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Study on quench effects in liquid scintillation counting during tritium measurements

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Abstract Quench effects can cause a serious reduction in counting efficiency for a given sample/cocktail mixture in liquid scintillation counting (LSC) experiments. This paper presents a simple experiment performed in order to test the influence of quenching on the LSC efficiency of ^3H . The aim of this study was to investigate the behavior of several quench agents with different quench strengths (nitromethane, nitric acid, acetone, dimethyl-sulfoxide) added in different amounts to tritiated water in order to obtain standard sets for quench calibration curves. The OptiPhase HiSafe 2 and OptiPhase HiSafe 3 scintillation cocktails were used in this study in order to compare their quench resistance. Measurements were performed using a low-level LS counter (Wallac, Quantulus 1220).

Keywords Standard quench parameter [SQP(E)] · Tritium measurements · Liquid scintillation counting · Scintillation cocktail

Introduction

There are mainly four different types of quenching that may occur in the mixture: absorption or physical quenching, chemical quenching, photon or color quenching and solvent dilution quenching [1]. Quenching is the most important factor responsible for a reduction in counting efficiency for a given sample/cocktail mixture in liquid scintillation counting (LSC), whereby the use of a liquid scintillation cocktail with an inherently high resistance to quenching is important [2]. Since chemical quenching is always present in LSC samples, dealing with this problem is necessary for the appropriate use of every LS counter. The evaluation of the overall performance of a cocktail involves the quantification of several factors: besides sample load capacity/compatibility, the effect of the sample load on ^3H counting efficiency, figure of merit (FOM) and sample/counting efficiency stability over time, as well as quench resistance estimation.

The present study involves an analysis of the performance of several quench agents added in aqueous samples in order to evaluate the quenching levels they induce through the transfer of nuclear decay energy to the scintillation cocktail solvent process. An investigation of prepared sets was also carried out for all the quenchers used in this study since the sample stability of the cocktail and counting efficiency become important in some specific cases where LSC vials have to be stored for longer periods of time after preparation before being counted or recounted [2].

It is possible to compensate for quenching and to determine the sample activity or DPM if the counting efficiency of the measured sample is known. Therefore, it is important that the system is equipped with a calibration curve, i.e. the counting efficiency of ^3H as a function of the

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quench-indicating parameter (QIP), which could be applied for each measured sample. As a QIP in liquid scintillation analysis, the standard quench parameter [SQP(E)] is a robust and widely used parameter in monitoring and correcting for sample quench levels in the determination of detection efficiencies [3].

The measurement of an external SQP(E) with the QuantulusTM counter requires the recording of two spectra: the first one is measured when the sample is exposed to γ -radiation from an external source of ^{226}Ra or ^{152}Eu . It contains the Compton electron events plus the sample events. The other spectrum is measured from the sample alone during the same counting time. The net external standard spectrum is obtained by subtracting the two spectra. The end point SQP(E) is calculated as the channel above which 1 % of all the signal of the net external standard spectrum is found. Such an approach gives a quick method of adjusting counting efficiency, which is very practical for environmental measurements [4].

With the development of the multichannel analyzer (MCA), sample spectrum QIPs have become more sophisticated, as all of the channels of the MCA can be used simultaneously to measure quench, since quenching manifests itself by shifting the energy spectrum toward the lower energy channels in the MCA [3]. The spectral quench parameter of the external standard SQP(E) is measured with ^{226}Ra or ^{152}Eu [5] as the standard external source of gamma radiation which creates a Compton spectrum in the scintillation cocktail as a tool for facilitating the measurement of QIP in the sample. The value of the QIP is then used to determine the reduction of radionuclide counting efficiency based on measured QIP, the creation of a quench correction curve and subsequently for the determination of radionuclide activity. This procedure does not correct for other effects such as chemiluminescence.

