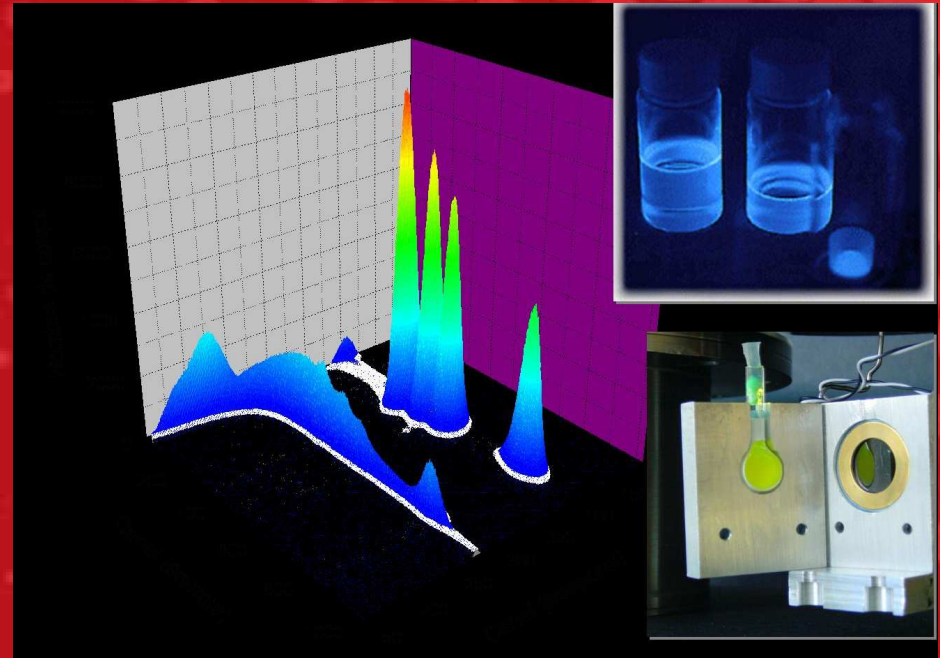


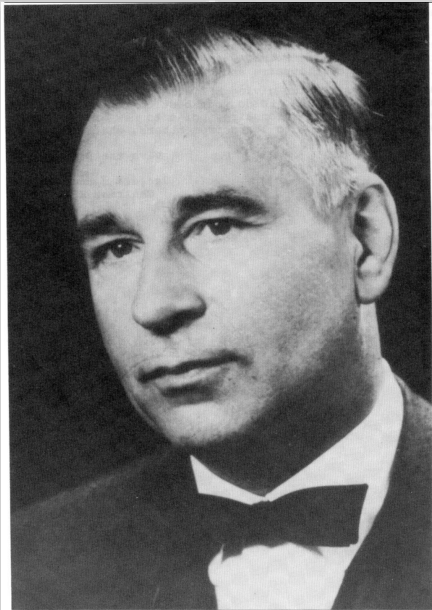
The logo for CEA (Commissariat à l'énergie atomique et aux énergies alternatives) is displayed in white lowercase letters on a red square background. A thin green horizontal line is positioned below the letters.

La scintillation liquide α

Licence Métrologie Chimique et Nucléaire

Commissariat à l'énergie atomique et aux énergies alternatives - www.cea.fr

J. AUPIAIS
CEA, DAM, DIF
91297 Arpajon



Theodor Förster
1910 - 1974

ASPECTS THEORIQUES

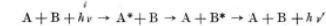
Experimentelle und theoretische Untersuchung des zwischenmolekularen Übergangs von Elektronenanregungsenergie

Von THEODOR FÖRSTER

Aus dem Max-Planck-Institut für physikalische Chemie, Göttingen
(Z. Naturforsch. 4a, 321-327 [1949]; eingegangen am 13. Januar 1949)

Im Anschluß an frühere orientierende Messungen wird die *wahre Löscherückung* von Rhodamin B auf die Fluoreszenz von Trypflavin in Methanol untersucht, indem diese von der durch Absorption bedingten Fluoreszenzschwächung experimentell getrennt wird. Es wird eine Theorie der Löscherückung durch *zwischenmolekularen Energieübergang* entwickelt und mit den Versuchsergebnissen verglichen.

In einer früheren Veröffentlichung¹ wurde über die experimentelle Untersuchung eines bisher wenig beachteten Typus von *Fluoreszenzlöscherückung* berichtet. Dieser liegt dann vor, wenn der Lösung eines fluoreszierenden Stoffes A ein anderer Stoff B zugesetzt wird, der bei *längeren* Wellen als der erste absorbiert. Die dabei auftretende Verringerung der Fluoreszenzintensität von A geschieht dabei außer durch Absorption des erregenden Lichtes und des Fluoreszenzlichtes durch den zugesetzten Stoff B auch durch *wahre Löscherückung*, die auf unmittelbarer Wechselwirkung der Moleküle von A und B beruht. Falls der Stoff B selbst fluoreszenzfähig ist, tritt dabei dessen sensibilisierte Fluoreszenz auf. Mit *Trypflavin* als Stoff A und *Rhodamin B* als Stoff B ergab sich für die wahre Löscherückung in Methanol eine Halbwertskonstante von etwa $1 \cdot 10^{-3}$ Mol/l. Selbstverständlich ist dies eine Fluoreszenzlöscherückung nur insofern, als die Beobachtung auf den Spektralbereich der Trypflavinfluoreszenz beschränkt bleibt. Die indirekt festgestellte *Verringerung* der *Abklingdauer* der Trypflavinfluoreszenz bei der Löscherückung zeigt, daß diese nicht statisch durch Assoziation zu einer fluoreszenzunfähigen Molekülverbindung, sondern *dynamisch* durch einen molekularen Prozeß folgender Art zu deuten ist:



Dabei ist eine gegenseitige Annäherung der Moleküle durch Diffusion, wie sie in anderen Fällen von Fluoreszenzlöscherückung stattfindet, wegen der nur geringen Abhängigkeit von Temperatur und

¹ Th. Förster, Z. Elektrochem. 53, 93 [1949]; vgl. auch Angew. Chem. 59, 181 [1947]; 60, 163 [1948].

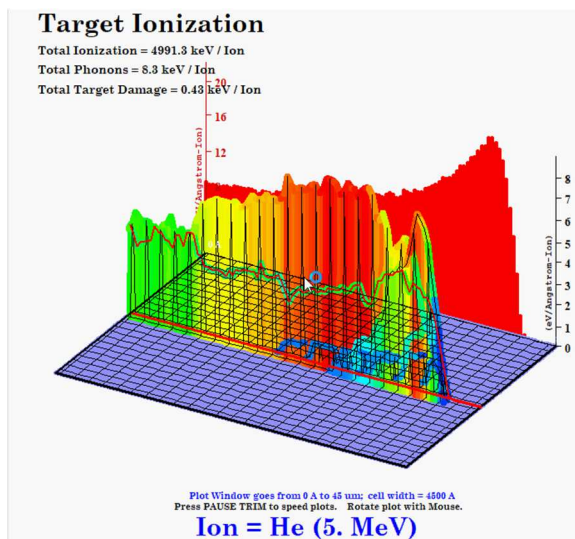
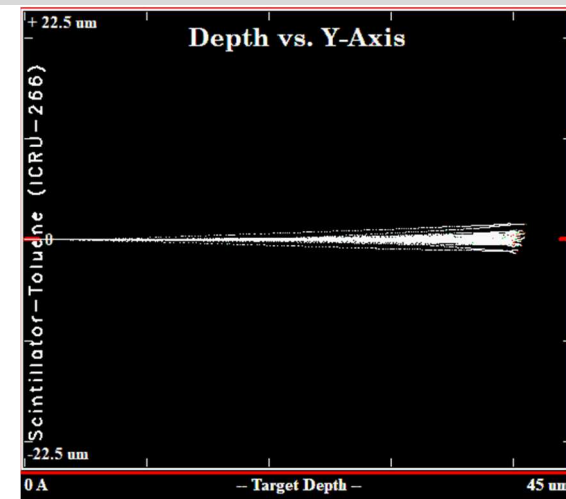
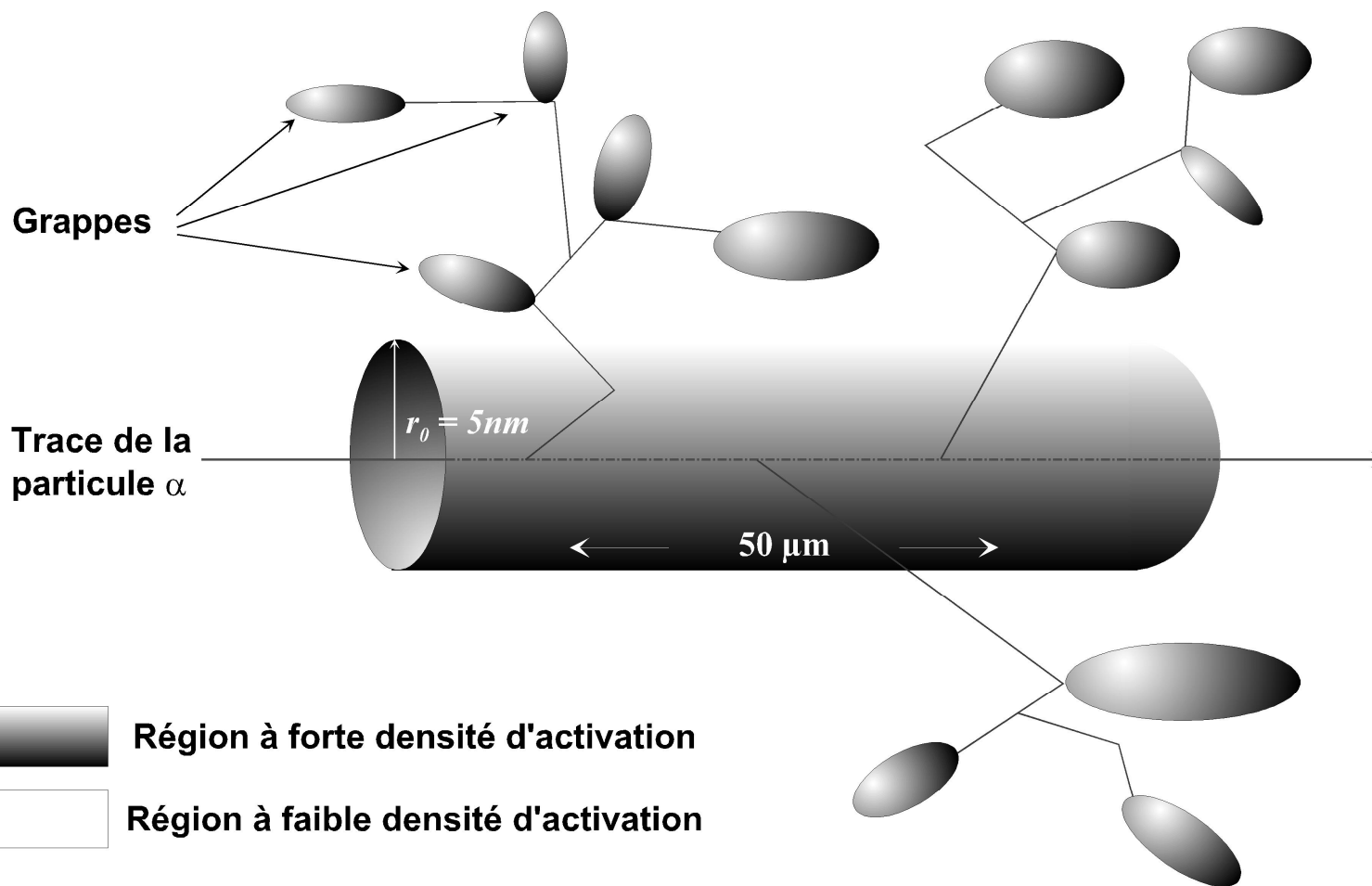
Lösungsmittelzähigkeit nicht anzunehmen. Der Übergang der Anregungsenergie muß vielmehr über die zwischenliegenden Lösungsmittelmoleküle hinweg auf eine Entfernung von vielen Moleküldurchmessern geschehen.

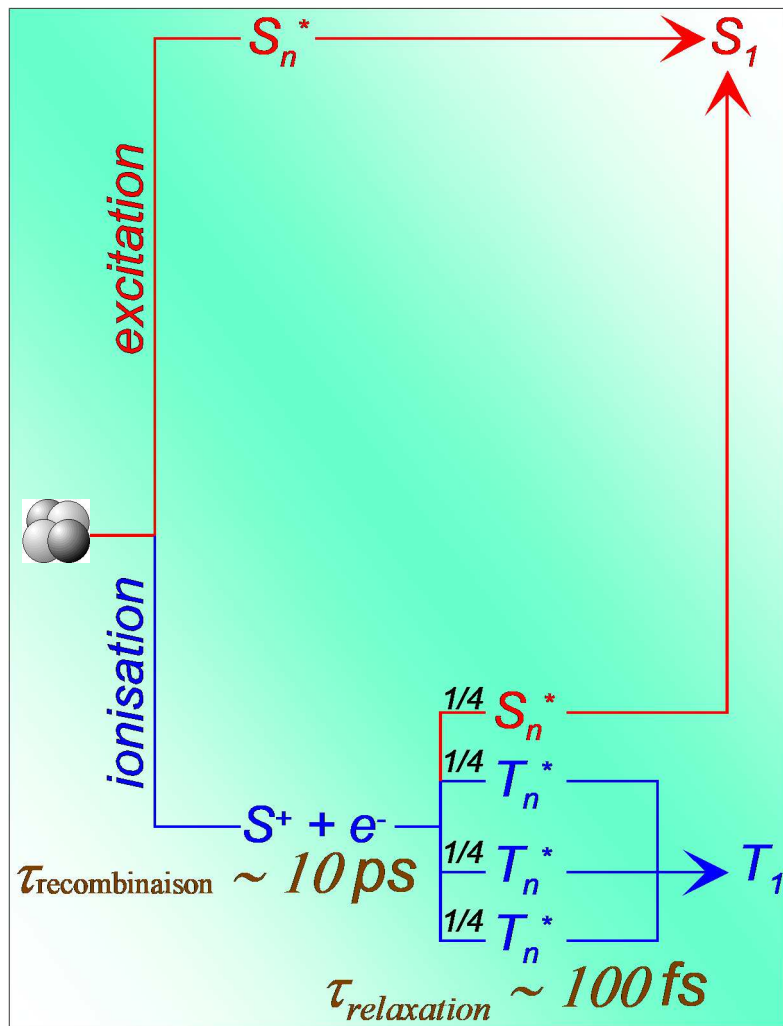
Wenn auch in den bereits vorliegenden Versuchen die Existenz der wahren Löscherückung sichergestellt werden konnte, so war deren quantitative Trennung von der durch Absorption vergetauschten Löscherückung doch unvollkommen. Da so die genaue Feststellung der Größe der Löscherückung, insbesondere bei geringen Konzentrationen, schwierig war, erschien die Weiterführung der Versuche mit einer verbesserten Methode erwünscht. Es wurde dazu eine solche benutzt, die bereits von J. Perrin und Choucrroun² bei einer orientierenden Untersuchung dieser Art von Fluoreszenzlöscherückung angewandt wurde. Sie beruht auf einem Vergleich der Fluoreszenzintensitäten verschieden konzentrierter Mischlösungen beider Stoffe in gleich absorbierenden Schichten. Bei Gültigkeit des Beerschen Absorptionsgesetzes werden dazu die Schichtdicken umgekehrt proportional den Konzentrationen beider Stoffe in den verschiedenen Lösungen gewählt. Es ist dann bei parallelem Erregungslicht der Einfluß der Absorption auf ein paralleles Bündel des Fluoreszenzlichtes der gleiche. Die relative Veränderung der gemessenen Fluoreszenzintensität I ist in diesem Falle gleich derjenigen der inneren Fluoreszenzausbeute τ und ergibt somit die wahre Löscherückung.

Für die Messungen wurden wieder die Farbstoffe Trypflavin und Rhodamin B in Methanol-Lösungen benutzt:

² J. Perrin u. Mlle. Choucrroun, C.R. hebdom. Séances Acad. Sci. 184, 1097 [1927]; 189, 1213 [1929].

Förster, v. T. Z. Naturforsch. 1949, 4 a, 321-327





Voie principale scintillation β

2 pour ^{244}Cm dans le stilbène
5 pour ^{244}Cm dans le stilbène

2 Voies pour scintillation α

3 pour ^{244}Cm dans le stilbène
1.5 pour ^{244}Cm dans le stilbène

EXEMPLE COCKTAIL EXTRACTANT-SCINTILLANT COMMERCIAL ALPHAEX™

①

- **Contient une molécule extractante spécifique à un émetteur α**

Note : Pour ALPHAEX™, c'est l'acide di-2éthylhexylphosphorique

- **Contient 3 molécules spécifiques fluorescentes**

– Solvant :

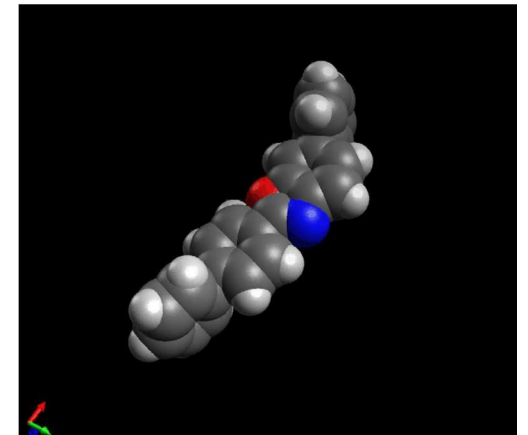
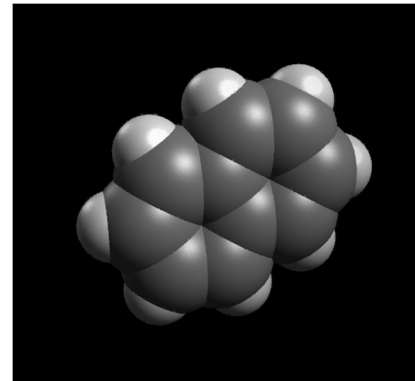
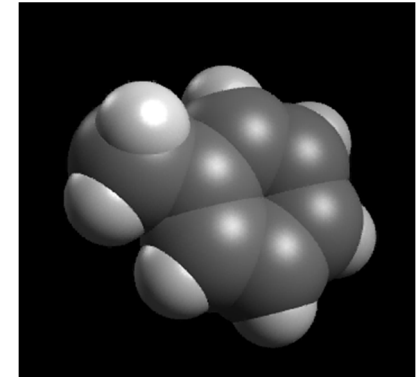
① Toluène (7,5 M)

– Amplificateur de discrimination α/β :

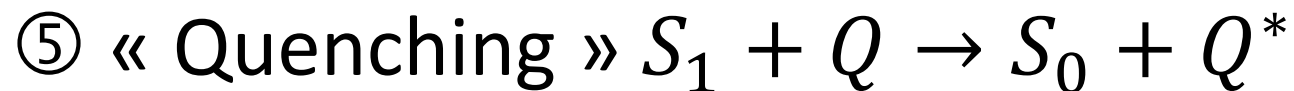
② Naphtalène (1,5 M)

– colorant UV :

③ PBBO (10^{-2} M) 2(4biphenyl) 6-phenylbenzoxazole



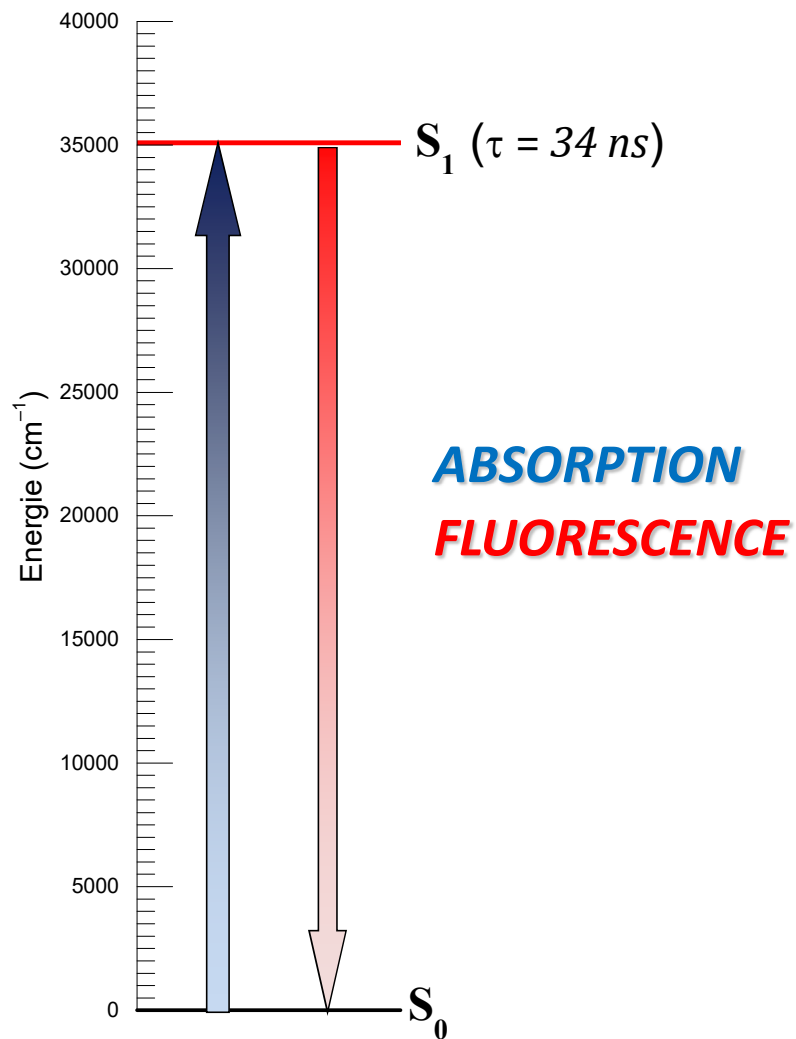
Les voies de désexcitation :



Rendement quantique de fluorescence

$$\Phi^F = \frac{\textcircled{1}}{\textcircled{1} + \textcircled{2} + \textcircled{3}}$$

Fluorescence $S_1 \xrightarrow{h\nu} S_0$

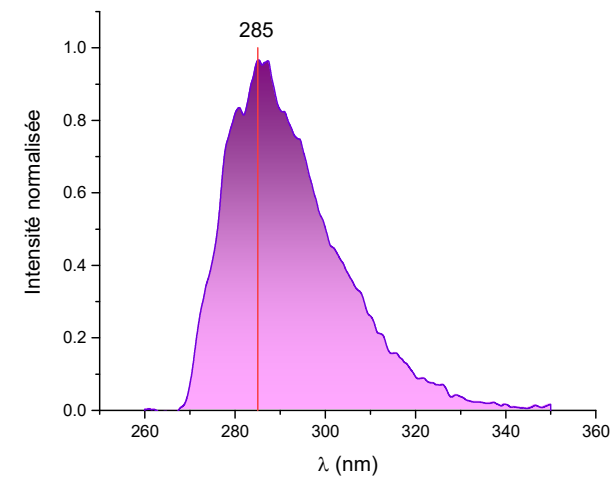


Mécanisme	k (s^{-1})
$S_1 \xrightarrow{h\nu} S_0$	$4,1 \cdot 10^6$
$S_1 \rightarrow T_1$	$1,6 \cdot 10^7$
$S_1 \rightarrow S_0$	$9,8 \cdot 10^6$

$$\Phi^F =$$

$$\tau =$$

Fluorescence toluène dans solvant toluène

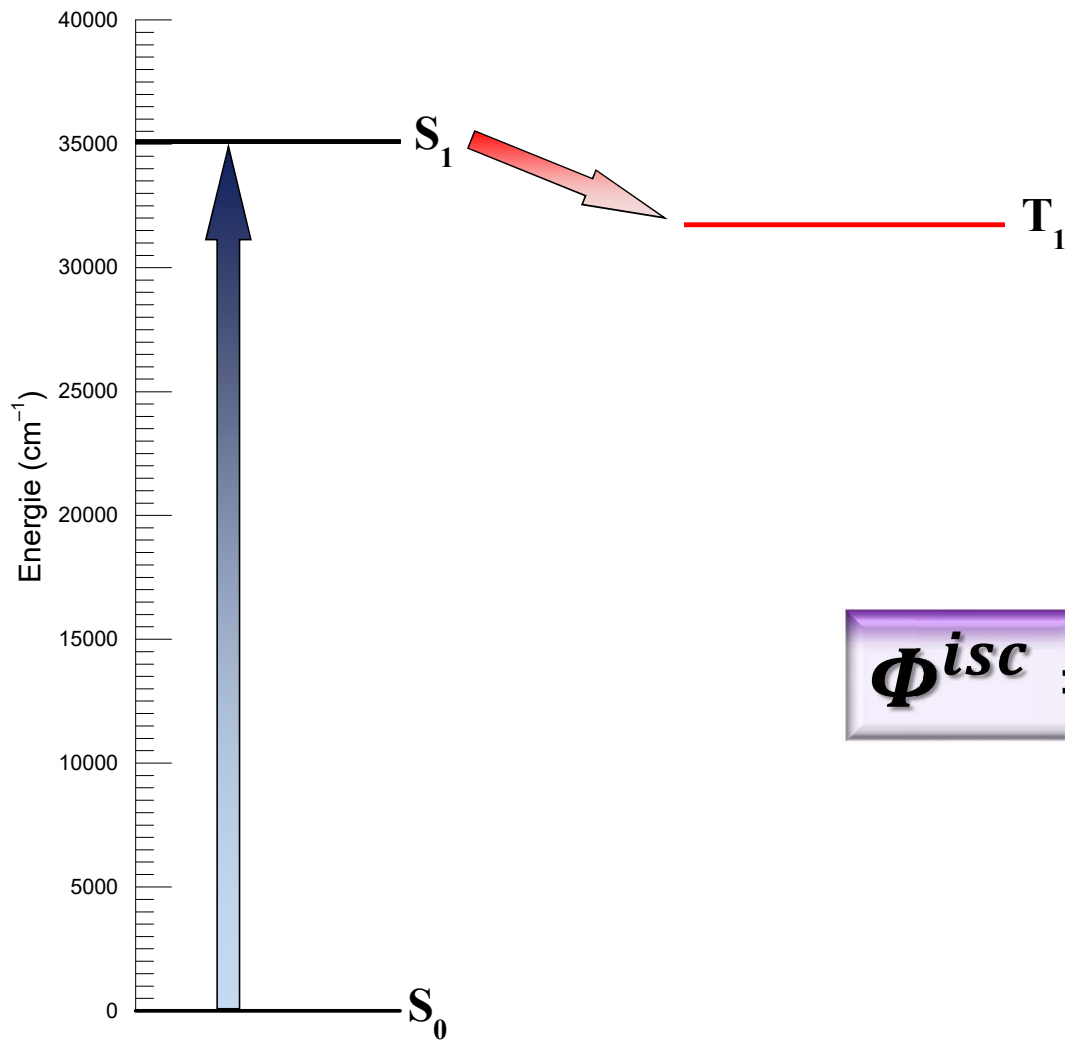


$$E(J) = ?$$

$$E(eV) = ?$$

$$E(\text{cm}^{-1}) = x \times 8065,7$$

$$E(\text{cm}^{-1}) =$$



$$E(\text{cm}^{-1}) = \mathbf{31733}$$

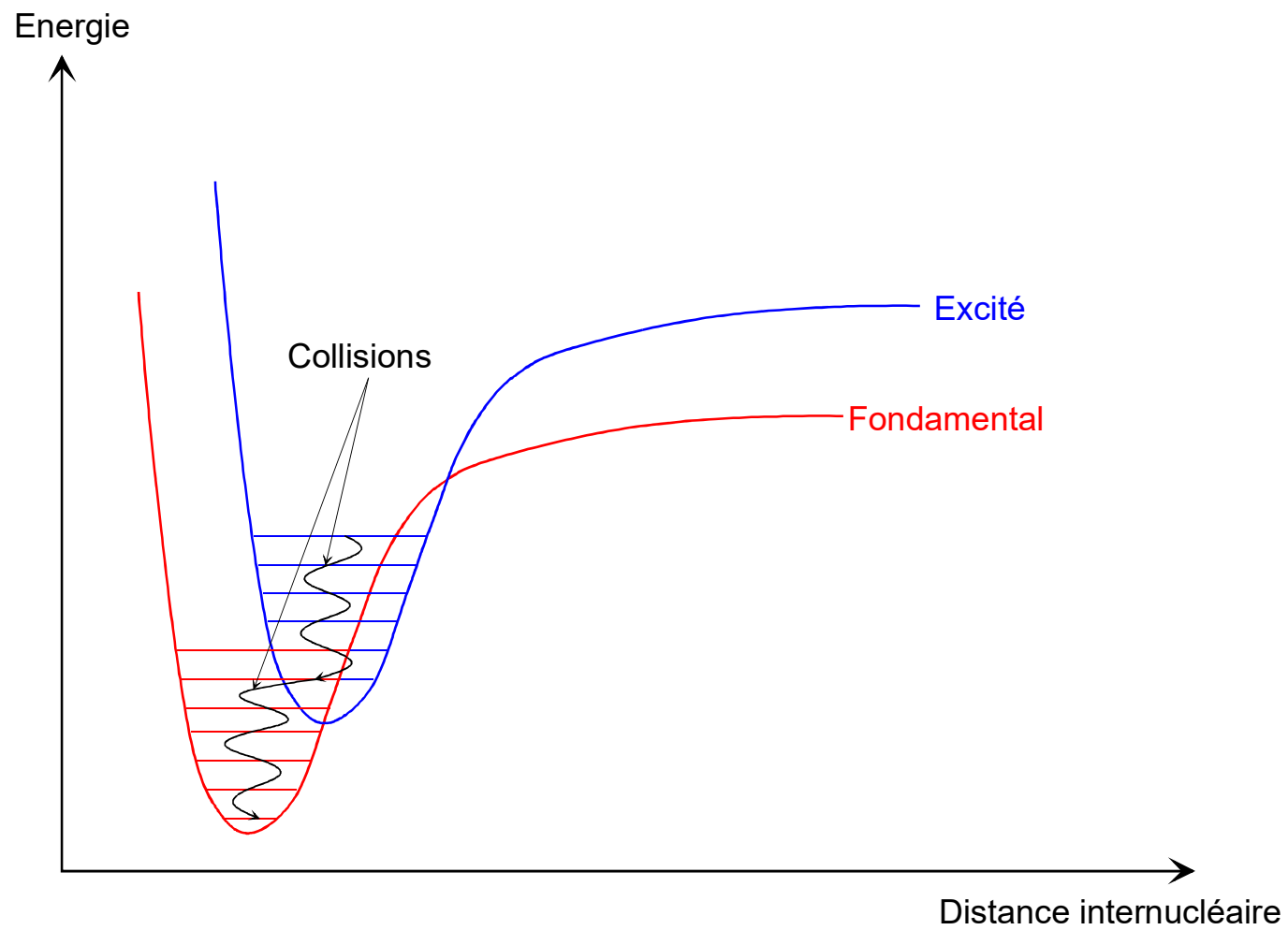
$$E(\text{eV}) =$$

$$E(\text{J}) =$$

$$\lambda(\text{nm}) = \frac{hc}{E(\text{J})} =$$

$$\Phi^{isc} =$$

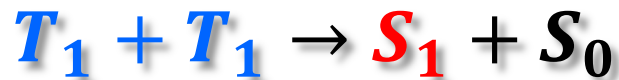
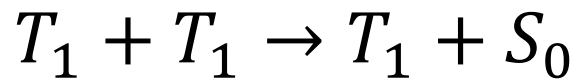
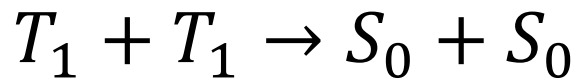
$$\lambda(\text{nm}) =$$



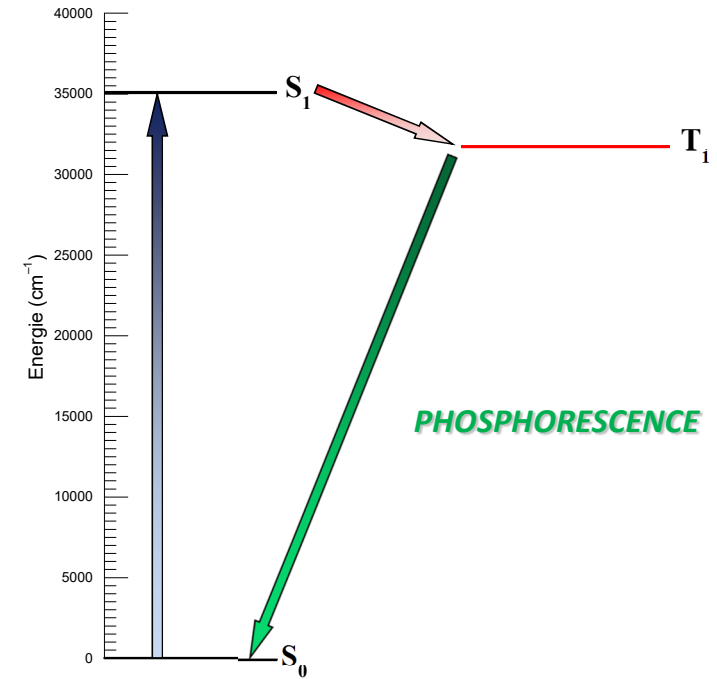
$$\Phi^{nr} =$$

Les voies de désexcitation :

- ① Phosphorescence $T_1 \xrightarrow{h\nu} S_0$
- ② Désexcitation interne $T_1 \rightarrow S_0$
- ③ « Quenching » $T_1 + Q \rightarrow S_0 + Q^*$
- ④ Annihilations T_1-T_1



Rendement quantique de phosphorescence



$$\Phi^P = \frac{\textcircled{1}}{\textcircled{1} + \textcircled{2}} \times \Phi^{isc}$$

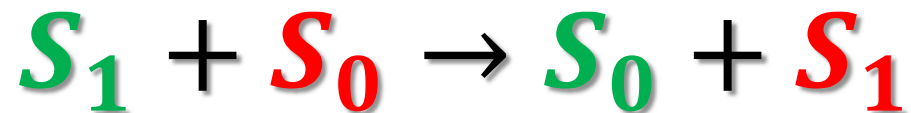
Fluorescence

Mécanisme	k (s ⁻¹)
$S_1 \xrightarrow{h\nu} S_0$	$4,1 \cdot 10^6$
$S_1 \rightarrow T_1$	$1,6 \cdot 10^7$
$S_1 \rightarrow S_0$	$9,8 \cdot 10^6$

Phosphorescence

Mécanisme	k (s ⁻¹)
$T_1 \xrightarrow{h\nu} S_0$	$4,7 \cdot 10^{-2}$
$T_1 \rightarrow S_0$	$8,2 \cdot 10^{-2}$

$$\Phi^P =$$

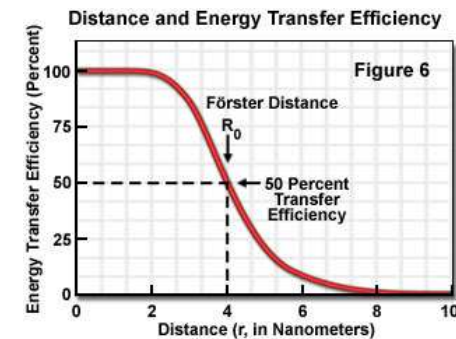


La cinétique de transfert k_{SF} (et donc l'efficacité du transfert ϵ_{SF}) dépend de la distance r entre les 2 molécules en interaction (donneur **D** et accepteur **A**).

$$k_{SF} = \frac{1}{\tau_D} \left(\frac{R_0}{r} \right)^6 \quad \epsilon_{SF} = \frac{1}{1 + \left(\frac{R_0}{r} \right)^6}$$

La distance d'interaction peut être quantifiée en calculant le rayon critique R_0 correspondant à une efficacité ϵ_{SF} de 0,5.

$$R_0^6 = \frac{9000 \ln 10 \kappa^2 \phi_D}{128 \pi^6 n^4 \mathcal{N}} \int_0^\infty f_D(\nu) \epsilon_A(\nu) \frac{d\nu}{\nu^4}$$



On doit tenir compte de la diffusion simultanée au transfert par dipôle-dipôle. La solution exacte dépendante du temps qui prend en compte simultanément la diffusion et le transfert à longue distance ne paraissant pas possible, des techniques d'approximation ont été utilisées.

