

## EFFECT OF VISCOSITY ON QUENCH CHARACTERISTICS OF SOLVENTS FOR LIQUID SCINTILLATION COUNTING

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**ABSTRACT.** In liquid scintillation counting (LSC) chemical and/or color quench reduce counting efficiency for low-energy radionuclides. Color quench usually involves absorption of produced photons by colored chemical components. Chemical quench follows a different pathway; the energy transfer efficiency is reduced by quenching of the solvent excitation processes. Introduction of solvents with high boiling points offered numerous advantages for LSC users. In addition, the quench characteristics appeared to be favorable compared to traditional solvents. Quench characteristics of LSC solvents with strong chemical quenchers, *e.g.*, carbon tetrachloride, in relation to the solvent viscosity, are reviewed and compared.

### INTRODUCTION

Organic solvents have been the subject of many theoretical studies in the early development of the liquid scintillation counting (LSC) technique for quantification of alpha-, beta- and gamma-emitting radionuclides. Practical considerations of environmental factors have led to the introduction of solvents with improved safety characteristics, when compared to traditional solvents, *e.g.*, toluene and pseudocumene. Considerable research has been devoted to understanding LSC processes; Birks (1971, 1975) discussed the importance of solvent parameters. These reviews helped to improve solvent quality with respect to purity.

Quench, the process of the reduction of the number of photons observed for a given amount of energy input to an LS solution, was thought to be a well-characterized phenomenon. The introduction of solvents with improved safety characteristics, *e.g.*, di-isopropylnaphthalene (DIPN), caused quench characteristics to show differences when compared to traditional, more volatile solvents. The decrease in counting efficiency for a given radionuclide, in particular, tritium, when the amount of quench was increased, is less favorable in modern solvents (Neumann, Roessler & ter Wiel 1991). Assuming that most of the quench parameters are relatively constant or can be kept relatively constant in a given solvent, one can vary the light output by adding different types of quench or amounts of quenching agent. The mechanisms by which chemical and color quench act in a scintillation solvent are known to be different (Gibson 1980). Consequently, at high quench levels, curves for these types of quench are not completely superimposable over a complete quench range for a given radionuclide.

Ross (1965) and ten Haaf (1974) have studied color quench, which is caused by any absorbing material that reduces the number of photons transmitted through the scintillation medium. Consequently, the number of photons seen by the photomultiplier is reduced, thus causing a decrease in counting efficiency. This molecular absorption of the fluorescent radiation follows Beer's Law

$$I = I_0 e^{-alc}$$

where I = number of transmitted photons

$I_0$  = number of initial photons

a = absorptivity coefficient

l = path length of photons

c = concentration of absorbent.

*Liquid Scintillation Spectrometry 1992, edited by*

*J. E. Noakes, F. Schönhofer and H. A. Polach. RADIOCARBON 1993, pp. 185-191*

Chemical quench (or impurity quench) prevents the production of photons. A competition for the excited molecules between scintillator and impurity molecules is the origin of this reduced light output. Birks (1971) studied these effects on the scintillation process. An important factor is excitation quenching. Factors affecting the excitation quenching are dissolved oxygen, temperature, density of solvent and type of quenching agent. I will compare the characteristics of quenching agents as they affect some organic solvents used in LSC.

## METHODS

Counting efficiency was measured on a Packard Tri-Carb® 2250CA/LL LS counter operating at 22°C, using standard settings for counting <sup>3</sup>H, according to manufacturer's instructions. The efficiency of a <sup>3</sup>H-sealed standard was 64.8 ± 0.2%. After light and temperature stabilization, samples were counted for 10 min each. Viscosity of solvents was determined on a Haake Viscotester VT01 at 22°C.

PPO and bis-MSB scintillators (Packard) were used in a concentration of 7 g liter<sup>-1</sup> of PPO and 1 g liter<sup>-1</sup> of bis-MSB in the solvents studied. Solvents were purified prior to use by column chromatography, consisting of basic and acidic alumina. Dodecyl benzene and pseudocumene were obtained from Packard Instrument B. V., Groningen, di-isopropylnaphthalene from Rütgers Kureha Solvents, Duisberg, Germany, phenylxylyl ethane and isopropyl biphenyl research samples from Koch Chemicals, Corpus Christi, Texas, USA, 2-ethyl naphthalene and phenyl cyclohexane from Aldrich, Milwaukee, Wisconsin, USA. Carbon tetrachloride (Merck, Darmstadt, Germany) was used as such, dimethyl yellow (Merck) was used at a concentration of 0.01% in di-isopropylnaphthalene, methyl salicylate (Merck) used as such. Counting efficiency for <sup>3</sup>H (absolute) of the samples was determined by using tritiated hexadecane as label; 30 μl of tritiated hexadecane was spiked to each vial. The activity was calculated from the spiked amount, applying the conversion factor for <sup>3</sup>H decay. Absolute counting efficiency is defined as

