CHAPTER 6

Advances In Scintillation Cocktails

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Liquid scintillation counting techniques have become a wide-spread method to obtain quantitative data for α, β, and γ emitting radionuclides. The detection sensitivity and efficiency for measuring soft β-emitters, tritium, and ^{14}C made liquid scintillation counting the accepted analysis technique.

Ever since the very beginning of liquid scintillation counting, the improvement in instrumentation is clearly demonstrated. The continuous increasing demand for multipurpose scintillation cocktails contributed to the development of a series of investigations leading to a better understanding of the scintillation process and the development of new cocktails.

Early requirements not taken into consideration, liquid scintillation cocktails have been improved in the 70's, and progress was made concerning

- increased sensitivity
- improved compatibility with samples
- volume reduction
- safety of handling and storage
- disposal

The present situation is a result of a development which started in the early 80's. A growing concern of health risk handling scintillation cocktails led to the introduction of new liquid scintillators. Besides the above mentioned, economical factors and continuous development of new surfactant systems contributed considerably to the desires of scientific and routine laboratories using liquid scintillation counting as an analytical tool.

The introduction of new cocktails based on solvents with a high flashpoint with a minimum of safety restrictions was a step forward.

The improvement of surfactants applied in LS cocktails contributed significantly to the simplification of sample preparation procedures. The well known classical sol-gel cocktails have been replaced by cocktails exhibiting a continuous clear liquid phase in applications with aqueous samples. An early example of new types of cocktail construction was discussed by O'Conner and Bransome.[1]

In the newest generation of liquid scintillators, a series of improvements combine a high degree of aqueous sample compatibility with progressive safety characteristics.

COCKTAILS, ASPECTS AND REQUIREMENTS

The major part of samples for radioactivity determination by liquid scintillation counting is of aqueous origin. The requirements to apply the technique in a proper way have been discussed in review articles and conference proceedings (Peng).[2] The general theory is assumed to be known.

Constituents of Cocktails:

The original construction of a cocktail remained the same throughout the years:

- solvent
- surfactant system (emulsifiers)
- scintillators

It is obvious that organic samples or samples soluble in an organic solvent can be quantified in a system without surfactants.

The advances of liquid scintillators are mainly based on progress in application of new solvents and surfactant systems, which will be discussed in general.

Scintillators

The solid primary and secondary scintillators did not change in fact.The most common primary scintillator is still PPO (diphenyl oxazole). Bis-MSB, together with POPOP, are the secondary scintillators in most cocktails.

Solvents

Toluene, dioxane, and xylene were applied initially in liqiud scintillation cocktails, followed by pseudo-cumene (1,2,4-trimethylbenzene). The newest generation of aromatic solvents all have in common the high flashpoint, accompanied by much more preferred safety characteristics. Some influences and requirements have been important in improving the quality of solvents.

Economical:
- availability of aromatic solvents in large quantities
- availability of aromatic solvents economically priced
- improvement of quality
- broadening of range available

Safety/
Economical:
- demand for less volatile products
- application in polyethylene vials
- less restricted storage, handling and transport

Safety:
- reduction of volatility of organic solvents resulting in reduced risk to personnel
- reduction of toxicity
- reduced fire and hazard risks
- growing concern of environment

Surfactants

The incorporation of water or aqueous samples in aromatic solvents was initially solved by using, e.g., dioxane and methylglycol. A solution was proposed by Bray.[3] Application of Triton-X-100[4] for example produces results comparable to many commercially available sol-gel scintillation cocktails. Triton-X-200 is a trademark of Rohm and Haas.

As the acceptance of the LSC technique became more important and widespread, its uses demanded improvements. Some criteria of influence were:

- increased detection sensitivity
- compatibility with various types of aqueous samples
- increased sample load in the fluid region
- higher resistance to quench
- economical reasons (counting in small vials)

A combination of investigations on solvents and surfactants created a new generation of cocktails for liquid scintillation counting.

EXPERIMENTAL

Counting efficiencies were determined on Packard Tri-Carb liquid scintillation counters model 2250CA or 1900CA as indicated in the tables. Instrument settings for tritium resulted in 64.1% efficiency for the 1900CA and 67–68% efficiency for the 2250CA for a sealed tritium standard. Instrument efficiency for ^{14}C is 95.8%. All efficiency determinations were performed at room temperature.

Counting efficiency of aqueous samples was obtained by spiking 10 μL tritiated water corresponding to 19,384 dpm in a glass vial containing the sample of interest, all in triplicate. Nonaqueous sample efficiency was obtained by spiking 10 μL tritiated toluene corresponding to 14,000 dpm into the samples, all in triplicate. For determining the counting efficiency of ^{14}C the same procedure as for tritium was followed, except for the amount of ^{14}C, a aliquot of 10 μL ^{14}C corresponding to 3814 dpm was spiked.

All efficiency determinations were obtained by using 20 ml low potassium borosilicate vials.