Although the quench curves are specific to the counter and to the sample composition, this paper presents an example how quench effects can manifest themselves in everyday routine measurements. The aim of this study was to parameterize quench effects for different quench agents with varying quench levels in our laboratory. The addition of any chemical changes the composition of a liquid scintillation sample and, consequently, the cross section for photon interaction is changed, which also has an influence on the measured SQP(E) value. The presented experiments could be used as a “recipe” for other similar setups.

There are more sophisticated LSC methods as well, triple-to-double coincidence ratio for example (TDCR), used for the measurement of absolute activity [6]. The method is based on a free parameter model describing the process of light emission and detection in a scintillation counter. It is to be noted that the TDCR value is neither a quenching indicator nor an efficiency value. The TDCR value as a

quenching indicator is only applicable if the relation between the TDCR value and the efficiency is unambiguous. This is the case with pure beta emitters but not radionuclides decaying by electron capture (EC) or radionuclides with complex decay schemes, where up to three efficiency values can correspond to the same TDCR value [7].

Experimental setup

Sample preparation, materials, and equipment

The results of the experiments were obtained using a Wallac 1220 Quantulus Ultra Low Level Liquid Scintillation Spectrometer manufactured by PerkinElmer (Finland, 2002), with EASYView and WinQ software. The tritium window was fixed to channels 1–250 [8].

To obtain an ultra low level count, this instrument uses a passive radiation shield to reduce natural background radiation and an active guard detector to remove the natural background fluctuation [9]. The system is provided with two pulse analysis circuits that are accessible to the users: a pulse shape analysis (PSA) and pulse amplitude comparator (PAC) circuit. There is also a delayed coincidence circuit (DCOS) inside the Quantulus, which is useful for the correction of chemiluminescence [5]. The Quantulus 1220 has two MCA, one is used for the active shield and the second one is used for spectra recording. The tritium 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 one half of the MCA, the whole sample spectrum being recorded in the other half of the MCA [5].

Tritiated water with an activity concentration of $1.61 \times 10^6 \text{ Bq L}^{-1}$ was used as a standard. All LSC samples were prepared in 20 mL low diffusion polyethylene anti static vials (PerkinElmer). The cocktails we have access to in our laboratory at this moment are OptiPhase HiSafe 2 and OptiPhase HiSafe 3 which were used for the comparison of their quench resistance. Their chemical composition is given in Table 1. A series of quench standards were prepared with quench agents with different quench strengths according to [3] for the creation of quench correction curves. All quench standards were prepared with 8 mL of tritiated water and 12 mL of scintillation cocktail, by adding increasing amounts of quenching agents listed here by their quench strength: nitromethane (CH_3NO_2 , 100 %), which is known as one of the strongest quenchers [3]; acetone ($(\text{CH}_3)_2\text{CO}$); nitric acid (2 M HNO_3 and 3 M HNO_3) as the mildest among these agents, and dimethylsulfoxide ($(\text{CH}_3)_2\text{SO}$). Because of the similar structure of $(\text{CH}_3)_2\text{SO}$ with $(\text{CH}_3)_2\text{CO}$ it was assumed that DMSO could induce similar quench effects. Calibration samples were

Table 1 Chemical composition of scintillation cocktails used (manufacturer's Material Safety Data Sheet) [11]. The manufacturer of both is PerkinElmer

Cocktail	Solvent and additives	Scintillator
OptiPhase HiSafe 2	DIN >70 %	PPO
		≤2.5 %
	Sodium dioctyl-sulfosuccinate <14 %	Bis-MSB
		≤2.5 %
	Poly(ethyleneglycol)mono(4-nonylphenyl)ether <7 %	
	2-(2-Butoxyethoxy)ethanol <5 %	
	N-lauroyl sarcosine <5 %	
	Propylene glycol butyl ether <3 %	
OptiPhase HiSafe 3	Sodium borohydride <1 %	
	Diethanolamine <1 %	
	DIN >60 %	PPO ≤1 %
	Poly(ethyleneglycol)mono(4-nonylphenyl)ether <25–30 %	
	α-Phenyl-ω-hydroxypoly(oxo-1,2-ethanediy)l phosphate <10 %	Bis-MSB
		≤0.1 %

PPO 2,5-diphenyloxazole, Bis-MSB 1,4-bis(2-methylstyryl)-benzene, DIN di-isopropyl naphthalene isomers, Pseudocumene 1,2,4-trimethylbenzene

stored for 6 h [10] before counting to avoid chemiluminescence and were counted for 5 min, 4 cycles each.

