

Optimization of low-level LS counter Quantulus 1220 for tritium determination in water samples

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Motivation

- ^3H low level in the environment → special conditions have to be fulfilled in order to obtain accurate and reliable measurements by liquid scintillation counting (LSC) .
- To optimize tritium analysis in waters by ultra-low background LS spectrometer Quantulus 1220 the influence of sample/scintillant ratio, choice of appropriate scintillation cocktail and comparison of their efficiency, background, minimal detectable activity (MDA) and FOM value, the effect of chemi- and photoluminescence and combination of scintillant/vial was investigated.
- Development and optimization of new direct method (faster and simpler than ASTM) [Pujol and Sanchez-Cabeza 1999] is presented → ^3H level was determined in Danube river samples and several samples within intercomparison with Ruđer Bošković Institute (IRB).

Experimental setup

- Ultra Low Level Liquid Scintillation Spectrometer Wallac 1220 Quantulus (PerkinElmer, Finland, 2002) with EASYView and WinQ software
- background reduction system around the vial chamber - an active and passive shield
- two pulse analysis circuits accessible for the users: a pulse shape analysis (PSA) and pulse amplitude comparator (PAC) circuit
- a delayed coincidence circuit (DCOS)
- two multichannel analyzers (MCA)
- quenching was quantified with the external standard quenching parameter, SQP(E)
- ^3H configuration of the MCA's setting eliminates the random noise of phototubes, inhibits the coincidence pulse from the guard and the sample, and monitors the random coincidence by DCOS in a half of the MCA, the whole sample spectrum being recorded in the other half of the MCA
- ^3H window was fixed to channels 1-250

Direct method of ^3H determination

Pujol, Ll., Sanchez-Cabeza, J.A., 1999. Optimization of liquid scintillation counting conditions for rapid tritium determination in aqueous samples. *J. Radioanal. Nucl. Chem.* 242 (2), 391–398.

- Each water sample was filtrated through a slow depth filter (cellulose nitrate filter pore size $0.45\ \mu\text{m}$)
- 8 ml of sample was mixed with 12 ml of the cocktail in a 20 ml vial
- background preparation: 8 ml of distilled raw water (deep well water) was mixed with 12 ml of the scintillation cocktail.
- Two organic commercial standards made with 1-pentanol and 1,3-butanediol (Perkin Elmer), tritium activities of 52510 (+/- 3%) dpm/ml (reference date July 9, 2008) and $1.48 \cdot 10^6$ (+/- 3%) dpm/ml (reference date July 9, 2008)

Direct method of ^3H determination. Calculations

- the counting efficiency ε_t :

V [ml] sample volume analyzed;

T_2 [Bq ml $^{-1}$] the standard dilution activity;

R_s [cps] standard count-rates for ^3H spectrum;

$$\varepsilon_t = \frac{R_s}{V T_2}$$

- ^3H activity concentration [Bq ml $^{-1}$]:

R_a [cpm] sample count-rates for ^3H spectrum;

R_b [cpm] background count-rates for ^3H spectrum;

r_q [cpm] count-rates in chemiluminescence spectrum;

$$A = \frac{R_a - (R_b + r_q)}{60 \varepsilon_t V}$$

- The minimum detectable tritium activity (MDA) for a counting time T [min]:

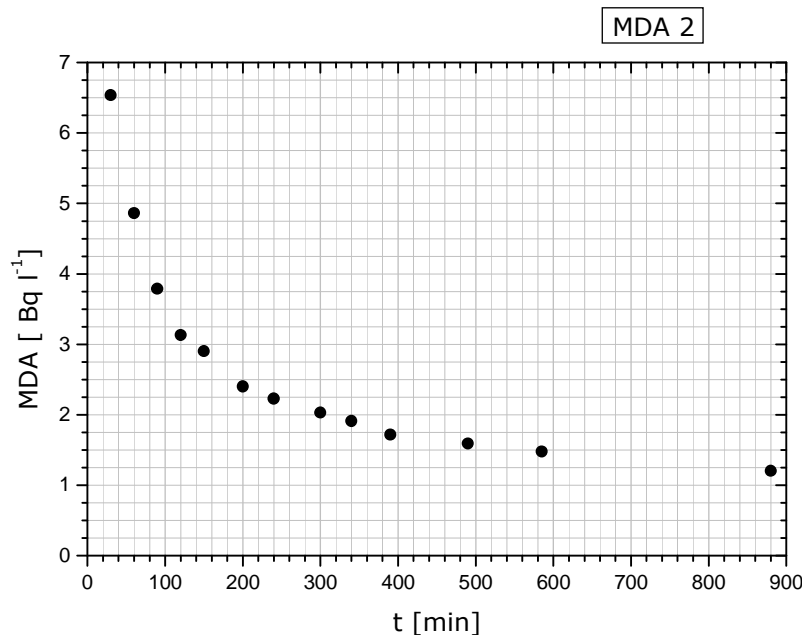
$$MDA = \frac{2.71 + 4.65 \sqrt{(R_b + r_q) T}}{60 \varepsilon_t V T}$$