Efficiency (abs.) was obtained by calculating:

$$\frac{\text{cpm}}{\text{dpm}} \times 100 = \%\ \text{efficiency}$$

Samples were visually and instrumentally checked for homogeneity

$$\% \text{ sample load} = \frac{\text{volume of sample}}{\text{volume of sample} + \text{volume of cocktail}} \times 100$$

Phase diagrams were obtained by adding the aqueous buffer or salt solutions to 10 mL of cocktail with increments of 0.5 mL. Near phase separations, increments of 0.1 mL were taken. Counting of samples was started after equilibration for light and temperature, all samples were counted for 4 min.

Cocktails

Ultima-Gold, Opti-Fluor, Pico-Aqua, Pico-Fluor 40, Emulsifier Safe, and Insta-Gel are commercially available products from Packard Instrument.

The cocktail phenylxylyl ethane was prepared by adding 40% w/w nonionic emulsifier blend to phenylxylyl ethane including 5 g PPO and 0.2 g of bis-MSB (PXE N) per liter cocktail.

SOLVENTS

Physical Constants, Classification:

Some characteristic data of common scintillation solvents are summarized in Table 1. The data show that a considerable improvement on safety has been made:

- Increased boiling point and flashpoint, and decreased vapor pressure indicate a reduced risk in the release of solvent vapors, thus reducing the danger to personnel and increasing laboratory safety.
- Lower flammability not only contributes to less restricted transport and storage regulations, but also lessens the chance of a possible fire hazard.
- Stopping the penetration of solvents through plastic vials is significant to all safety aspects.
- High flashpoint solvents received no TLV values; it is unlikely that vapors will be released in the working atmosphere under normal conditions.

The high flashpoint solvents, e.g., phenylalkane and diisopropylnaphthalene have been well investigated concerning their toxicological properties.[5] Extensive investigations for diisopropylnaphthalene have been performed on bioaccumulation and biodegradability and the outcome is very positive. According to the EEC-directive 79/831 EEC Annex VII, diisopropylnaphthalene is considered a non dangerous substance, having a biodegradability of more than 80% 28 days after it is determined.[6]

Scintillation Characteristics

The question remains whether high flashpoint solvents can compete with established solvents concerning counting efficiency. Tables 2 and 3 summarize

Table 1. Characteristics of Common Scintillation Solvents

Solvent	Boiling Point°C	Flash-Point°C	TLV ppm	Vapor Pressure 25°C mmHg	CLASSIFICATION		Scintillation Yield
					International	U.S.A.	
Dioxane	101	11	50	40	Flammable liquid	Flamm. class. IB	
Toluene	110	4	100	28	Same	Same	100
Xylene	137–139	25	100	8	Same	Flamm. class. IC	110
Cumene	152	31	50	5	Same	Combustible class. II	100
Pseudo-cumene	168	50	25	2	Same	Same	112
Tri-methyl-benzenes	166–178	50	100	2	Same	Same	100
Phenyl cyclohexane	235–236	100	n.a.		Harmless chemical	Combustible class. IIIB	103
Phenyl alkane (alkylbenzene)	290–310	130–150	n.a.	0,76	Same	Same	94
Phenylxylyl ethane	302–309	150	n.a.	<1	Same	Same	110
Diisopropyl naphthalene	290–299	132–140	n.a.	1,1	Same	Same	112

TLV = threshold limit value and n.a. = not assigned.

some experimental data for tritium counting efficiency of some commercially available solvents containing PPO and bis-MSB as scintillators.

These data show clearly a very important fact: without suffering in tritium counting efficiency, the safety aspects can be increased significantly.

Table 2. Percentage Tritium Counting Efficiency (TRI CARB 1900 CA)

Pseudo-cumene	Phenylalkane	Phenylxylyl-ethane (PXE)	Diisopropylnaphthalene (DIPN)
63.6	55.2	62.2	62.8

Table 3. Quench Characteristic with Carbon Tetrachloride; Tritium Counting Efficiency (TRI CARB 1900 CA)

μl Carbon Tetrachloride	Pseudo-Cumene	PXE	Diisopropyl Naphthalene
0	63.3	62.2	62.8
10	50.8	51.8	51.7
20	44.5	43.3	47.5
30	38.5	36.6	41.9
40	33.9	29.5	38.8
50	30.8	23.8	34.4

SURFACTANTS

Surfactant Systems

Surfactants have to be added to organic solvents when, in particular, aqueous samples are the subject of analysis in activity determination. The very well known sol-gel scintillators are most widely used because of their wide applicability. The surfactants, nonionics, applied to obtain these types of cocktails are discussed by Benson[7] and Lieberman and Moghissi.[8] The increasing demand of applications led to the introduction of cocktails based on nonionic and anionic surfactants, an example is given by O'Conner and Bransome.[1] An important advantage is obtained; with aqueous samples give a clear non viscous homogeneous sample, important when small (e.g., 6 mL) counting vials are used.

The diversification of sample types, increase of sample amounts, and whenever possible, minimum of sample preparation procedures influenced the development of new scintillation cocktails, in which in a combination with anionic and nonionics, additional anionic surfactants are applied, e.g., Hegge and Wiel,[9] Sena et al.,[10] Mallik,[11] and references cited therein. The additional surfactants all have improved characteristics of cocktails in common. Some general formulas of surfactants are given in Figure 1.