L'équation de Gösele (1975) donne la probabilité de vie d'un état excité dépendante du temps

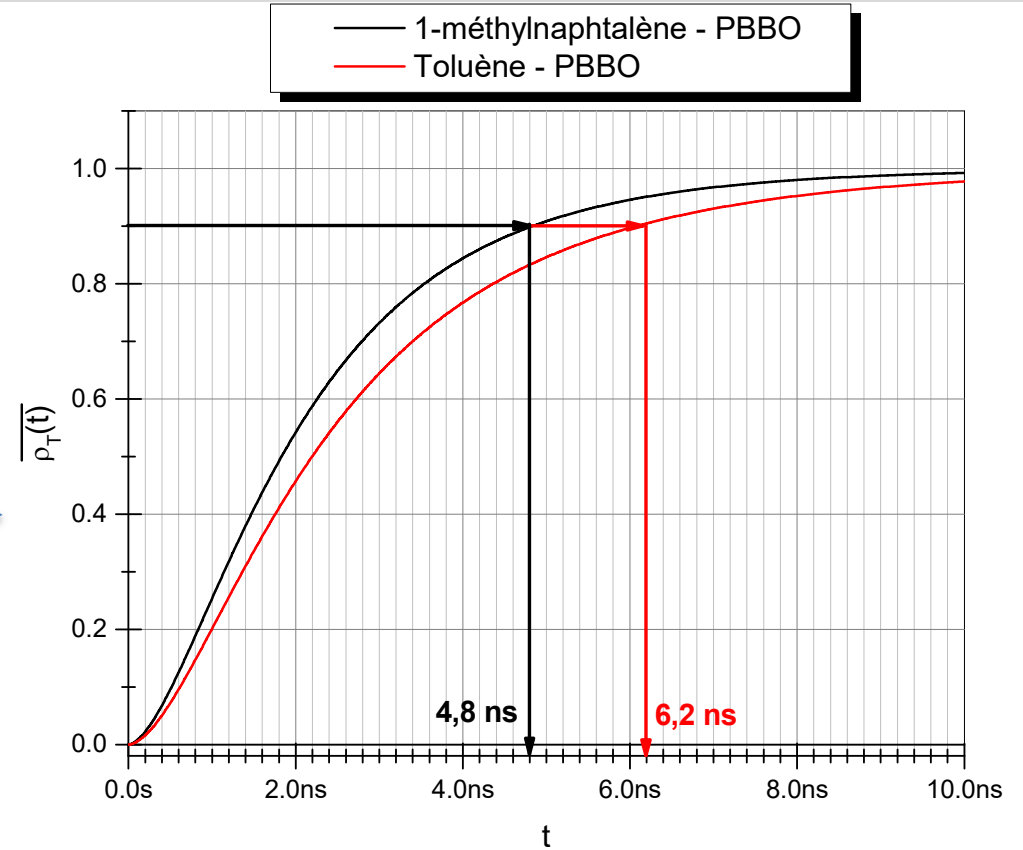
$$\rho(t) = \exp \left(\underbrace{\left(-\frac{t}{\tau_D} \right)}_{\text{Fluorescence}} \underbrace{- 4\pi D r_F n_A t}_{\text{Diffusion}} \underbrace{- g \frac{4}{3} \pi^{3/2} n_A R_0^3 \sqrt{\frac{t}{\tau_D}}}_{\text{Interaction coulombienne}} \right)$$

Avec r_F rayon effectif de piégeage : $r_F \approx 0,676 R_0 \sqrt[4]{g^2 \frac{R_0^2}{\tau_D D}}$
 $g = 0,845$

Cas pour 2 molécules

$$\overline{\rho_T(t)} = [1 - \rho_{1 \rightarrow 2}(t)] \times \left(1 - e^{-\frac{t}{\tau_1}}\right)$$

1 = toluène ou 1-méthylnaphtalène
2 = PBBO

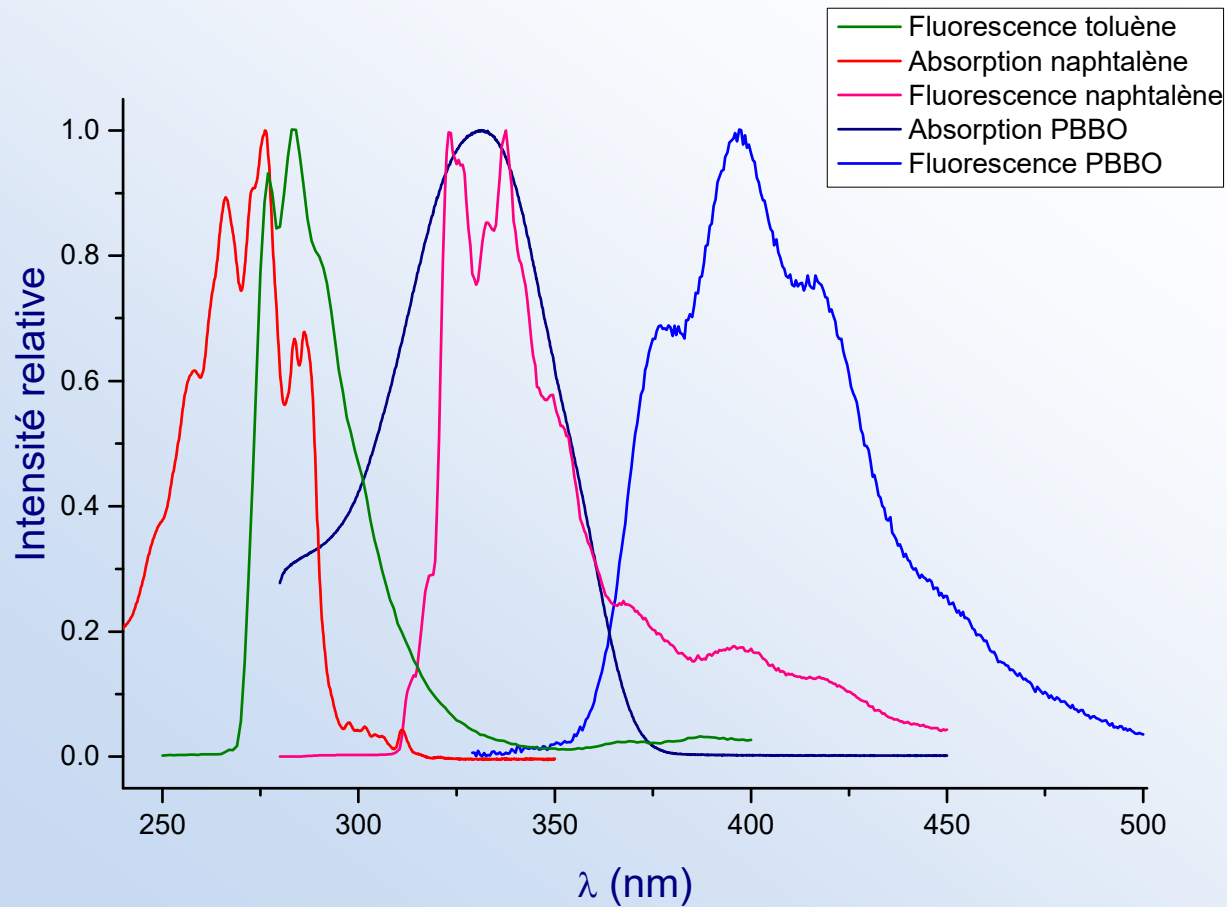


Cas pour 3 molécules (liquide scintillant)

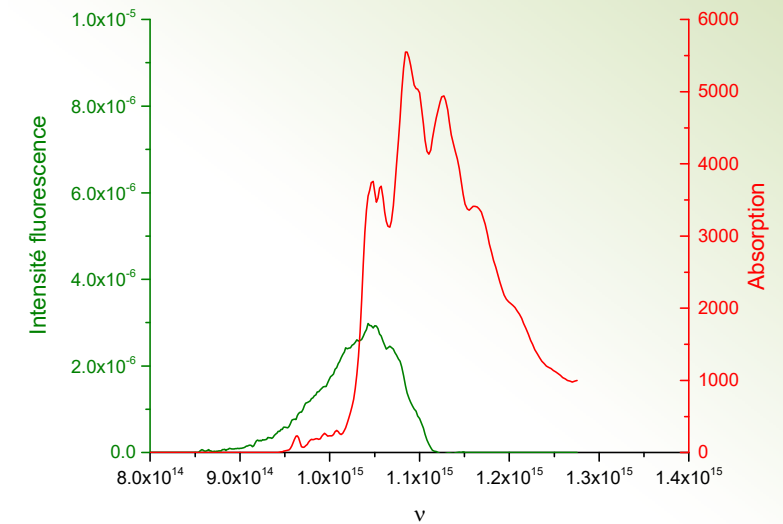
$$\overline{\rho_T(t)} = [1 - \rho_{1 \rightarrow 2}(t)] \times [1 - \rho_{2 \rightarrow 3}(t)] \times \left(1 - e^{-\frac{t}{\tau_3}}\right)$$

(par exemple pour AlphaexTM 1 = toluène, 2 = naphtalène, 3 = PBBO)

$$R_0^6 = \frac{9000 \ln 10 \kappa^2 \phi_D}{128 \pi^6 n^4 \mathcal{N}} \int_0^\infty f_D(\nu) \epsilon_A(\nu) \frac{d\nu}{\nu^4}$$



Le calcul réel doit être réalisé dans les unités S.I. !





Mécanisme	Toluène k_i (s^{-1})	Naphtalène k_i (s^{-1})	PBBO k_i (s^{-1})
$S_1 \xrightarrow{h\nu} S_0$	$4,1 \cdot 10^6$	$2,0 \cdot 10^6$	$8,3 \cdot 10^8$
$S_1 \rightarrow T_1$	$1,6 \cdot 10^7$	$7,8 \cdot 10^6$	—
$S_1 \rightarrow S_0$	$9,8 \cdot 10^6$	$6,3 \cdot 10^5$	—
$S_1 + O_2 \rightarrow S_0 + O_2^*$	$2,8 \cdot 10^{10} M^{-1}s^{-1}$ (dans cyclohexane)	$2,7 \cdot 10^{10} M^{-1}s^{-1}$ (dans cyclohexane)	?
$T_1 \xrightarrow{h\nu} S_0$	$4,7 \cdot 10^{-2}$	$1,4 \cdot 10^{-2}$	—
$T_1 \rightarrow S_0$	$8,2 \cdot 10^{-2}$	0,42	—
$T_1 + O_2 \rightarrow S_0 + O_2^*$	$1,3 \cdot 10^{10} M^{-1}s^{-1}$ (dans benzène)	$1,5 \cdot 10^9 M^{-1}s^{-1}$ (dans benzène), $2,4 \cdot 10^9$ dans toluène	?



$$6,9 \cdot 10^{10}$$

$$1,5 \cdot 10^8$$

Les états triplets ne sont pas des dipôles (pas d'interaction coulombienne). Le transfert est essentiellement dû à la diffusion.

Généralement une réaction de pseudo premier ordre quantifie assez bien le temps de transfert.

$$\frac{1}{t} = k_{diffusion}[Accepteur]$$

N.B. : La constante de diffusion dans les solvants organiques est d'environ $10^{10} \text{ M}^{-1}\text{s}^{-1}$

Dans le cas du cocktail Alphaex™ :

① [Toluène] = 7,5 M

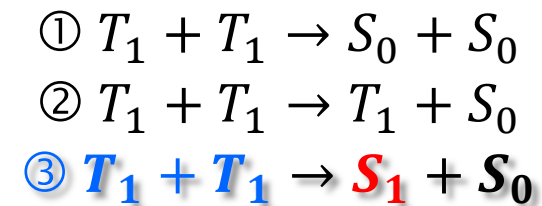
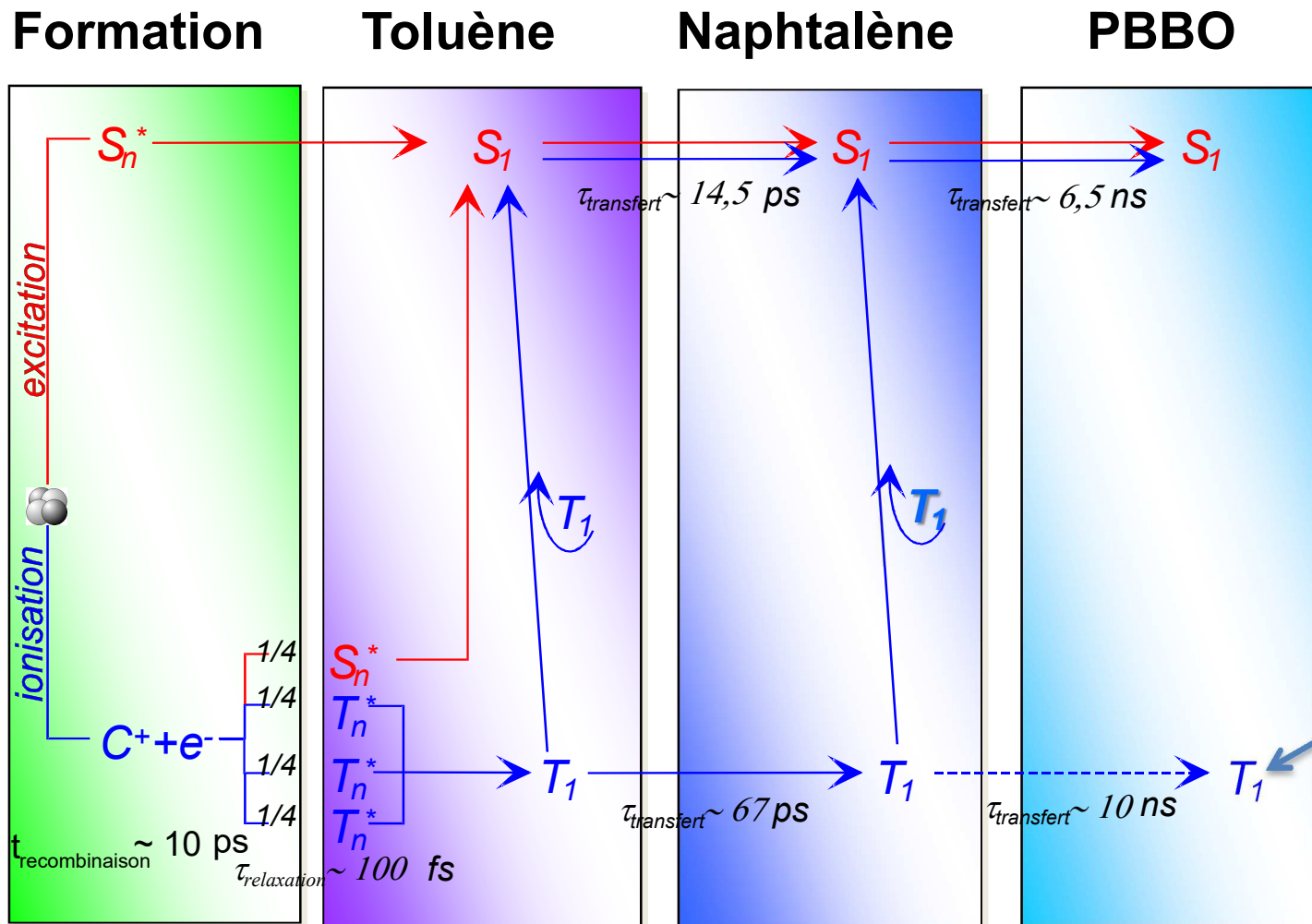
② [Naphtalène] = 1,5 M

③ [PBBO] = 0,01 M



$t_{1 \rightarrow 2} =$ ps soit $k_{1 \rightarrow 2} =$ s^{-1}

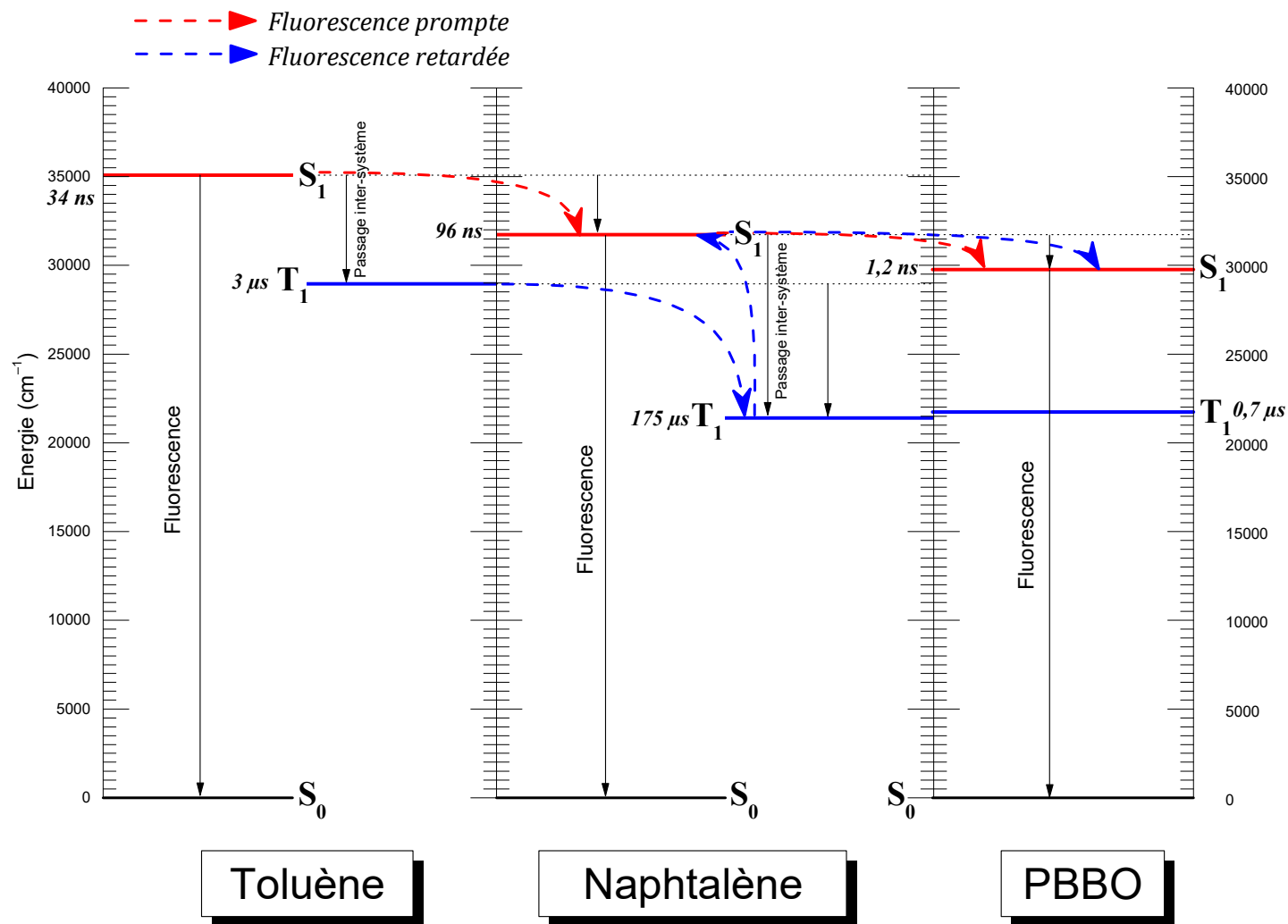
$t_{2 \rightarrow 3} =$ ns soit $k_{2 \rightarrow 3} =$ s^{-1}



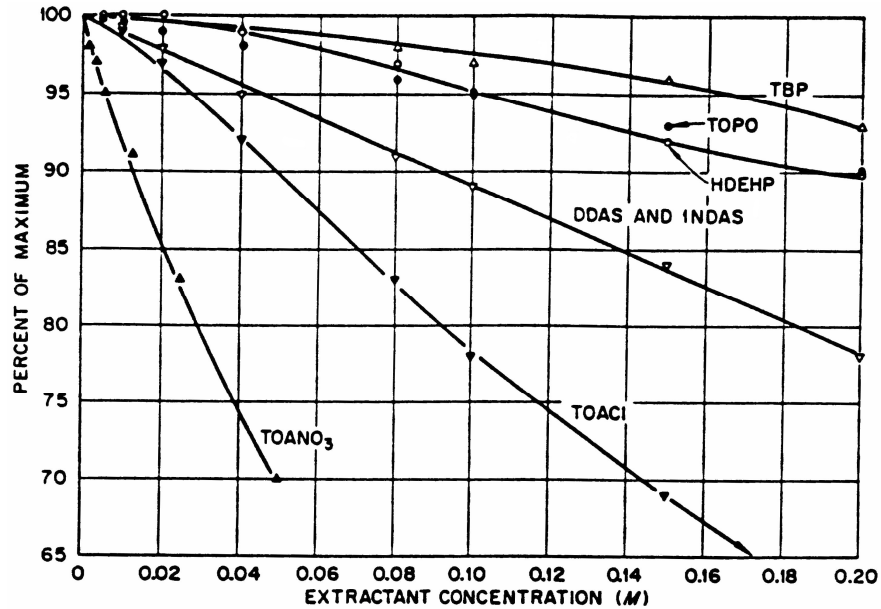
$$\Phi_{\textcircled{3}} = \frac{\textcircled{3}}{\textcircled{1} + \textcircled{2} + \textcircled{3}} = \mathbf{0,56}$$

Non favorable,
 $E_{T_1}(\text{PBBO}) > E_{T_1}(\text{Naphtalène})$

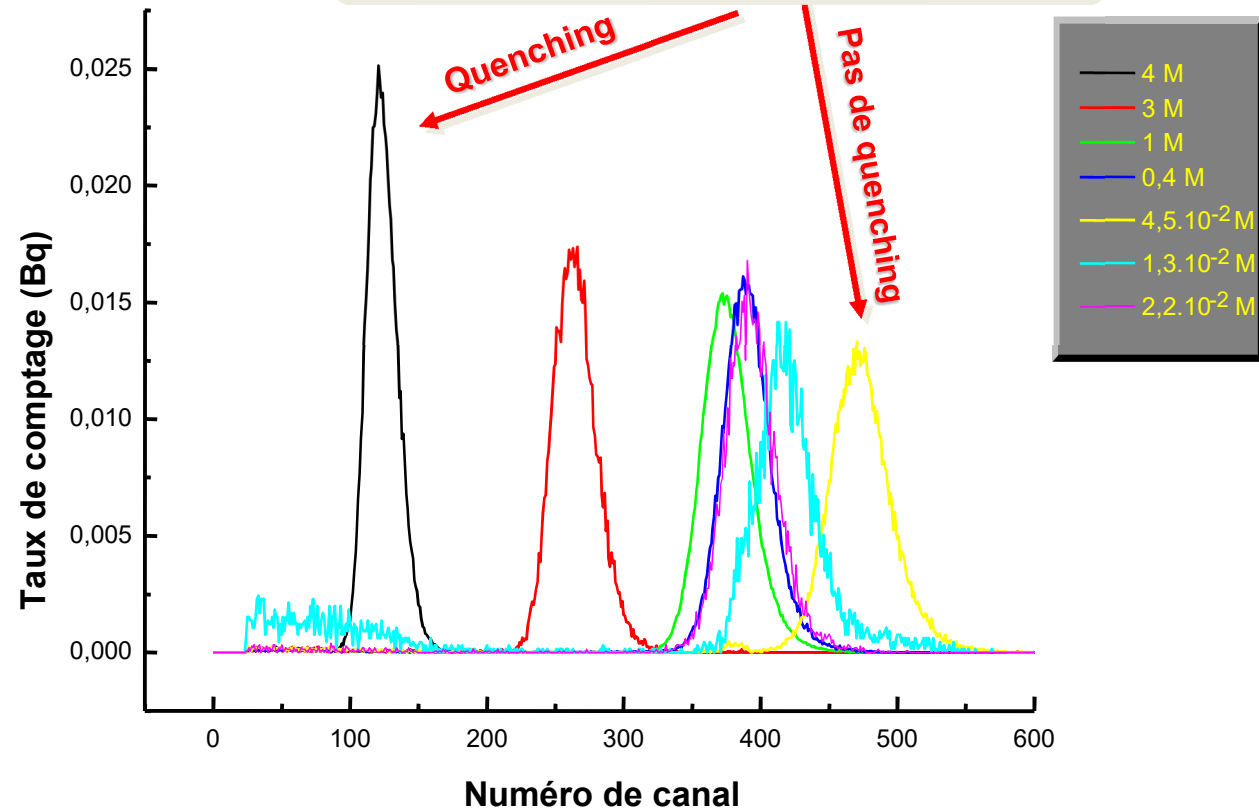
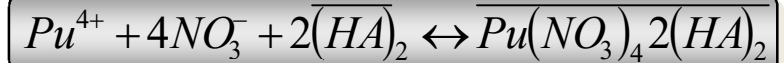
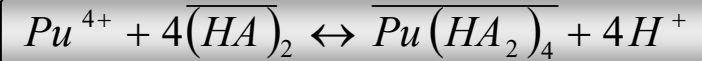
Niveaux d'énergie des états excités des composés de Alphaex™

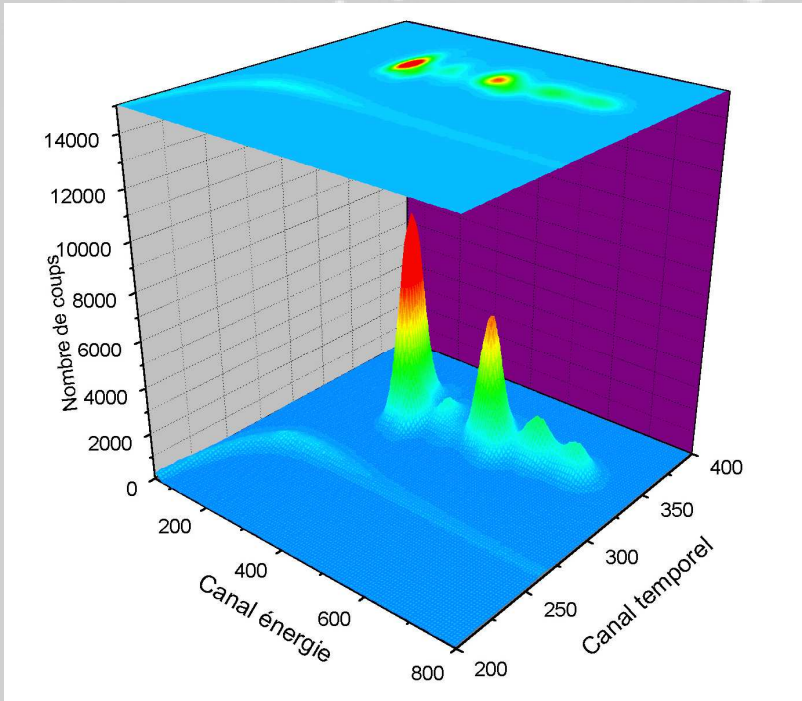


Présence de molécule extractante



The Quenching Effect of Various Extractants: TBP = tributylphosphate, TOPO = trioctylphosphine oxide, DDAS = didecylamine sulfate, 1NDS = 1-nonyldecylamine sulfate, TOACI = trioctylamine chloride, and TOANO₃ = trioctylamine nitrate.





TRAITEMENT DU SIGNAL

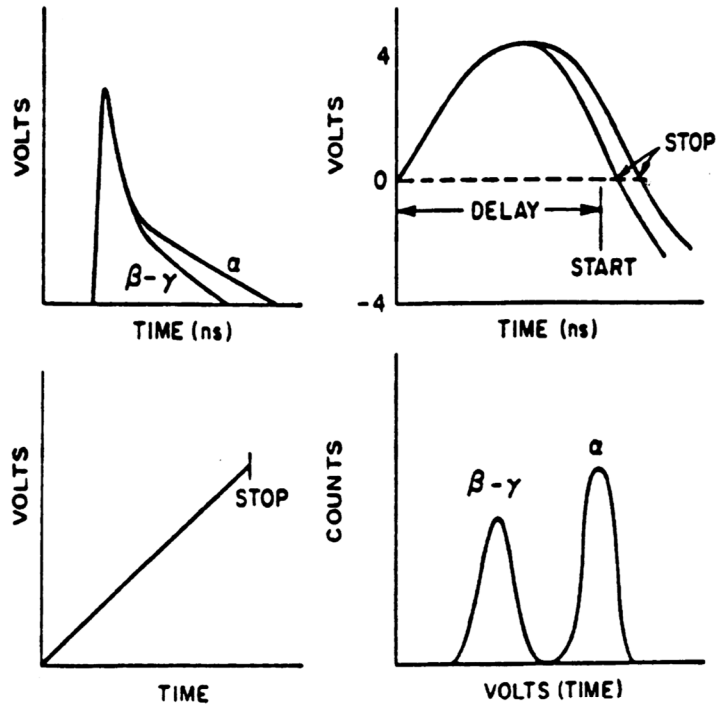
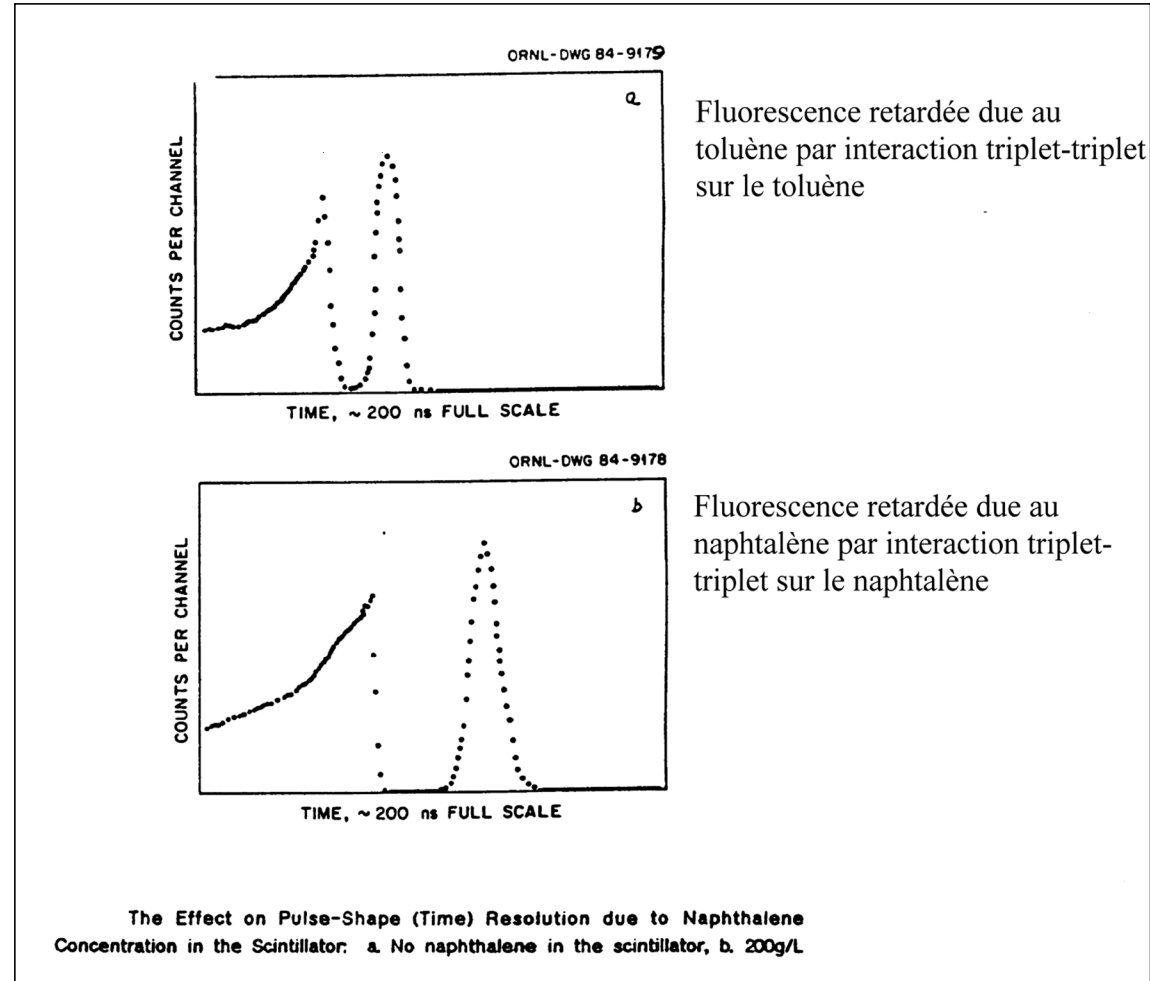
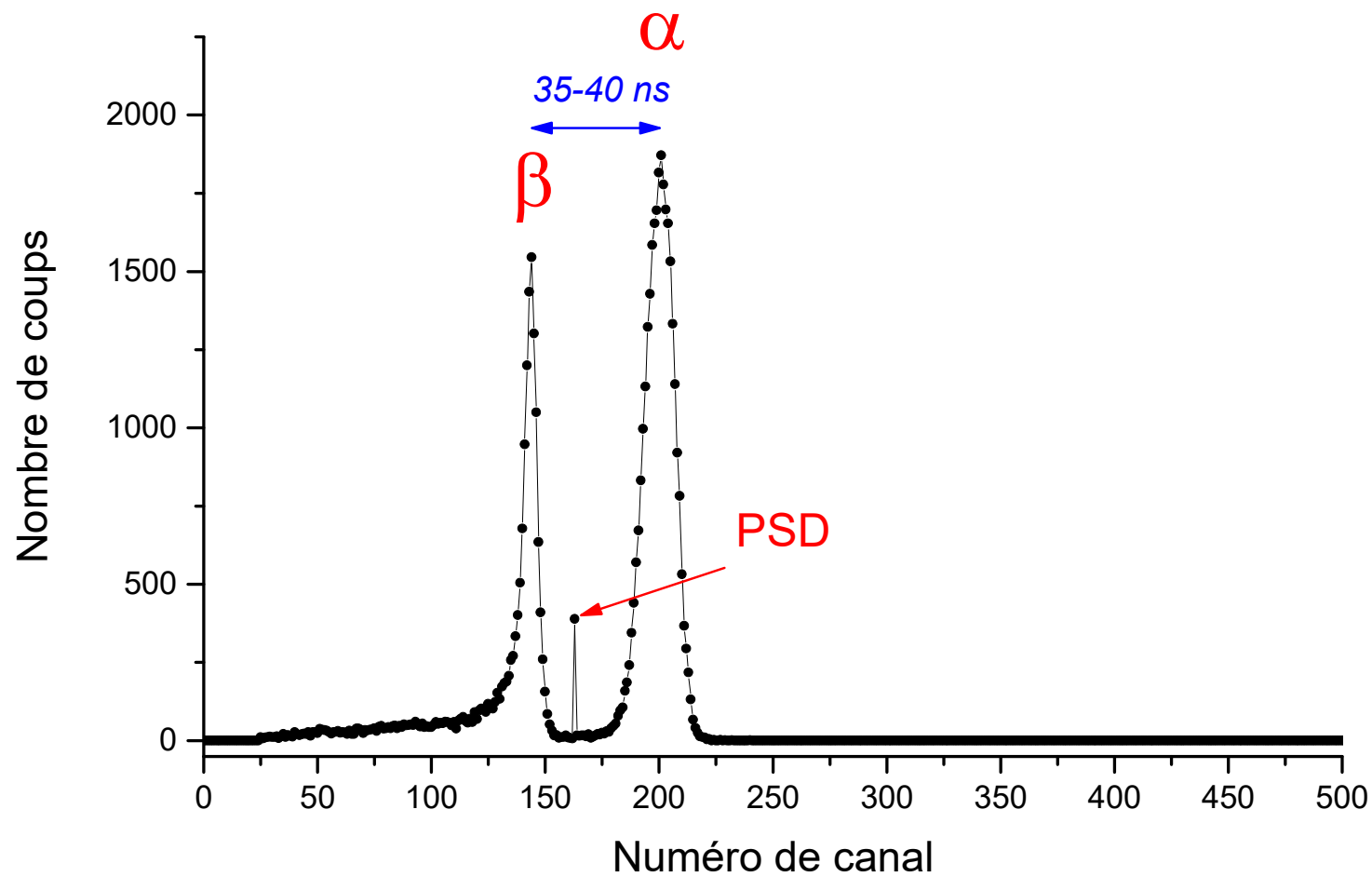


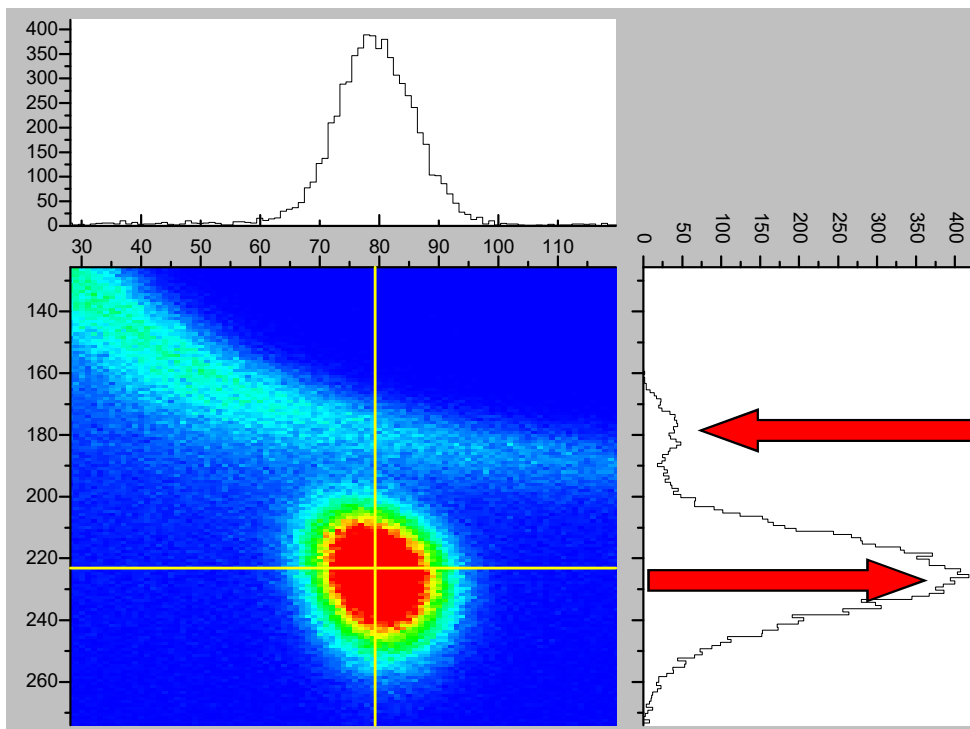
Fig. 21. Pulse-Shape Discrimination. This is possible because the detectable portion of alpha-produced light pulses (upper left) last about 30 nanoseconds longer than beta- or gamma-produced pulses. Since the integrated pulses (upper right) are about a microsecond long, the beginning of timing is delayed for about 800 nanoseconds. A voltage ramp (lower left) is then started and rises linearly with time until the pulse crosses zero. The spectrum of these voltage pulses (lower right) represents alpha (right) and beta-gamma pulses (left).



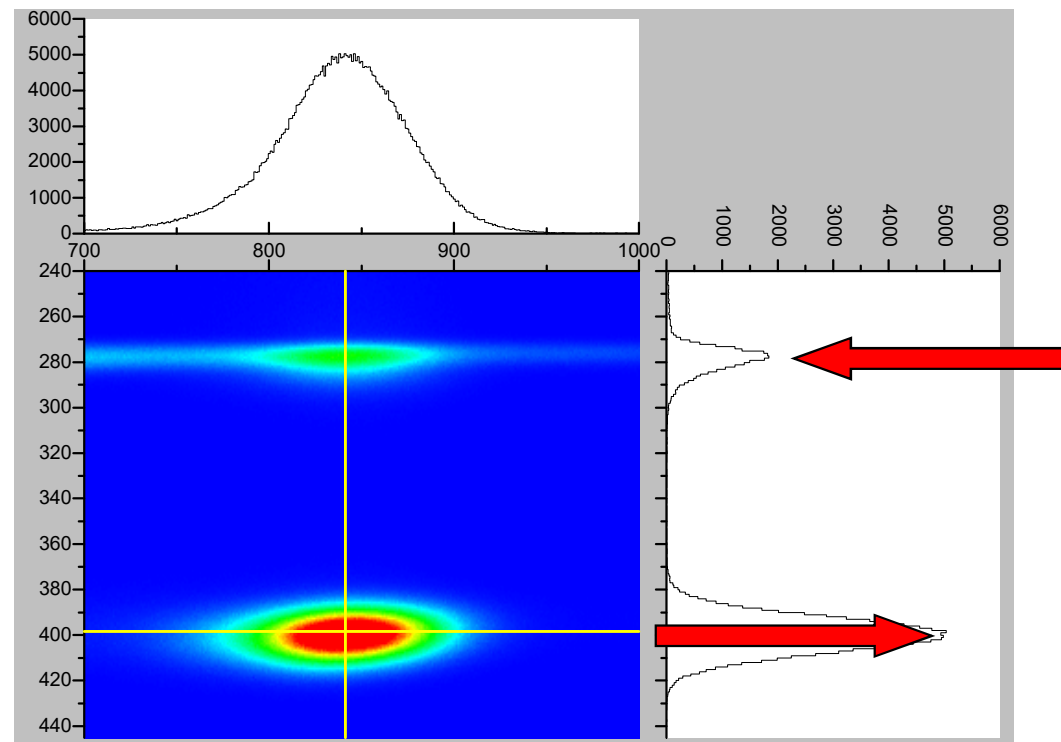
PSD = Pulse Shape Discrimination

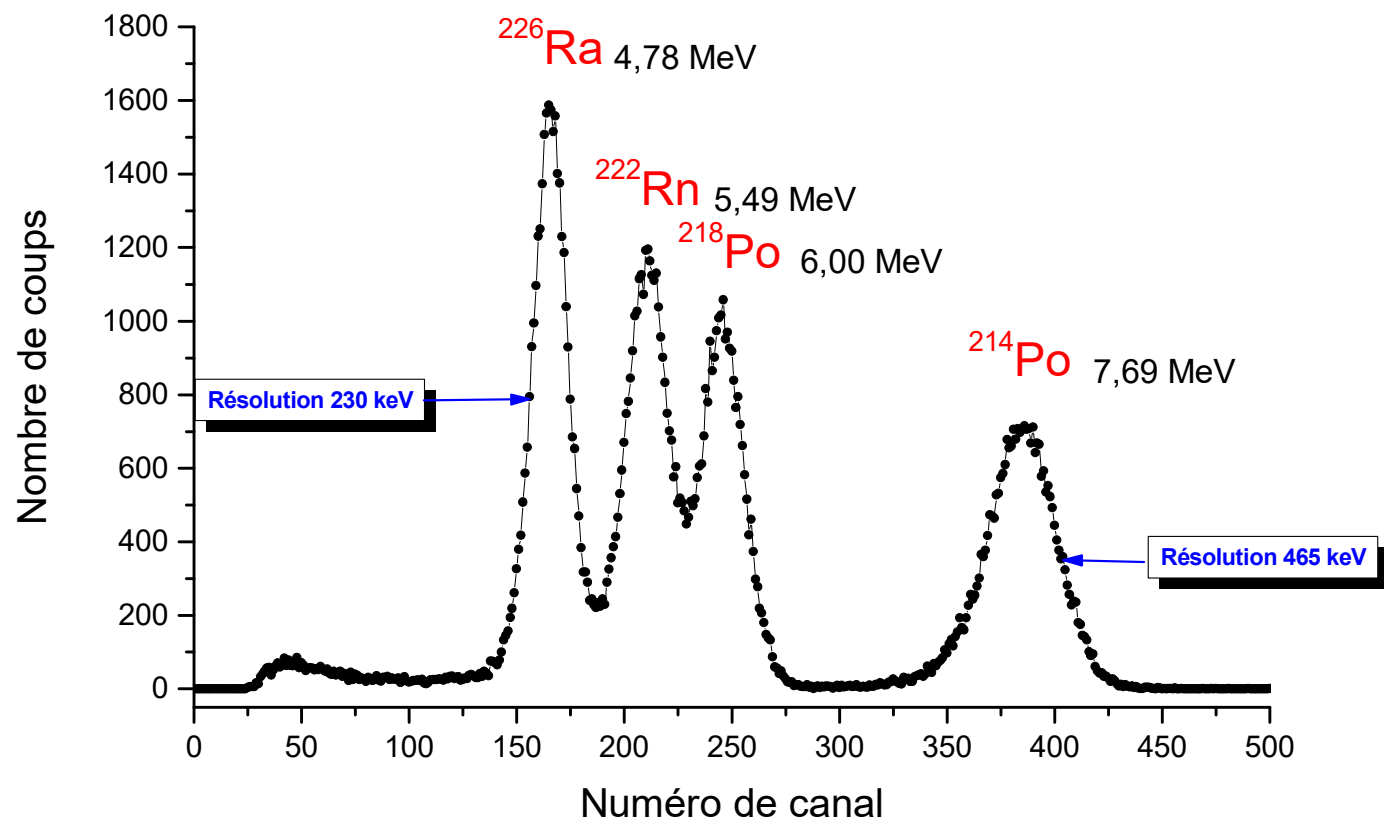


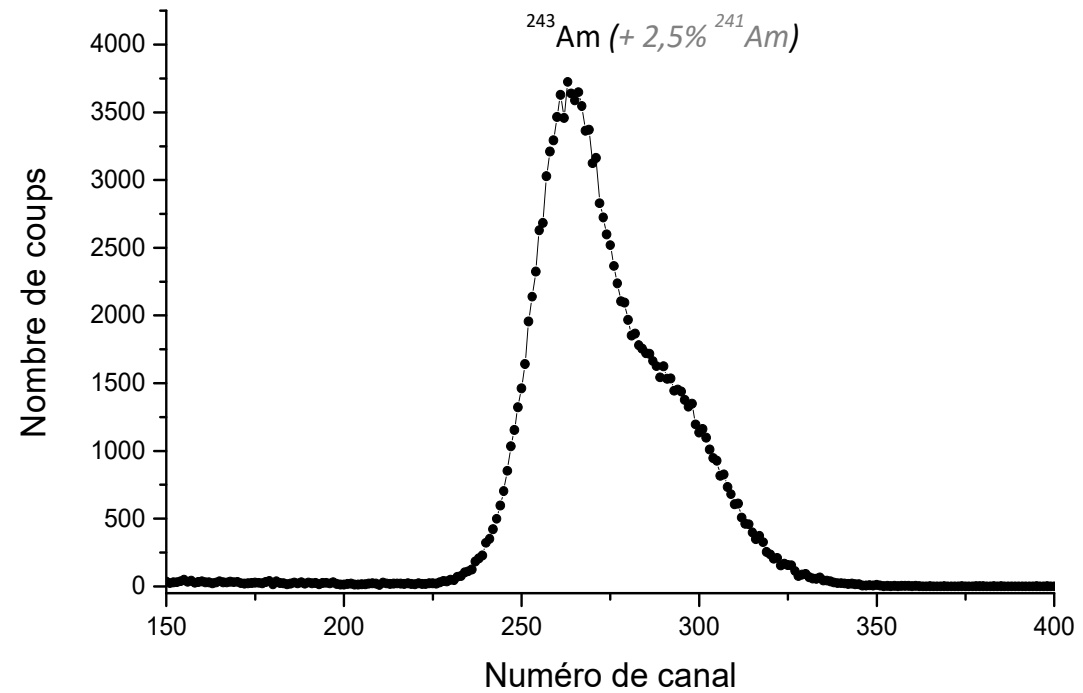
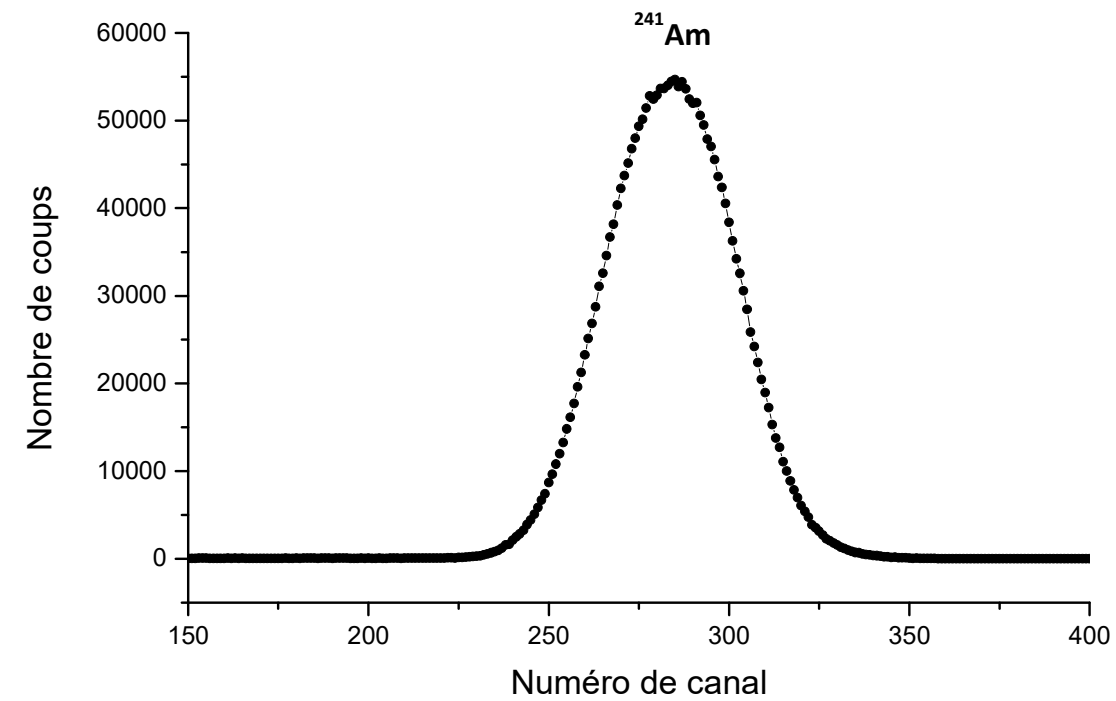
^{147}Sm
 $E_{\alpha} = 2233 \text{ keV}$