Results and discussion

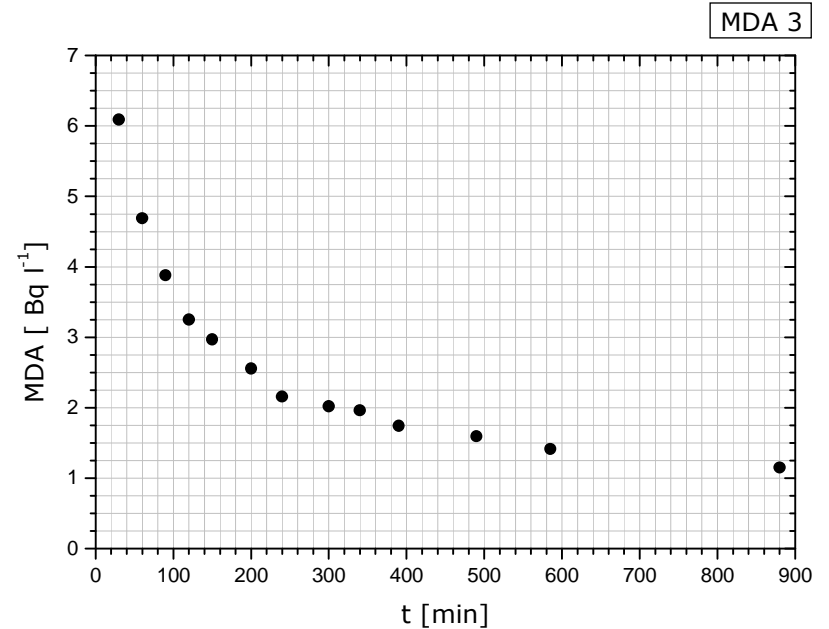
MDA achieved

$$MDA = \frac{2.71 + 4.65 \sqrt{(R_b + r_q) T}}{60 \epsilon_t V T}$$

- The minimum detectable ^3H activity for total counting time of 300min $\sim 2.0 \text{ Bq}\cdot\text{l}^{-1}$ for both cocktails



OptiPhase HiSafe 2

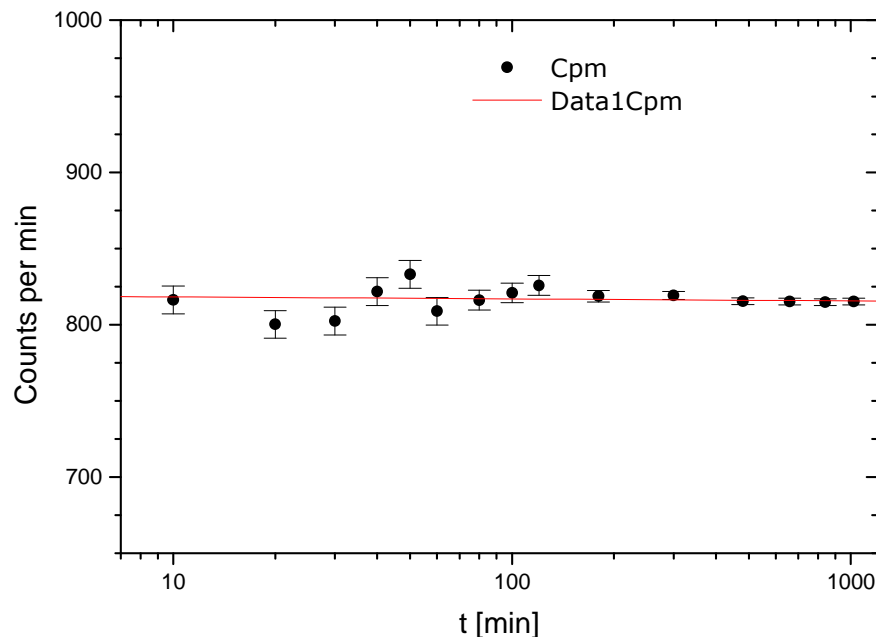


OptiPhase HiSafe 3

Results and discussion

Chemiluminescence study

- Quantulus already has a built-in monitor for detection of chemiluminescence events (emission of single photon), Delayed Coincidence Circuitry, DCOS