Alkylphenolethoxylates were the first applied nonionic surfactants, followed by succinates. Some general structures of additional surfactants show that these all have an anionic character.

The characteristics of products differ considerably, as can be seen in Figure 2. Instead of a gel area when a nonionic surfactant is applied, a clear homogeneous fluid results when a combination of non ionics and anionics in an aromatic solvent are the constituents of a cocktail. A general advantage shows that in the application of a nonionic/anionic combination, whatever the solvent is, the relative independence of sample load capacity of temperature. Introduction of combined surfactants results in different sample load capacities for water and 0.01M Pbs (phosphate buffered saline), as shown in Figure 2. This is a general behavior although a wide range of samples is applicable. To each sample type belongs a unique sample load capacity.

Counting Efficiency for Liquid Scintillation Types

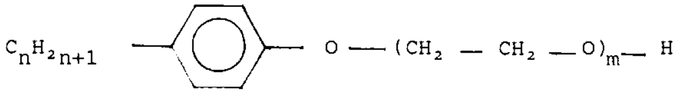
The counting efficiency for tritium of cocktails depends on solvent, surfactant system, and amount of surfactants dissolved in the original solvent, assuming the concentration of scintillators is at optimum. Counting efficiency of aforementioned products is given in Table 4.

The counting efficiency with sample of Pico-Aqua is comparable to the sol-gel scintillator, but the surfactant system applied has the advantage that compatible samples form a clear homogeneous mixture.

The other two products contain an anionic/nonionic surfactant system about 25% w/w in different solvents. The lower efficiency of Opti-Fluor is a consequence of the solvent applied.

NONIONIC

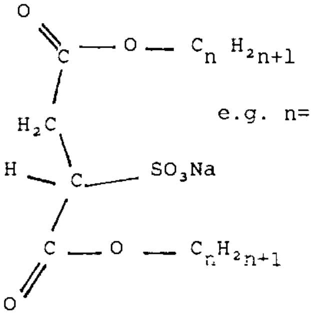
alkyl phenol ethoxylates



e.g. n=9 M=4 to 20

ANIONIC

SUCCINATES



e.g. n=6

ANIONIC

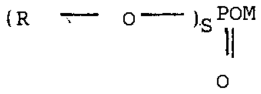
additional

R = e.g. alkyl
ethoxylated alkyl
ethoxylated aryl

$R-COONa$ carboxylates

$R-SO_3Na$ sulfonates

$R-O-SO_3M$ sulphates



$(R-O-)_S\overset{\overset{}{}}{\underset{\underset{O}{\|}}{P}}OM$ phosphates

S=1,2

Figure 1. General formulas of surfactants.

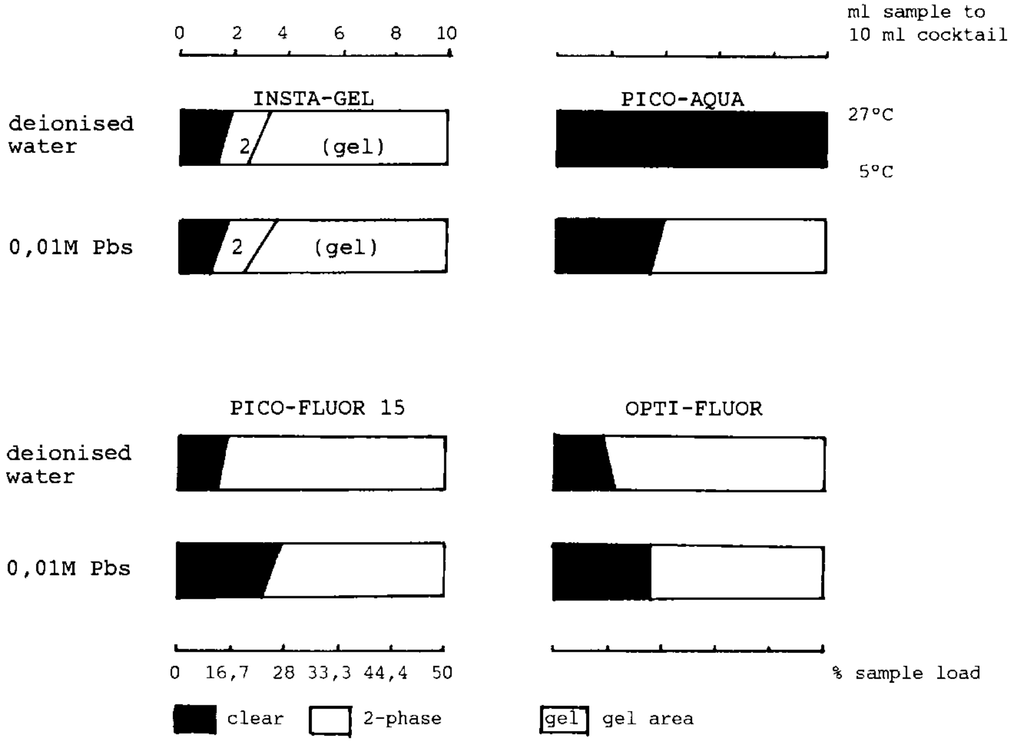


Figure 2. Sample capacities for different types of cocktail:

- Insta-Gel—classical sol-gel liquid scintillator—pseudocumene/xylene based.
- Pico-Aqua—modern liquid scintillator—pseudocumene based.
- Pico-Flour 15—nonionic/anionic scintillator—psuedocumene based.
- Opti-Flour—nonionic/anionic scintillator—phenylalkane based.

