

## ANALYSIS OF SOLVENT COMPONENTS IN COMMERCIAL LIQUID SCINTILLATION COCKTAILS

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**ABSTRACT.** Solvent components of commercial liquid scintillation (LS) cocktails were analyzed by gas chromatography (GC) on polar and non-polar fused-silica capillary columns. Together with GC/MS analysis, the GC data were interpreted using a structure-retention index relation to gain structure information of the solvent components. Based on the analytical results, the LS cocktails could be classified into five categories. The structure information thus obtained serves as a basis for understanding the function of LS cocktails and for safe handling and intelligent disposal of LS wastes.

### INTRODUCTION

In liquid scintillation counting (LSC), the counting efficiency of an LS system depends on the energy transfer coefficient of the solvent. Different classes of solvents vary in energy transfer efficiency. Among them, aromatic hydrocarbons have high excitation energy transfer coefficients and are classified as efficient LS solvents. Toluene and xylene were used widely in the past, but concerns about their flammability, toxicity and negative impact on the environment have led manufacturers to introduce "improved" LS cocktails. The improved LS cocktails have been advertised as safe, non-toxic and biodegradable, but because of proprietary interest, the identities of their solvent components have not been divulged. Scanning by gas chromatography/mass spectrometry (GC/MS) of the improved LS cocktails to identify the solvent components was reportedly unsuccessful (McCormick 1990). To better understand the properties and biohazards of the improved LS cocktails, we need to identify these solvent components.

The purpose of this study is threefold: 1) to determine the structures of solvent components in a liquid scintillator from gas chromatographic data, using a structure-retention index relation that we developed; 2) to understand the structural basis of biodegradability, non-toxicity and non-flammability of some liquid scintillators as advertised; and 3) to allow safe and intelligent handling of LS wastes. GC analysis is simple and yields structural information of the solvent components in an LS cocktail.

### METHODS

The following commercial liquid scintillators were analyzed: Ready-Solv™ MP, Ready-Solv™ GP and Filter-Solv™ Solution from Beckman Instruments; Uni/verse LSC cocktail from J. T. Baker; Universol Cocktail, EcoLite™(+), and EcoLume™ from ICN Biomedicals; Hydrofluor™ from National Diagnostics; Formula-989 from NEN (DuPont); Insta-Gel® XF, Flo-Scint™ II, III, IV, V, and Opti-Fluor® from Packard Instrument Co.; Econo-Safe and Bio-Safe II from Research Products International Corporation. The LS cocktails (20 µl) were diluted with n-hexane (1.0 ml), and the dilute solutions (1.0 µl) were injected by an automatic sampler into the gas chromatograph for analysis.

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### GC Analysis

Samples were analyzed on fused-silica capillary columns coated with non-polar and polar stationary phases (30 m × 0.53 mm ID, film thickness 1.0 μm for DB-Wax and 1.5 μm for DB-1, from J&W Scientific, Folsom, California) in Hewlett-Packard Model 5890 and 5880A gas chromatographs, equipped with automatic samplers (Model 7673), thermal conductivity detectors and electronic integrators (Model 3393A). The temperature of the injection port was set at 250°C and the detector at 300°C. The oven temperature was programmed linearly during the run. The oven temperature for the DB-1 column was set initially at 40°C for 4 min, and then increased at 8°C/min to 200°C, maintained for 1 min, and then increased at 5°C/min to 280°C. The oven temperature for the DB-Wax column was set initially at 40°C for 24 min, and then increased at 4°C/min to 200°C. The maximum oven temperature was maintained for 20 min for both columns before the run was terminated. A mixture of n-alkanes from n-hexane to n-tricontacosane (C<sub>6</sub>–C<sub>32</sub>) were used as markers for the calculation of Kováts retention index as previously reported (Peng *et al.* 1988; Peng, Yang & Ding 1991). The linear temperature program allows the n-alkane standards to emerge from the column separated at equal distance from adjacent homologs. The raw run data from HP 5890 gas chromatograph were stored on diskettes and replotted on the integrator as unigrams for better comparison with other samples.

### GC/MS Analysis

For GC/MS analysis, we used a fused-silica capillary column (30 m × 0.32 mm ID) coated with DB-1 stationary phase. For MS analysis, we used a V670-SE instrument (VG Analytical, Manchester, UK). The instrument was operated in the electron impact mode. The source temperature was 270°C, the interface temperature was 280°C, the filament current was 200 μA, and the electron energy was 70 eV. The data were acquired by scanning from 30 to 500 dalton at 0.7 sec per decade. We used a V6 Opus Data System for data acquisition and processing.