Methods

A set of quenched standards represents samples with a known and constant radionuclide activity but varying levels of quench. From the count rates of each standard and SQP(E) value measured by the LSA, a standard curve of counting efficiency versus SQP(E) is plotted. When a sample of unknown activity is analyzed in the LSA, the instrument will determine the SQP(E) value of the sample, and extract the counting efficiency from the standard curve.

The external standard method was used for quench correction in this paper. This method can be the most reliable when very accurate DPM values are required, because the users can control all aspects of the preparation of the quenched standards in order to represent the chemistry of their experimental samples most closely [3]. A detailed description of the procedure for the preparation of quenched standards and a quench correction curve from the quenched standards is provided in [3].

Results and discussion

Before carrying out the measurements of the calibration samples, it was necessary to previously determine efficiencies for ^3H measurements without the addition of

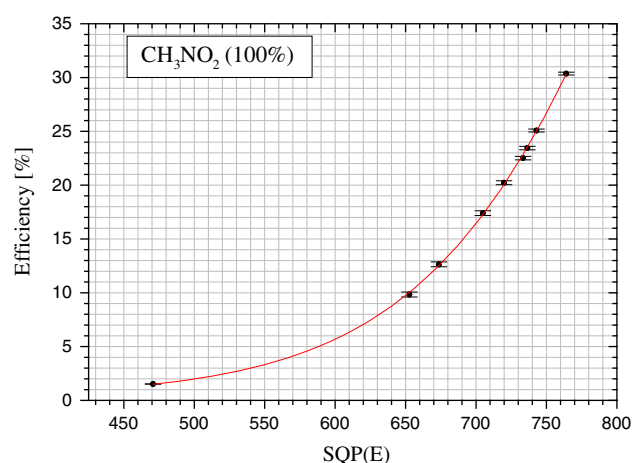


Fig. 1 The quench curve obtained by adding the quench agent CH_3NO_2 (100 %), using the OptiPhase HiSafe 3 cocktail. A sigmoidal fit produced the following quench equation:

$$y(x) = \frac{0.322 - 116.99}{1 + e^{\frac{x - 832.4}{-832.4}}} + 116.99$$

quenching agents, which was done according to the method suggested by Pujol and Sanchez-Cabeza [12]. The obtained efficiencies were as follows: 35.1 ± 0.5 % for OptiPhase HiSafe 2 and 30.5 ± 0.6 % for OptiPhase HiSafe 3. HiSafe 3 contains surfactants (organic phosphates) in its chemical composition, which lowers its efficiency [13].

Nitromethane as a quenching agent

CH_3NO_2 is known as one of the strongest quenchers (Fig. 1), and the preparation of samples was carried out according to the recommendation in [3]. Figure 1 represents the quench correction curve obtained by adding the quench agent CH_3NO_2 (100 %), using the OptiPhase HiSafe 3 cocktail and the efficiency values were fitted to a sigmoidal fit.

Measurements of the same set of quenched samples with OptiPhase HiSafe 2 during the first 2 weeks after its preparation gave different results. In Fig. 2 it can be noticed that both the efficiency and SQP(E) of samples decrease during time, the explanation follows from the chemical composition of OptiPhase HiSafe 2 (Table 1), namely that it is most probably the effect of the reduction reaction that sodium borohydride (NaBH_4) induced. During that time NaBH_4 was interacting with CH_3NO_2 (possibly creating aminomethane), which initially diminished the quench effect produced by CH_3NO_2 . After ~ 2 weeks the NaBH_4 was probably spent, which allowed the remaining free CH_3NO_2 to quench samples in a constant manner. The sequence of this reaction could be discovered based on the quench curves given in Fig. 3, parameterized in Table 2.

