used as supplied.

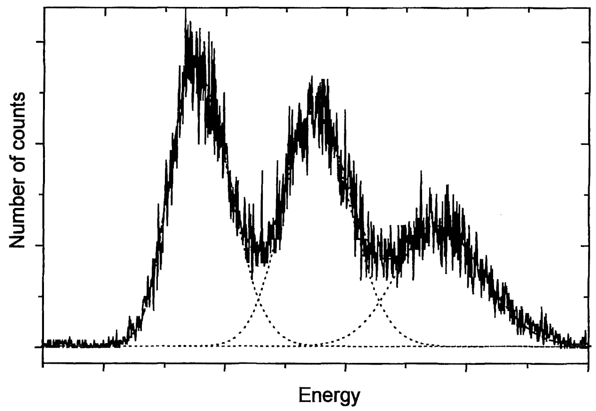

Fig.5 Scintillation spectrum of uranium isotopes with Ultima Gold LLT without detergents.

The Stoke's shift, however high it may be, leads to a self-absorption and then to a lower resolution. It is the consequence of the Beer-Lambert's law expressed as following:

$$\log\frac{I}{I_0} = \varepsilon \cdot l \cdot C, \qquad (5)$$

ε is the molar extinction coefficient, l the optical path and C the concentration of the scintillator. Lower is the optical path, higher is the photons detected by the P.M. Therefore, the solution is to decrease the optical path. Thus, we have used small vials for which the external diameter was equal to 16 mm instead of 26 mm for the usual vials. An increase of 18 % has been noticed and give resolution almost equal to that of observed for the PERALS spectrometer (Figure 6).

The sensitivity of alpha liquid scintillation depends on the resolution. A higher resolution leads to an increase of the signal/background ratio and thus better sensitivity as shown in Table 2.

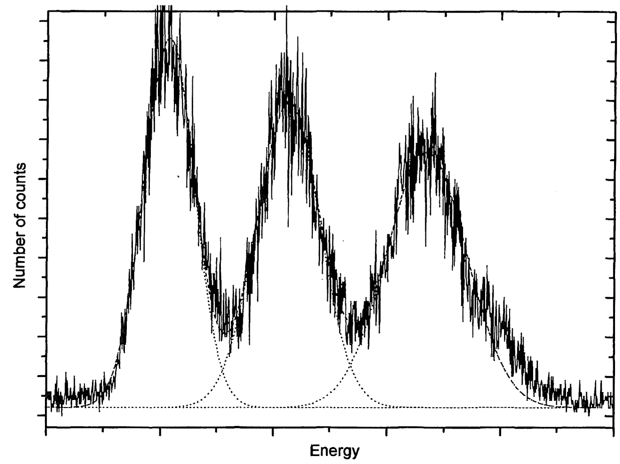

Fig.6 Scintillation spectrum of uranium isotopes with Ultima Gold LLT without detergents and using vials of 16 mm instead of 26 mm.

Table 2 Detection limits (in mole.l^{-1}) of some actinides with TRICARB and PERALS spectrometers using commercialised and modified scintillating cocktails

Isot.	Alphaex (PERALS)	Alphaex (TRI-CARB)	DIN (TRI-CARB)	Ultima Gold (TRI-CARB)
^{232}Th	$1.5\ 10^{-8}$	$2.8\ 10^{-8}$	$2.7\ 10^{-8}$	$1.1\ 10^{-7}$
^{234}U	$2.6\ 10^{-13}$	$4.9\ 10^{-13}$	$4.7\ 10^{-13}$	$1.9\ 10^{-12}$
^{238}U	$4.8\ 10^{-9}$	$9.3\ 10^{-9}$	$8.5\ 10^{-9}$	$3.6\ 10^{-8}$
^{237}Np	$2.4\ 10^{-12}$	$4.3\ 10^{-12}$	$4.1\ 10^{-12}$	$1.7\ 10^{-11}$
^{238}Pu	$9.6\ 10^{-17}$	$1.8\ 10^{-16}$	$1.7\ 10^{-16}$	$6.9\ 10^{-16}$
^{239}Pu	$2.6\ 10^{-14}$	$4.9\ 10^{-14}$	$4.6\ 10^{-14}$	$1.9\ 10^{-13}$
^{241}Am	$4.8\ 10^{-16}$	$8.4\ 10^{-16}$	$8.2\ 10^{-16}$	$3.4\ 10^{-15}$
^{244}Cm	$2.0\ 10^{-17}$	$3.6\ 10^{-17}$	$3.5\ 10^{-17}$	$1.4\ 10^{-16}$

The detection limit is about 300 % better with no-water miscible cocktail in comparison with the commercialised cocktail Ultima Gold LLT as shown in Table 2. This performance is still 40 % lower than the Alphaex cocktail in a PERALS spectrometer. Two reasons are involved: a lower optical path in the PERALS spectrometer (diameter 10 mm) in comparison with the standard vial used with a TRICARB (diameter 26 mm) and a better β/γ discrimination efficiency equal to 99.95 % instead of about 95 % for TRICARB.

IV. Conclusion

Better detection limits are achieved if resolution is enhanced. The improvement of resolution is possible by the optimisation of the energy transfer. In particular the knowledge of the spectroscopic data like the fluorescence and absorption spectra, the fluorescence lifetime or the fluorescence quantum yield is of importance. Moreover, more efficient photomultiplier tubes, small vials and no-water miscible cocktails are the conditions required for the actinide measurement in environmental samples and to access to isotopic information.

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