$$\frac{\text{cpm observed}}{\text{dpm calculated}} \times 100 .$$

Samples were counted in high-performance glass vials (Packard 6000128). Quench studies were performed on a series of solutions prepared as follows: To 10 ml of LSC solvent were added increments of 160 μl of the dimethyl yellow solution, 20 μl of carbon tetrachloride or 46 μl methyl salicylate. Unless otherwise noted, scintillator concentrations were used as described above.

## RESULTS

Table 1 gives the viscosities and boiling points of the solvents. Table 2 summarizes the decrease in counting efficiency produced in some of the solvents. Aliquots of 160 μl quenching agent were added to the scintillator solutions. Because the results are similar for most of the solvents in this study, selected solvents were used to study color quench characteristics of a low-, medium- and high-viscosity solvent (Fig. 1).

Table 3 illustrates the decrease in counting efficiency as a function of chemical quench in different LS solvents, which were selected to compare different levels of viscosity and boiling point. Pseudocumene has low viscosity, EN and PCH have middle viscosity; the others have relatively high viscosities. Table 3 also summarizes data obtained on characteristics with the chemical quench, carbon tetrachloride. Figures 2 and 3 display chemical quench data.

TABLE 1. Physical Data of Solvents

Solvent	Abbreviation	Boiling point (°C)	Viscosity (m Pa.s)
Pseudocumene	PS	168	2.0
2-ethyl naphthalene	EN	251–252	6.1
Phenyl cyclohexane	PCH	240	5.3
Dodecyl benzene (tech)*	DDB	290–310	11.4
Di-isopropylnaphthalene*	DIPN	290–300	14.8
Phenyl xylyl ethane*	PXE	302–319	16.2
Isopropyl biphenyl*	IPB	290–316	13.8

\*Solvents are technical products; boiling ranges given are from manufacturers' literature.

TABLE 2. Color Quench: % <sup>3</sup>H Counting Efficiency vs. Added Color Quench\*

Quench agent (μl)	Solvent		
	PS	EN	DIPN
0	60.7	61.8	60.9
160	46.9	46.3	46.3
320	35.8	33.1	34.5
480	28.4	25.1	26.8
640	23.0	21.1	21.8

\*Tri-Carb® 2250CA/LL; Scintillators in solvents: 7 g PPO liter<sup>-1</sup>; 1 g bis-MSB liter<sup>-1</sup>; Quenching agent: 0.01% dimethyl yellow solution

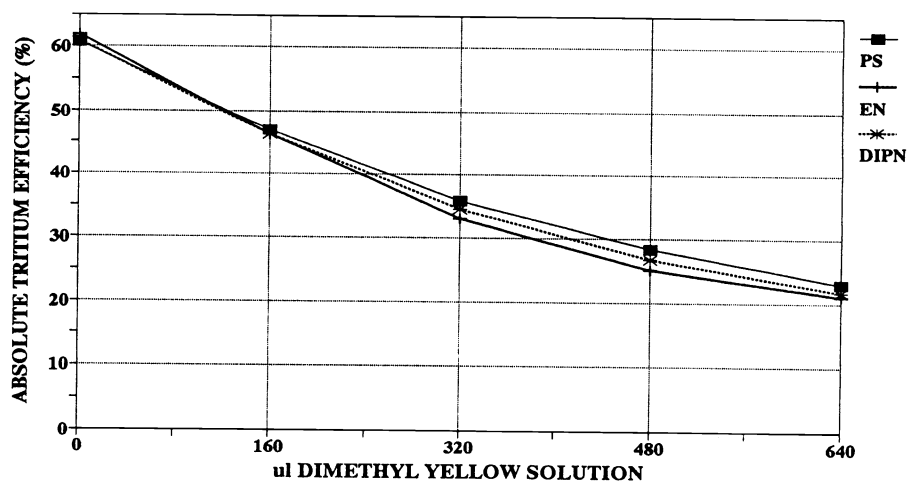


Fig. 1. Effect of color quench on various solvents

TABLE 3. Chemical Quench: %  $^3\text{H}$  Counting Efficiency (Absolute) at the Indicated Quench Levels\*