Table 4. Counting Efficiency for Tritium for Cocktails from Figure 1 (TRI CARB 2250 CA at 67% Efficiency)

ml of 0.10*M* Pbs to 10 mL of Cocktail	Insta-Gel	Pico-Aqua	Pico-Fluor 15	Opti-Fluor	% Sample Load
0	54.5	48.8	56.9	46.7	0
1	47.3	42.3	52.1	42.2	9.7
3	38.4	36.5	48.2	38.3	23.0
10	27.2	25.3	n.c.	n.c.	50.0

Note: n.c. = no capacity; two-phase sample.

Surfactant Types, Sample Load Capacity

Another illustration showing surfactant influence on sample load capacity of a cocktail for aqueous samples is given in Figure 3. The cocktails differ in composition concerning percentage nonionic surfactants and anionic surfactants as mentioned in, e.g., Benson, Hegge, and O'Conner.

The result is extraordinary. The sample load capacity of a product depends on concentration of buffer (salts) present in the aqueous sample.

COMPARISON OF COCKTAILS

Counting Efficiency General

For a comparison of tritium counting efficiency between some different types of cocktails, data are put together in Figures 4–9, using some typical samples.

The pseudo-cumene based products have the advantage of large sample holding capacities in the fluid region, while a very fast mixing of sample and cocktail is observed. Very high counting efficiency is achievable too, but consequently sample load capacity is smaller.

On the other hand, when applying high flashpoint solvents, reasonable to excellent counting efficiencies are obtained compared to pseudo-cumene based cocktails. A comparison for a common sample type is given in Figures 4 and 5.

It is obvious that the difference observed in tritium counting efficiency is much less pronounced when ^{14}C labeled samples have to be analyzed. In Table 5 some typical examples are given.

Difference in Quenching Agents

A striking difference is observed when tricholoracetic acid solutions are the subject of analysis. The application of aforementioned surfactant systems shows a remarkable difference, as shown in Figures 6 and 7.

The decrease in counting efficiency is much smaller in Pico-Aqua, Pico-Fluor 40, and Ultima-Gold compared to nonionic surfactant based products.

The example given in Figures 8 and 9 of dark yellow colored urine, a big

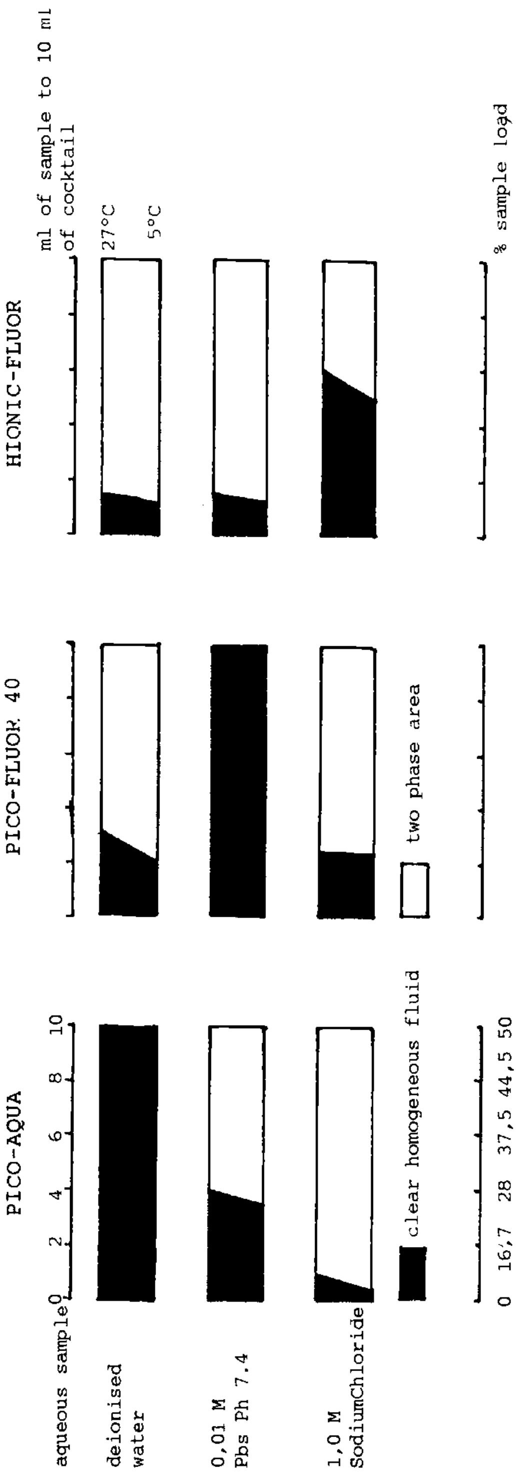


Figure 3. Sample load capacities.