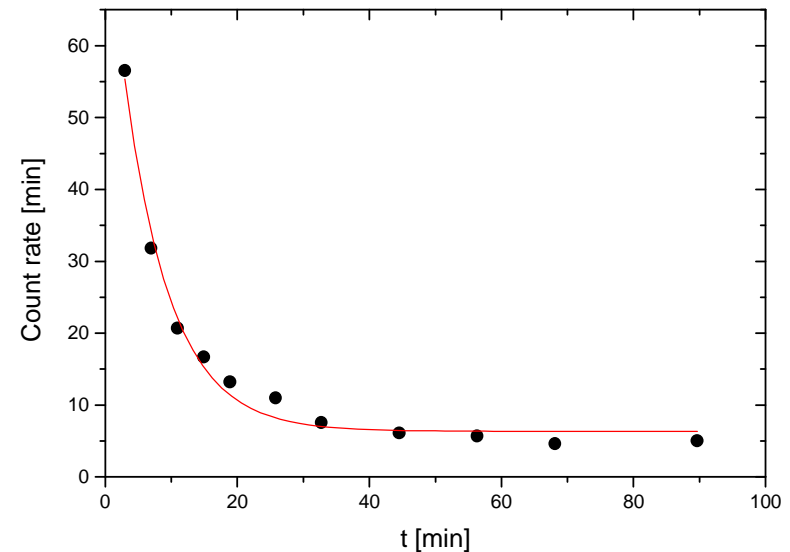
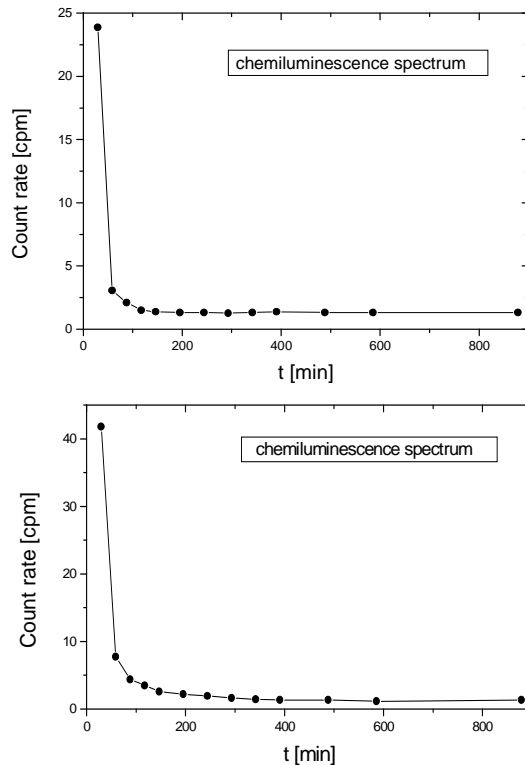
No visible deviation on count rate for active samples during time that would come as consequence of chemical reactions if the sample was counted straightaway after its preparation

Despite conclusions that 1 day waiting time is adequate for Quantulus performances, when measuring active samples, it is not necessary in our procedure if we monitor chemiluminescence spectrum

Results and discussion

Chemiluminescence study

- For samples with very low activity (blank samples) there is some indication for chemical reactions taking place during first 3 hours after its preparation