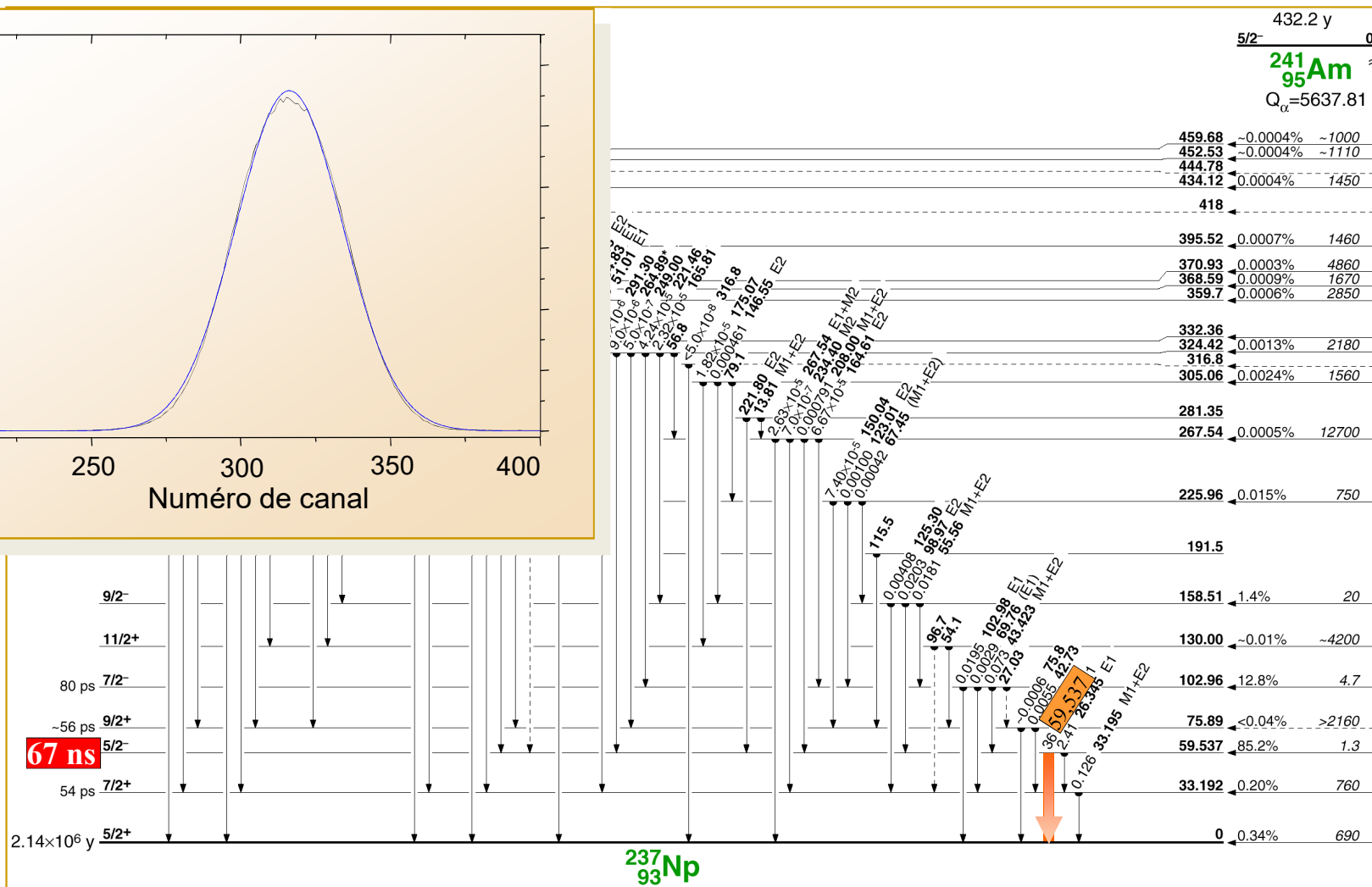
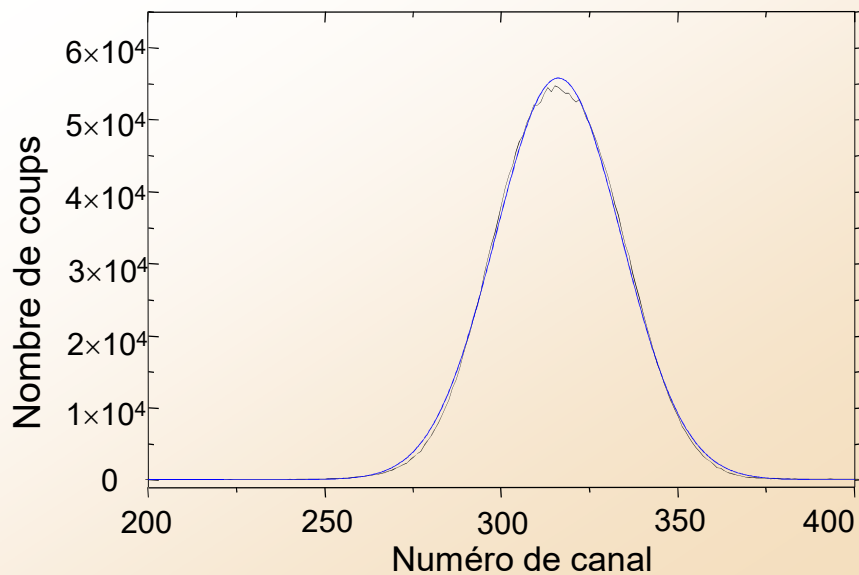


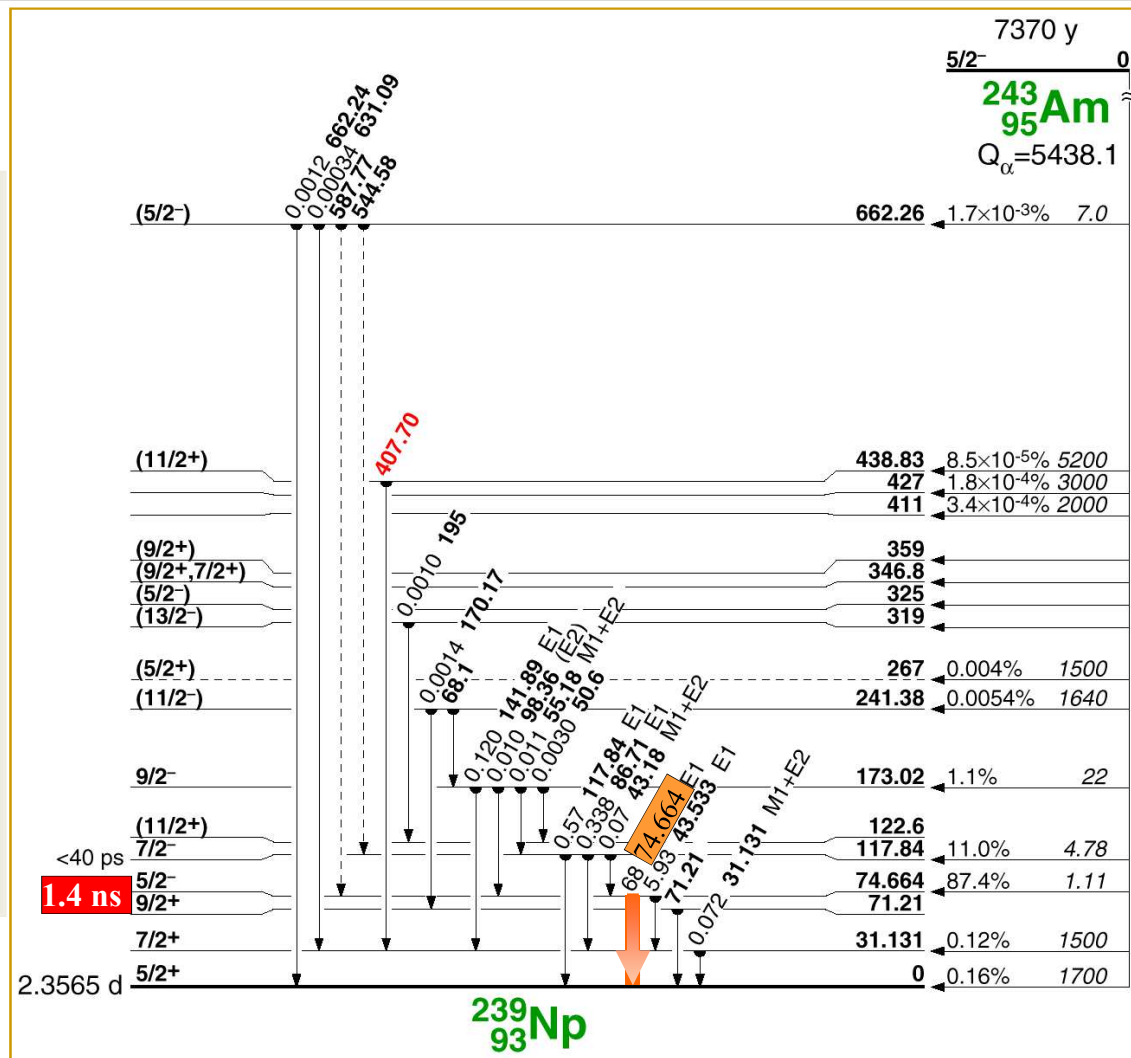
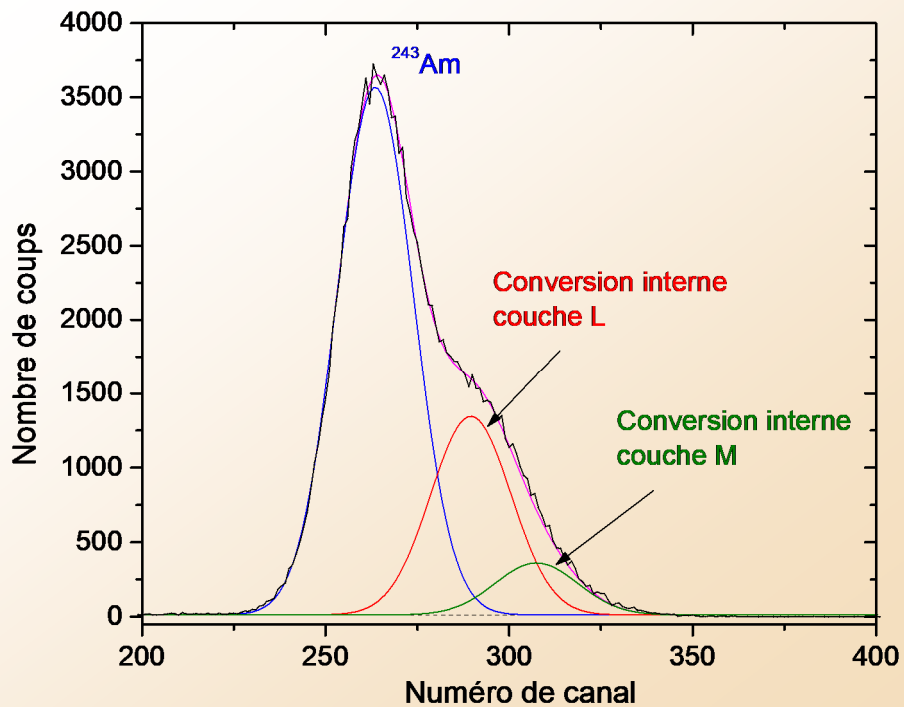
^{214}Po
 $E_{\alpha} = 7687 \text{ keV}$











Conversion interne totale : $\alpha_T = \alpha_K + \alpha_L + \alpha_M + \dots = \frac{I_{ic}}{I_\gamma}$

Conversions internes dans chaque couche :

$$\alpha_K = \frac{I_{ic,K}}{I_\gamma}$$

$$\alpha_{L_i} = \frac{I_{ic,L_i}}{I_\gamma} \quad (i = 1, 2, 3)$$

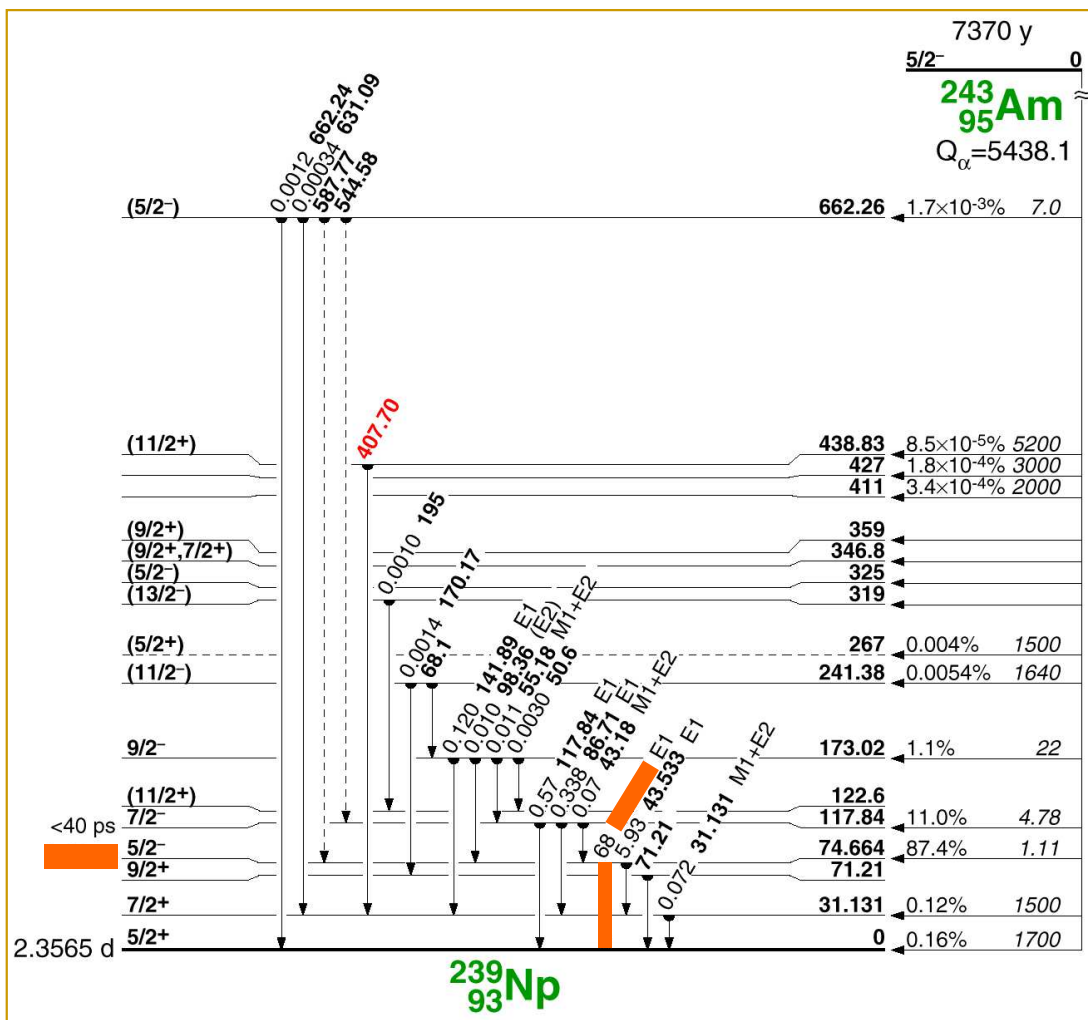
$$\alpha_{M_i} = \frac{I_{ic,M_i}}{I_\gamma} \quad (i = 1, 2, 3, 4, 5)$$

$$\alpha_L = \sum_{i=1}^3 \alpha_{L_i}$$

$$\alpha_M = \sum_{i=1}^5 \alpha_{M_i}$$

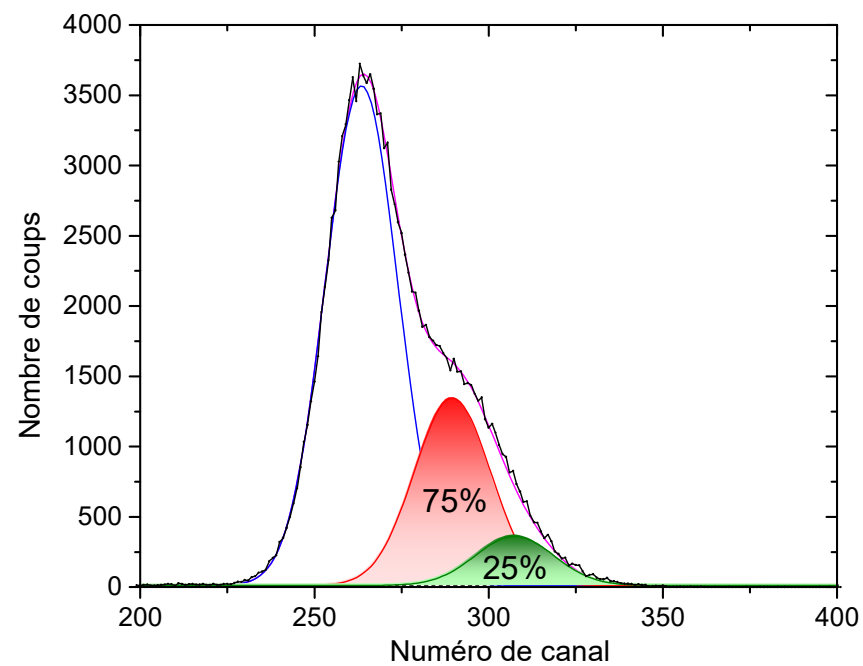
$$I_{ic} = \frac{\alpha_T}{1 + \alpha_T}$$

$$I_\gamma = \frac{1}{1 + \alpha_T}$$



Isot.	α_T	α_L	α_M	$\alpha_{N+\dots}$
^{243}Am	0,280	0,210	0,0518	0,0183

$\frac{\alpha_L}{\alpha_T}$	$\frac{\alpha_M}{\alpha_T}$	$\frac{\alpha_M}{\alpha_L}$



Isot.	α_T	α_L	α_M	$\alpha_{N+\dots}$
^{243}Am	0,280	0,210	0,0518	0,0183

I_{ic}	I_γ	$E_{\alpha_{0,3}}$

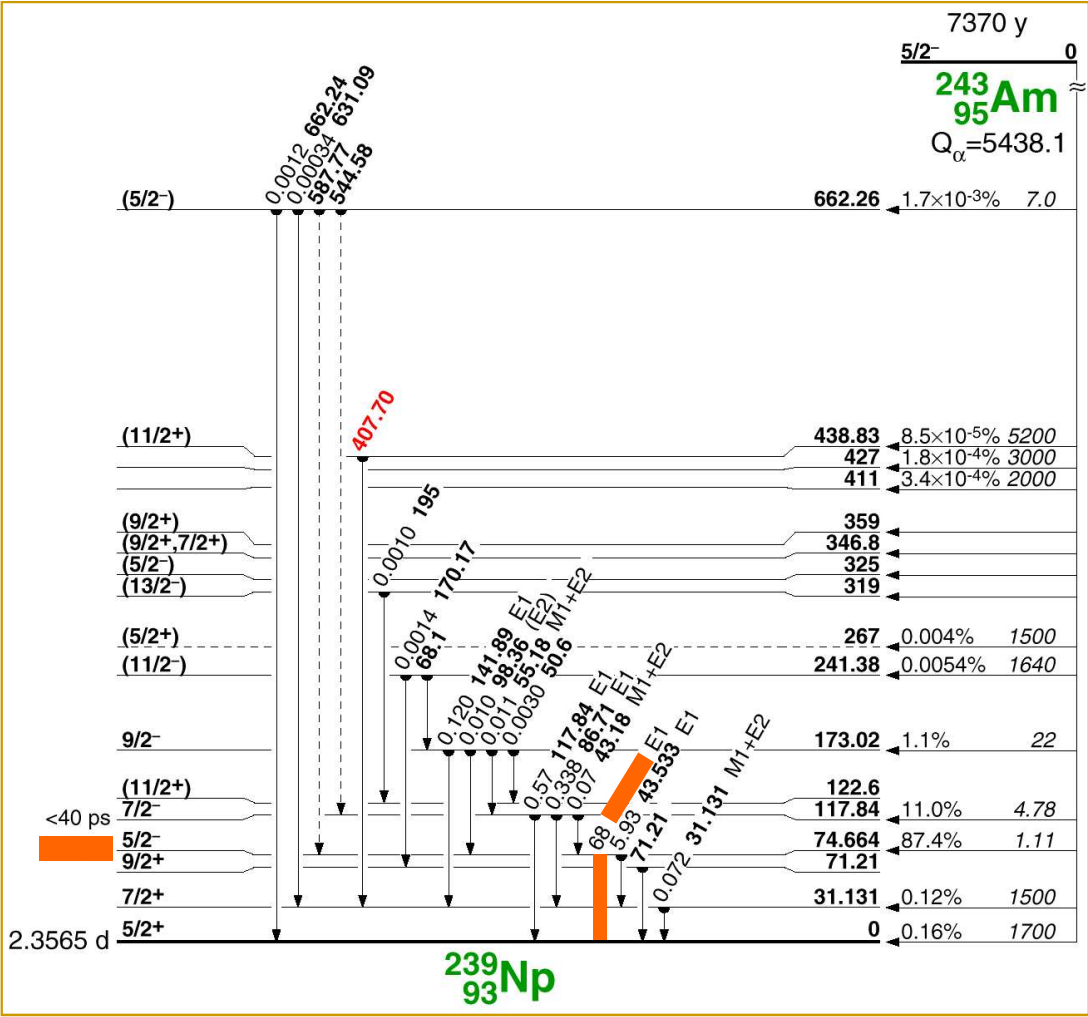
$$E_{\alpha_{0,3}} = (Q_\alpha - E_{5/2^-}) \times \frac{\mathcal{M}_{^{239}\text{Np}}}{\mathcal{M}_{^{243}\text{Am}}}$$

Couche	i = 1	i = 2	i = 3	i = 4	i = 5	\bar{E}
L	23,808 (2s)	22,952 (2p _{1/2})	18,510 (2p _{3/2})			
M	6,133 (3s)	5,739 (3p _{1/2})	4,698 (3p _{3/2})	4,096 (3d _{3/2})	3,890 (3d _{5/2})	

Energie en keV

$$E_{e,ic_L} = \quad \text{keV}$$

$$E_{e,ic_M} = \quad \text{keV}$$



Un électron (particule β^-) produit **8** à 10 fois plus de photons qu'une particule α à même énergie. La position des raies alpha converties devrait donc être déplacée de :

$$E_{ic} = E_{\alpha} + kE_{\text{électron}}$$

Exemple pour la raie alpha principale convertie sur les couche L et M :

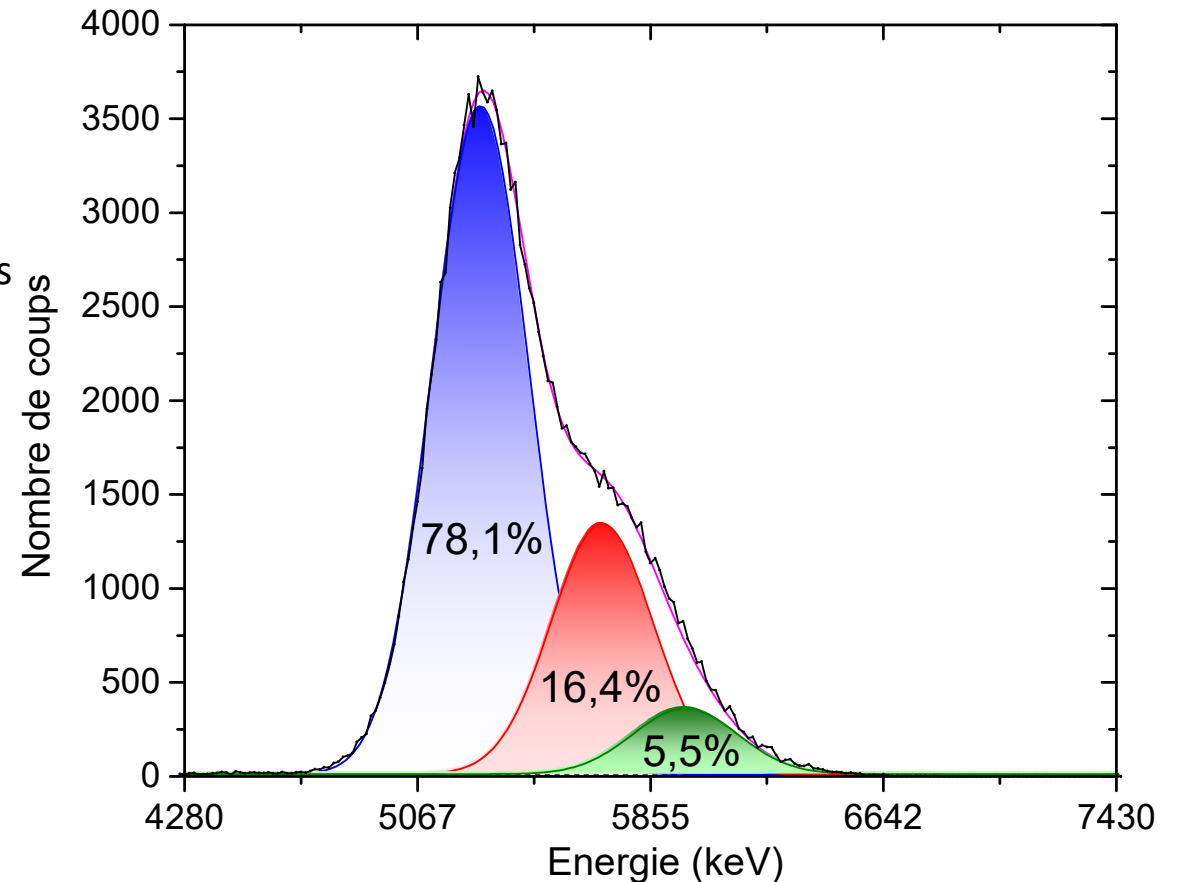
$$E_{ic} = 5275 + 8 \times \quad = \quad \text{keV}$$

$$E_{ic} = 5275 + 8 \times \quad = \quad \text{keV}$$

Avec des intensités respectives de :

$$I_{ic,L} = I_{ic} \times \frac{\alpha_L}{\alpha_T} =$$

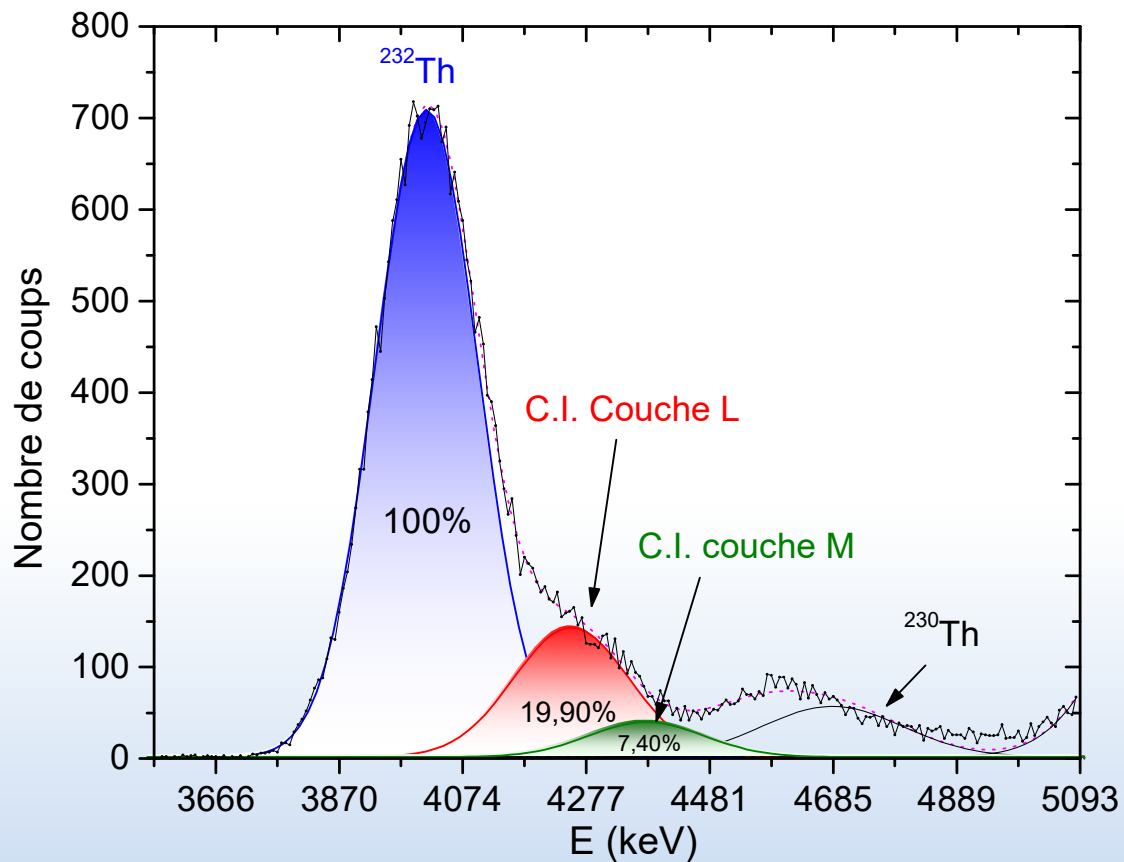
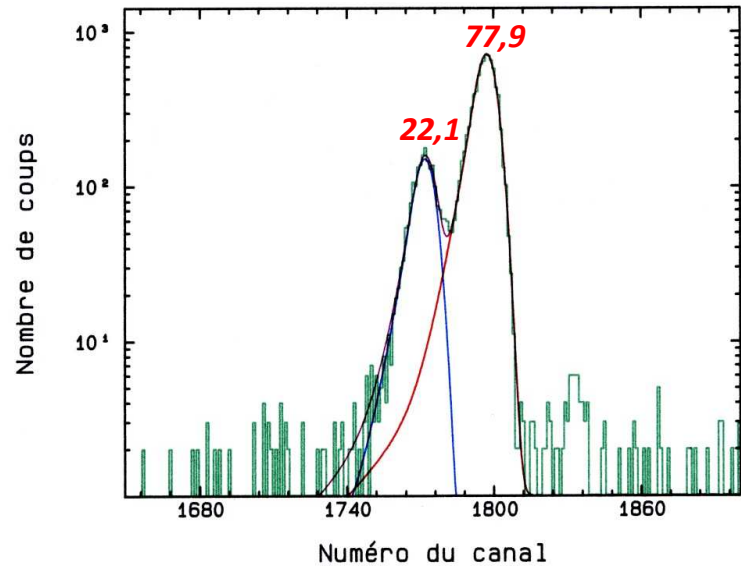
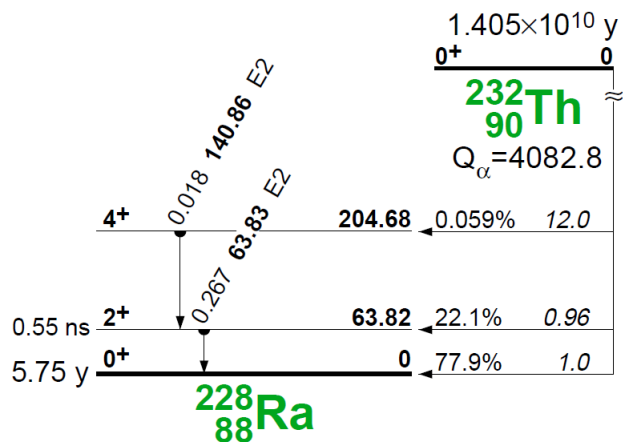
$$I_{ic,M\dots} = I_{ic} \times \left(1 - \frac{\alpha_L}{\alpha_T}\right) =$$



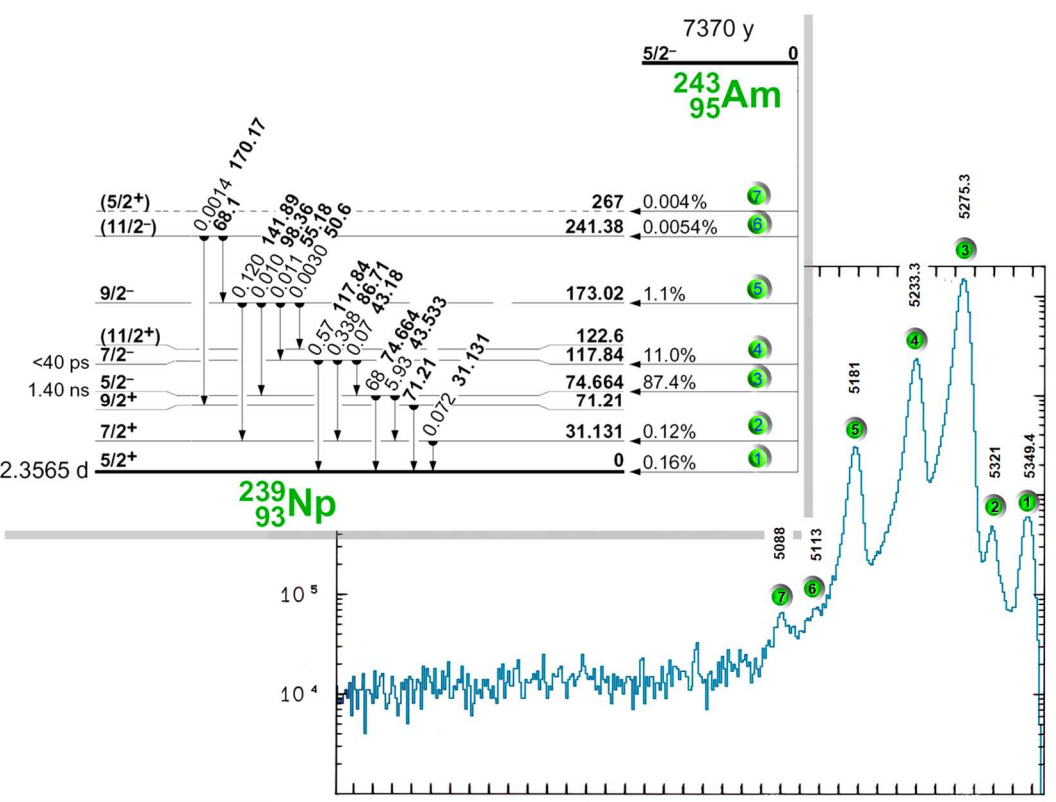
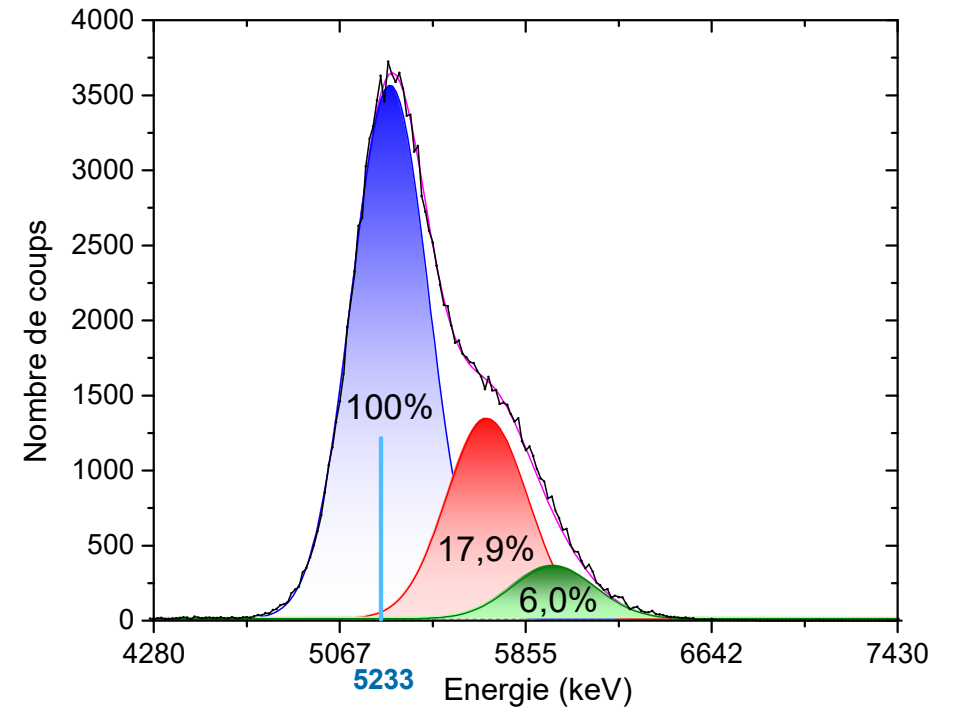
Ces intensités ne sont pas exactes car toutes les transitions n'ont pas été prises en compte