Quench agent ( $\mu\text{l}$ )	Solvent						
	PS	EN	PCH	DIPN	PXE	DDB**	IPB
0	60.7	61.6	60.2	61.0	61.2	55.7	57.1
20	48.3	52.3	49.4	53.7	53.4	46.6	48.7
40	39.1	43.7	40.3	46.4	46.0	38.6	41.8
60	31.0	36.3	32.7	40.0	39.5	32.2	36.2
80	24.8	29.9	26.4	34.5	33.8	26.8	31.2
100	19.5	24.7	21.4	29.5	29.4	22.2	26.7
120	15.2	19.9	17.5	24.7	23.7	18.0	22.2
140	12.2	16.6	15.1	21.2	20.3	15.0	19.1

\*Tri-Carb® 2250CA/LL; Scintillators in solvents: 7 g PPO liter<sup>-1</sup>; 1 g bis-MSB liter<sup>-1</sup>

\*\*DDB: 7 g PPO liter<sup>-1</sup>; 0.5 g bis-MSB liter<sup>-1</sup>; Quenching agent: carbon tetrachloride

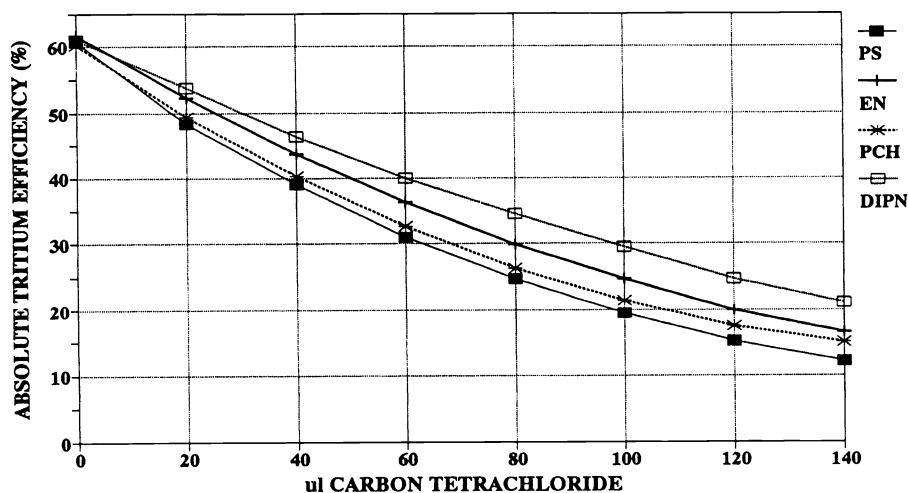


Fig. 2. Effect of chemical quench on various solvents

Having obtained data on color and chemical quenching agents, I studied quench properties of methyl salicylate in two solvents (PS and DIPN). The objective was to gain insight into the quench action of methyl salicylate in LSC. This compound should be a very mild chemical quenching agent. However, compounds with similar structures are known to be ultraviolet (UV) absorbers. Table 4 summarizes and Figure 4 shows these data.

## DISCUSSION

It is well known that different scintillation properties of organic solvents result in differences in counting efficiency of  $\beta$ - and  $\alpha$ -emitting radioisotopes. The data and figures obtained for color quench show minor differences when the yellow color quench is added to the solutions. As color quench involves the absorption of photons produced in the LSC medium and, follows Beer's law,

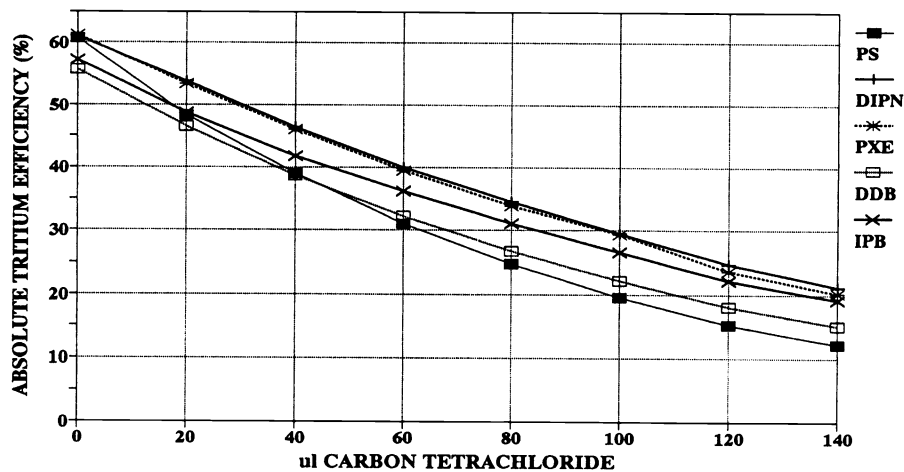


Fig. 3. Effect of chemical quench on various solvents

TABLE 4. Methyl Salicylate Quench: % <sup>3</sup>H Counting Efficiency (Absolute) of DIPN and PS vs. μl Added Quench Agent\*