Table 5. Counting Efficiency for ^{14}C (TRI CARB 1900 CA)

Cocktail Type	Capacity	% C.E.
Pseudo-cumene based	Moderate/high	95.6
Pseudo-cumene based	High	92.1
Phenylalkane based	Moderate/high	92.3
Diisopropylnaphthalene based	Moderate/high	92.5

Table 6. Counting Efficiency for Tritium Modern Cocktail (TRI CARB 2250 CA at 68% cH), Example Ultima-Gold

	1 mL of Sample to 10 mL of Cocktail					
Cocktail	None	Water	HC104 1 M	Pbs 0,01 M	TCA 10%	Sucrose 30%
Ultima-Gold	57.6	54.4	54.5	53.8	53.9	53.0

color quencher besides chemical quencher, shows good quench characteristics for modern cocktails compared to established examples.

Background Decay

Another typical aspect of the application of different types of surfactants is background decay when alkaline samples are applied. Sol-gel scintillators, with quaternary ammonium hydroxide solutions, exhibit quite large background levels. Acidification is an answer to this problem, but it needs an extra

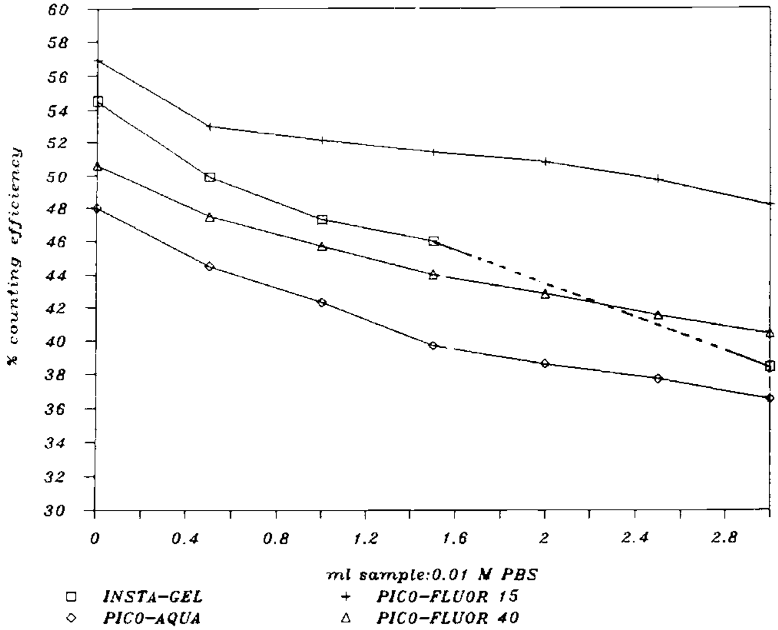


Figure 4. Counting efficiency cocktails, pseudocumene (or xylene) based solvents.

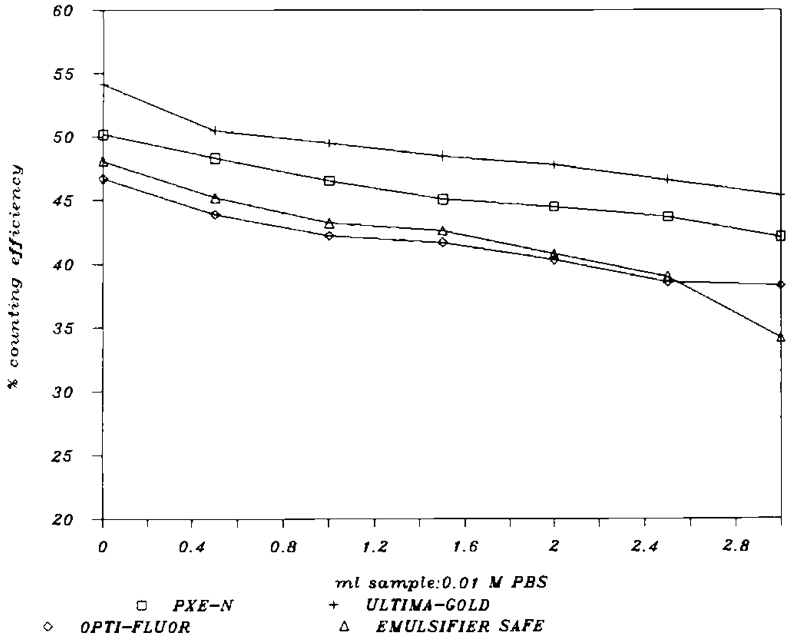


Figure 5. Counting efficiency cocktails, high flashpoint solvents.