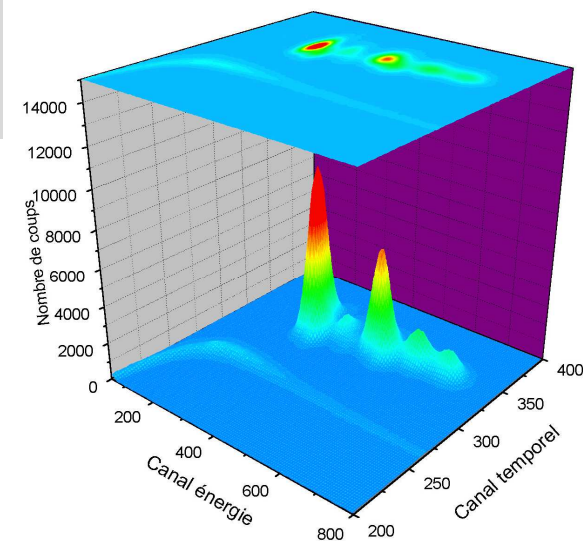
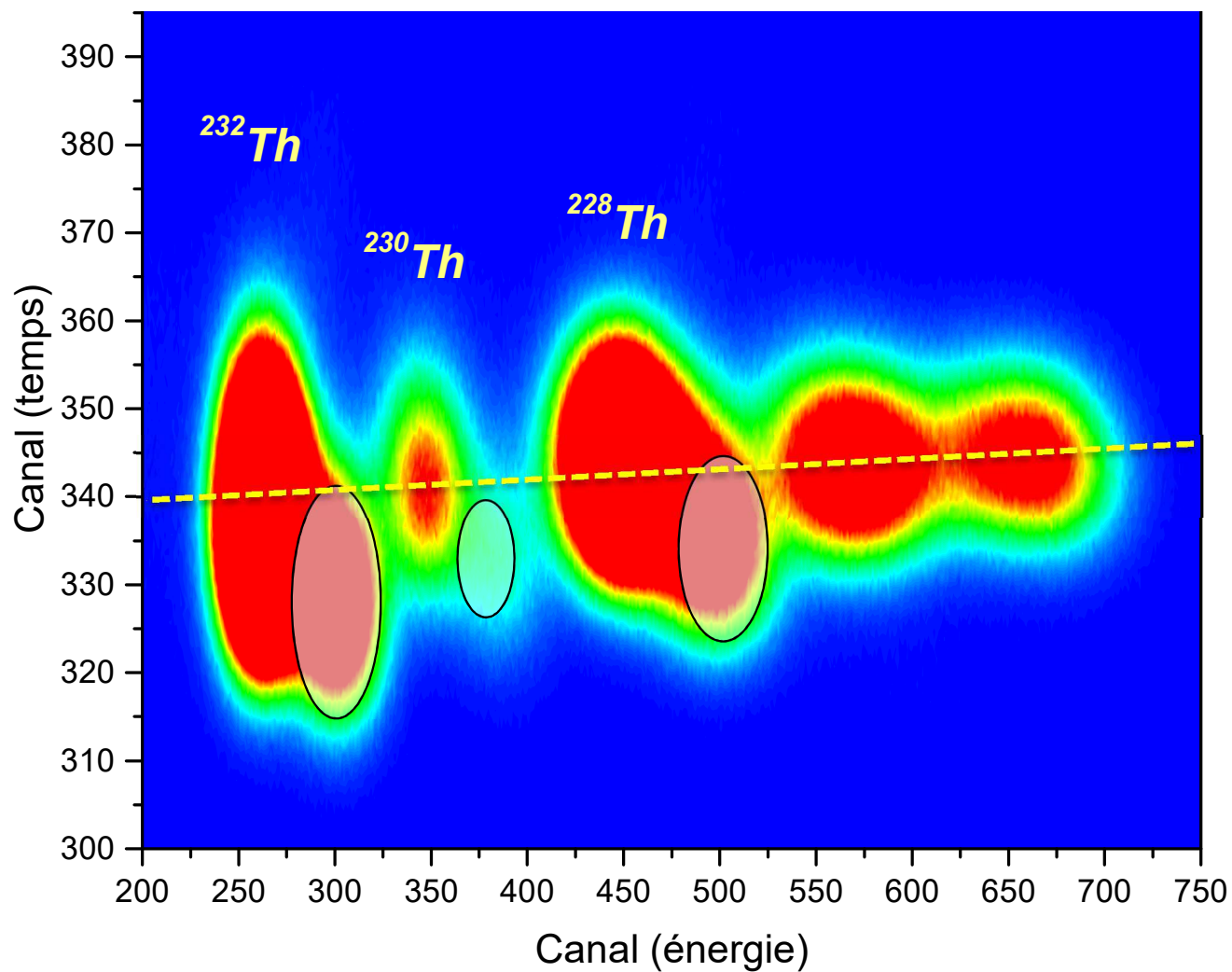
Isotope	E_α (keV)	$I_\alpha^{abs.}$ (%)	$I_\alpha^{rel.}$ (%)	Isotope	E_α (keV)	$I_\alpha^{abs.}$ (%)	$I_\alpha^{rel.}$ (%)
^{238}U	4196	76,16	100	^{239}Pu	5157	88,54	100
Couche L	4388	15,17	19,16	Couche L	5349	8,32	9,40
Couche M	4512	5,67	7,16	Couche M	5480	3,14	3,55
^{234}U	4775	71,70	100	^{240}Pu	5168	72,94	100
Couche L	4988	20,60	28,73	Couche L	5313	19,86	27,23
Couche M	5112	7,70	10,74	Couche M	5448	7,20	9,87
^{232}U	5320	68,65	100	^{236}Pu	5768	68,37	100
Couche L	5566	22,82	33,24	Couche L	5933	23,41	34,24
Couche M	5690	8,53	12,43	Couche M	6064	8,22	12,02
^{232}Th	4010	78,56	100	^{243}Am	5233	12,10	–
Couche L	4307	15,63	19,90		5275	68,65	100
Couche M	4386	5,81	7,40	Couche L	5275	14,44	17,88
				Couche M	5698	4,81	5,96
^{230}Th	4688	76,97	100				
Couche L	5011	16,81	21,40				
Couche M	5128	6,22	7,92				
^{228}Th	5423	74,00	100				
Couche L	5865	18,98	25,65				
Couche M	5982	7,02	9,49				

Aupiais, J., Deconvolution of alpha liquid scintillation spectra for quantitative analysis of actinide elements in water samples. *Radiochim. Acta* **2004**, 92 (3), 125-132.

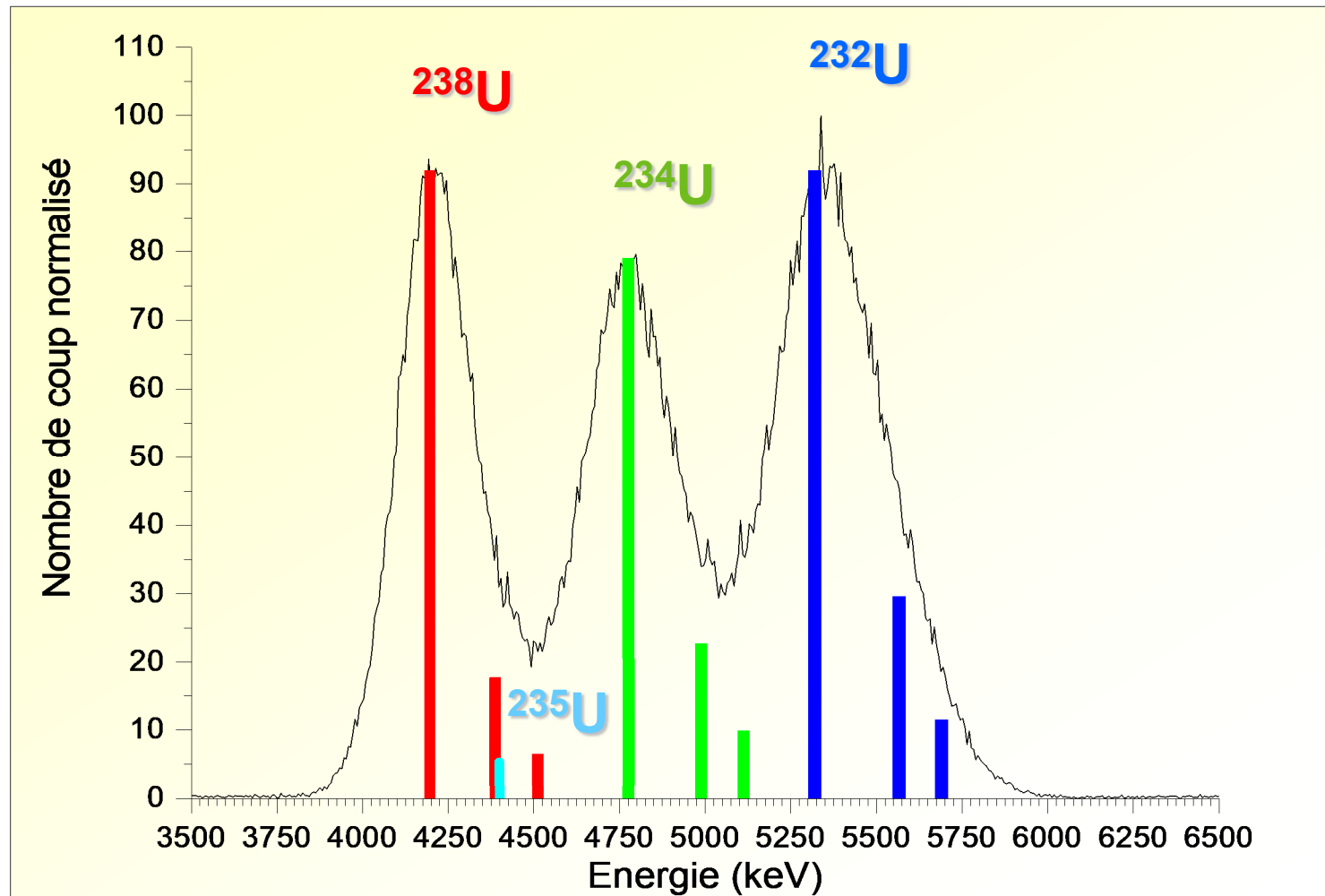


5233	12,10
5275	68,65
5275	14,44
5698	4,81

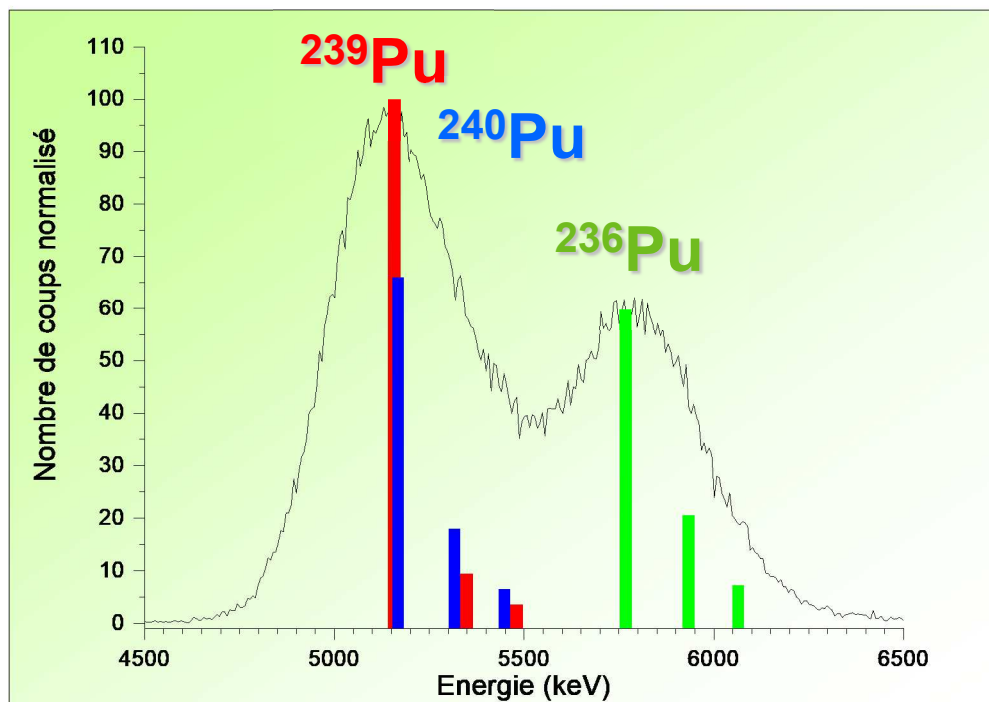




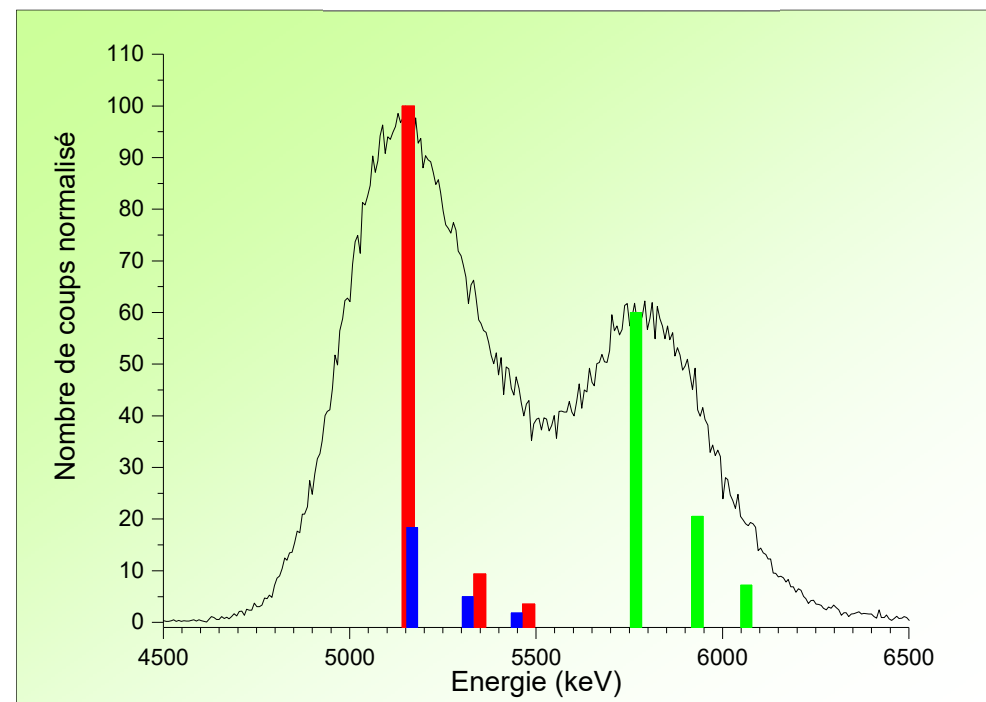
Combinaison linéaire de 2 signaux de temps de vie différent (celui des α et celui des β)

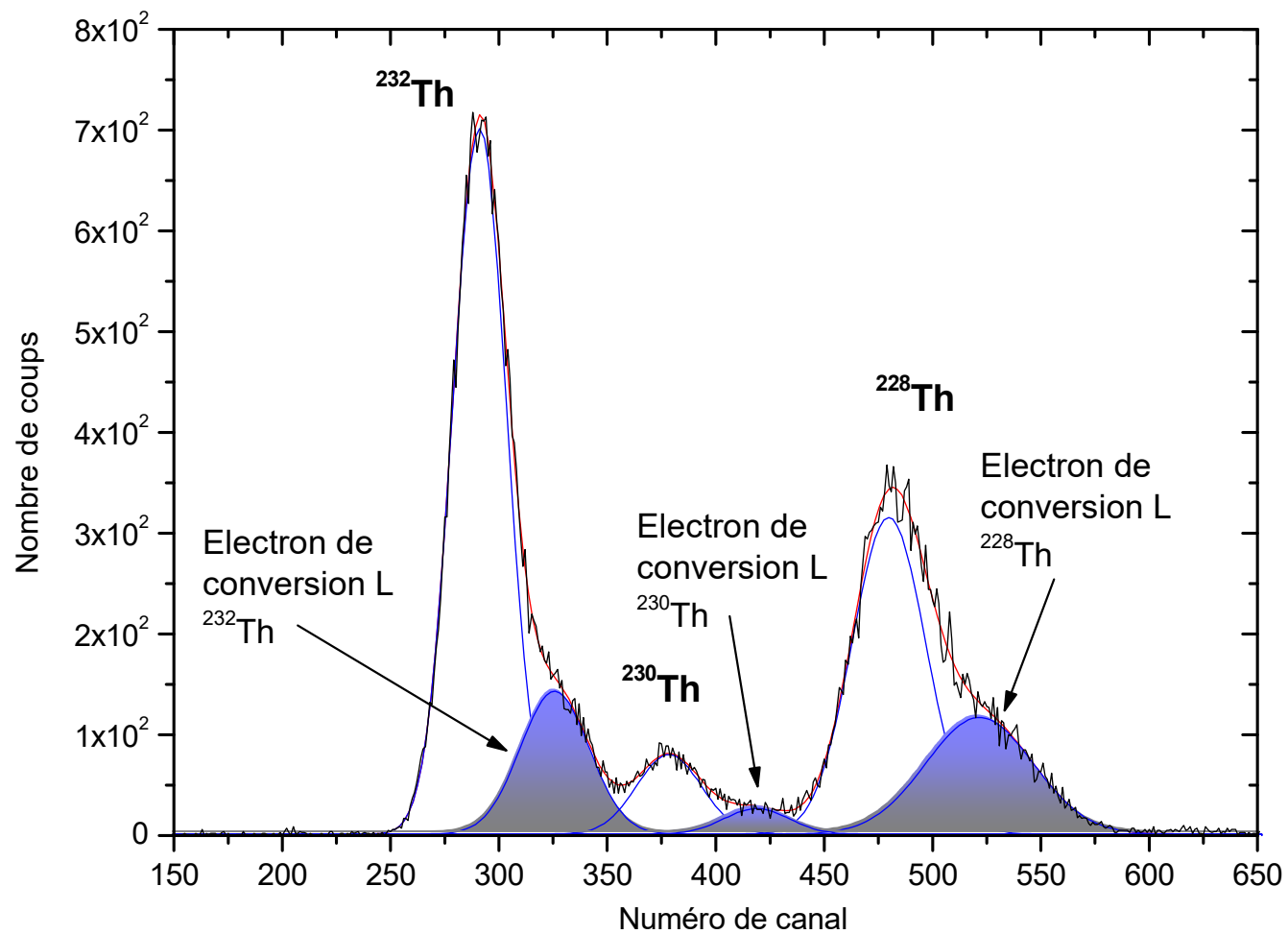


Retombées mondiales



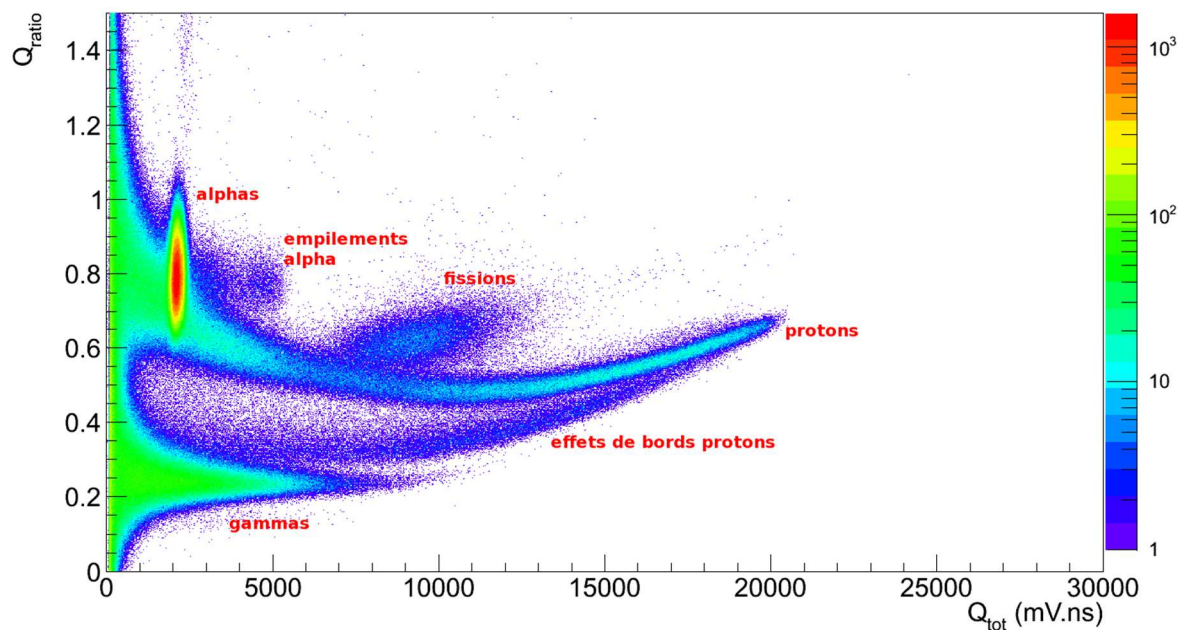
Qualité militaire



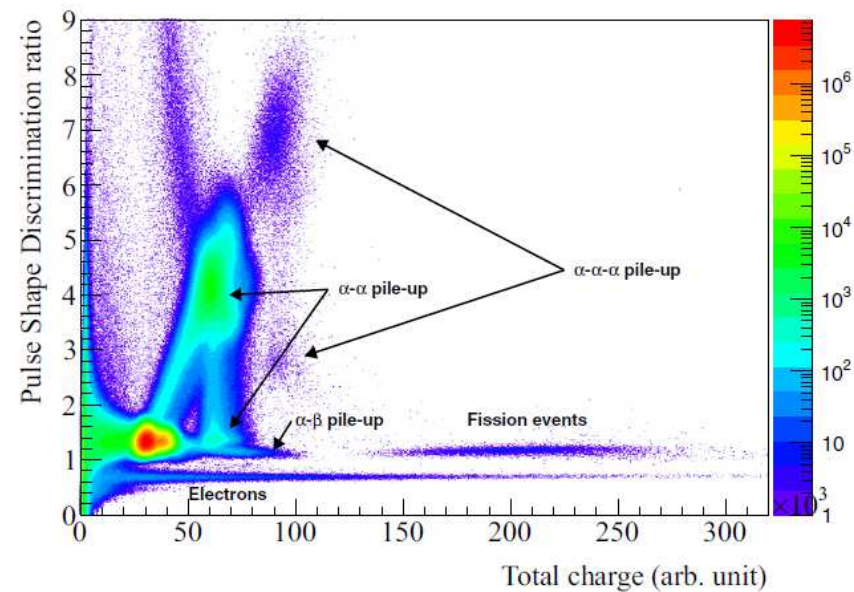


Remarque : les conversions sur la couche M ont été omises pour les 3 isotopes du thorium

Fissions induites par neutrons rapides



Histogramme de discrimination : irradiation par des neutrons de 18 MeV d'une solution de ^{252}Cf (2 kBq), solvant DIN

Fission spontanée ^{242}Pu 

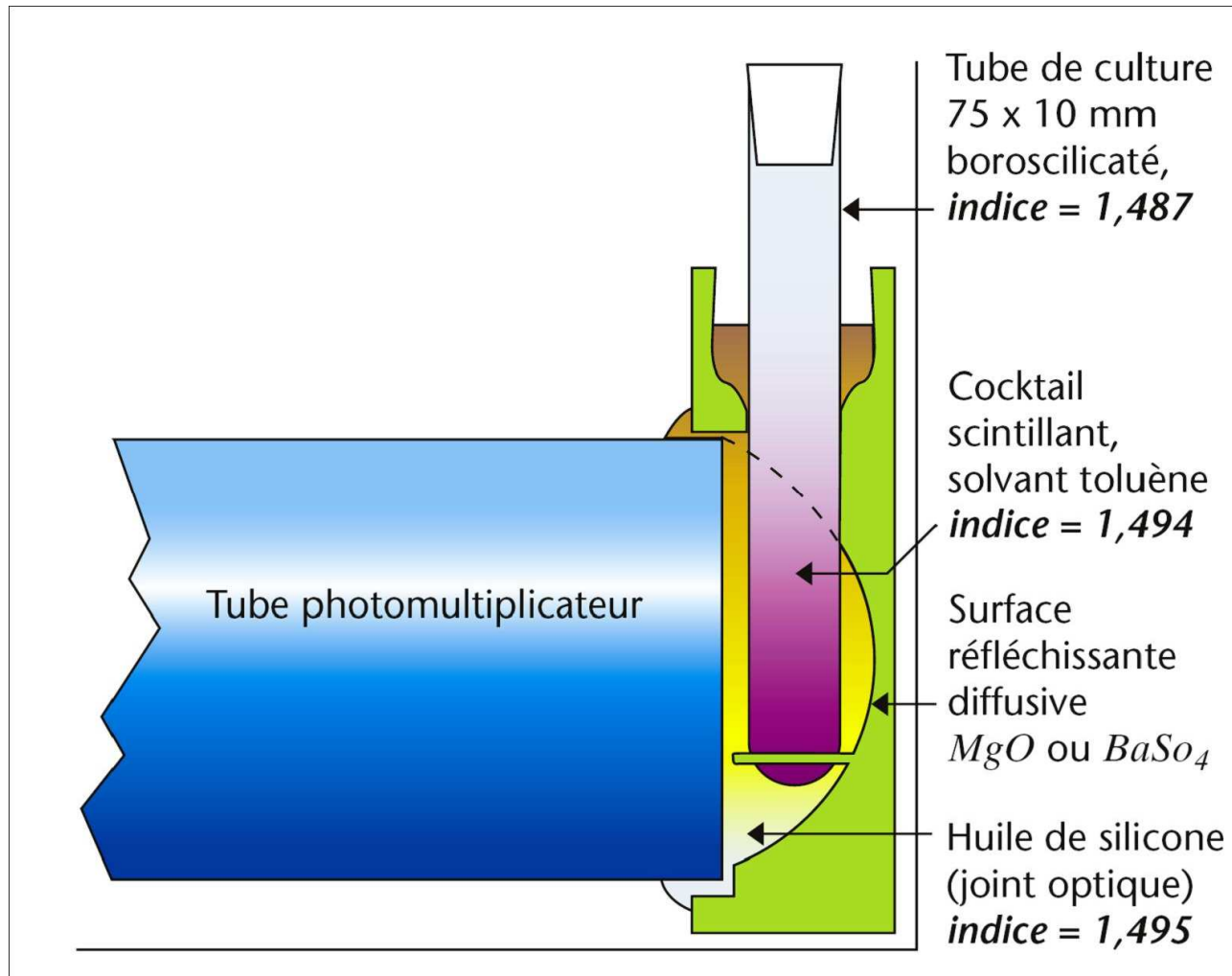
Isotope	Ce travail	Évaluation [6]	État de l'art
^{240}Pu	$1,132(8) \times 10^{11}$	$1,140(10) \times 10^{11}$	$1,165(13) \times 10^{11}$
^{242}Pu	$6,77(7) \times 10^{10}$	$6,77(6) \times 10^{10}$	$1,132(8) \times 10^{10}$
^{252}Cf	85,245(270)	86(1)	85,54(22)

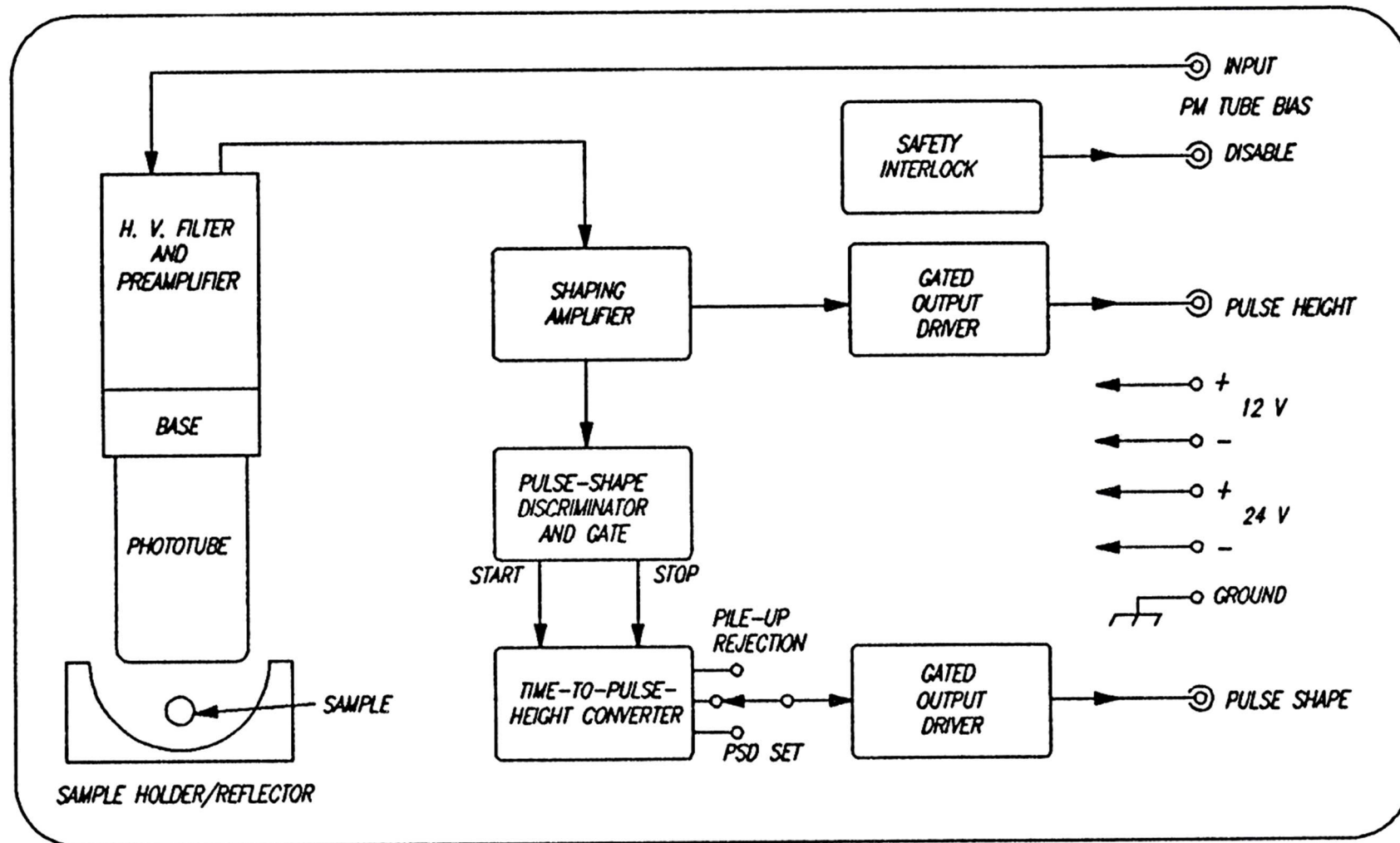
Béliet G. et al, High-precision spontaneous fission branching-ratio measurements for $^{240,242}\text{Pu}$ and ^{252}Cf isotopes, *Phys. Rev. C* 98 (2018) 034612

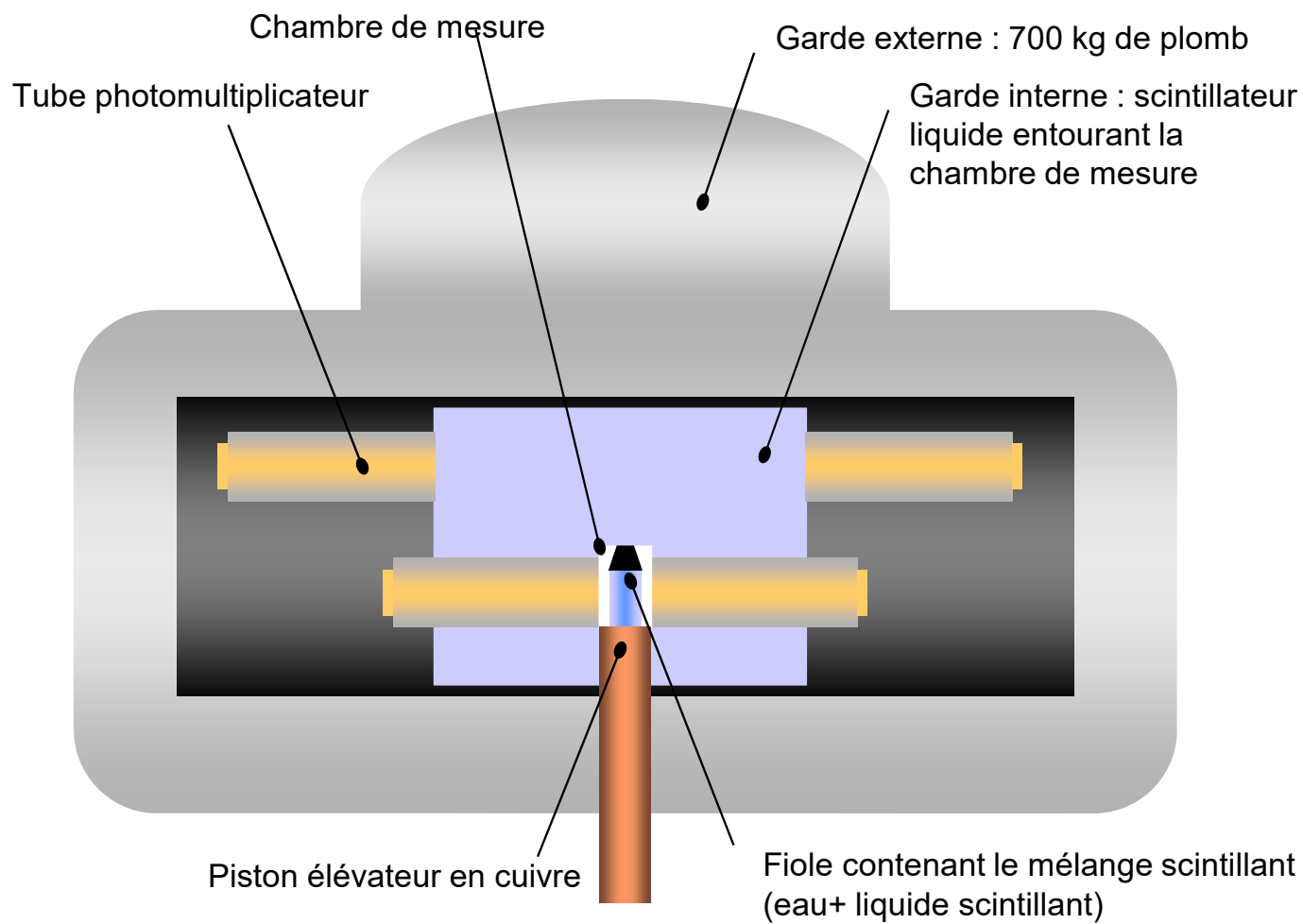


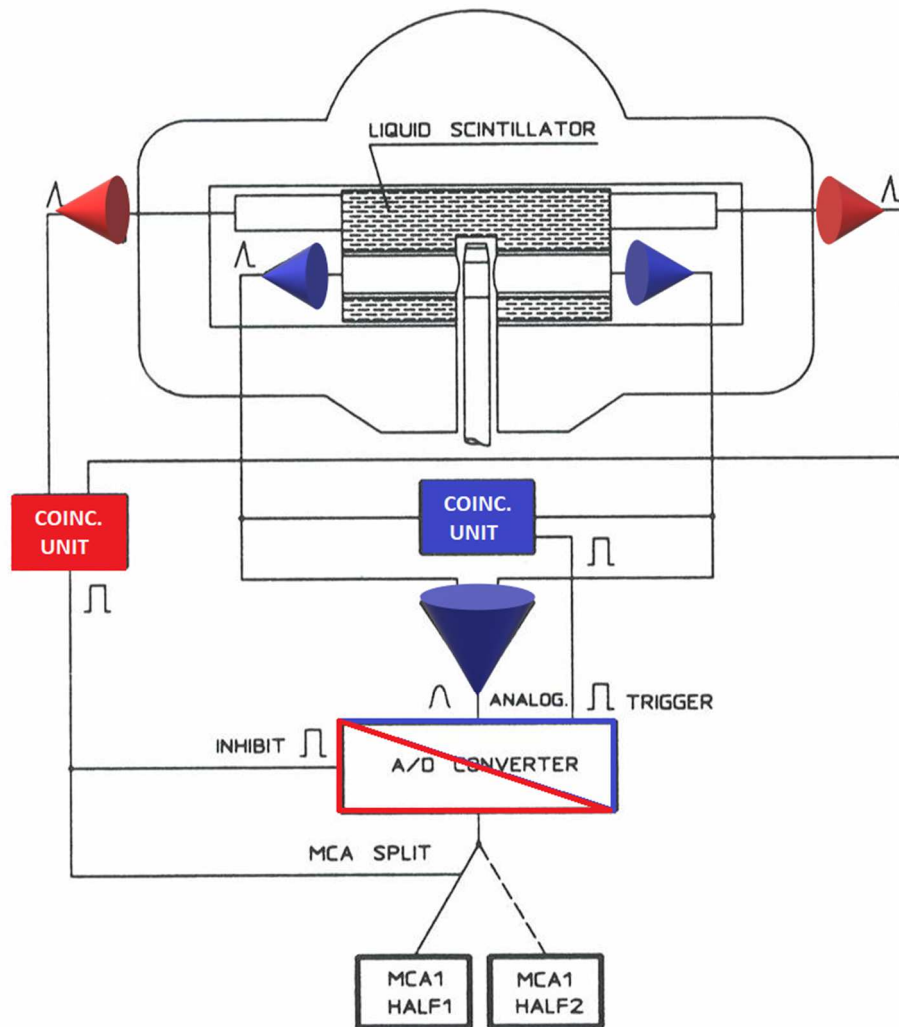
APPAREILS

Commissariat à l'énergie atomique et aux énergies alternatives - www.cea.fr

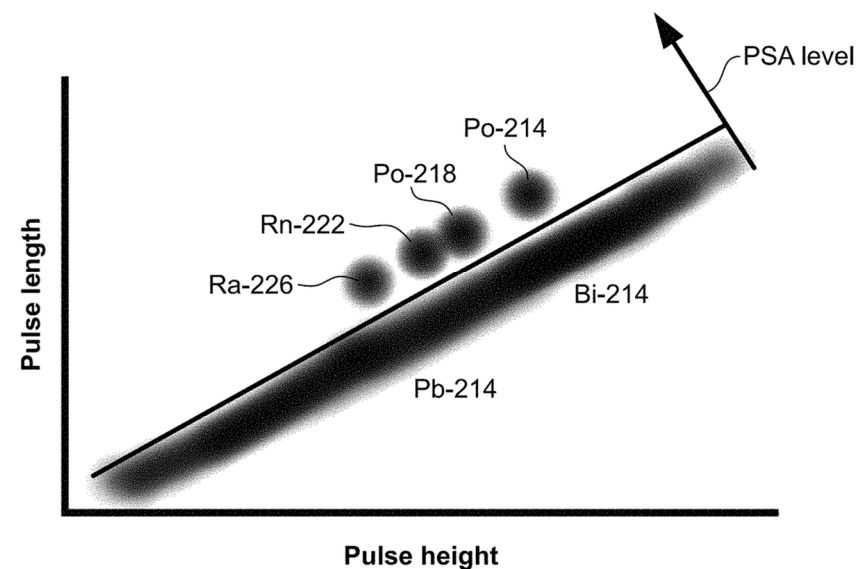






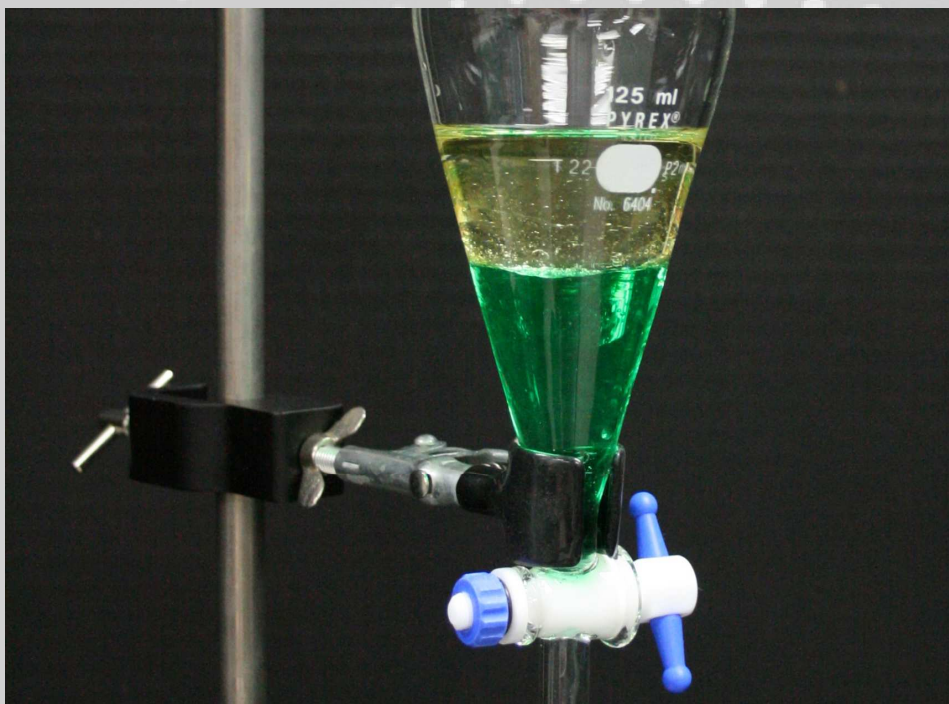


PSA = Pulse Shape Analysis



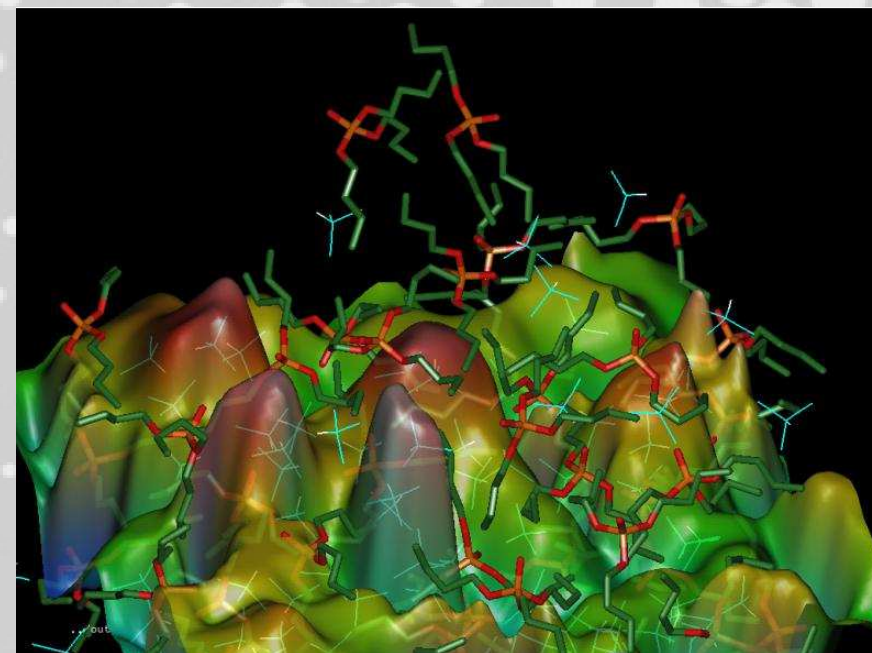
Discrimination α/β

Le PSA intègre la traîne du pulse de scintillation et compare la valeur obtenue à l'intégrale totale du signal.