The conclusion that follows from these experiments is that the set of samples prepared for obtaining a quench correction curve with CH_3NO_2 (100 %), using the

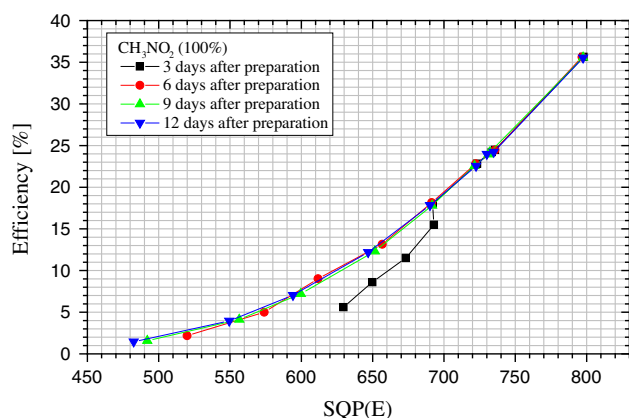


Fig. 2 A set of quench curves measured in different periods of time after sample preparation with the added quench agent CH_3NO_2 (100 %), using the OptiPhase HiSafe 2 cocktail

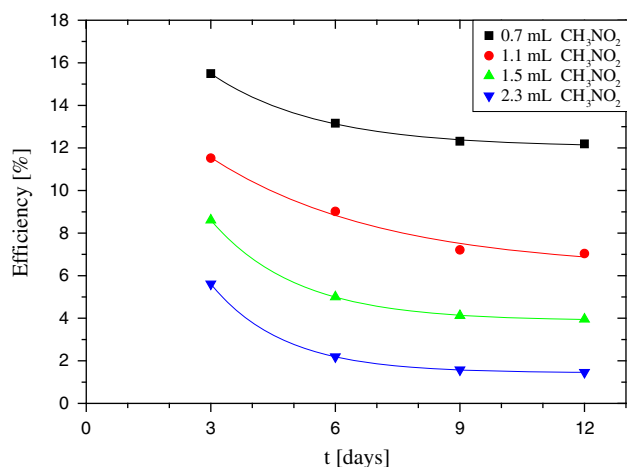


Fig. 3 Time dependence of detection efficiency when different volumes of the quenching agent CH_3NO_2 (100 %) are added, using the OptiPhase HiSafe 2 cocktail

Table 2 Quench resistance equations for different volumes of nitromethane added (corresponding Fig. 3) fitted to exponential functions

Volume of CH_3NO_2 added (mL)	Quench equation
0.7	$y(x) = 12.04 + 3.45 \exp\left[-\frac{x-3}{2.6}\right]$
1.1	$y(x) = 6.3 + 5.26 \exp\left[-\frac{x-3}{4.12}\right]$
1.5	$y(x) = 3.88 + 4.73 \exp\left[-\frac{x-3}{2.07}\right]$
2.3	$y(x) = 1.44 + 4.18 \exp\left[-\frac{x-3}{1.76}\right]$

OptiPhase HiSafe 2 should be stored for at least 2 weeks for reduction reactions to take place and to gain the stability of the samples.

On the other hand, the set of samples quenched with OptiPhase HiSafe 3 did not show any serious deviations

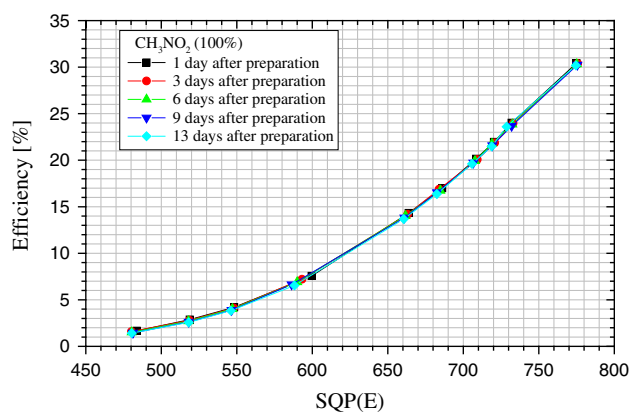


Fig. 4 A set of quench curves measured in different periods of time after sample preparation with added quench agent CH_3NO_2 (100 %), using the OptiPhase HiSafe 3 cocktail