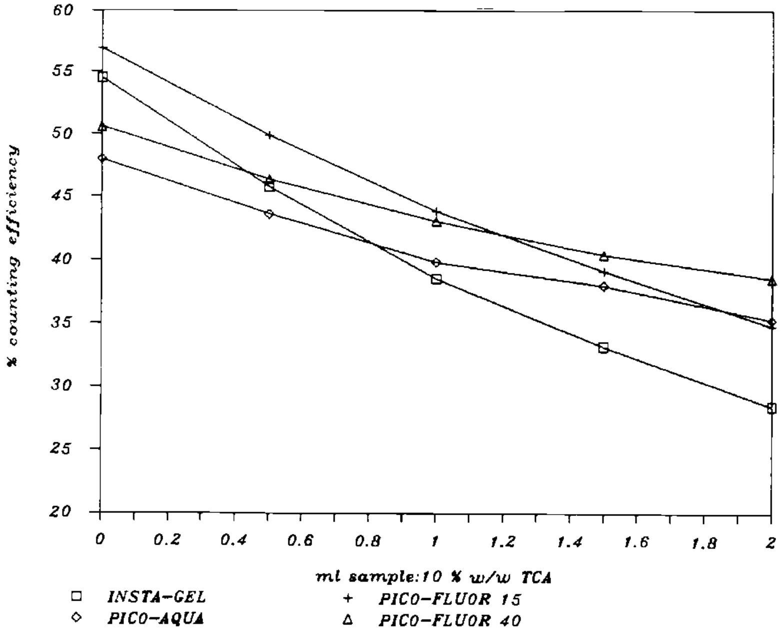


Figure 6. Counting efficiency cocktails, pseudocumene (or xylene) based solvents.

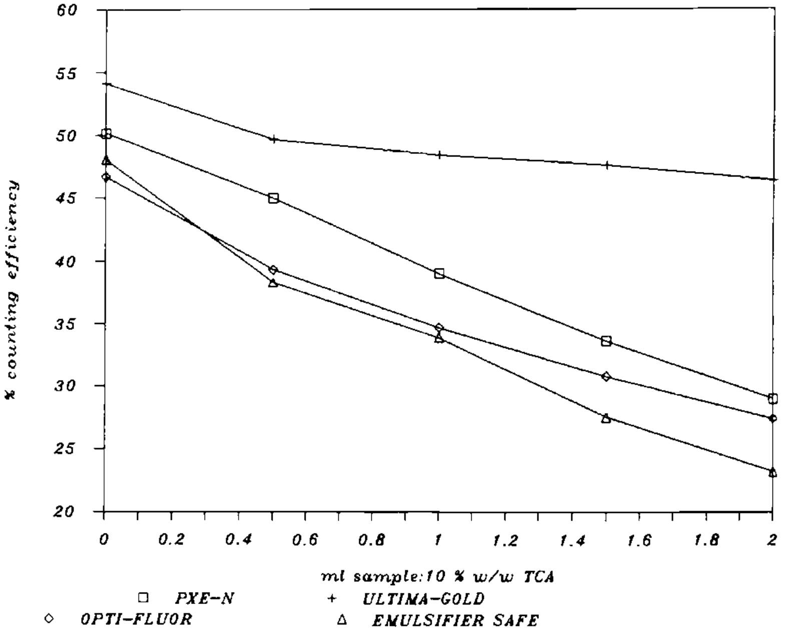


Figure 7. Counting efficiency cocktails, high flashpoint solvents.

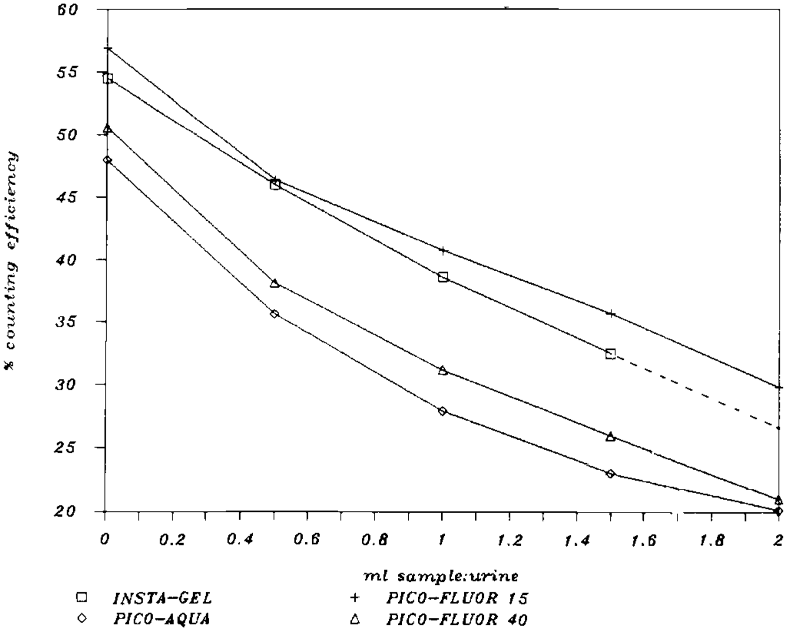


Figure 8. Counting efficiency cocktails, pseudocumene (or xylene) based solvents.