Par PRHaney — Travail personnel, CC BY-SA 3.0,
<https://commons.wikimedia.org/w/index.php?curid=9472662>

EXTRACTION LIQUIDE-LIQUIDE



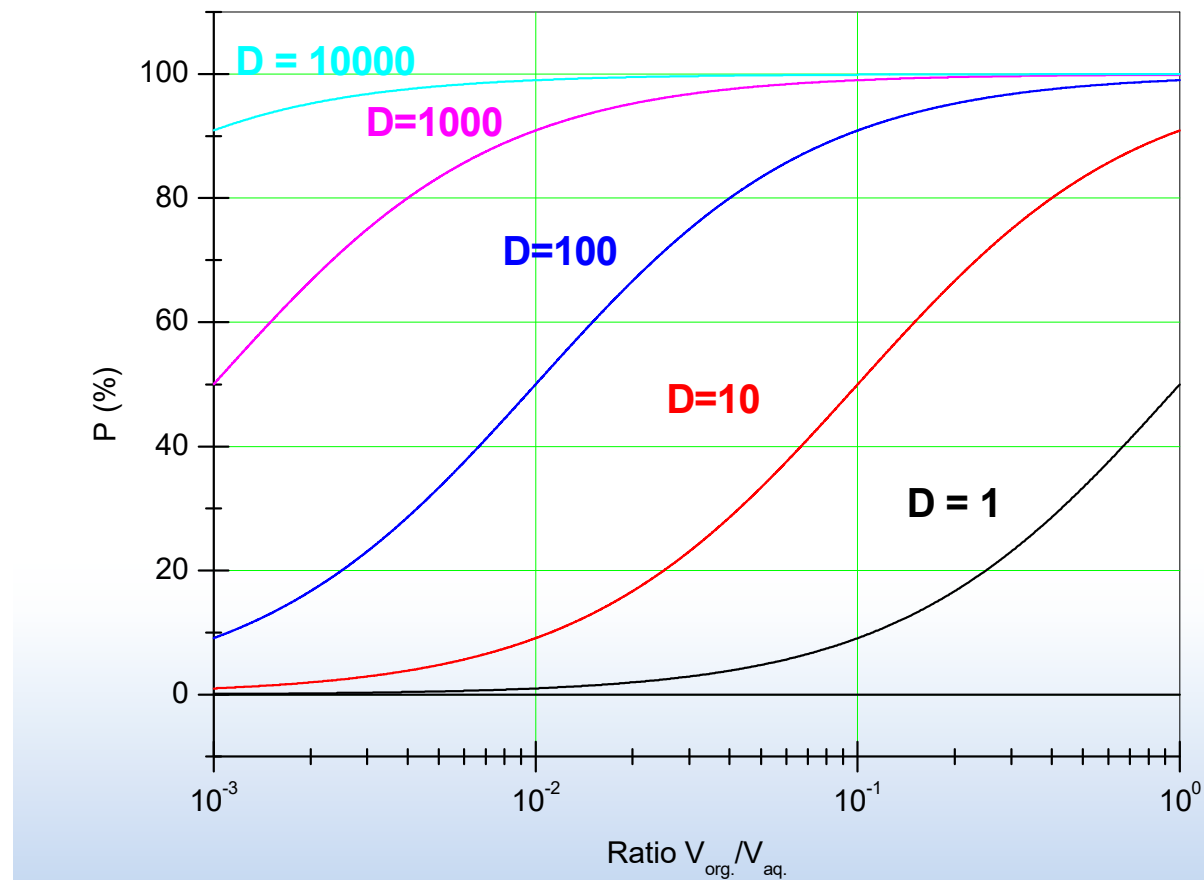
M. Baaden, M. Burgard et G. Wipff: "TBP at the water-oil interface: the effect of TBP concentration and water acidity investigated by molecular dynamics simulations", J.Phys.Chem.B. 105, 2001, 11131-11141

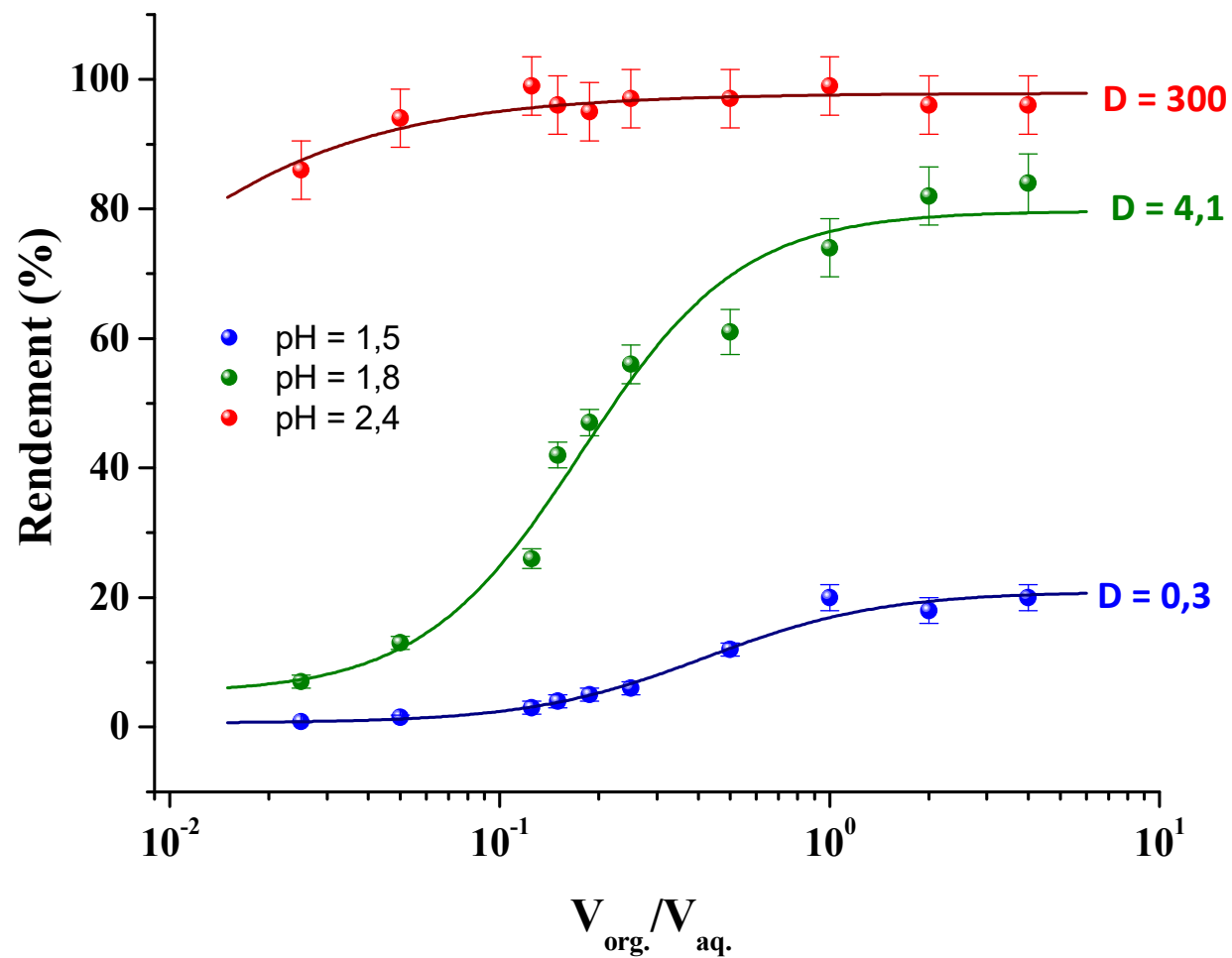
$$P = \frac{D \times \bar{V}}{1 + D \times \frac{\bar{V}}{V}}$$

D : coefficient de distribution du cation

\bar{V} : volume de phase organique

V : volume de phase aqueuse





Dacheux, N.; Aupiais, J., Determination of low concentrations of americium and curium by photon/electron rejecting alpha liquid scintillation. *Anal. Chim. Acta* **1998**, 363, 279-294.

1. RADONS_α : toluène
2. STRONEX_α : éther couronne dicyclohexano-18-couronne-6
3. RADAEX_α : éther couronne dicyclohexano-21-couronne-7 + acide heptanoïque
4. POLEX_α : oxyde de trioctylphosphine
5. THOREX_α : 1-nonyldécylamine en milieu sulfate
6. URAEX_α : tri-*n*-octylamine en milieu sulfate
7. ALPHAEX_α : acide di-2-éthyl-héxylphosphorique

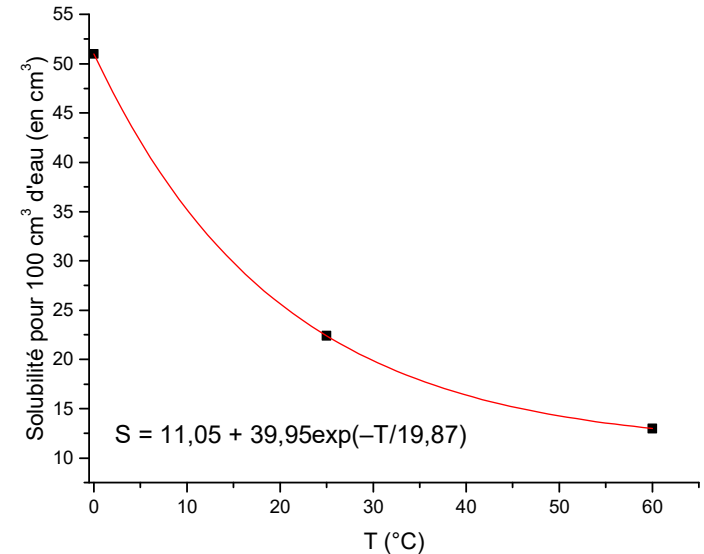
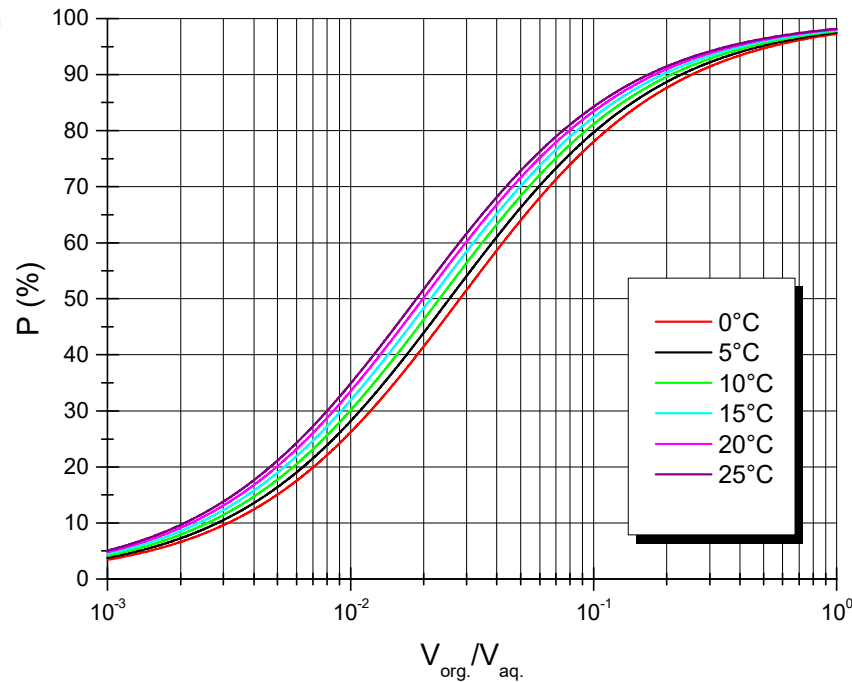
Ce cocktail n'est pas à proprement parlé un cocktail extractant car basé sur la différence de solubilité du radon entre une phase aqueuse et une phase organique

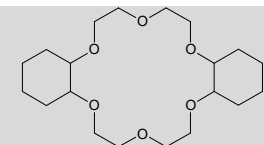
Solubilité du radon dans l'eau @25°C = **22,4** cm³

Solubilité du radon dans le toluène @25°C = **1279,47** cm³

Le coefficient de distribution est de **53,74**

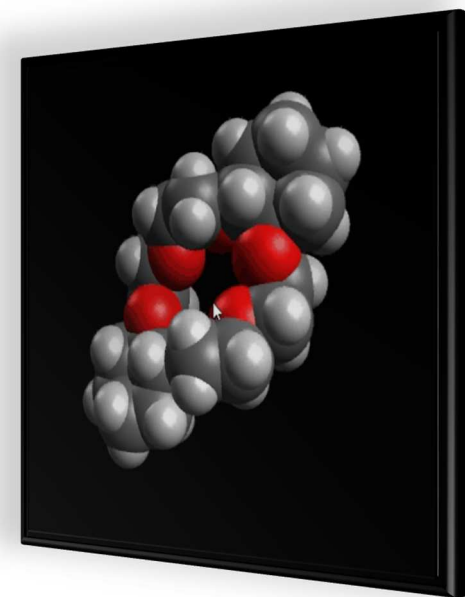
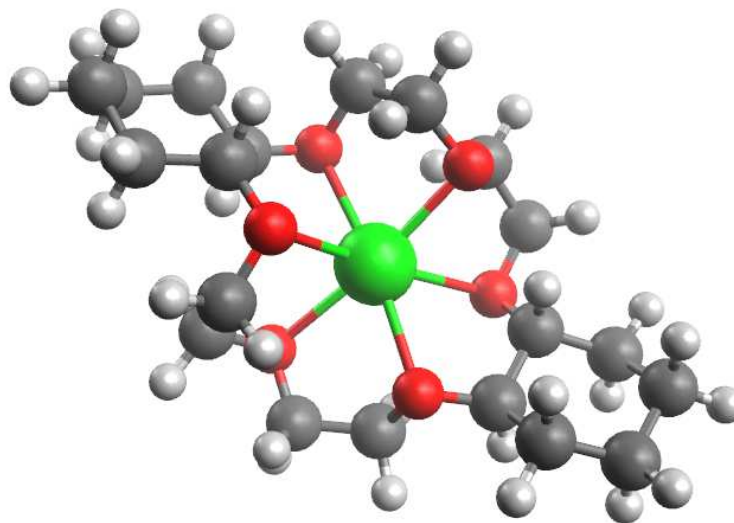
Soit **P = 98,17 %**

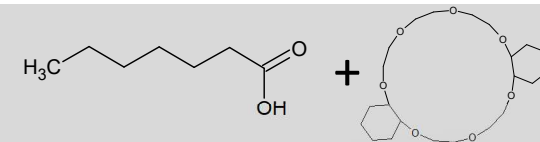




Coefficient de distribution dans HNO₃ 0,2 M (+ acide didodécyl naphthalène sulfonique)

Elément	D
Sr	6000
Ca	80
K	46
Rb	16
Ba	6000





Diapo #94

Conditions :



$$R_{\max} = 80 \%$$

- $V_{\text{aq}} = 6 \text{ ml max}$
- $\text{pH} > 10,0$ (NH_4OH , pas de Na^+)
- Quantification : dopage 2nde aliquote
- C.I. = 2,26%

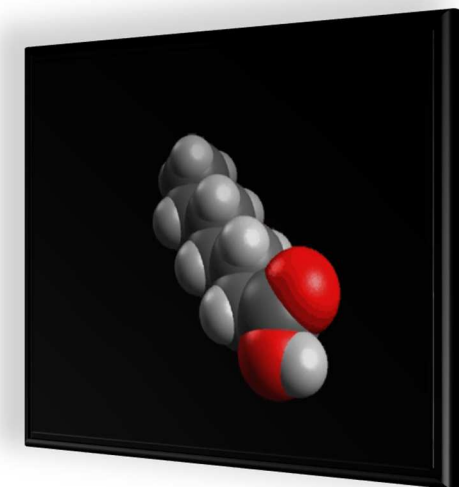
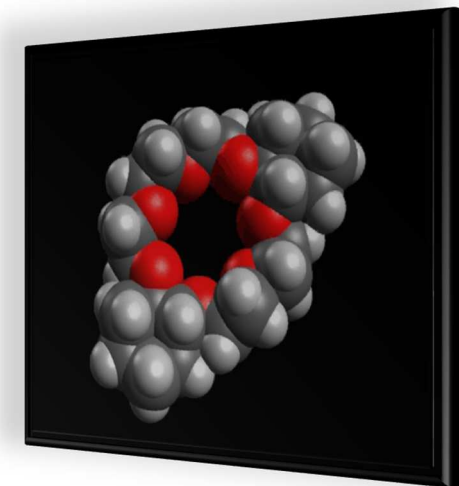
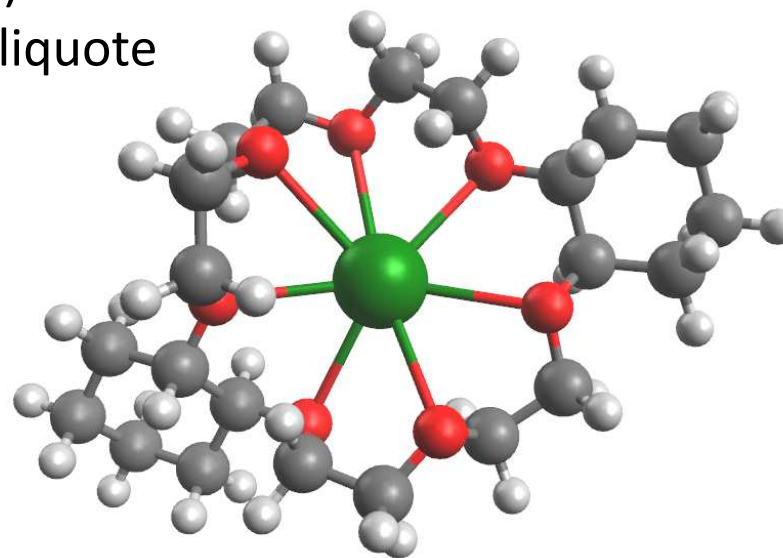
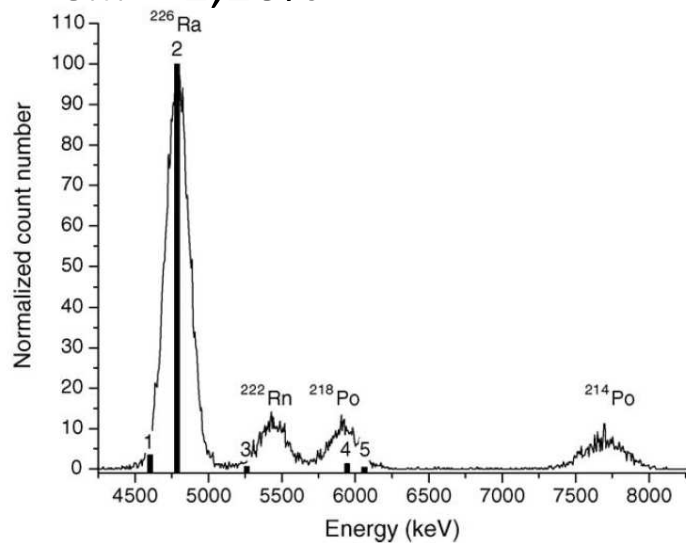
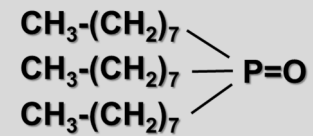
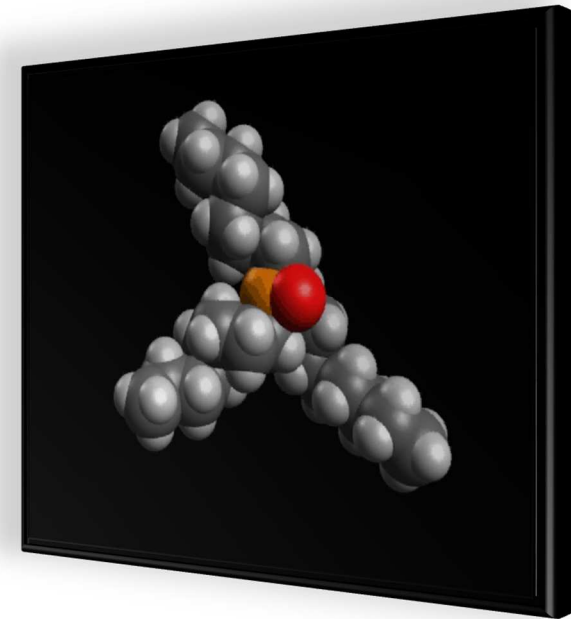
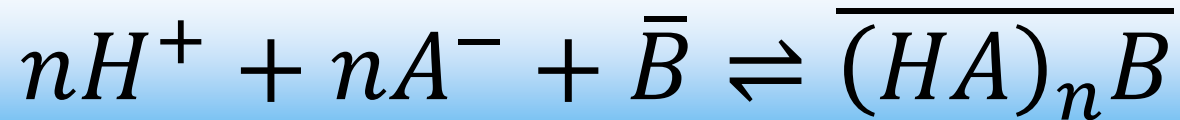
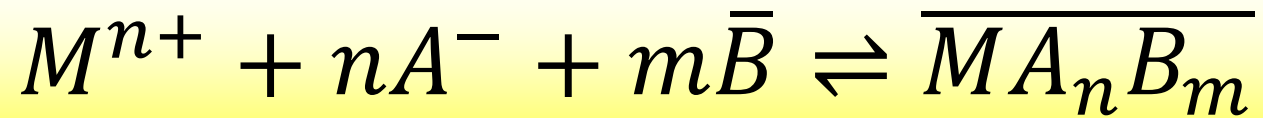


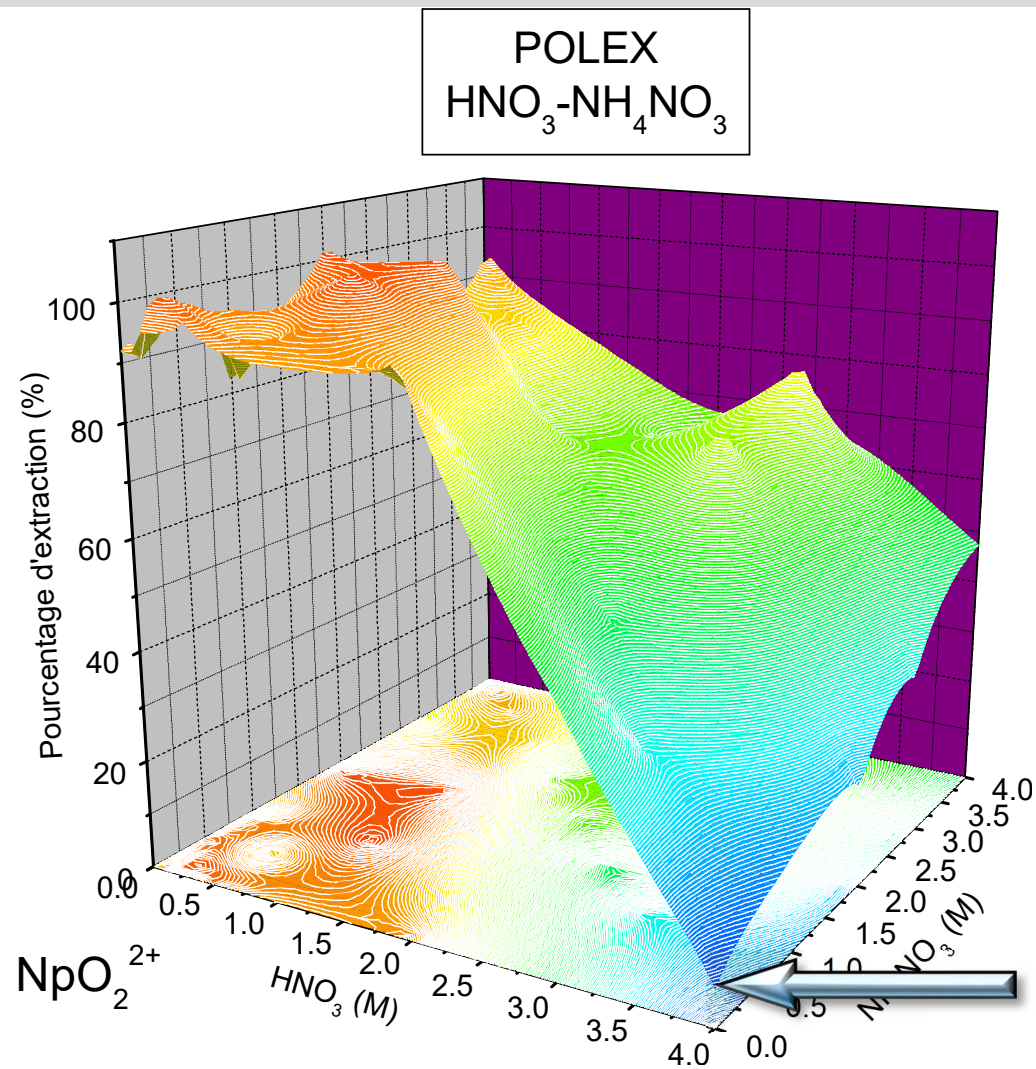
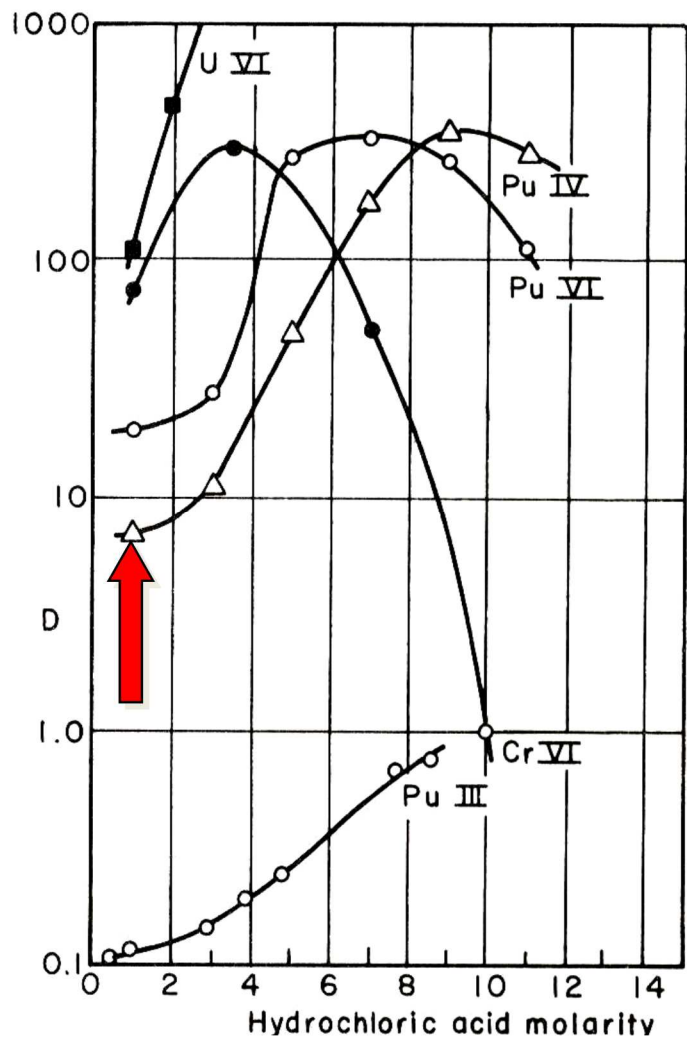
Fig. 1. Typical α -energy spectrum of radium 226 obtained from a natural water (IAEA 425): (1) secondary α -ray at 4685 keV; (2) main α -ray at 4871 keV; (3) secondary α -ray + IC K-shell peak at 5343 keV; (4) secondary α -ray + IC L-shells peak at 6033 keV; (5) secondary α -ray + IC M+...-shells peak at 6144 keV.

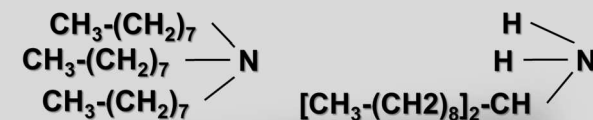
Aupiais, J., Radium measurement in water samples by α -liquid scintillation counting with a/b discrimination. *Anal. Chim. Acta* **2005**, *532*, 199-207.



Mécanismes d'extraction :

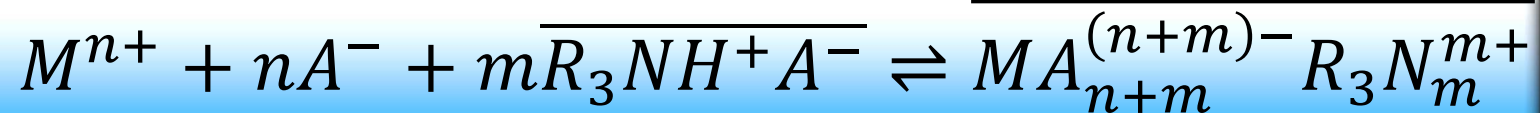
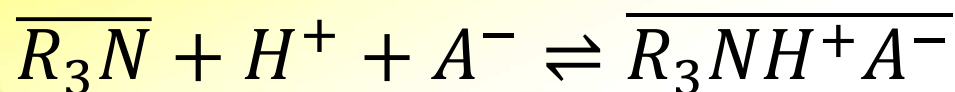
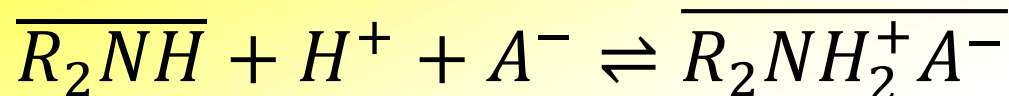
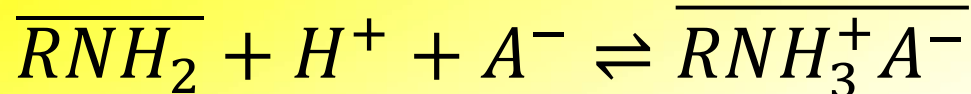






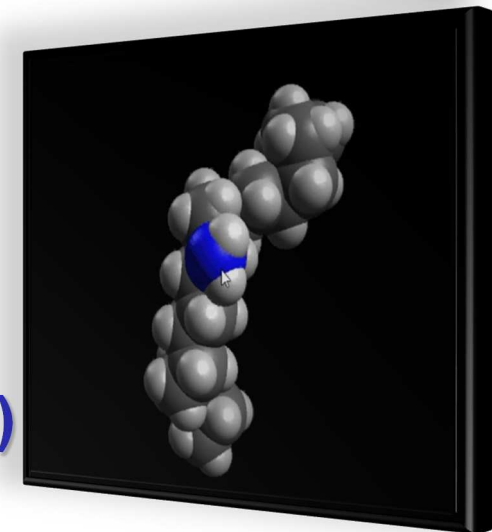
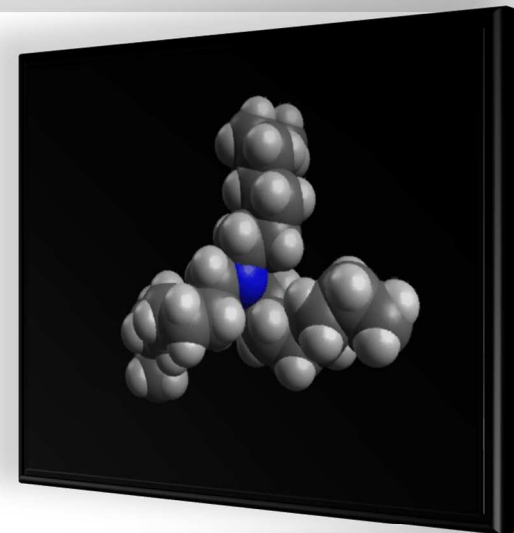
Tri-*n*-octylamine (TNOA)

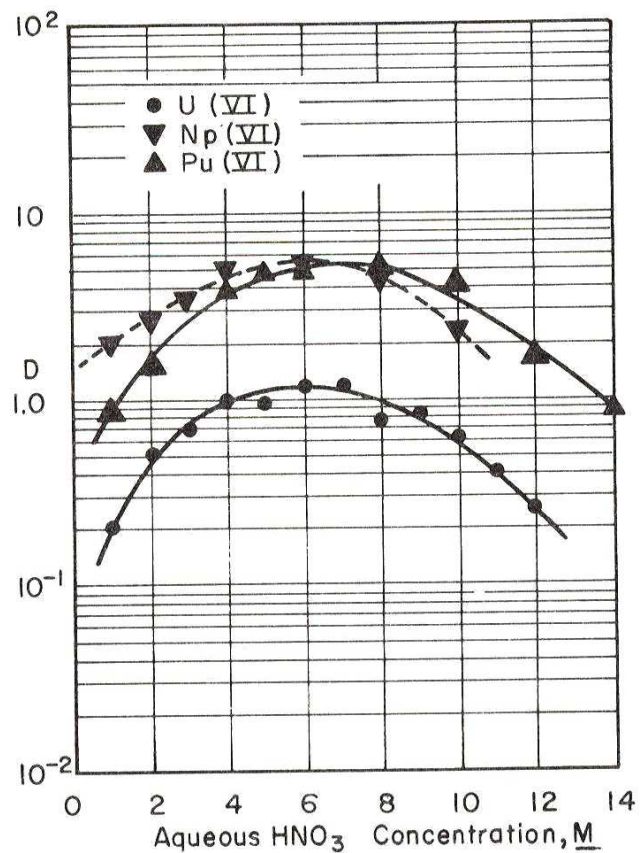
(U)



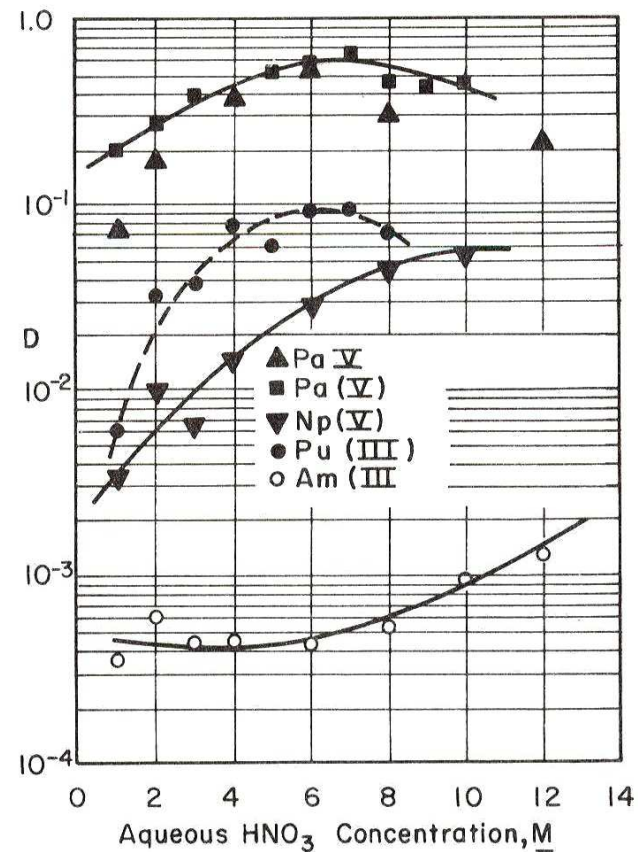
1-Nonyldécylamine (NDA)

(Th)



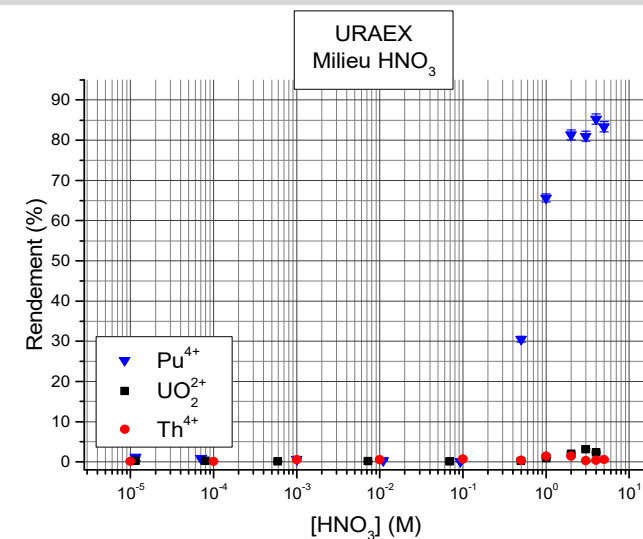
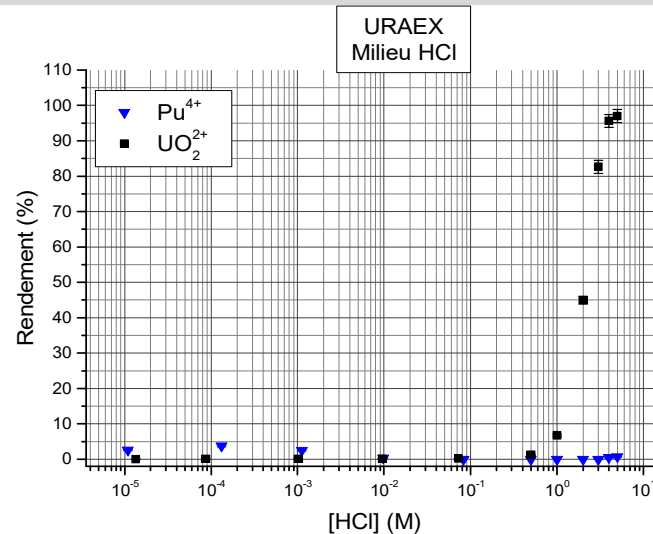
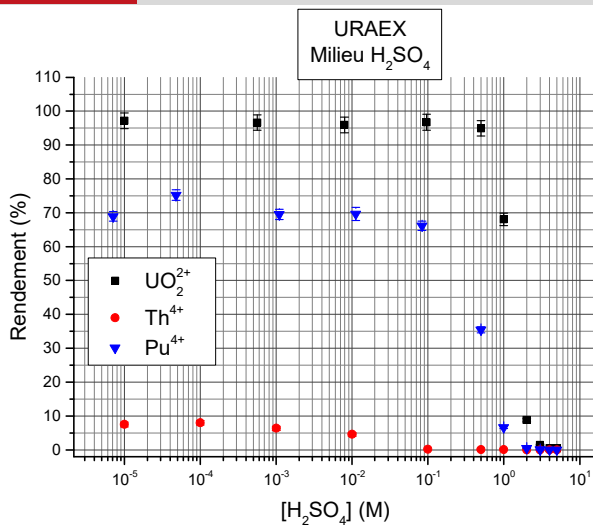