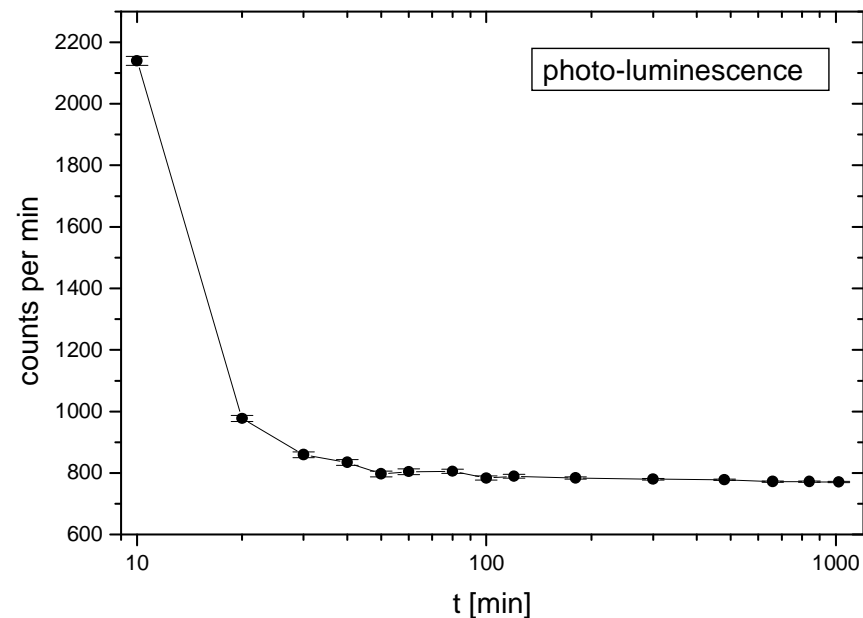
Half-life of chemiluminescence
decay estimation: $T_{1/2} \sim 16.4$ min

8ml distilled water+12 ml OptiPhase HiSafe2 (up)
8ml distilled water+12 ml OptiPhase HiSafe3 (down)
counted immediately after its preparation

Results and discussion

Photoluminescence study

- Reactions of photoluminescence due to activation of cocktail by ultraviolet light have a relatively rapid decay rate, these don't affect spectrum after ~2 hours

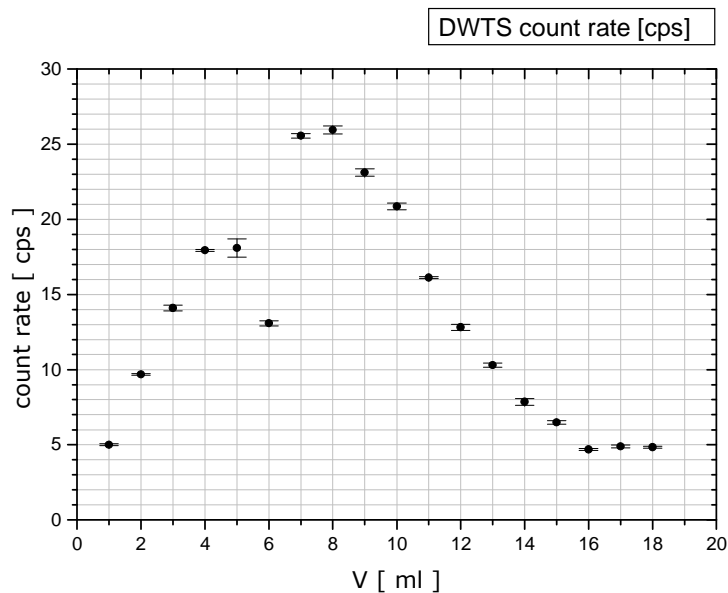


Count rates of sample - 8ml tritiated water + 12 ml OptiPhase HiSafe 3, measured immediately after its exposure to sunlight.