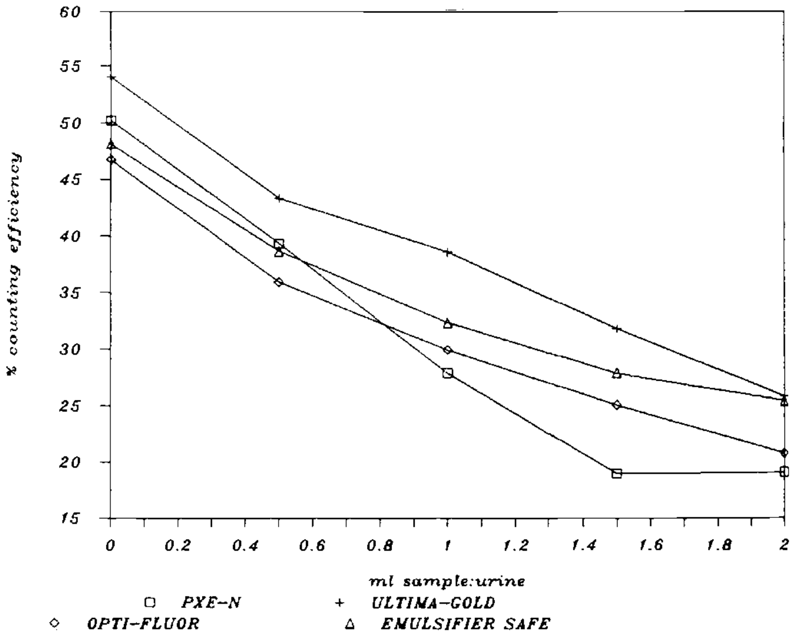


Figure 9. Counting efficiency cocktails, high flashpoint solvents.

processing step. Some modern cocktails, however, make acidification superfluous. An example is given in Figure 10.

Newest Generation Cocktail

An example of the newest generation cocktails is described below, Ultima-Gold is based on diisopropylnaphthalene:

- high flashpoint solvent, e.g., diisopropylnaphthalene
- safety, no vapor release, very low toxicity
- easy transport and storage
- EPA classified as nonhazardous
- no bioaccumulation
- single phase sample accommodation (some examples are given in Figure 11)
- high quench resistance and counting efficiency for tritium (see Table 6)
- compatibility with alkaline samples

CONCLUSION

Advances in liquid scintillation counting are clearly demonstrated. The application of both new solvents and surfactant systems contributed to the progress. Pseudo-cumene was a first step forward, and it is still important. The introduction of new high flashpoint solvents such as alkylbenzenes and