The extraction of the hexavalent actinide nitrates by 10 v/o TOA in xylene.²¹⁹



The extraction of pentavalent and trivalent actinide nitrates by 10 v/o TOA in xylene.²¹⁹

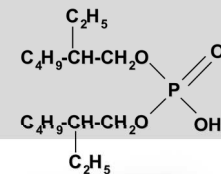
Rendements d'extraction de quelques actinides par URAEX dans divers milieux



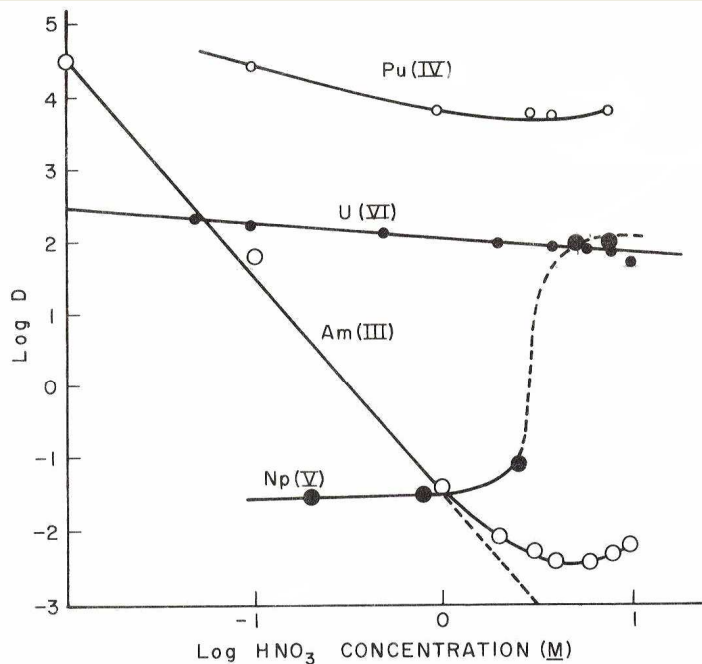
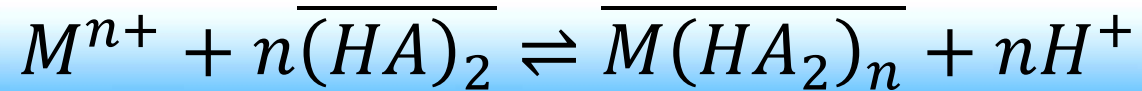
Élément	Extraction	
	faible acidité	forte acidité
U	✓	✗
Th	✗	✗
Pu	✓	✓

Élément	Extraction	
	faible acidité	forte acidité
U	✗	✓
Th	✗	✗
Pu	✗	✗

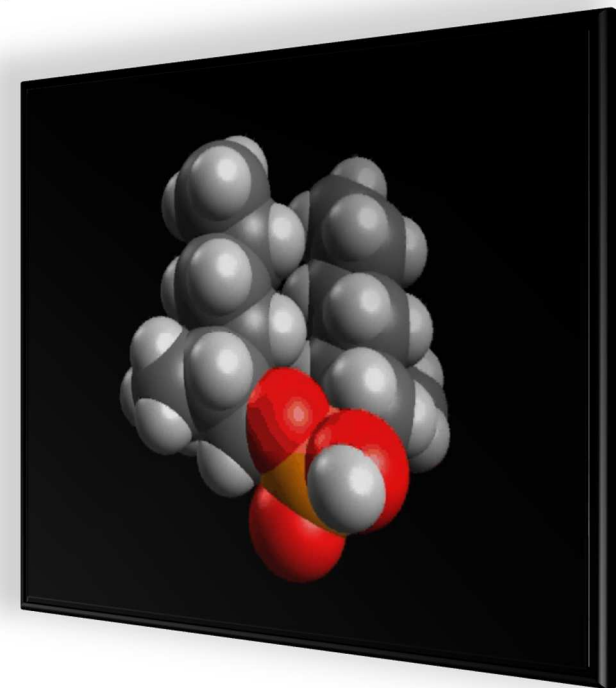
Élément	Extraction	
	faible acidité	forte acidité
U	✗	✗
Th	✗	✗
Pu	✗	✓

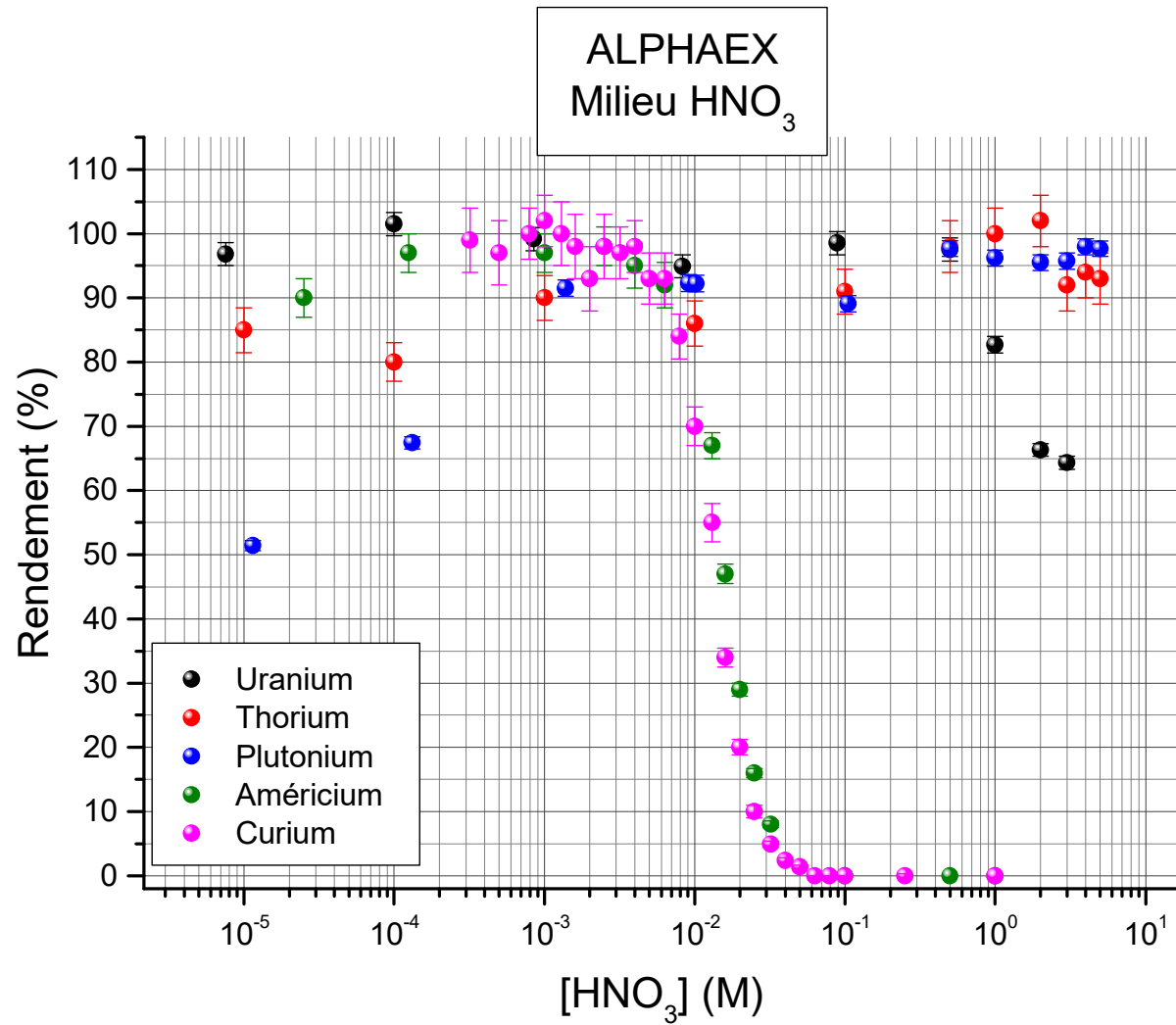


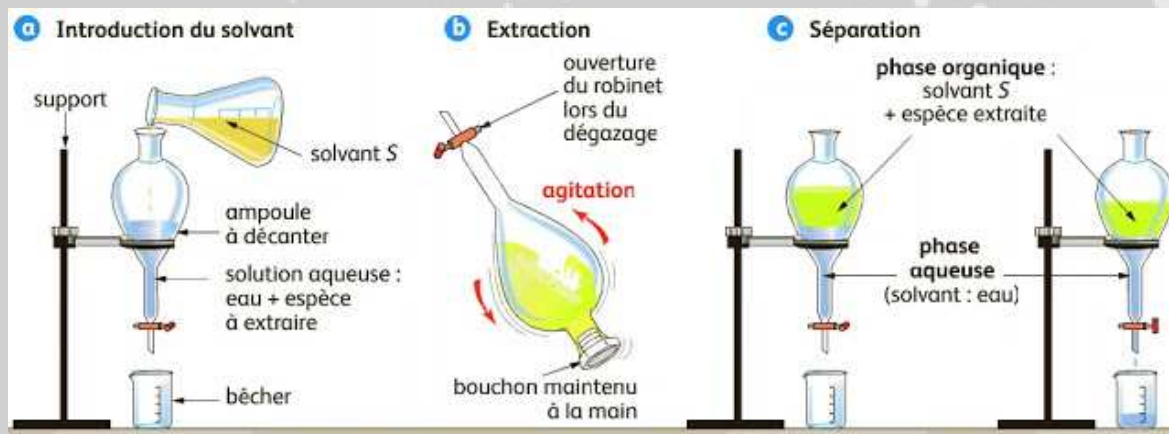
Molécule sélective des actinides aux degrés d'oxydation +3, +4 et +6



Extraction of various actinides into 0.5 M HDEHP (isooctane diluent) from HNO₃ solutions.²³⁸

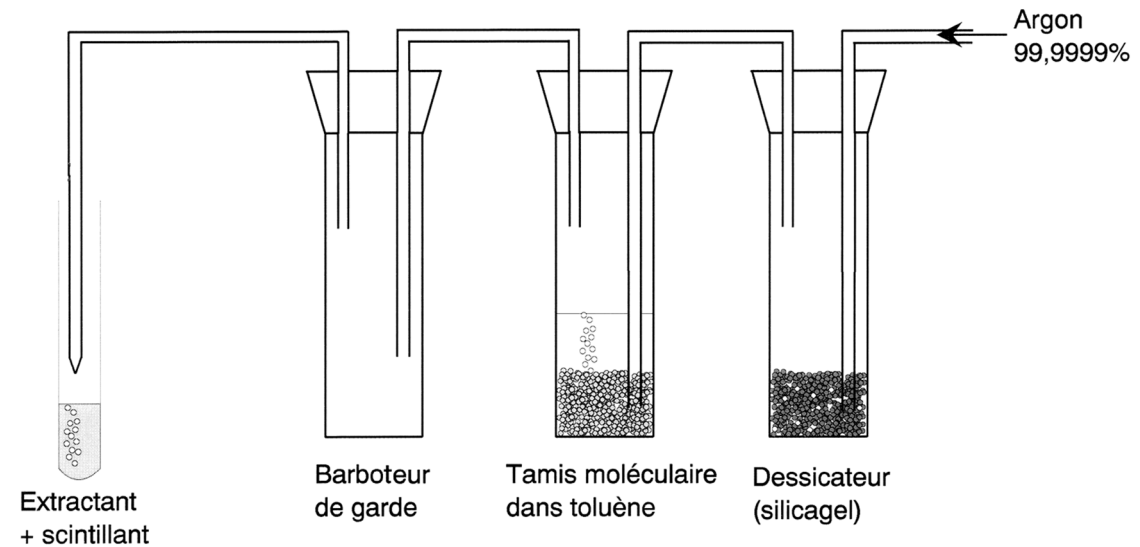


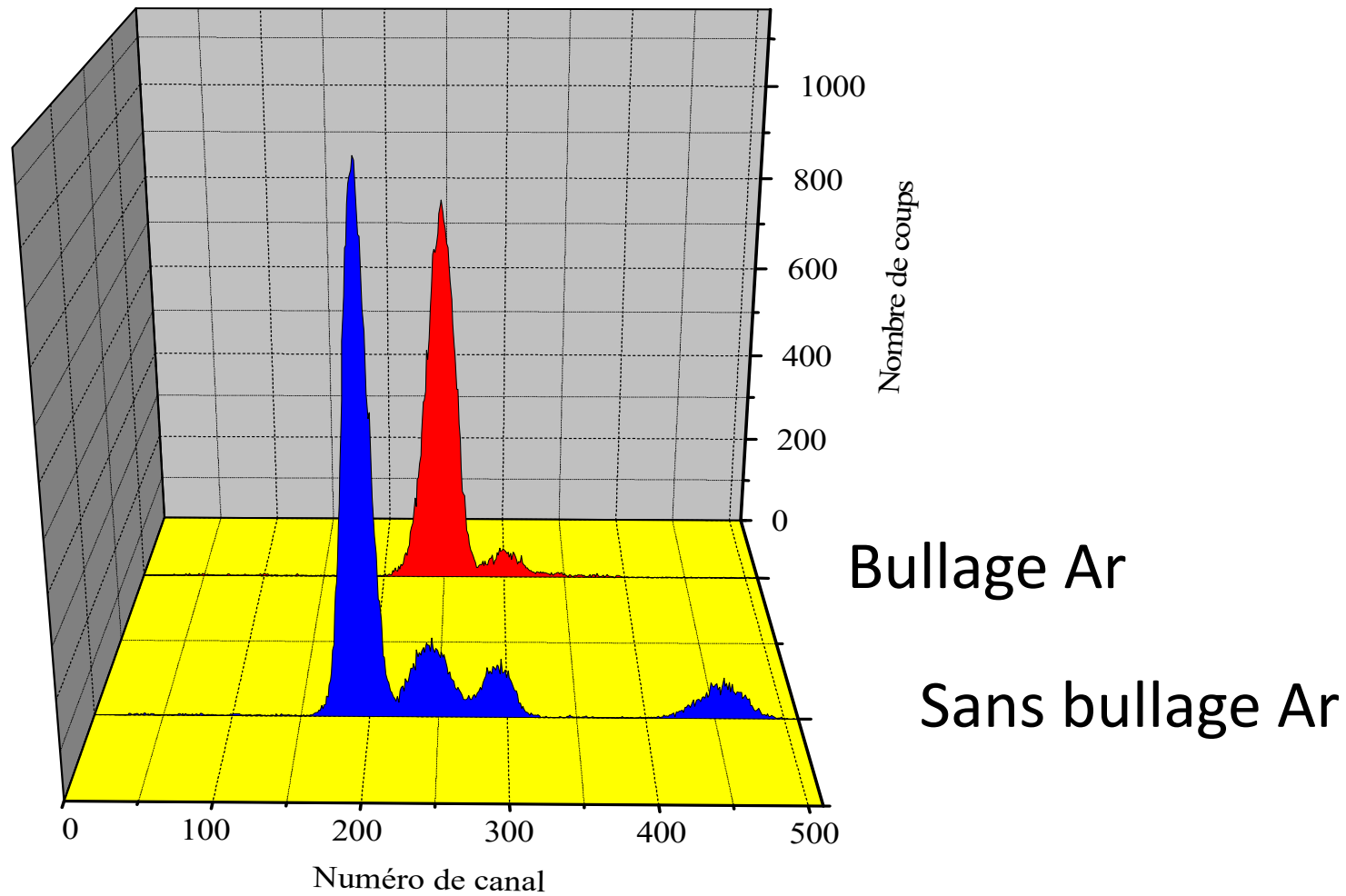


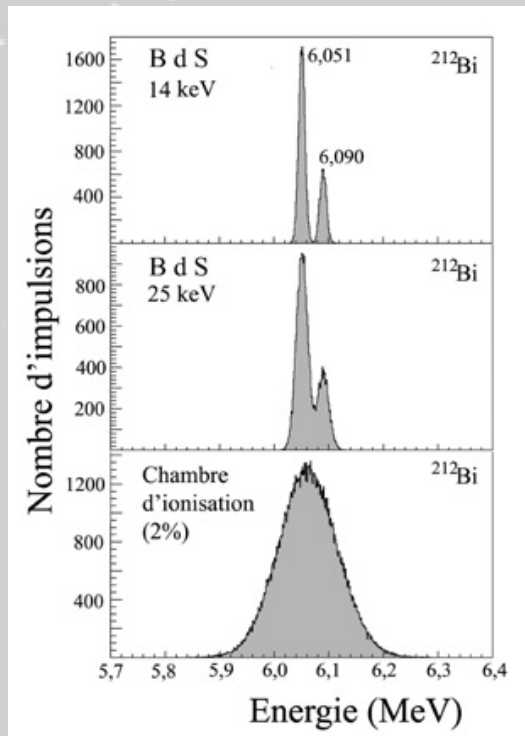


Préparation des échantillons

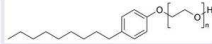


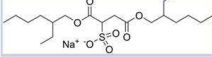
1. Ajustement du milieu
2. Agitation (vigoureuse) des phases
3. Centrifugation (pour séparer les 2 phases)
4. Prélèvement précis d'une aliquote de phase scintillante ($\bar{V} = 1,0 \text{ mL}$)
5. Désoxygénation de la phase scintillante par Ar saturé en toluène ($t = 5 \text{ min}$)
6. Scellement du tube (un simple bouchon suffit si temps de comptage pas trop long cad $t_{\text{comptage}} < 3 \text{ j}$)
7. Comptage dans le spectromètre







Résolution – paramètres influant et optimisation

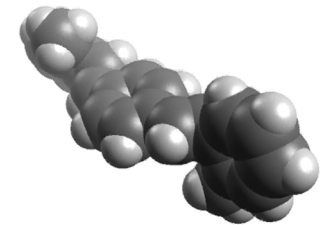
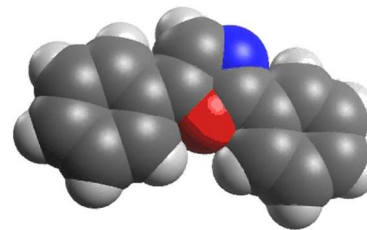
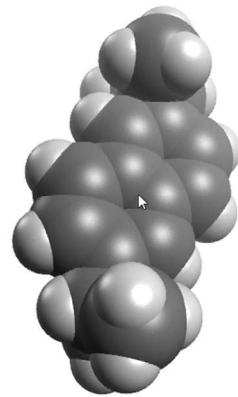
Surfactants		
Surfactant	Molecular structure	Surfactant type
Ethoxylated Alkylphenol		Non-ionic
Alcohol Ethoxylate		Non-ionic
Mono-/Di-Phosphate ester		Anionic
Sodium di-octylsulphosuccinate		Anionic

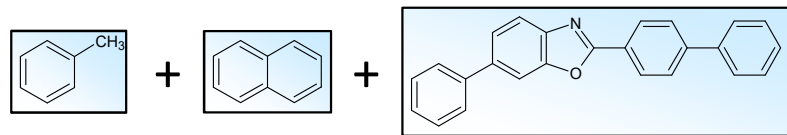
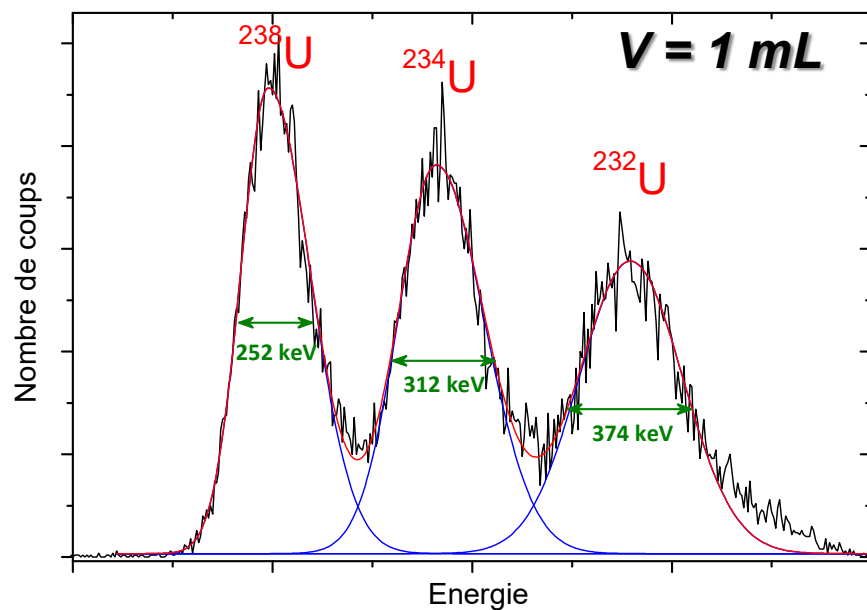
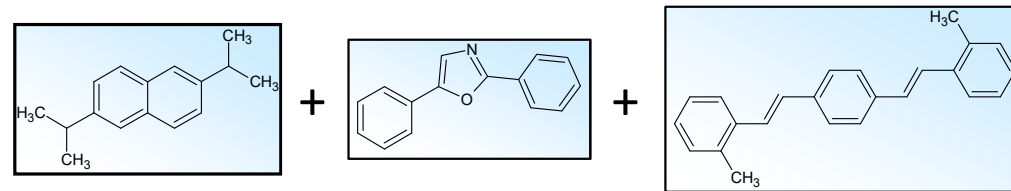
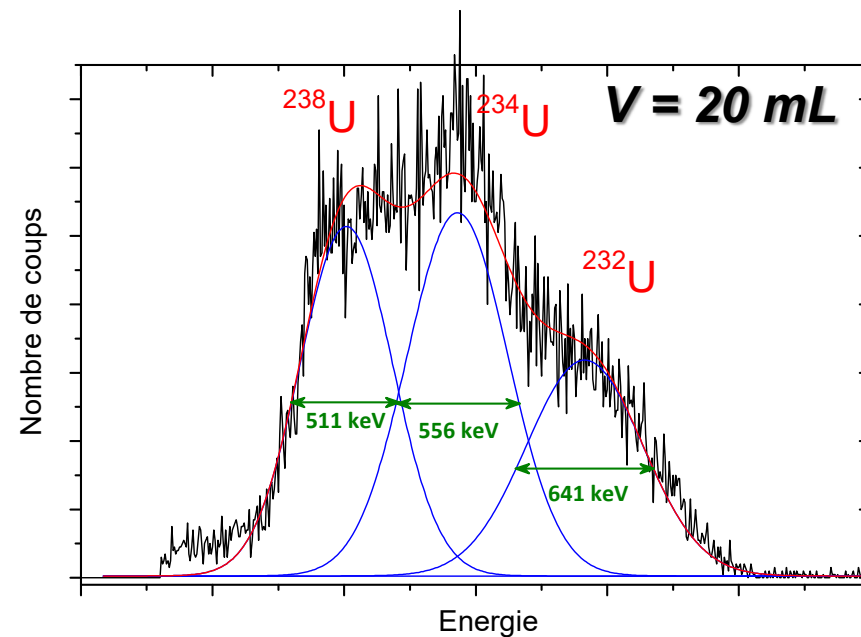
Spectromètre PERALS™

- **Extractant**
 - HDEHP 0,2 M
- **Mélange scintillant**
 - Toluène 7,5 M
 - Naphtalène 1,5 M
 - PBBO 0,01 M

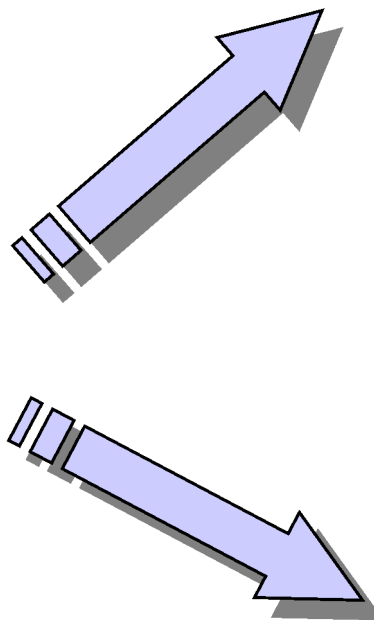
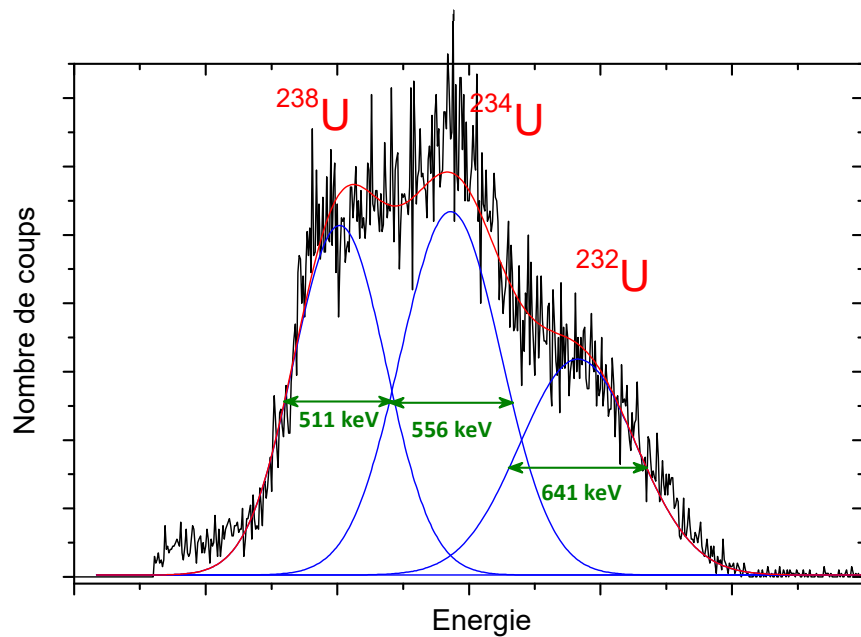
Spectromètre TRICARB™ ...

- **Tensio-actifs**
 - Non-ioniques et anioniques 27-42 %
- **Mélange scintillant**
 - Disopropylnaphtalène 3 - 4,5 M (5 isomères principaux 1,3- ; 1-4-; 1,7- ; **2,6-** et 2,7-)
 - PPO 0,025 M
 - Bis-MSB 0,0015 M

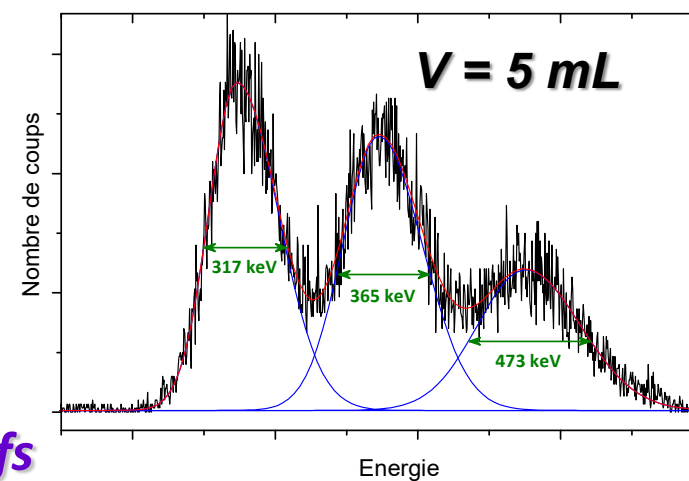
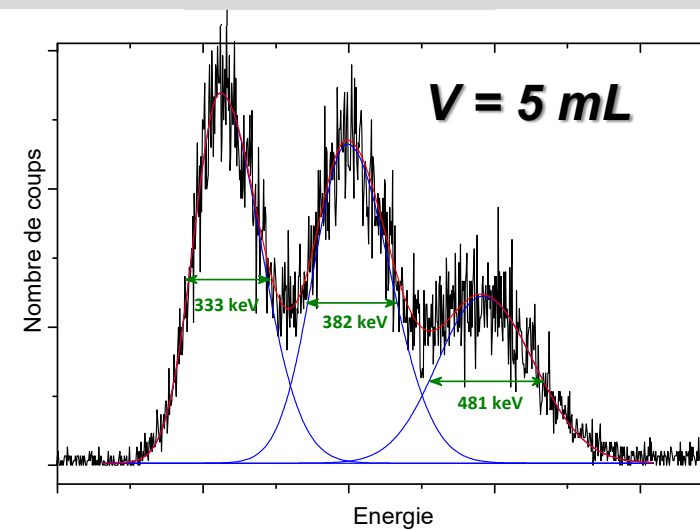


ALPHAEX_α dans PERALS™**ULTIMA Gold™ dans TRICARB™**

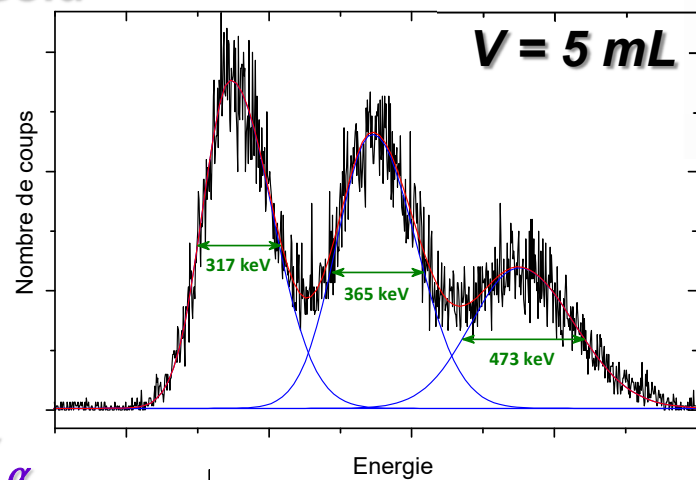
ULTIMA Gold™



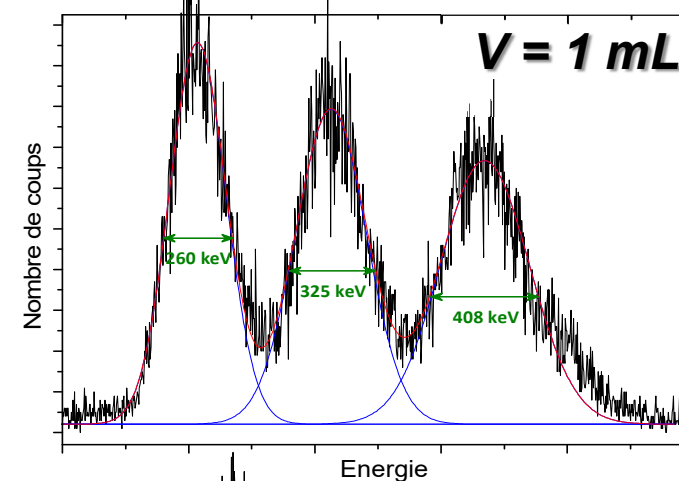
ULTIMA Gold™#
sans tensio-actifs



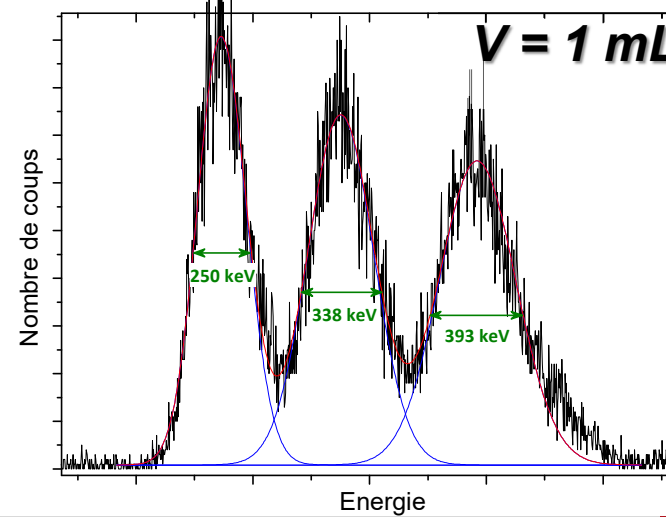
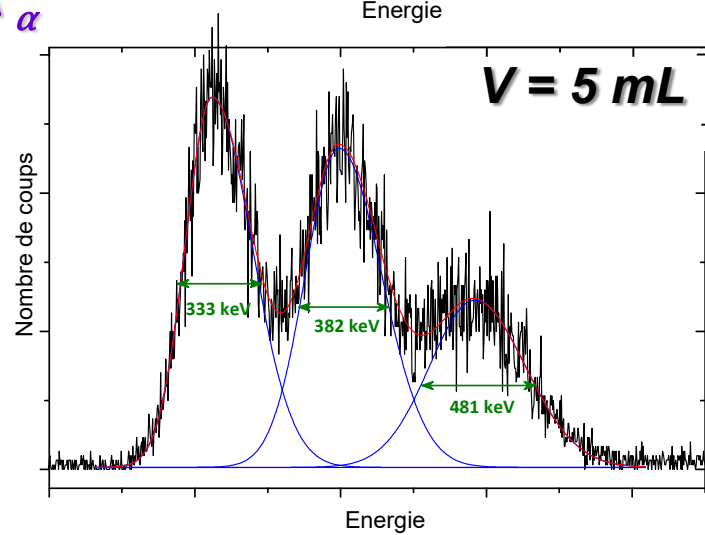
ULTIMA Gold™# $L = 26 \text{ mm}$



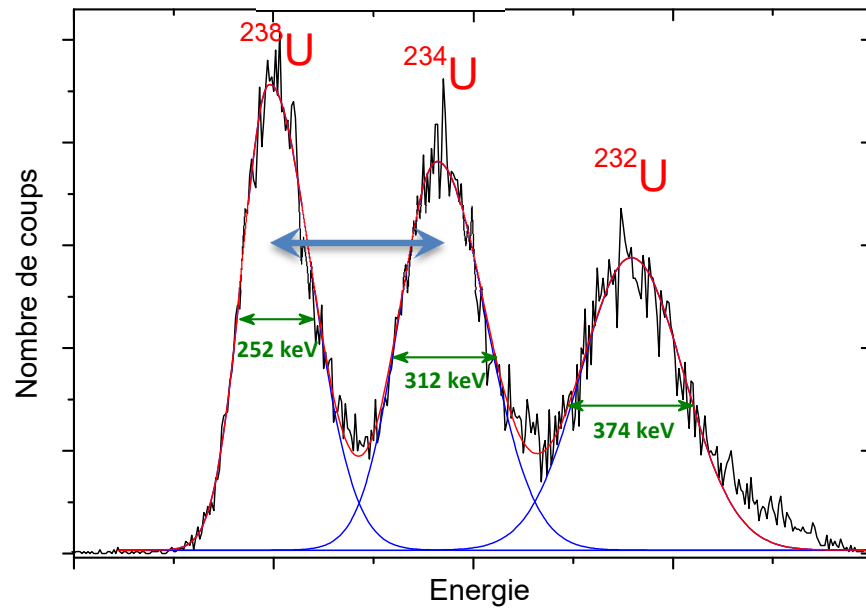
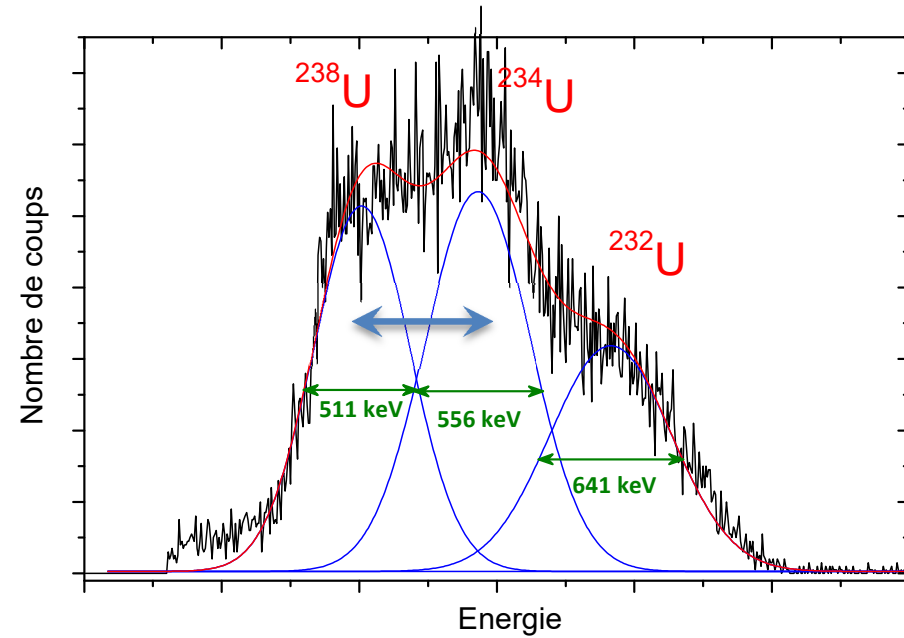
$L = 16 \text{ mm}$