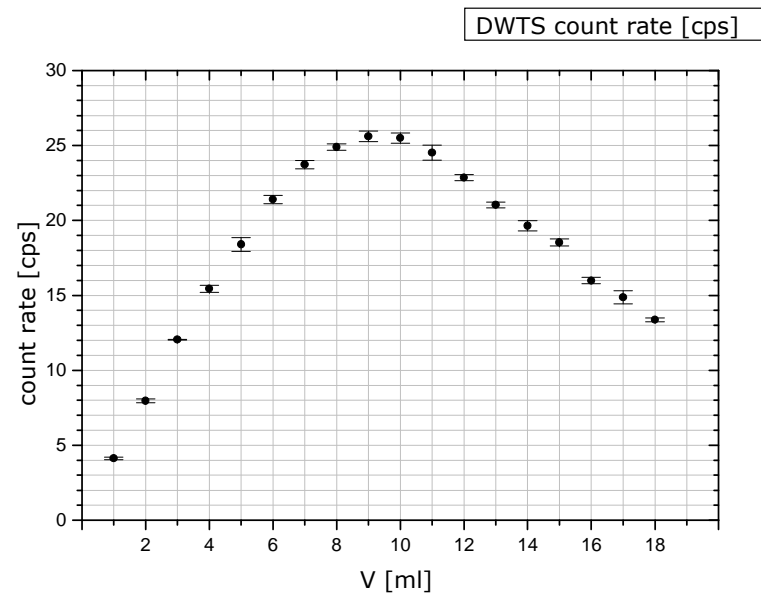
Results and discussion

Sample/scintillant ratio optimization

- Measurements of samples with different ratios of tritiated water and cocktail (keeping the total volume 20 ml) were performed. The optimal water : cocktail ratio is 9 : 11 ml, but as environmental samples may induce phase separation, we decide to use 8ml sample+12 ml LS cocktail, as suggested by various authors.



OptiPhase HiSafe 2



OptiPhase HiSafe 3

Results and discussion

Scintillant/vial combination crosscheck

Chemical composition of scintillation cocktails used (manufacturer's Material Safety Data Sheet). The manufacturer of all is PerkinElmer.

Cocktail	Solvent and additives	Scintillator
OptiPhase HiSafe 2	DIN > 70% Sodium dioctyl-sulfosuccinate < 14% Poly(ethyleneglycol)mono(4-nonylphenyl)ether < 7% 2- (2-butoxyethoxy)ethanol < 5% N-lauroyl sarcosine < 5% Propylene glycol butyl ether < 3% Sodium borohydride < 1% Diethanolamine < 1%	PPO ≤ 2.5% bis-MSB ≤ 2.5%
OptiPhase HiSafe 3	DIN > 60% poly(ethyleneglycol)mono(4-nonylphenyl)ether < 25-30% α -phenyl- ω -hydroxypoly(oxo-1,2-ethanediyl) phosphate < 10%	PPO ≤ 1% bis-MSB ≤ 0.1%
Ultima Gold LLT	DIN 40-60% Ethoxylated nonylphenol 20-40% 2-(2-butoxyethoxy)ethanol 2.5-10% Ethoxylated fatty alcohol ≤ 2.5% Nonylphenyl polyoxyethylene ether phosphate < 2.5% 3,6-dymethyl-4-octyne-3,6-diol ≤ 2.5%	PPO ≤ 2.5% bis-MSB ≤ 2.5%

PPO – 2,5 - diphenyloxazole

DIN – *di*-isopropylnaphtalene isomers

bis-MSB – 1,4 -bis(2-methylstyryl)-benzene

Pseudocumene – 1,2,4-trimethylbenzene

Results and discussion

Scintillant/vial combination crosscheck

Two vial types : 20 ml glass vials (low potassium borosilicate glass),
20 ml plastic vials (low diffusion polyethylene anti static)

Comparison of tritium standard count rates ($A=5612 \text{ Bq}\cdot\text{l}^{-1}$) for two different scintillation cocktails and two types of 20ml vials used. Water : scintillation cocktail ratio was set to 8:12 ml.

Cocktail	Plastic vials			Glass vials		
	cps	Efficiency [%]	FOM	cps	Efficiency [%]	FOM
OptiPhase HiSafe 2	15.75 (21)	35.1 (5)	1080.7	16.33 (29)	36.4 (6)	109.9
OptiPhase HiSafe 3	13.69 (25)	30.5 (6)	816.0	13.81 (26)	30.8 (6)	79.1

$$\varepsilon_t = \frac{R_s}{V T_2}$$

$$\text{FOM} = \frac{(\text{Efficiency } [\%])^2}{\text{Background [cpm]}}$$

- Background (and ~blank samples) should be prepared exclusively in plastic vials to avoid natural radioactivity contained in glass of the vial ($^{40}\text{K} \rightarrow ^{40}\text{Ar}$, which emits X-rays).

Results and discussion

Scintillant/vial combination crosscheck

Environmental samples (Danube samples) with low activity expected (close to background). Water:cocktail ratio was set to 8:12 ml. Counting time was 600min.