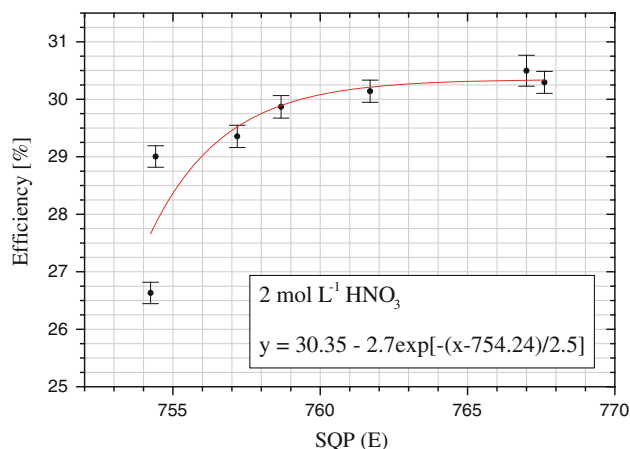


Fig. 5 A quench curve obtained by adding HNO_3 (concentration of 2 mol L^{-1}) as a quench agent, using the OptiPhase HiSafe 3 cocktail, fitted to an exponential function

during time (Fig. 4), as it was expected according to the chemical composition (given in Table 1) of this cocktail in which no reducing agents are present. It can be concluded that the experimental data obtained for the quench curve with OptiPhase HiSafe 3 are relevant as early as 1 day after sample preparation when the samples become stable.

Nitric acid as a quenching agent

As shown on Figs. 5 and 6, nitric acid is a very mild quencher, and later measurements of the same sets of samples showed that the addition of HNO_3 does not trigger any additional reactions in samples during time and that they are stable. The maximum added volume in 20 mL of radioactive sample was determined as 0.75 mL of 2 M HNO_3 and 0.5 mL of 3 M HNO_3 , since HNO_3 is a strong electrolyte that in higher concentrations causes nitrification

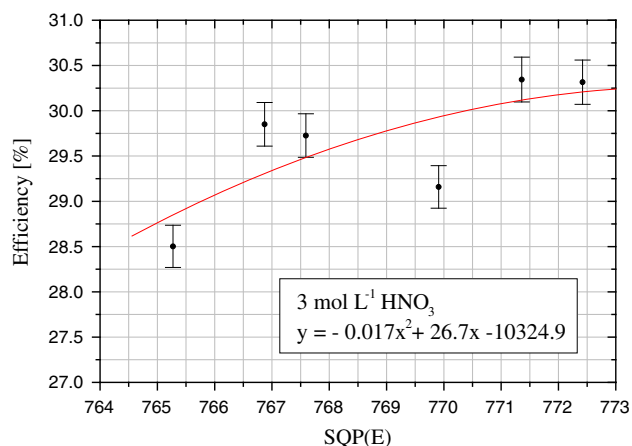


Fig. 6 A quench curve obtained by adding HNO₃ (concentration of 3 mol L⁻¹) as a quench agent, using the OptiPhase HiSafe 3 cocktail, with a second-order polynomial fit

of aromatic components in the scintillator and, therefore, invalidates its performance.

The effect of coagulation occurring in the set of samples on the overall optical characteristics of the cocktail, which could, besides the obvious chemical quench, generate the possible occurrence of color quench at higher concentrations of HNO₃, would require a more careful analysis.