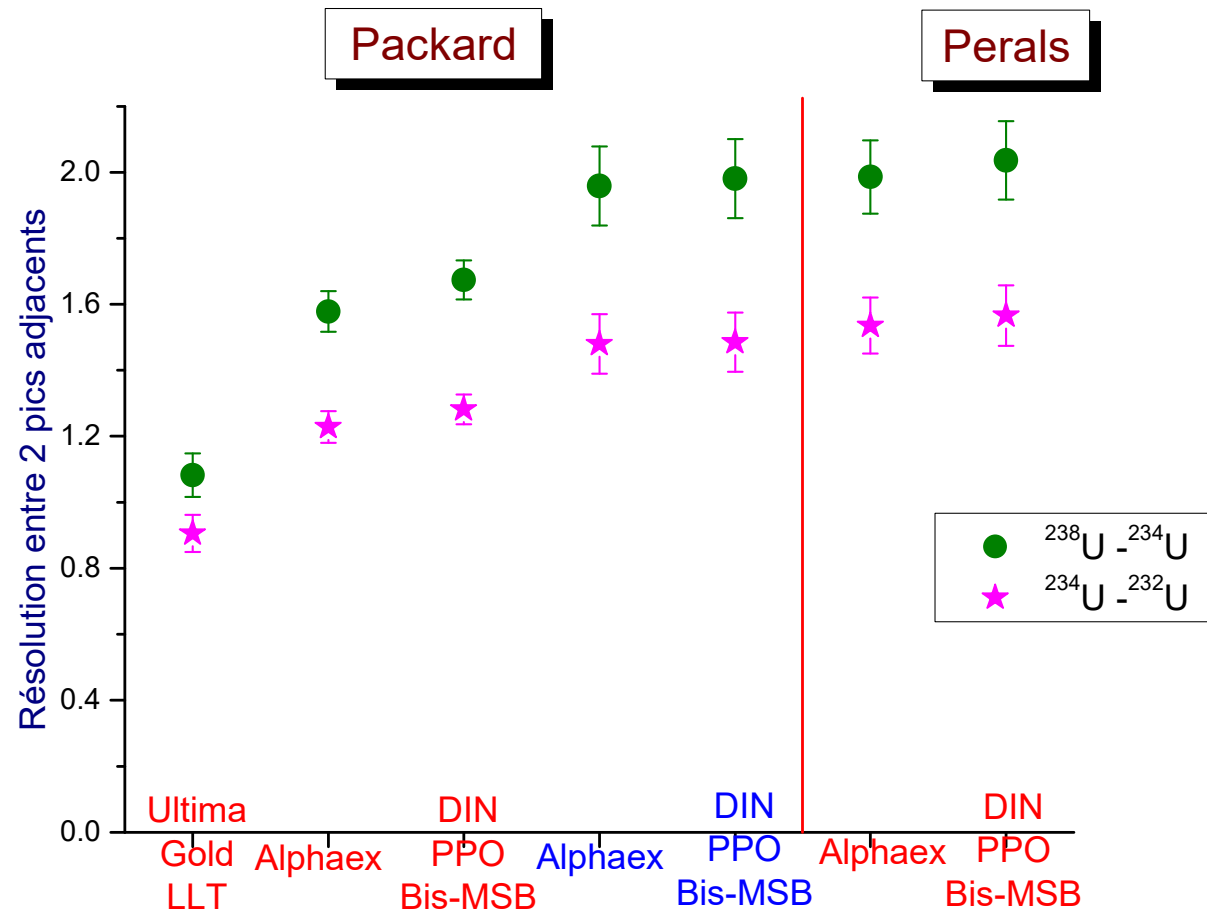


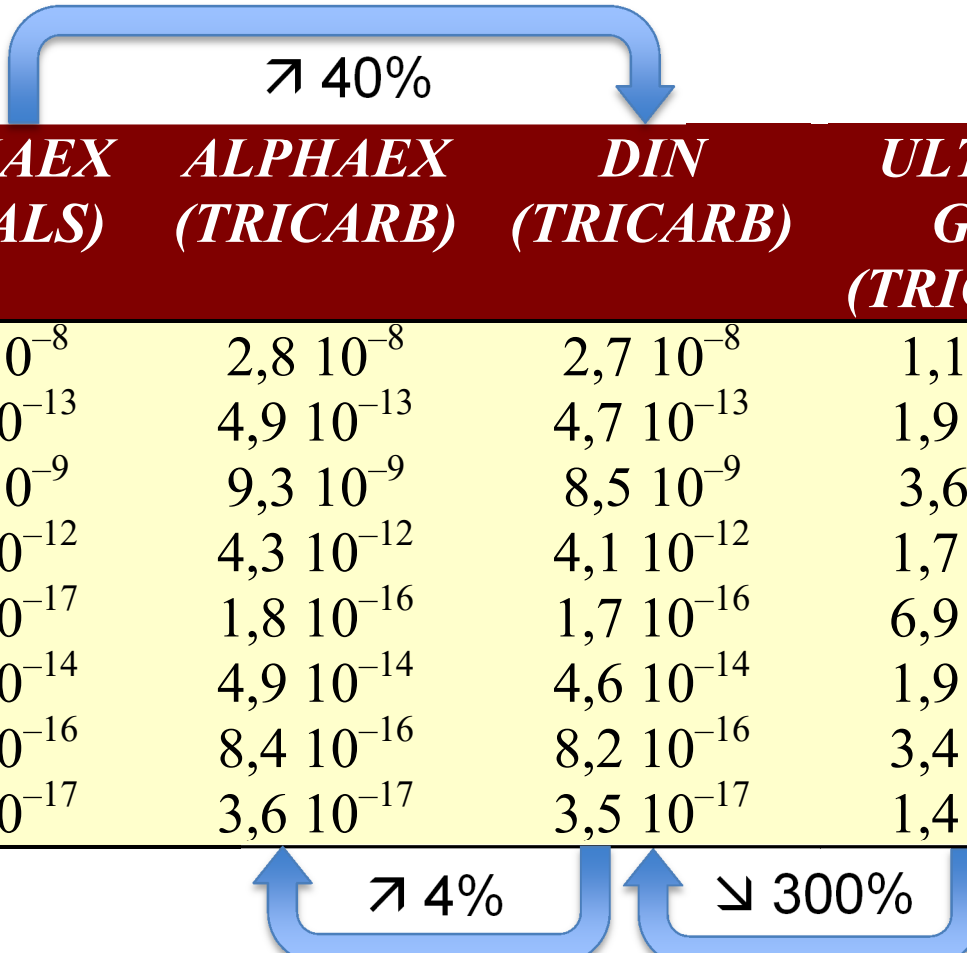
ALPHAEX α



$$R_s = 2 \frac{t_2 - t_1}{\omega_1 + \omega_2}$$

 $R_s = 2,0$  $R_s = 1,1$ 

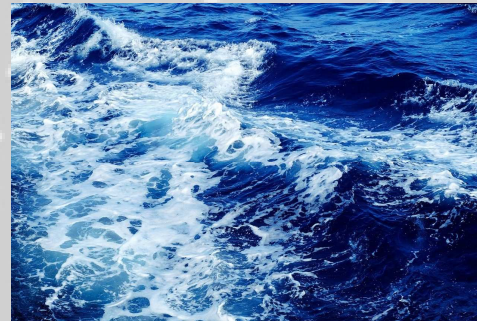




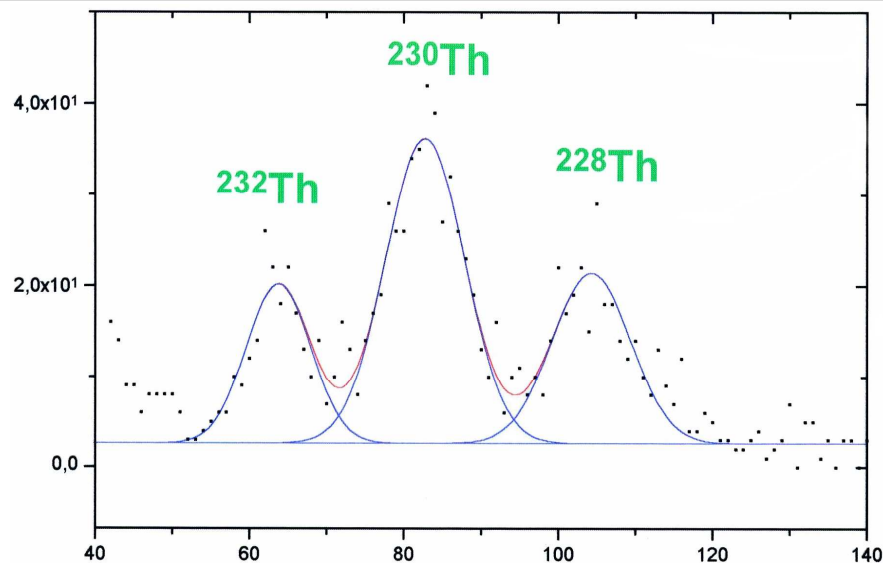
<i>Isotope</i>	<i>ALPHAEX (PERALS)</i>	<i>ALPHAEX (TRICARB)</i>	<i>DIN (TRICARB)</i>	<i>ULTIMA Gold (TRICARB)</i>
^{232}Th	$1,5 \cdot 10^{-8}$	$2,8 \cdot 10^{-8}$	$2,7 \cdot 10^{-8}$	$1,1 \cdot 10^{-7}$
^{234}U	$2,6 \cdot 10^{-13}$	$4,9 \cdot 10^{-13}$	$4,7 \cdot 10^{-13}$	$1,9 \cdot 10^{-12}$
^{238}U	$4,8 \cdot 10^{-9}$	$9,3 \cdot 10^{-9}$	$8,5 \cdot 10^{-9}$	$3,6 \cdot 10^{-8}$
^{237}Np	$2,4 \cdot 10^{-12}$	$4,3 \cdot 10^{-12}$	$4,1 \cdot 10^{-12}$	$1,7 \cdot 10^{-11}$
^{238}Pu	$9,6 \cdot 10^{-17}$	$1,8 \cdot 10^{-16}$	$1,7 \cdot 10^{-16}$	$6,9 \cdot 10^{-16}$
^{239}Pu	$2,6 \cdot 10^{-14}$	$4,9 \cdot 10^{-14}$	$4,6 \cdot 10^{-14}$	$1,9 \cdot 10^{-13}$
^{241}Am	$4,8 \cdot 10^{-16}$	$8,4 \cdot 10^{-16}$	$8,2 \cdot 10^{-16}$	$3,4 \cdot 10^{-15}$
^{244}Cm	$2,0 \cdot 10^{-17}$	$3,6 \cdot 10^{-17}$	$3,5 \cdot 10^{-17}$	$1,4 \cdot 10^{-16}$

Isotope	Limite de détection (M)		Limite de détection (pg/L)	
	3	10	3	10
²³² Th	1.10^{-9}	3.10^{-10}	3.10^5	6.10^4
²³⁸ U	2.10^{-10}	9.10^{-11}	6.10^4	2.10^4
²³⁸ Pu	5.10^{-18}	2.10^{-18}	1.10^{-3}	4.10^{-4}
²³⁹ Pu	1.10^{-15}	5.10^{-16}	3.10^{-1}	1.10^{-1}
²⁴⁰ Pu	3.10^{-16}	1.10^{-16}	8.10^{-2}	3.10^{-2}
²⁴¹ Am	2.10^{-17}	9.10^{-18}	5.10^{-3}	2.10^{-3}
²⁴³ Am	4.10^{-16}	1.10^{-16}	9.10^{-2}	4.10^{-2}
²⁴⁴ Cm	9.10^{-19}	4.10^{-19}	2.10^{-4}	9.10^{-5}

≈ 200000 at./L



APPLICATIONS ENVIRONNEMENTALES



$$C(^{232}\text{Th}) = 11 \mu\text{g/L}$$

Thorex_α

H_2SO_4 2 M

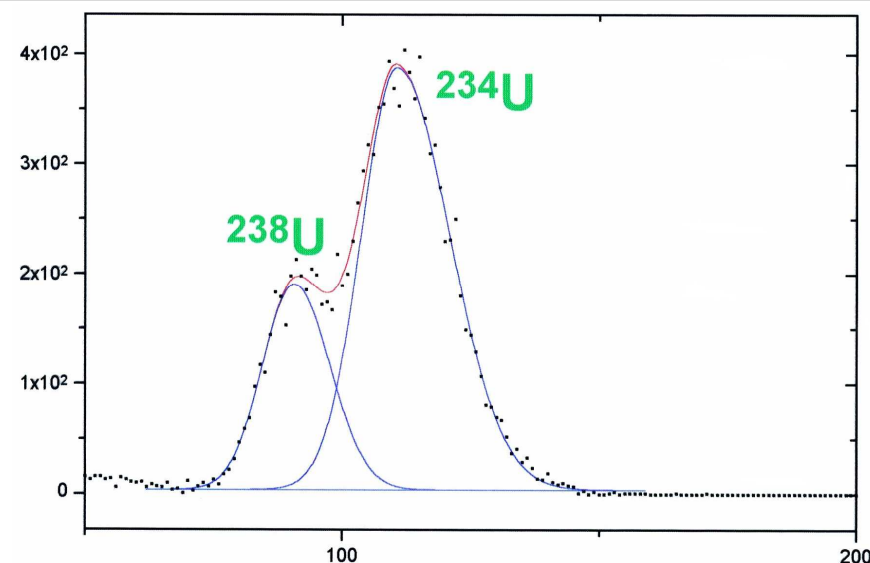
\bar{V}

$$\frac{\bar{V}}{V} = 0,1$$

R = 99 %

Table 4. Activities Expected and Measured in Badoit French Granitic Mineral Water

radionuclide	activity (Bq/L)	
	expected	measured
^{228}Th	0.065	0.06 ± 0.02
^{230}Th	0.107	0.11 ± 0.03
^{232}Th	0.046	0.07 ± 0.02
^{234}U	2.38	2.26 ± 0.07
^{238}U	0.91	0.88 ± 0.04



$$C(^{238}\text{U}) = 80 \mu\text{g/L}$$

Uraex_α

H_2SO_4 0,5 M

\bar{V}

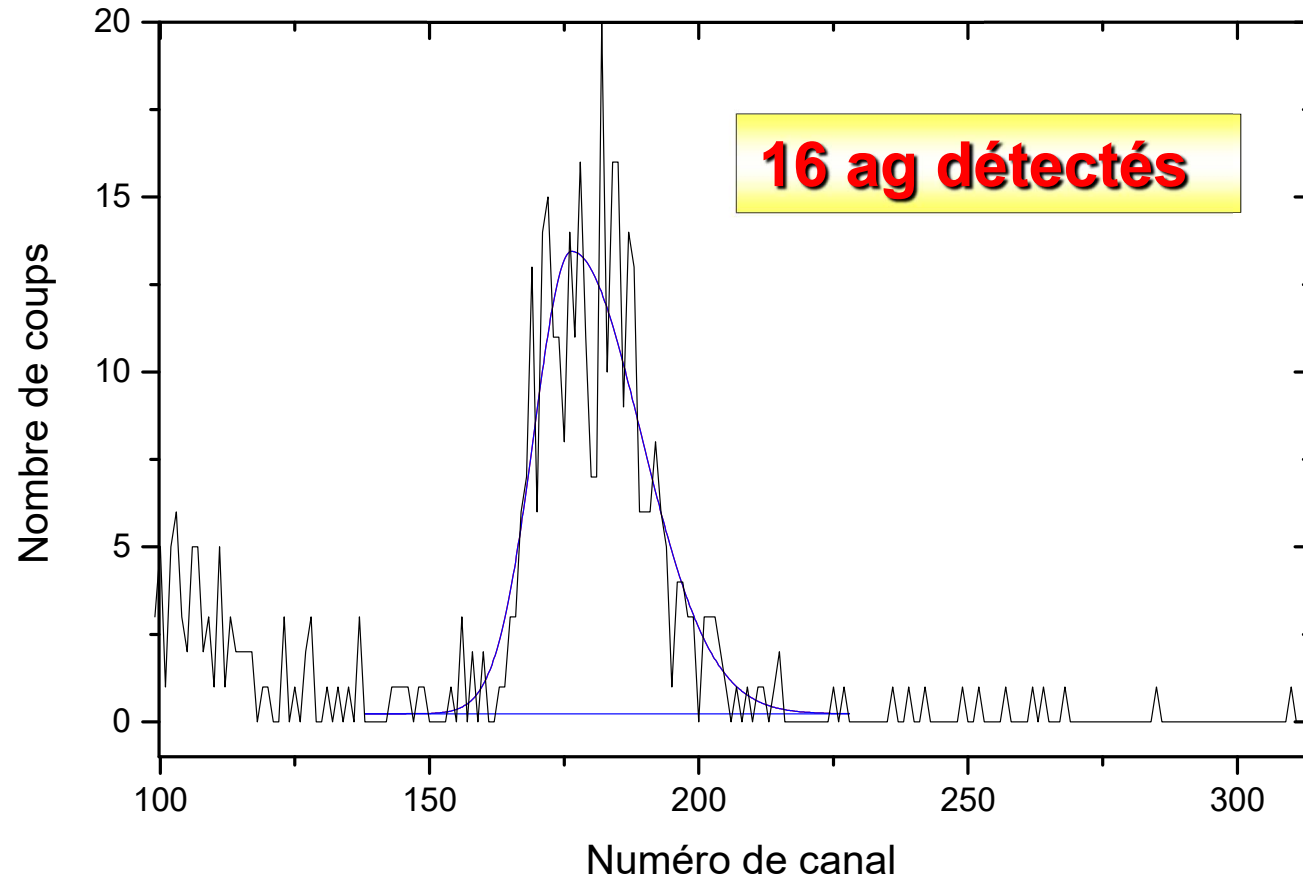
$$\frac{\bar{V}}{V} = 0,1$$

R = 98 %

Dacheux, N.; Aupiais, J., Determination of uranium, thorium, plutonium, americium and curium ultratraces by photon electron rejecting a liquid scintillation. *Anal. Chem.* **1997**, *69* (13), 2275-2282.

A = 19,7 ± 1,6 mBq/L

16 ag détectés



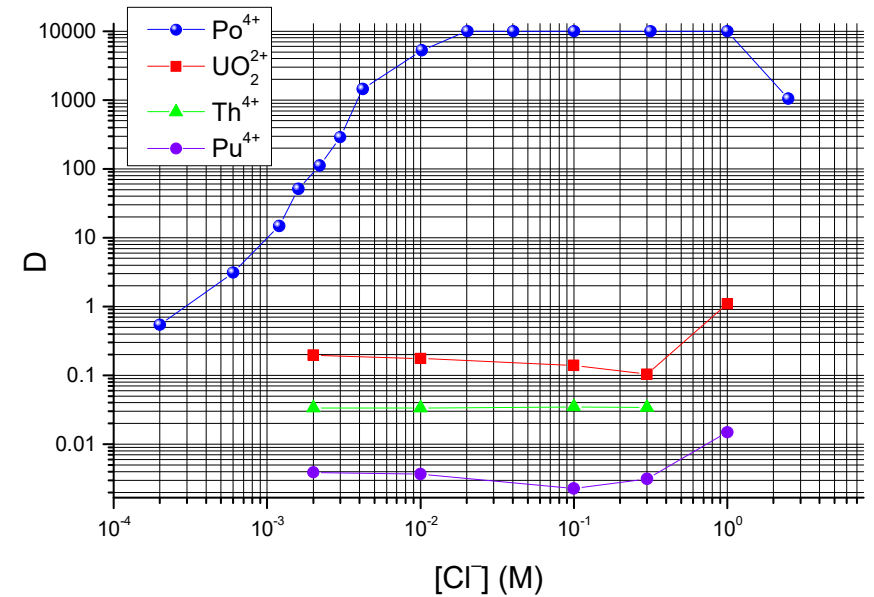
Uraex_α

H_2SO_4 3 M

NaCl 0,01 M

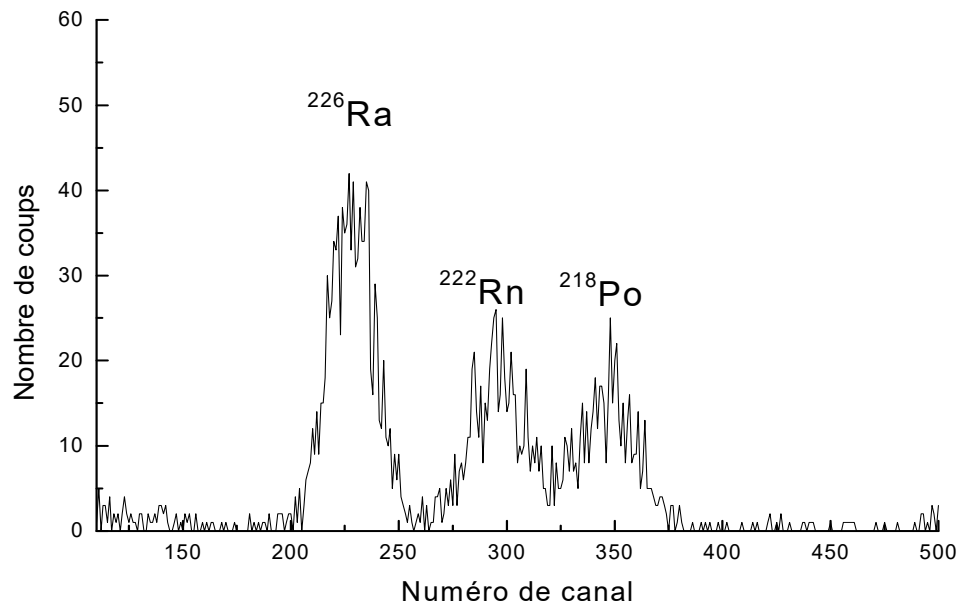
\bar{V}

$\frac{\bar{V}}{V} = 0,0075$



Uraex_α : $\frac{\bar{V}}{V} = 0,006$, H_2SO_4 3 M

Véronneau, C.; Aupiais, J.; Dacheux, N., Selective determination of polonium by photon electron rejecting alpha liquid scintillation (PERALS system). *Anal. Chim. Acta* **2000**, 415, 229-238



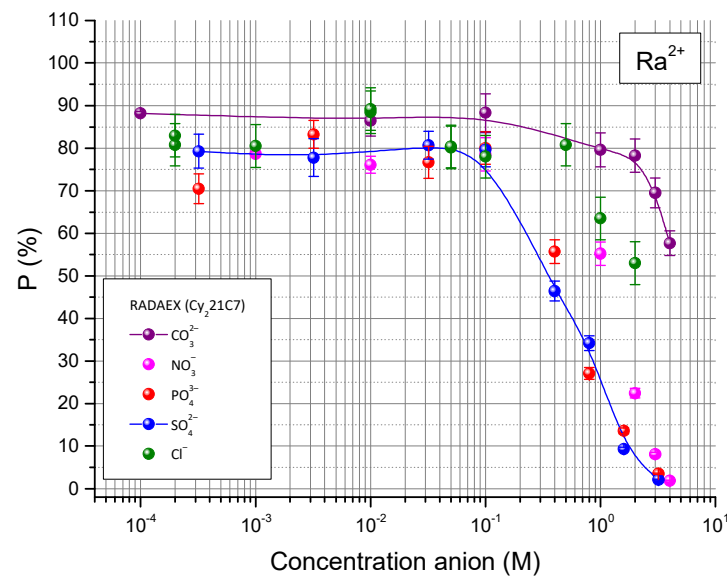
Radaex $_{\alpha}$

pH > 10 + αHIB 0,1 M

$$\frac{\bar{V}}{V} = 0,3$$

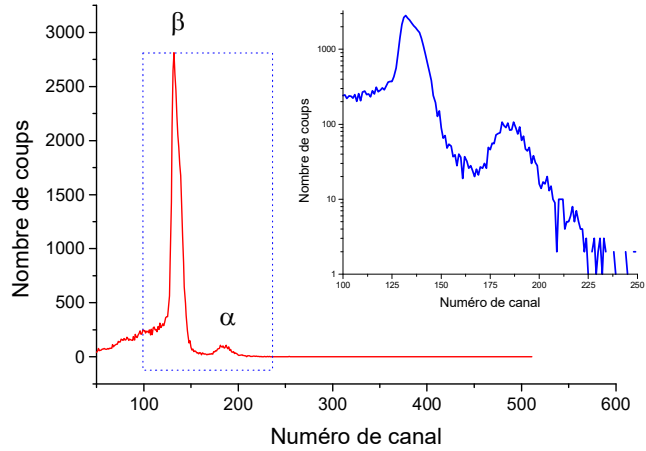
Echantillon	Rendement (%)	^{226}Ra (mBq.L $^{-1}$)	^{238}U ($\mu\text{g.L}^{-1}$)	
			ICP/MS	SLRT
Volvic	74 \pm 4	28 \pm 13	0,956 \pm 0,016	0,82 \pm 0,09
Cristaline	76 \pm 4	< 39	2,03 \pm 0,09	1,92 \pm 0,05
Montjoie	81 \pm 4	< 28	0,275 \pm 0,012	0,8 \pm 0,2
Aulus *	73 \pm 3	254 \pm 81	0,834 \pm 0,035	
Chanteraine	83 \pm 4	93 \pm 18	(9,73 \pm 3,82).10 $^{-3}$	
Fontestorbes	78 \pm 4	< 24	0,377 \pm 0,017	0,9 \pm 0,1
Alet	79 \pm 4	50 \pm 12	2,30 \pm 0,10	3,7 \pm 0,5
Ax les thermes	70 \pm 4	< 6	(1,48 \pm 0,27).10 $^{-2}$	
Evian	67 \pm 3	< 24	1,82 \pm 0,08	
Badoit *	77 \pm 4	2100 \pm 250	76,6 \pm 3,3	79 \pm 2
Vittel	75 \pm 4	< 24	0,984 \pm 0,017	
Plancoët *	78 \pm 4	75 \pm 20	0,353 \pm 0,015	0,41 \pm 0,05
Contrex	65 \pm 3	< 39	1,54 \pm 0,07	1,4 \pm 0,9
La Bourboule-Choussy	78 \pm 4	3000 \pm 200		

* Aliquote 1 mL, sinon 6 mL

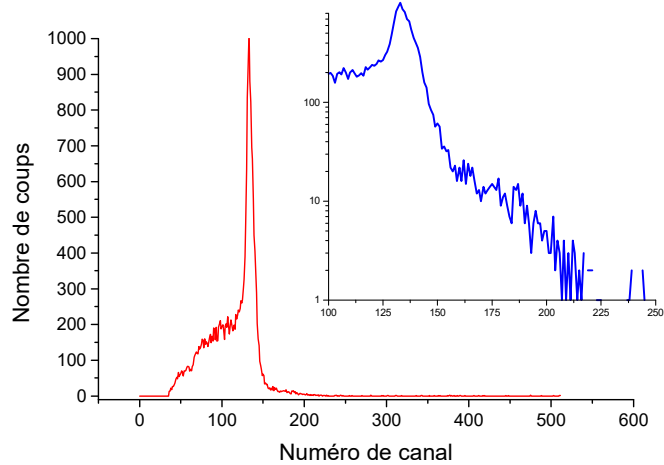


NF ISO 13165-1

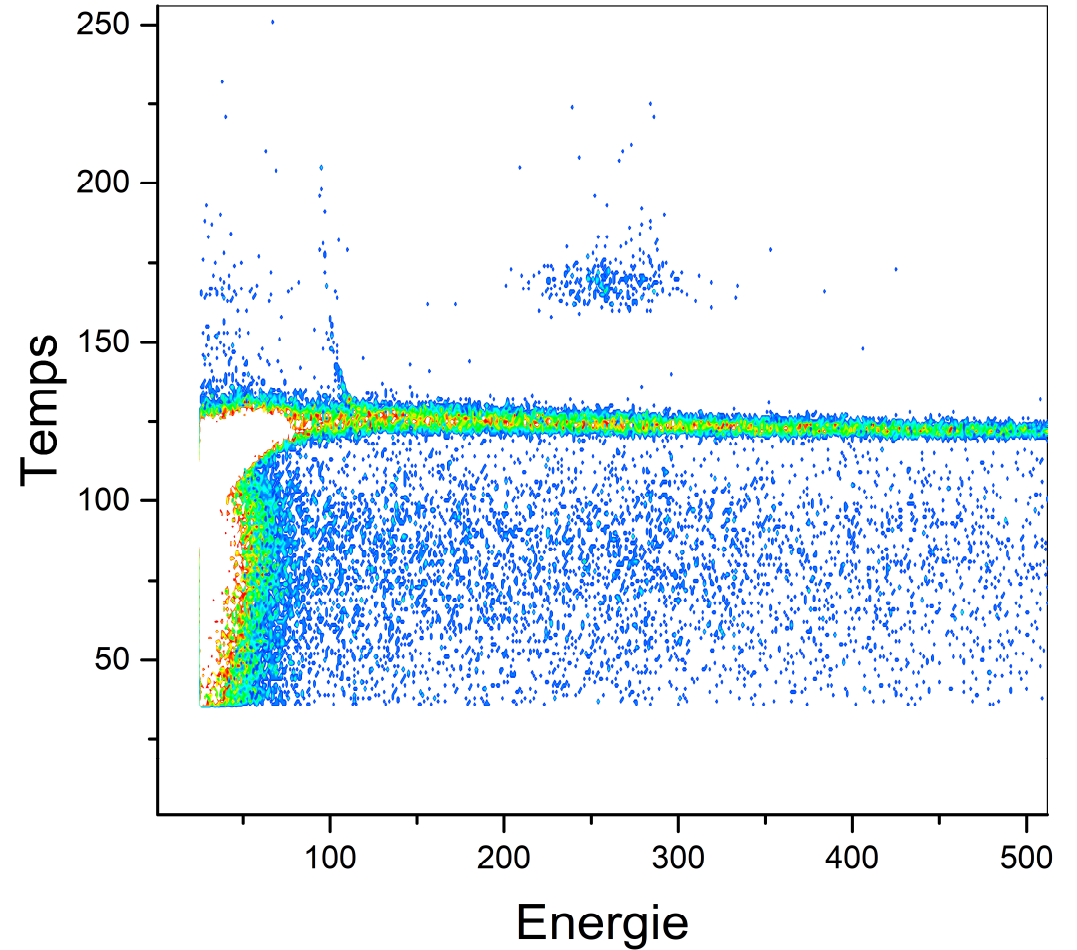
Aupiais, J., Radium measurement in water samples by α -liquid scintillation counting with α/β discrimination. *Anal. Chim. Acta* **2005**, 532, 199-207



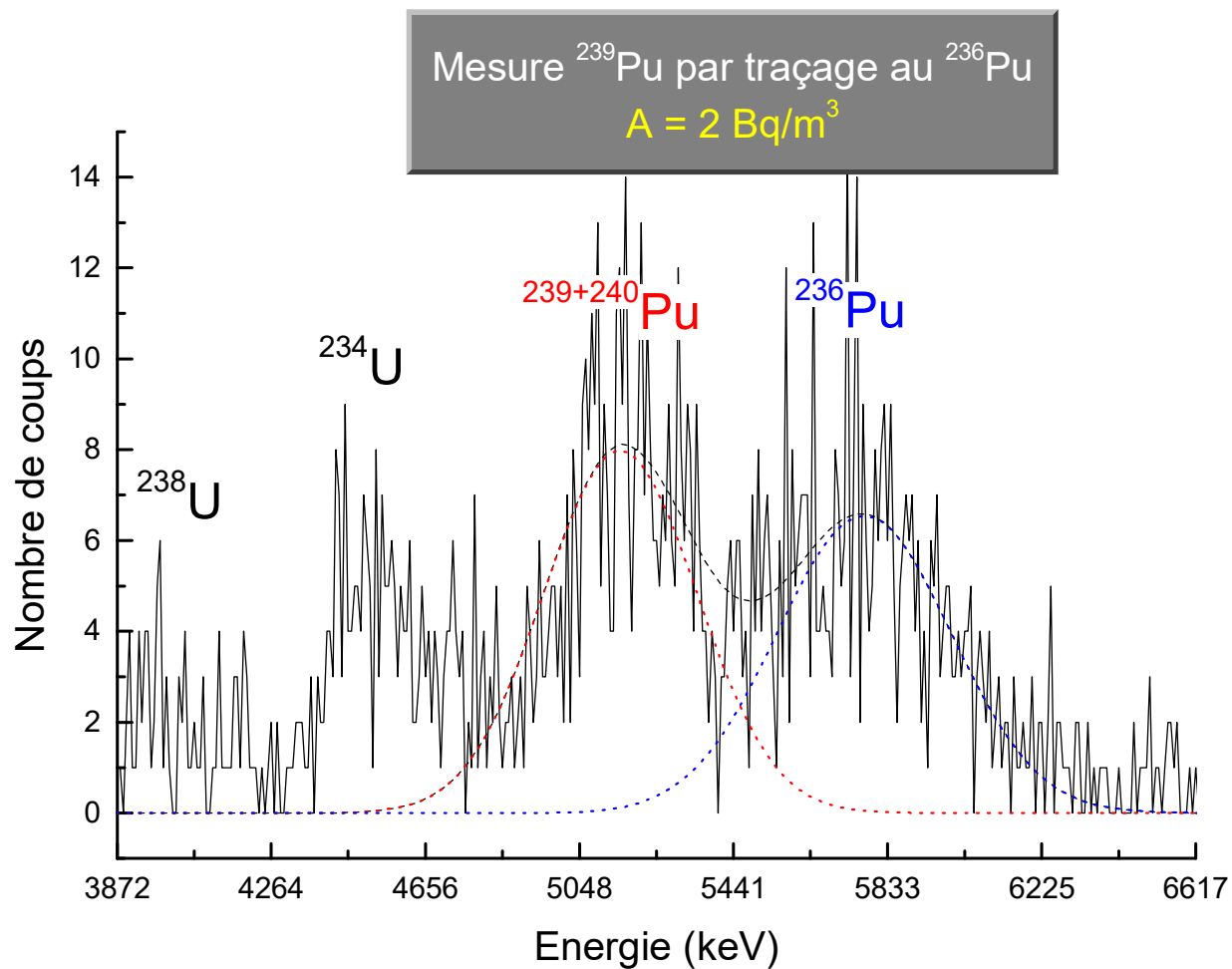
Rapport initial 10^5 avant extraction $A = 0,1$ Bq, $t = 7200$ s



Rapport initial 10^6 avant extraction $A = 0,1$ Bq, $t = 7200$ s

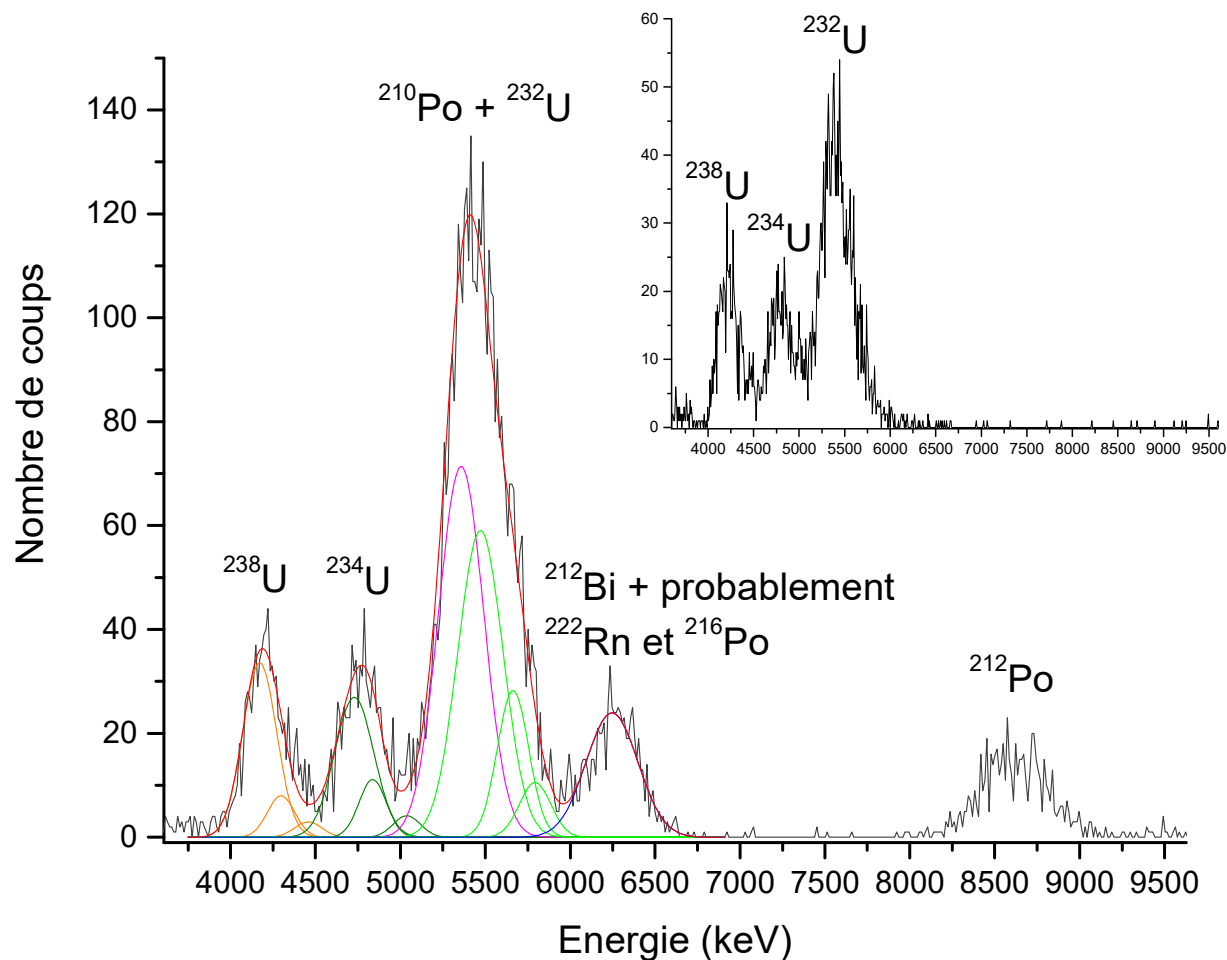


Spectre 2D – PSD = 0 ; $t = 7200$ s, $A = 6$ Bq/L



Limite de détection

 $0,5 \text{ Bq.m}^{-3}$



Alphaex_α

pH = 3,5 + DTPA 0,01 M

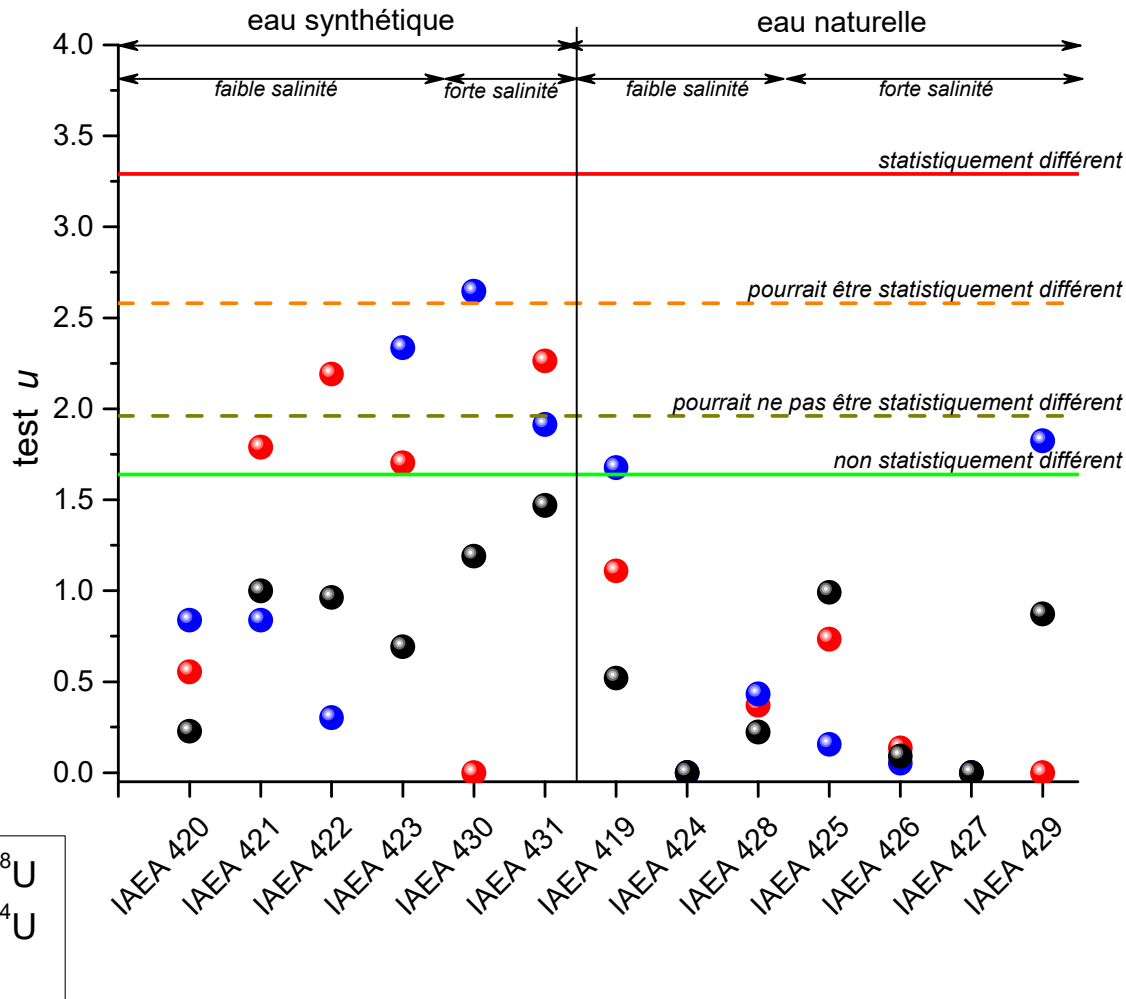
+ poudre Ag (si Po)

$$\frac{\bar{V}}{V} = 0,015$$



NF ISO 13169

Aupiais, J., *Rapid determination of uranium activity and concentration in water by alpha liquid scintillation with a/b discrimination.* *Anal. Chim. Acta* **2004**, 517 (1-2), 221-228.



$$u = \frac{|R\acute{e}sultat - Cible|}{\sqrt{u_{R\acute{e}sultat}^2 + u_{Cible}^2}}$$

Valeurs u $u < 1,64$ $1,64 < u < 1,96$ $1,96 < u < 2,58$ $2,58 < u < 3,29$ $3,29 < u$ **Conclusion****Résultat significativement non différent****Résultat pourrait ne pas être significativement différent.**

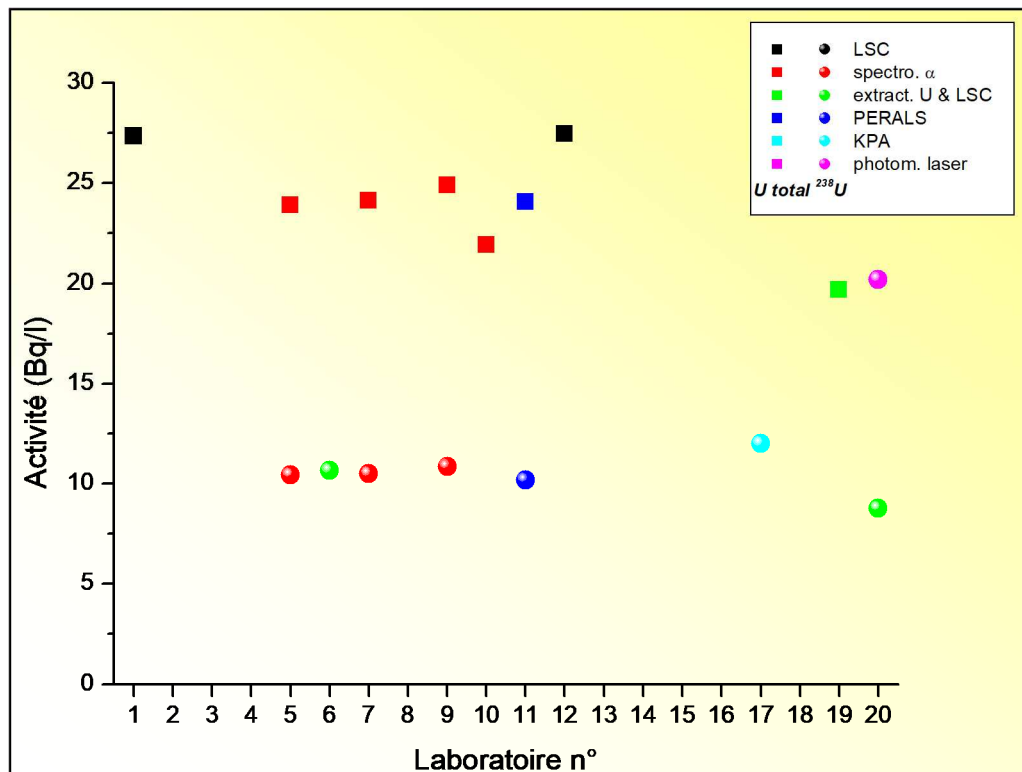
Autre détermination nécessaire

Aucune conclusion ne peut être tirée

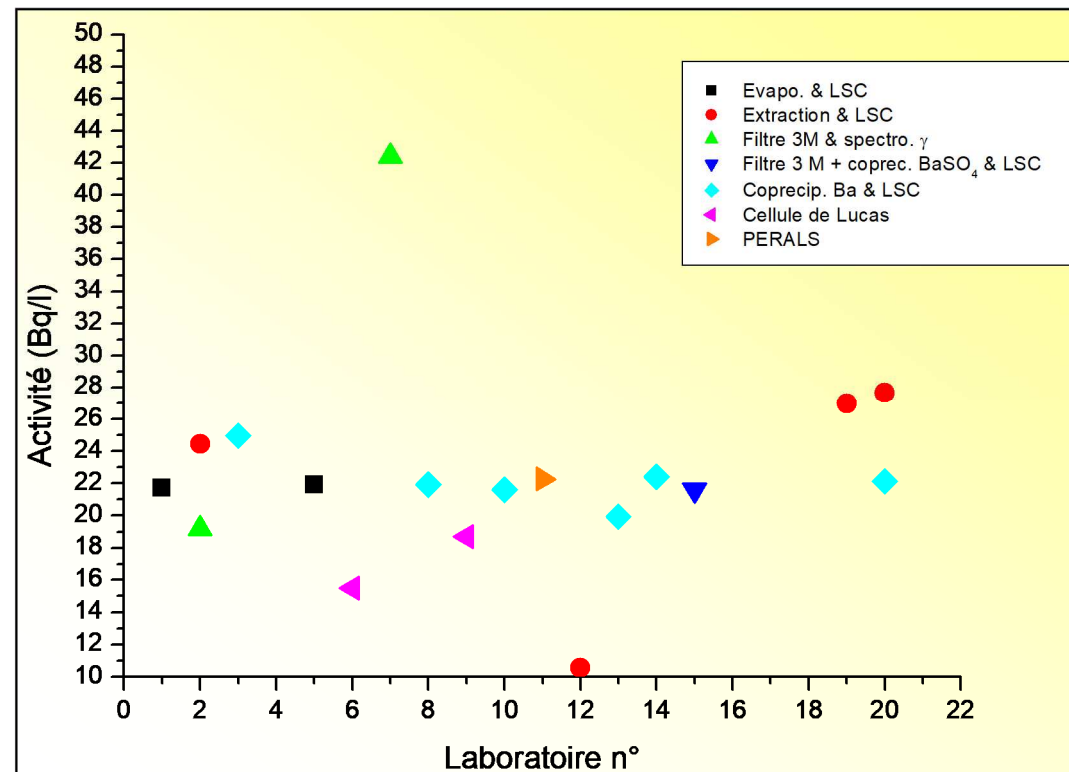
Résultat pourrait être significativement différent.