Sample	C o c k t a i l			
	OptiPhase HiSafe 2		OptiPhase HiSafe 3	
	Plastic vials Cpm	Glass vials Cpm	Plastic vials Cpm	Glass vials cpm
Blank	1.14 (4)	12.06 (14)	1.14 (4)	12.00 (14)
Karlovci	1.68 (5)	12.72 (15)	1.80 (6)	12.66 (15)
Oficirac	1.50 (5)	12.42 (15)	1.56 (5)	12.42 (14)
Becarac	1.44 (5)	12.66 (15)	1.74 (5)	12.48 (15)
Strand	1.68 (5)	12.96 (15)	1.86 (6)	12.66 (15)

Sample	OptiPhase HiSafe 2	OptiPhase HiSafe 3
	Activity concentration	
Karlovci	2.1 (4) Bq l ⁻¹	2.9 (5) Bq l ⁻¹
	18 (4) TU	24 (4) TU
Oficirac	2.5 (4) Bq l ⁻¹	2.9 (4) Bq l ⁻¹
	21 (4) TU	24 (4) TU
Becarac	< MDA	2.5 (4) Bq l ⁻¹
		20 (4) TU
Strand	3.2 (4) Bq l ⁻¹	4.5 (5) Bq l ⁻¹
	27 (4) TU	38 (4) TU

Calculated activity concentrations of Danube samples (plastic vials). Comparison of adequacy and behavior of two cocktails.

$$A = \frac{R_a - (R_b + r_q)}{60\varepsilon_f V}$$

The upper limit for tritium in drinking water is 100 Bq l⁻¹ (European Commission)

Results and discussion

Intercomparison with IRB for IAEA samples

Sample	*IRB result	IAEA ref.	OptiPhase HiSafe 3 used		OptiPhase HiSafe 2 used	
			NS result	z-score	NS result	z-score
IAEA TRIC2008 Intercomp. T17	14.44±0.40 TU 1.70±0.04 Bq l ⁻¹	14.46±0.08 TU	<MDA (electrolytic enrichment recommended)		<MDA (electrolytic enrichment recommended)	
IAEA TRIC2008 Intercomp. T19	576±13 TU 68.0±1.5 Bq l ⁻¹	568.7±2.3 TU	584±17 TU 68.9±2.0 Bq l ⁻¹	0.9 (for IAEA ref) 0.47 (for IRB ref)	724±16 TU 85.5±1.9 Bq l ⁻¹	9.7 (for IAEA ref) 9.25 (for IRB ref)
Sample 1	1.365·10 ⁸ TU (±12957) 1.61·10 ⁷ Bq l ⁻¹ (±1530)	very ³ H active	1.389·10 ⁸ TU (±2768880) 1.639·10 ⁷ Bq l ⁻¹ (±326750)	0.87	1.31·10 ⁸ TU (±1866610) 1.546·10 ⁷ Bq l ⁻¹ (±220275)	-2.95
Sample 2	47563±214 TU 5612±25 Bq l ⁻¹	-	47079±1202 TU 5556±142 Bq l ⁻¹	-0.40	46284±1016 TU 5462±120 Bq l ⁻¹	-1.26

*Two IAEA samples were measured using OptiPhase HiSafe 3 (for the first one electrolytic enrichment was performed), the other two were measured with Ultima Gold LLT

Conclusions

Optimization of detector system in order to apply direct method without distillation led to the following statements:

- Optimal sample/scintillant ratio - confirmed to be 8:12 ml
- Chemiluminescence is suppressed 3 hours after sample preparation. $T_{1/2} \sim 16.4$ min
- MDA ($t=300$ min)= 2.0 Bq l^{-1} both for OptiPhase HiSafe 2 and OptiPhase HiSafe 3
- Backgrounds and samples with low-level activity close to background are to be put strictly in plastic vials (to avoid natural radioactivity of glass vials which becomes dominant source of radiation)

Conclusions

- ^3H level of Danube samples is low as expected. Calculated activities obtained with OptiPhase HiSafe 2 are slightly higher compared to the ones measured with OptiPhase HiSafe 3.
- OptiPhase HiSafe 2 has better FOM values and higher efficiency ($35.1 \pm 0.5\%$) than OptiPhase HiSafe 3 but failed during intercomparison with IRB and IAEA. OptiPhase HiSafe 3 achieved modest FOM parameter and worse efficiency ($30.5 \pm 0.6\%$) but obtained excellent results in all measurements within intercomparison.
- Ultima Gold LLT remains the best choice for scintillation cocktail with highest efficiency (up to 56%) giving the most precise results as shown in IRB and IAEA data.



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Thank you for your attention!