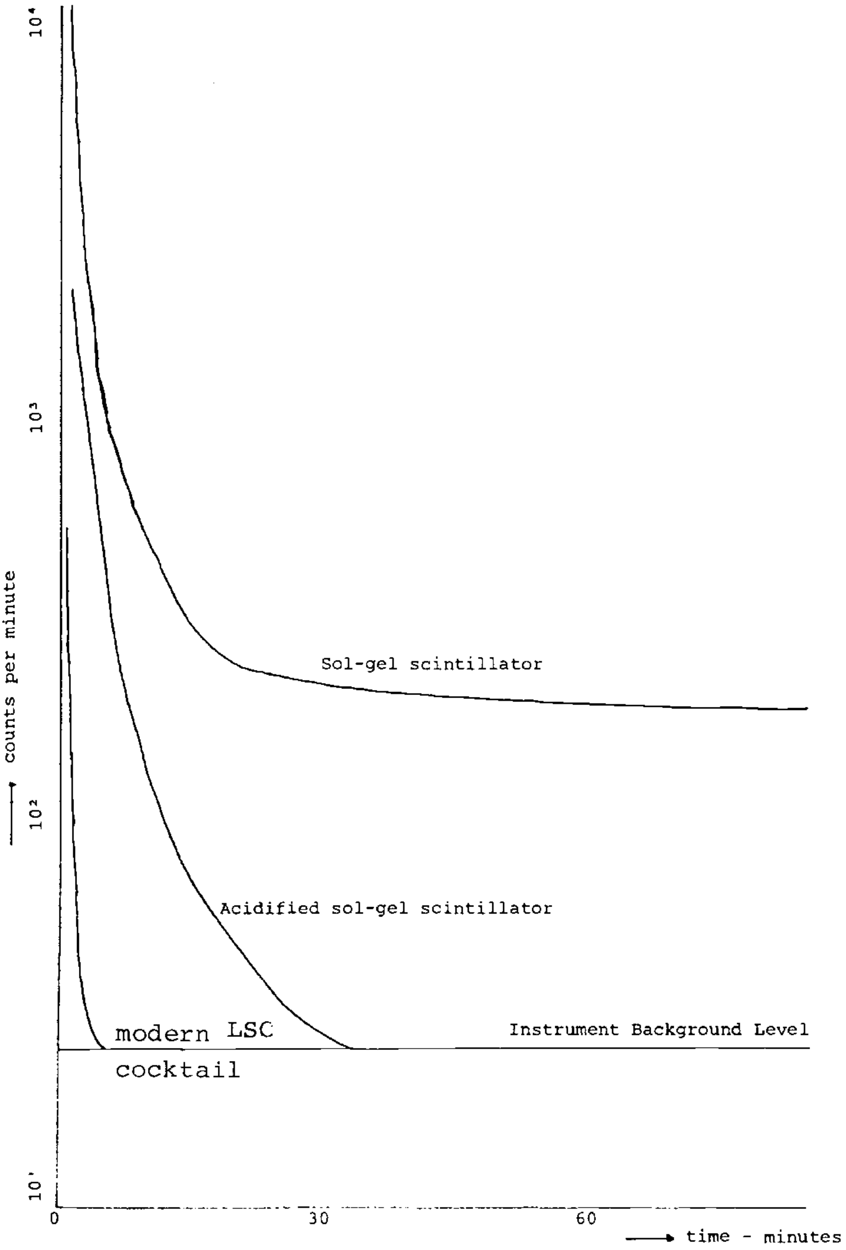


Figure 10. Some modern cocktails make acidification superfluous.

diisopropylnapththalene provided a significant increase in all safety, toxicity, and economic aspects.

The newest generation of liquid scintillation cocktails made improvements in many areas. A high tritium counting efficiency, a fast sample incorporation,

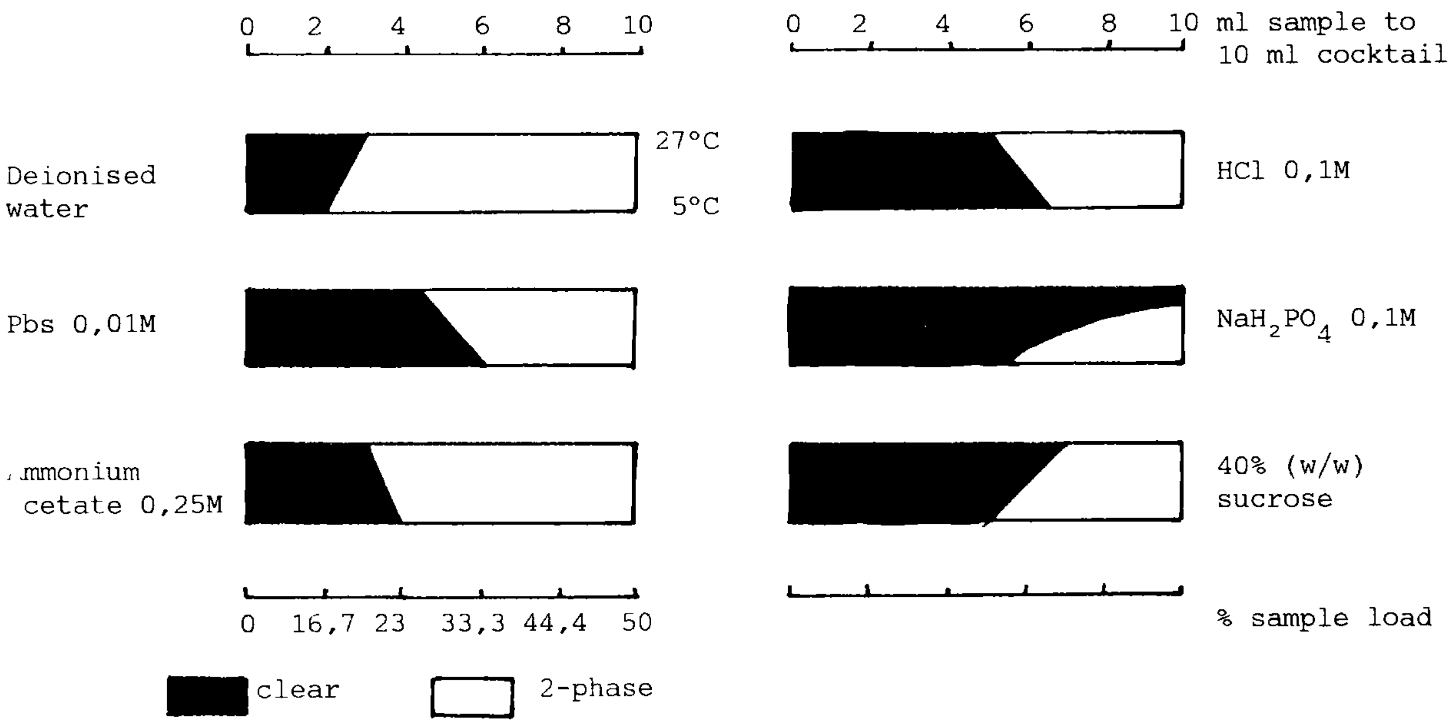


Figure 11. Phase diagram for aqueous samples of a modern high flashpoint liquid scintillation cocktail.

and a high and expanded sample load capacity are achieved. Until now a major drawback to cocktails based on a high flashpoint solvent was the higher viscosity, making sample handling a little more difficult.

These developments all contributed to the safer and easier use of the liquid scintillation technique while enhancing the quality of results.

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