Autre détermination nécessaire

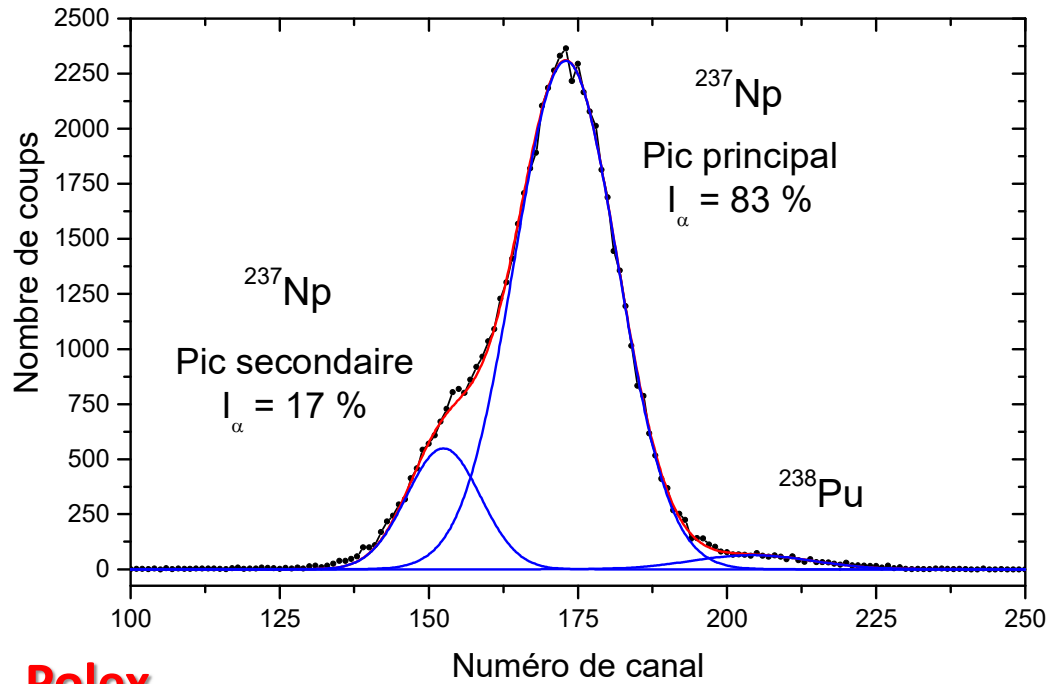
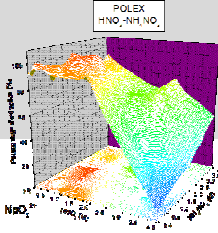
Résultat significativement différent



^{238}U , U_{total}



^{226}Ra



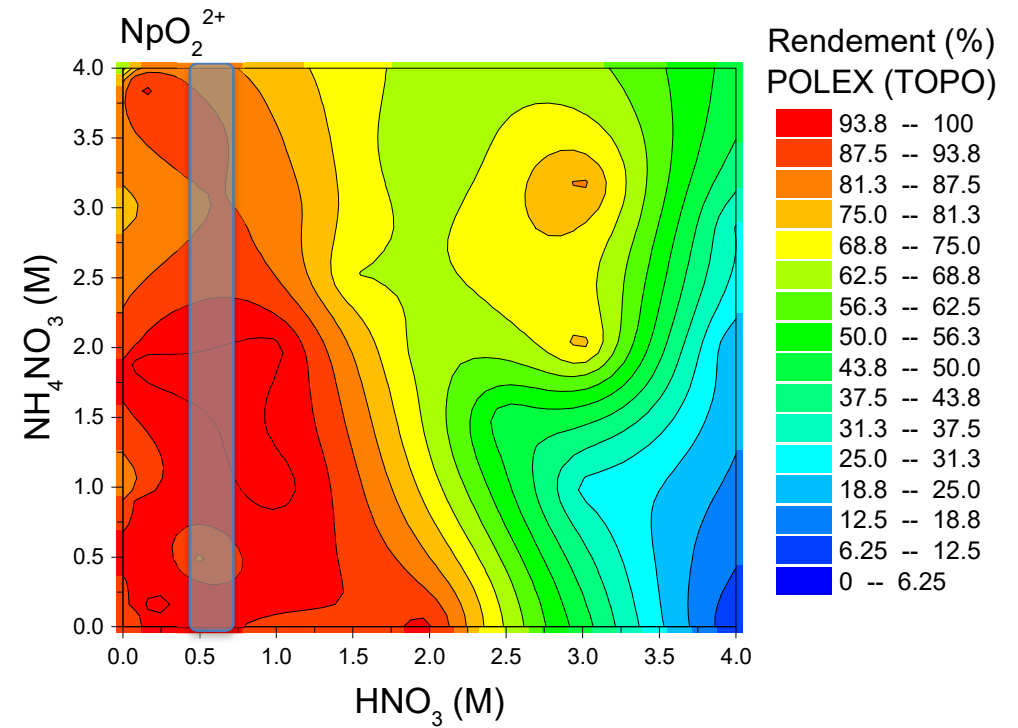
Polex_α

HNO_3 0,5–0,75 M

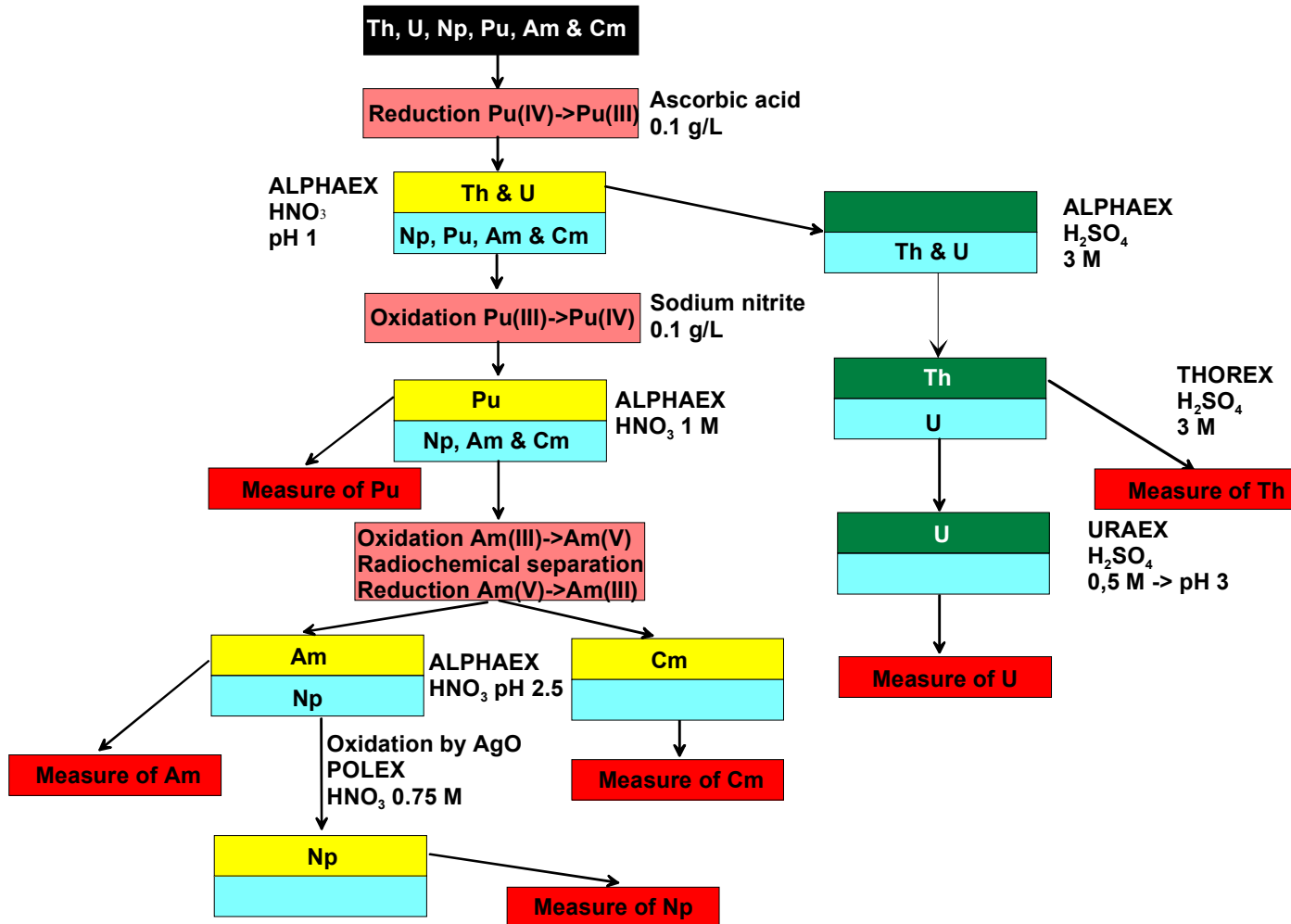
Oxydation Np^{VI} (AgO)

\bar{V}

$\frac{\bar{V}}{V} = 0,05$



Aupiais, J.; Dacheux, N.; Thomas, A. C.; Matton, S., Study of neptunium measurement by alpha liquid scintillation with rejection of b-g emitters. *Anal. Chim. Acta* **1999**, *398*, 205-218



Soit : A_T l'activité totale

A_1 l'activité trouvée 1^{ère} extr.

A_2 l'activité trouvée 2^{nde} extr.

R le rendement d'extraction

$$A_1 = R \times A_T$$

$$A_2 = R \times (A_T - A_1)$$

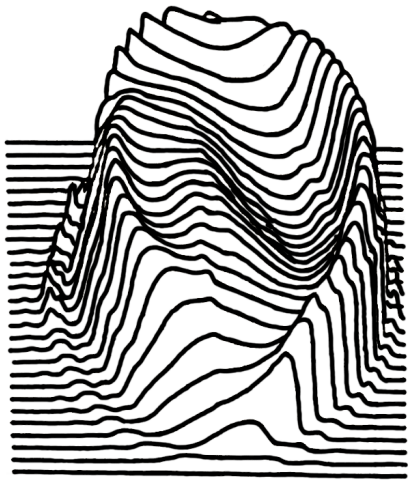
$$R = 1 - \frac{A_2}{A_1}$$



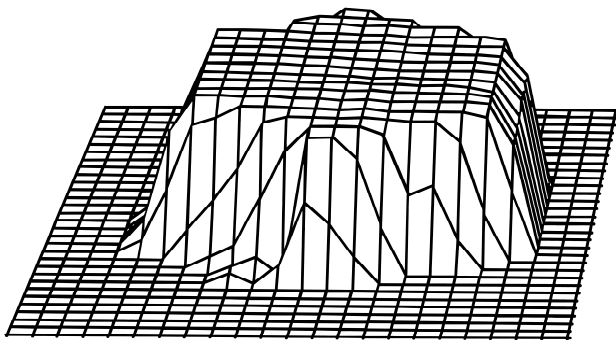
PERSPECTIVES

Commissariat à l'énergie atomique et aux énergies alternatives - www.cea.fr

Réponse uniforme

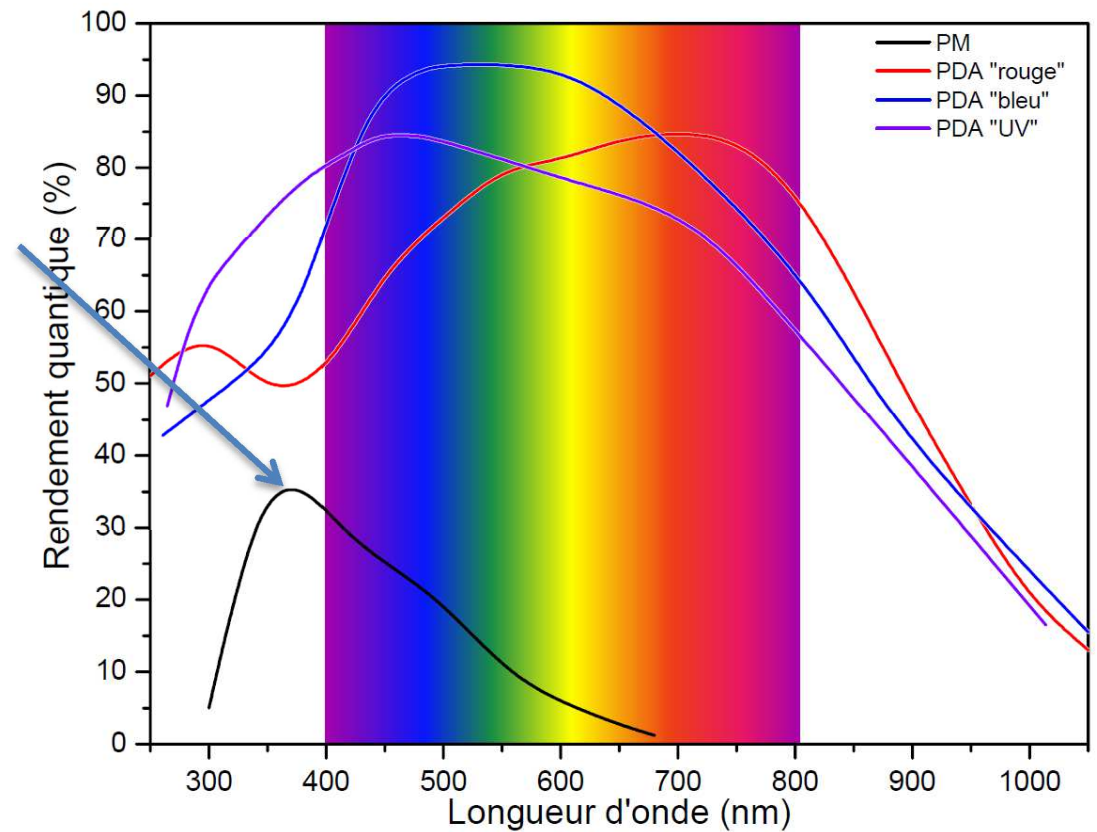


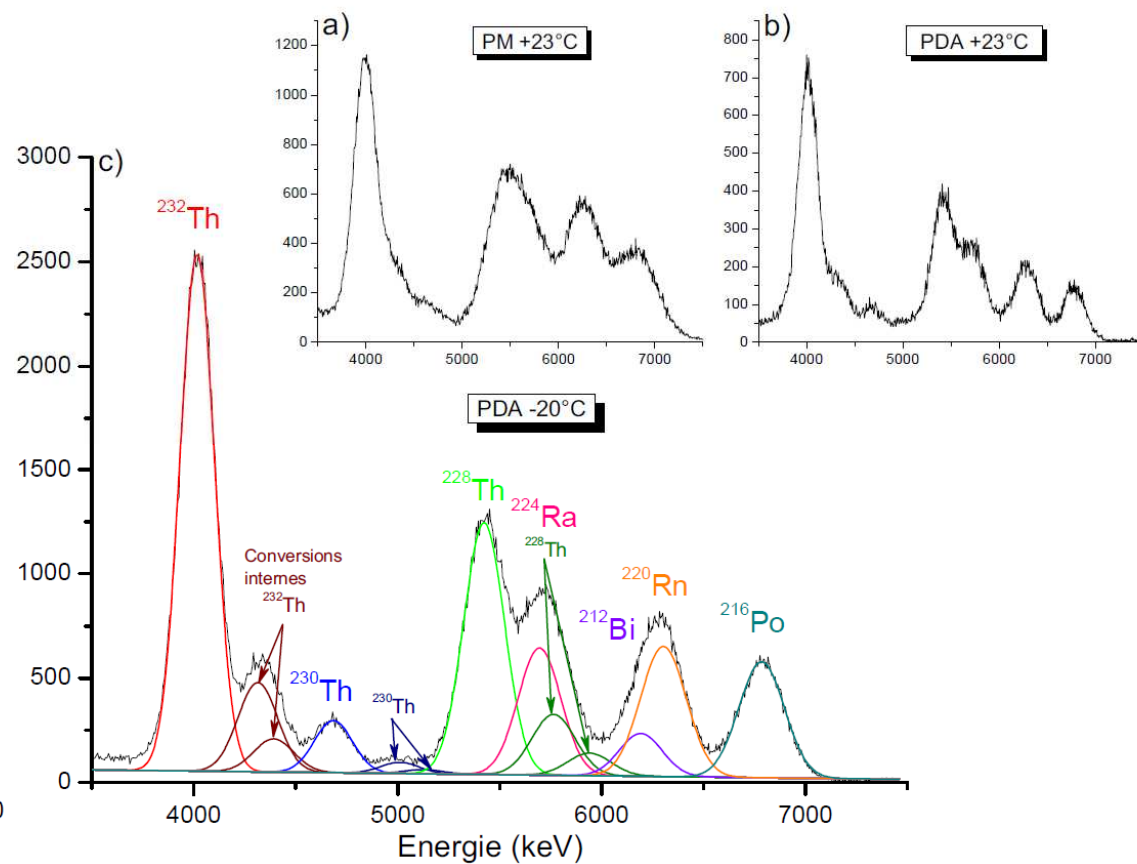
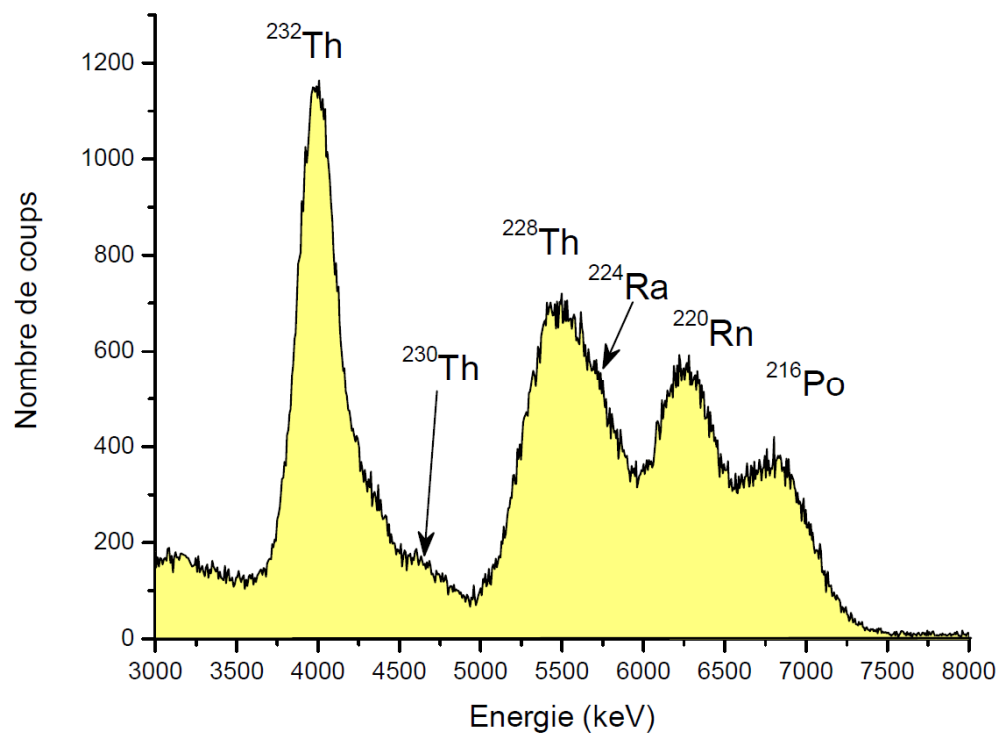
photomultiplicateur



photodiode

Rendement quantique supérieur





$$E_{ic} = E_{\alpha} + kE_{\text{électron}} \quad k = 7,6 \pm 0,2$$

Reboli, A.; Aupiais, J.; Mialocq, J. C., Application of large area avalanche photodiodes for alpha liquid scintillation counting. Nucl. Instr. and Meth. A **2005**, 550, 593-602.

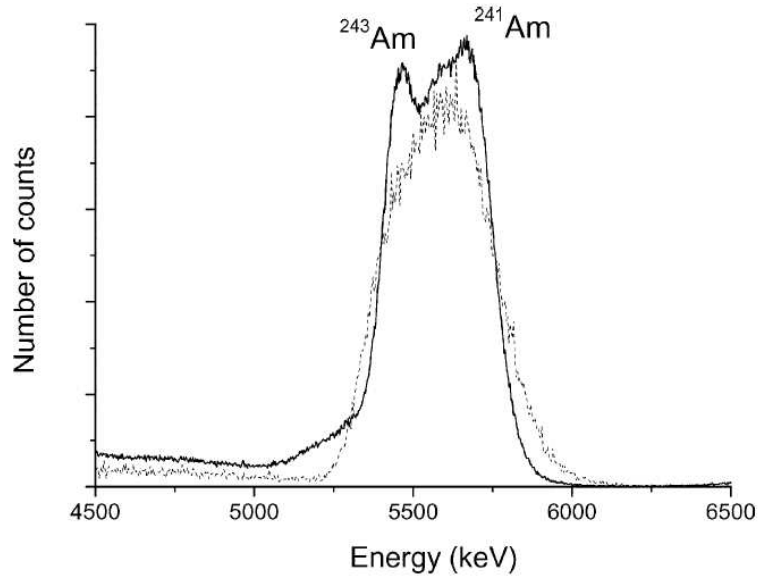


Fig. 6. Comparison of the pulse height spectra of ^{241}Am and ^{243}Am measured with the PERALS[®] spectrometer (dashed line) and with our experimental set-up and an APD at -40°C (straight line). ^{241}Am and ^{243}Am activities are 6 Bq each and counting time is 43 h.

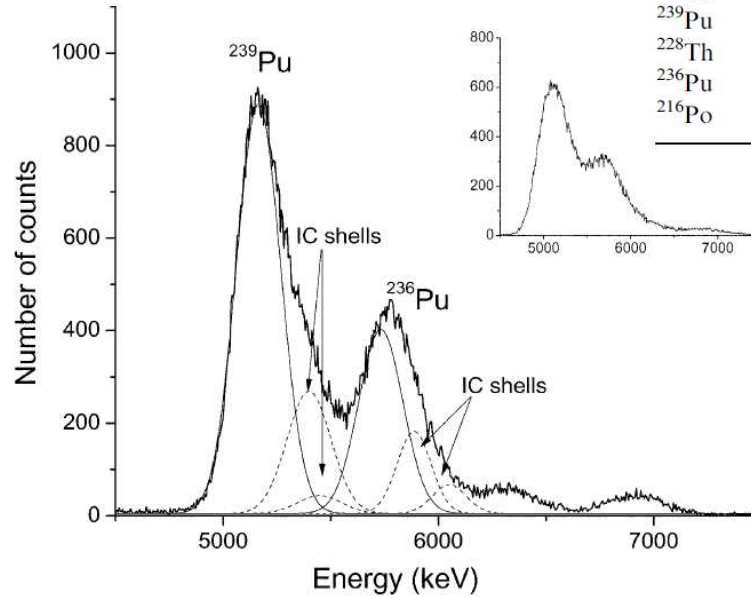


Fig. 7. Pulse height spectra of ^{239}Pu and ^{236}Pu at -40°C . The straight lines represent the main α -ray spectra. Dashed lines represent the pile-up of the main α -ray + IC-shells peaks. The resolution is approximately equal to 240 keV for the two isotopes. ^{236}Pu and ^{239}Pu activities are 4 and 8 Bq respectively, counting time is 17 h. The plot in the upper right shows the ^{239}Pu and ^{236}Pu spectrum measured with the PERALS[®] spectrometer.

Isotope	Energy (keV)	APD	PMT
		R (keV)	R (keV)
^{232}Th	4010	200 ± 13	210 ± 13
^{239}Pu	5157	242 ± 13	256 ± 14
^{228}Th	5423	235 ± 11	306 ± 14
^{236}Pu	5768	243 ± 11	293 ± 17
^{216}Po	6785	262 ± 14	448 ± 20



Merci pour votre attention

Vous en savez autant que moi, mais...





Annexes



Rendement de fluorescence $\Phi^F = \frac{k^F}{\sum_i k^i}$

Rappel : $\sum_i k^i = \frac{1}{\tau}$

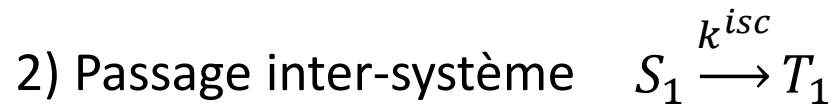
Constante cinétique de fluorescence $k^F = \Phi^F \sum_i k^i$

Temps de vie de fluorescence naturel $\frac{1}{\tau^F} = \Phi^F \frac{1}{\tau}$

Temps de vie de fluorescence $\tau = \Phi^F \tau^F$



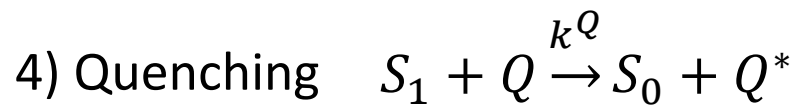
$$k^0 = \frac{1}{\tau^0}$$



$$k^{isc} = \frac{1}{\tau^{isc}}$$



$$k^{nr} = \frac{1}{\tau^{nr}}$$



$$k^Q = \frac{1}{\tau^Q}$$

Cinétique globale

$$-\frac{d}{dt}[S_1] = (k^0 + k^{isc} + k^{nr})[S_1] + k^Q[Q][S_1]$$

$$[S_1] = [S_1]_0 e^{-k^F t} \quad k^F = \frac{1}{\tau^F} = \sum_i k^i + k^Q[Q]$$



Table 1. Overlap calculations $\int f_D(\nu) \times \varepsilon_A(\nu) \frac{d\nu}{\nu^4} \times 10^{-27}$ for a couple donor-acceptor (in mole⁻¹ m⁶).

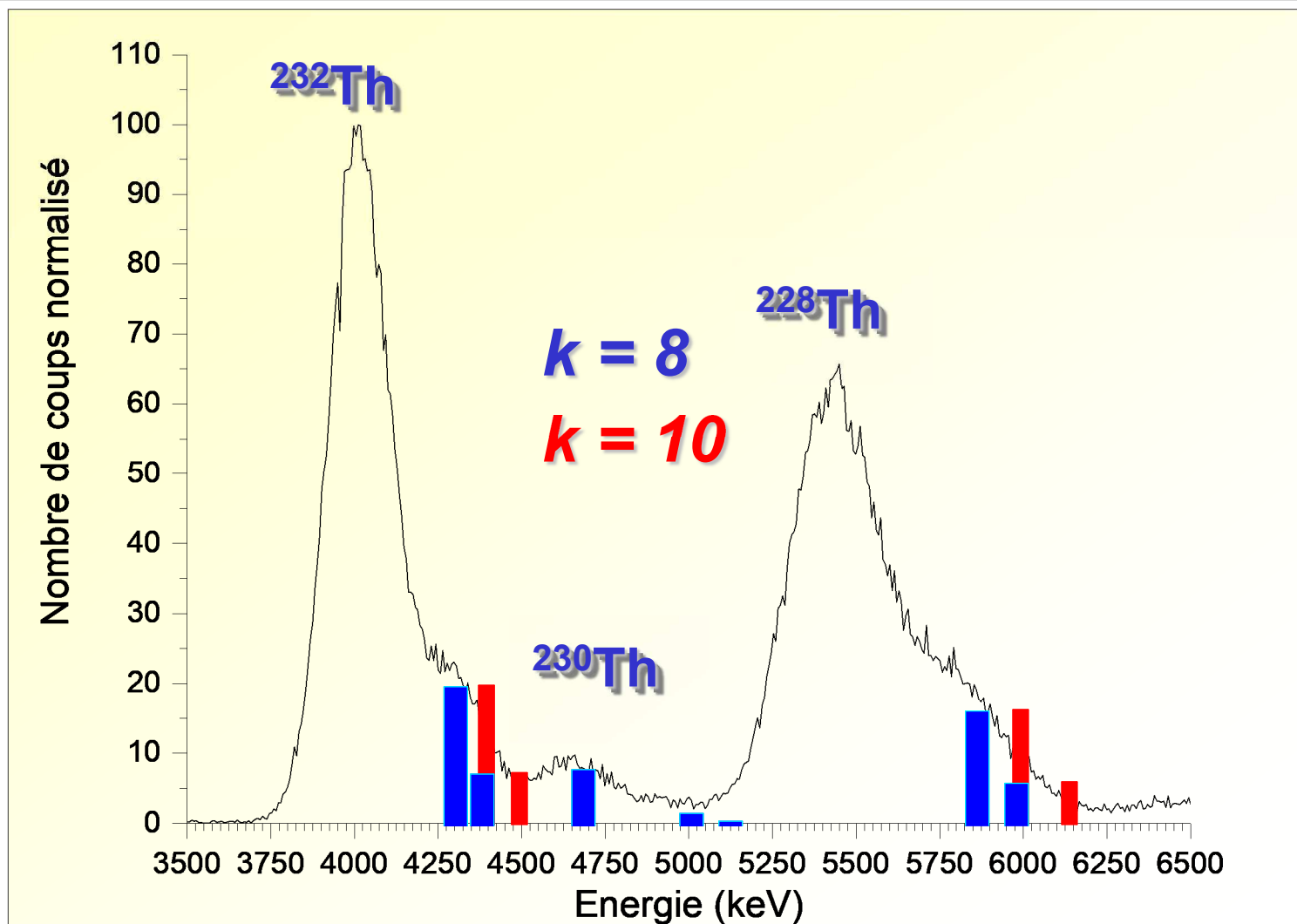
Donor	Acceptor	Overlap	Donor	Acceptor	Overlap
Toluene	Toluene	0.0021 ^a	DIN	PBBO	96.245
	Naphthalene	2.123 ^a		PPO	21.201
	PBBO	27.738		Bis-MSB	146.518
	PPO	23.820		PBBO	3.539
Naphthalene	Naphthalene	0.0056 ^a	PPO	PPO	1.544
	PBBO	92.504		Bis-MSB	128.325
	PPO	26.527		Bis-MSB	12.03
	Bis-MSB	129.411			

a: in cyclohexane else in toluene.

Table 2. Critical distances R_0 and parameters required by Eq. (1).

donor → acceptor	Φ_D (donor)	Refractive index n of the solvent	R_0 (in Å)
Toluene → naphthalene	0.14 [12]	1.4961 [15]	15.4
Naphthalene → PBBO	0.19 [13]	1.4961	28.0
Toluene → PBBO	0.14 [12]	1.4961	22.5
DIN → PPO	0.62 this work	1.6 ^a	30.2
PPO → bis-MSB	0.79 [14]	1.6 ^a	39.8
DIN → Bis-MSB	0.62 this work	1.6 ^a	38.8

a: assumption taking into account that derivative naphthalene molecules have refractive index close to about 1.6 like 1-methylnaphthalene ($n = 1.6170$) or β isopropylnaphthalene ($n = 1.58482$) [15].





Isotope	α_T	$\alpha(L)$	$\alpha(M)$	$\alpha(N+\dots)$	$\alpha(L)/\alpha_T$	$\alpha(M)/\alpha_T$	$\alpha(M)/\alpha_L$
²³⁰ Th	61.9	45.2	12.24	4.39	0.730	0.198	0.271
²³² Th	120	87.5	23.64	8.49	0.729	0.197	0.270
²³² U	156.1	113.6	31.1	11.44	0.728	0.199	0.274
²³⁴ U	232.9	169.6	46.3	17.07	0.728	0.199	0.273
²³⁶ Pu	461*	341*	94.1*	31.0*	0.740	0.204	0.276
²³⁸ Pu	731	530*	146*	48.1*	0.732	0.202	0.275
²³⁹ Pu	724*	—	—	—	—	—	—
317	—	—	—	—	—	—	—
²³⁹ Pu	318 ± 6*	231 ± 4*	—	—	0.726	—	—
²⁴⁰ Pu	597	—	—	—	—	—	—
610 ± 9*	448 ± 7*	—	—	0.734	—	—	—
²⁴¹ Am	1.16	0.84	0.226	0.094	0.724	0.195	0.269
²⁴³ Am	0.280	0.210	0.0518	0.0183	0.750	0.185	0.247
²⁴⁴ Cm	918	—	—	—	—	—	—
928 ± 9*	673 ± 7*	186*	61.5*	0.725	0.200	0.276	—

*: Ref. [15] else Ref. [16–27].

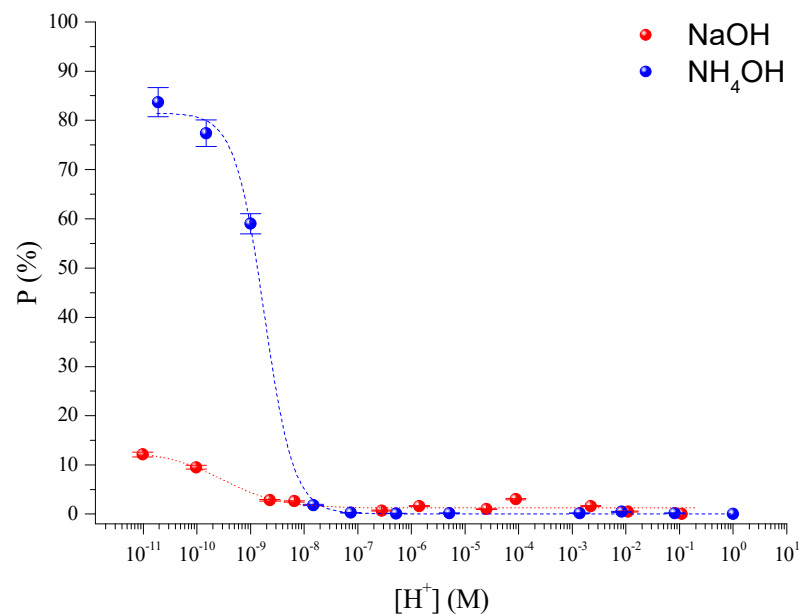
Table 2. Contributions of the *L*, *M*, etc. shells in the total *IC* (α_T) [6–17, 19].

Table 3. Data used for calculating the E_{ic} value [15–27].

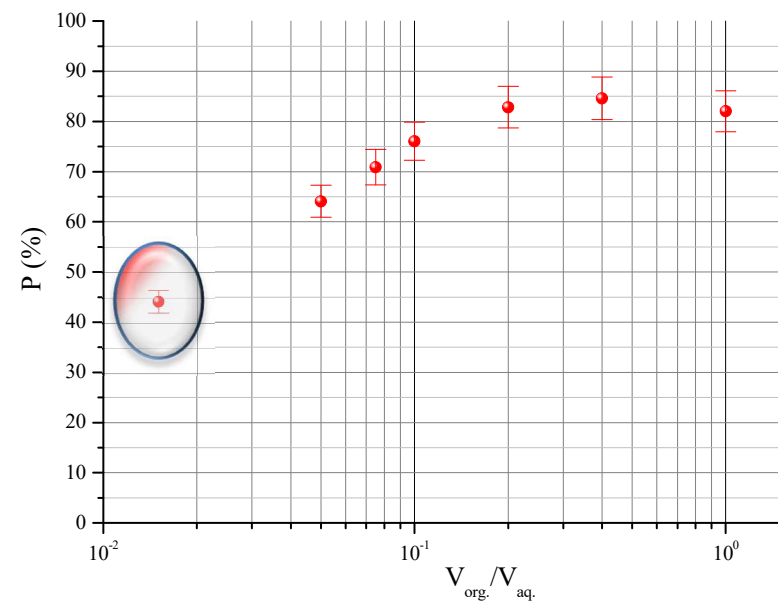
Isotope	E_α (keV)	I_α (%)	E_γ (keV)	τ (ns)	α_T	I_{ic}	I_γ	$E_{electron}$ (keV) (<i>L</i> shell)	$E_{electron}$ (keV) (<i>M</i> shell)
²²⁸ Th	5340.36	27.2	84.37	0.746	21.6	0.9558	0.0442	65.55	80.19
²³⁰ Th	4620.5	23.4	67.67	0.63	61.9	0.9841	0.0159	48.85	63.49
²³² Th	3947.2	21.7	63.81	0.55	81.9	0.9879	0.0121	45.00	54.82
²³² U	5263.36	31.55	57.78	0.406	156	0.9936	0.0064	37.82	53.32
²³³ U	4783	13.23	42.44	0.172	4500	0.9998	0.0002	22.48	37.98
²³⁴ U	4722.4	28.42	53.20	0.354	232.9	0.9957	0.0043	33.24	48.74
²³⁸ U	4151	20.9	49.55	0.37	326.4	0.9969	0.0031	29.59	45.09
²³⁶ Pu	5721	31.7	47.6	0.254	461	0.9978	0.0021	26.46	42.84
²³⁸ Pu	5456.3	28.84	43.50	0.252	731	0.9986	0.0014	22.36	38.72
²³⁹ Pu	5144.3	15.1	13.0	0.50	≈ 3 · 10 ⁴	1	0	—	—
	5105.5	11.5	51.62	0.191	317	0.9967	0.0031	30.48	46.86
²⁴⁰ Pu	5123.68	27.1	45.24	0.234	597	0.9983	0.0017	24.10	40.48
²⁴² Pu	4856.3	22.4	44.91	0.225	619	0.9984	0.0016	23.77	40.17
²⁴¹ Am	5485.56	84.5	59.54	67	1.16	0.537	0.463	37.78	54.63
	5442.80	13.0	102.98	0.08	0.121	0.108	0.892	81.22	98.07
²⁴³ Am	5275	87.9	74.67	1.40	0.280	0.219	0.781	52.91	69.76
	5233	10.6	117.66	< 0.04	—	—	—	—	112.75
²⁴⁴ Cm	5762.70	23.6	42.82	0.164	918	0.9989	0.0011	20.44	37.74

Aupiais, J.; Aubert, C.; Dacheux, N., Some rules to improve the energy resolution in alpha liquid scintillation with beta rejection. *Radiochim. Acta* **2003**, *91*, 63-69.

$D =$



Effet de la nature de la base



Effet du rapport des volumes de phase