It was not possible to perform the same measurements with OptiPhase HiSafe 2 since its chemical components would coagulate in the presence of a strong electrolyte such as nitric acid even at lower concentrations, leading to very inhomogeneous samples. These results confirmed that OptiPhase HiSafe 2 is not suitable for strong electrolytes and very high and very low pH values, as is stated by its producer.

Acetone as a quenching agent

Acetone is miscible with water and organic solutions at all concentrations. Our assumption is that at lower concentrations there is only chemical quench but at higher concentrations color quench could also be present. The set of samples quenched with acetone turned out to be stable over time as well. No reduction of efficiency was discovered in repeated measurements. It was concluded from the quench curve shown on Fig. 7 that acetone belongs among mild quenchers [since the set was prepared by adding from 0 to 2 mL (CH₃)₂CO into 20 mL vials].

DMSO as a quenching agent

As it was reported in [10], in our previous experiments, while performing routine distillation procedures with ³H standard according to the Standard Test Method [14], there

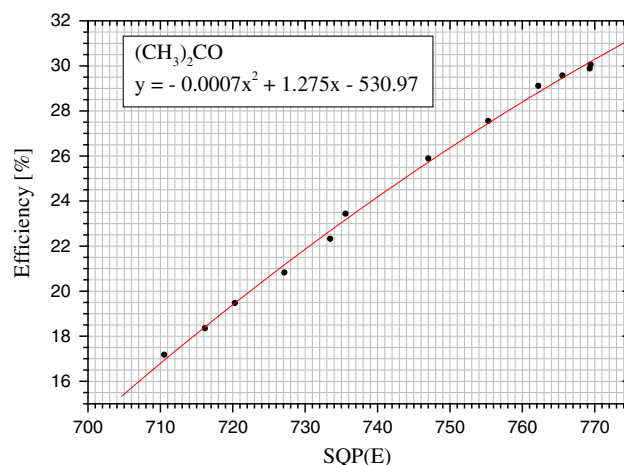


Fig. 7 A quench curve obtained by adding the quench agent acetone (CH₃)₂CO (100 %) using the OptiPhase HiSafe 3 cocktail with a second order polynomial fit

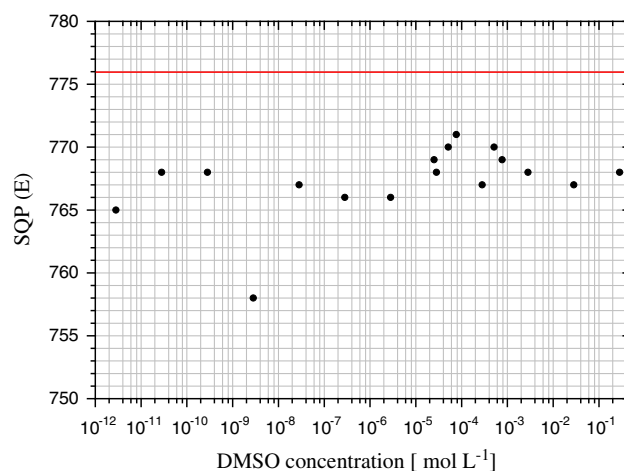


Fig. 8 SQP(E) variation in a wide range of dimethyl-sulfoxide concentrations, obtained with the OptiPhase HiSafe 3 cocktail. The line in the upper part of the graph indicates the SQP(E) value of non-quenched samples

was an odor of dimethylsulfoxide (CH₃)₂SO and detection efficiency was reduced.

Our first goal was to discover the relevant range of DMSO concentrations that could cause quench in count-rate measurements, so a series of measurements within a wide range of DMSO concentration levels was performed and the results have been presented in Figs. 8 and 9. It was not possible to complete the establishment of a quench curve with dimethyl-sulfoxide because of the obvious deviations in both SQP(E) and efficiency from non-quenched samples displayed on all levels of DMSO concentrations added. This behavior might be a consequence of constant chain reactions occurring at all DMSO concentrations in the samples.