Quench agent (μl)	Solvent	
	PS	DIPN
0	60.5	60.7
46	49.2	51.5
92	41.7	42.9
138	36.4	36.1
184	31.7	31.8
230	29.2	28.8

\*Tri-Carb® 2250CA/LL; Scintillators: PPO 7 g liter<sup>-1</sup>; bis-MSB 1 g liter<sup>-1</sup>; Quenching agent: methyl salicylate

TABLE 5. Reduction in % Counting Efficiency

	PS	EN	PCH	DIPN	PXE	DDB	IPB
% <sup>3</sup> H CE 0 μl tetra	60.7	61.6	60.2	61.0	61.2	55.7	57.1
% <sup>3</sup> H CE 100 μl tetra	19.5	24.7	21.4	29.5	29.4	22.2	26.7
Reduction %	41.2	36.9	38.8	31.5	31.8	33.5	32.4
Viscosity	Low	Medium		High			

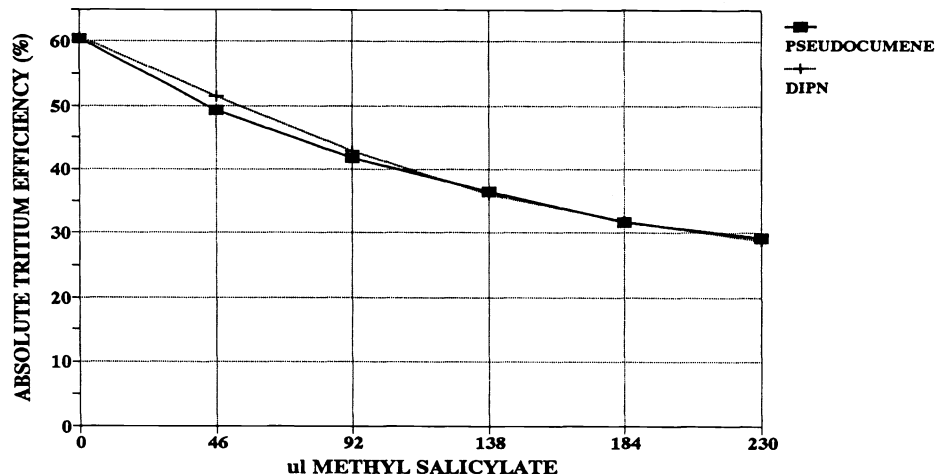


Fig. 4. Quench characteristics of methyl salicylate

one should not expect widely different quench curves. A slight preference of color quench can be observed for pseudocumene. However, the chemical quench leads to a different observation when comparing Figures 3 and 4. The results show three types of curves that appear to be related to solvent viscosity. One could differentiate between curves for low-viscosity pseudocumene, medium-viscosity phenyl cyclohexane, 2-ethyl naphthalene and high-viscosity DIPN, PXE, IPB and DDB.

Table 5 shows the calculated reduction in counting efficiency between the addition of 0 and 100  $\mu\text{l}$  of carbon tetrachloride. The differences obtained indicate that the quench resistance with respect to viscosity is better for solvents with high viscosity. It is known that the fluorescence quantum yield of dyes depends on temperature. Förster (1976) studied effects of temperature and solvent viscosity in fluorescence quantum yields of dyes, as Lutz (1983) did in liquid scintillators. One could expect to observe an influence of solvent viscosity on counting efficiency of an LSC medium. Chemical quenching reduces the fluorescence quantum yield by interfering through competitive processes in the diffusion-controlled transfer of energy from excited solvent molecules to the scintillators.

Differences in light output are known to depend on temperature and viscosity. From Figure 4, where the curves of PS and DIPN are compared for both chemical and color quench, one can conclude that methyl salicylate is predominantly a color-quenching agent.

## CONCLUSION

A comparison of quench characteristics of modern, more viscous solvents vs. traditional organic solvents indicates a relation between solvent viscosity and quench. I conclude that chemical quench is reduced in solvents with increased viscosity.

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