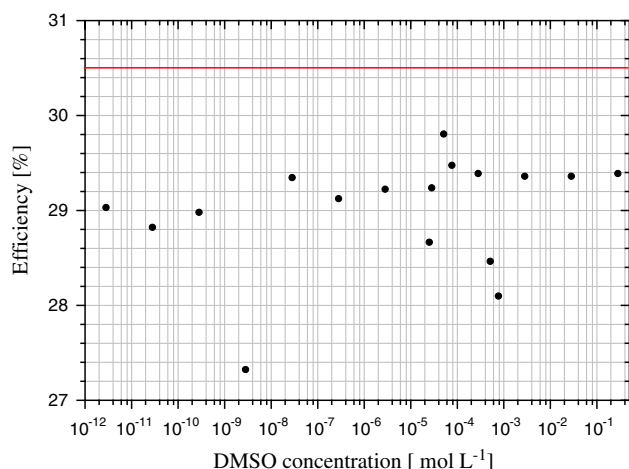


Fig. 9 Efficiency variation in a wide range of dimethyl-sulfoxide concentrations, obtained with the OptiPhase HiSafe 3 cocktail. The line in the upper part of the graph indicates the efficiency detection value of non-quenched samples

Significant quench was observed around 10^{-9} mol L⁻¹. This peak should be subjected to more detailed analyses, whereby an examination in a narrow region around 10^{-9} mol L⁻¹ concentration is suggested for further investigations.

Conclusions

The influence of quenching agents was investigated using LSC techniques. The quench correction curves obtained for several quenching agents (nitromethane, acetone, 2 and 3 M nitric acid) were plotted and efficiency values were fitted in order to obtain quench resistance equations. The experiments presented in this report intend to objectively quantify the quench resistance of two cocktails, OptiPhase HiSafe 2 and OptiPhase HiSafe 3. The Conclusions are as follows:

- (1) In case of nitromethane, the use of this agent in combination with OptiPhase HiSafe 2 demands storing the set of prepared quenched samples for at least 2 weeks after its preparation, probably in order for the reduction reactions induced by sodium borohydride to take place. As for the set of nitromethane quenched samples prepared with OptiPhase HiSafe 3, the samples become stable after 1 day of preparation.
- (2) Nitric acid can generate a very mild and stable quench in samples. Its application in combination with OptiPhase HiSafe 2 is not possible at all, since coagulations always take place. As for its combination with OptiPhase HiSafe 3, the limit of the maximum added volume in 20 mL of a radioactive sample was determined to be 0.75 mL for 2 M

HNO₃ and 0.5 mL for 3 M HNO₃, since at higher concentrations HNO₃ causes nitrification of the aromatic components in the scintillator.

- (3) Acetone is a somewhat stronger (and more stable) quencher than nitric acid, and the usage of its quench curve is appropriate when no serious quench is expected in samples.
- (4) DMSO is not a classical quencher so there was no usual correlation between efficiency and SQP(E) and it was not possible to obtain the quench curve. Investigation in a narrow region around 10^{-9} mol L⁻¹ concentration could show a more serious quench and indicate that the relevant range of DMSO concentrations within the quench curve could be completed.

Resistance of the two cocktails used in this study has shown that they don't behave similarly in the presence of various quenchers, OptiPhase HiSafe 2 being significantly less tolerant in the chemical sense, meaning it is not suitable for strong electrolytes and very high and very low pH values. In the process of creating quench curves with OptiPhase HiSafe 3, users will have more options when choosing what quench agent to add.

It is now possible to determine the counting efficiency for an unknown sample based on the measurement of SQP(E) according to the obtained quench curves. The quench curve obtained with nitromethane was chosen to be stored in Quantulus since it had shown the widest range of SQP(E) values and reduced efficiencies. This was expected as nitro groups are known to be the strongest quencher of all the used ones in this research.

Although there are more sophisticated LSC methods like TDCR, if someone uses Quantulus, the presented experiments could be applied as a "recipe" for similar setups.

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