## RESULTS AND DISCUSSION

### Rules of Interpretation of GC Data

Information about structures can be obtained from gas chromatographic data using rules that were established in our previous findings (Peng *et al.* 1988; Peng, Yang & Ding 1991; Peng, Hua & Maltby 1992; Peng 1992). These rules are stated as follows: 1) the retention index (*I*) on non-polar DB-1 column is determined by the number of atoms in the analyte molecule; 2) the *I* value on polar DB-Wax column is determined by both the number of atoms and the number, polarity and polarizability of the functional groups; 3) as a result, the difference between the *I* values of an analyte on polar and non-polar columns, known as the column difference ( $\Delta I$ ), can identify uniquely the functional or polarizable group, such as the phenyl ring in the molecule; 4) chain branching or the presence of tertiary or quaternary carbon atoms in the molecule decreases the *I* value; 5) the addition of one carbon atom to lengthen an alkyl chain will increase the *I* value by about 100 index units (iu), but the addition of one carbon atom to create a branched-chain isomer will increase the *I* value only by about 60; 6) positional isomers formed by changing the relative length of the branched alkyl chains or shifting of a methyl group from the meta or para to ortho positions in the phenyl ring will cause only small increments of 10–20 iu in the *I* value. In aromatic hydrocarbons, the ortho isomers show higher retention indexes than the meta or para isomers, and the distinction is more pronounced on a polar column.



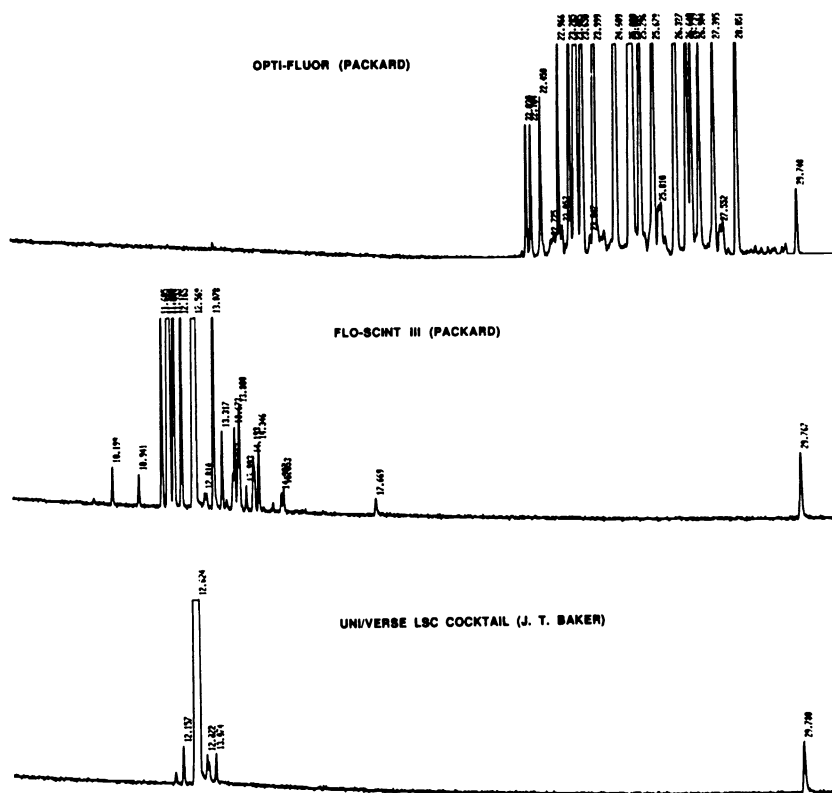


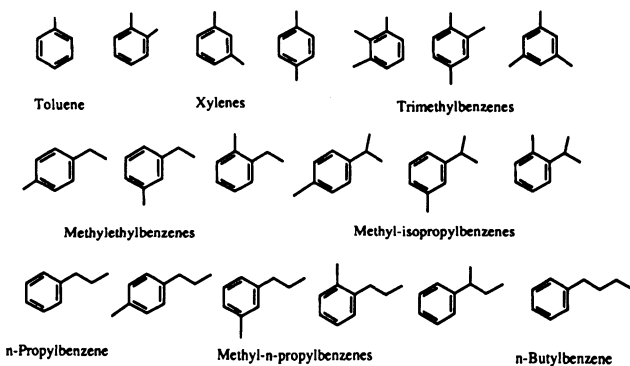
Fig. 2. Gas chromatograms (unigrams) of Uni/verse LSC cocktail, Flo-Scint™ III and Opti-Fluor® on DB-1 column. The lone chromatographic peak at the right side of the unigram, with a retention time of *ca.* 29.7 min and a retention index of *ca.* 1991 iu, is from the primary solute PPO (2,5-diphenyloxazole).

chromatograms. The *I* values corresponding to the chemical structures have been determined for the solvent components in Opti-Fluor® (Peng, Hua & Maltby 1992).

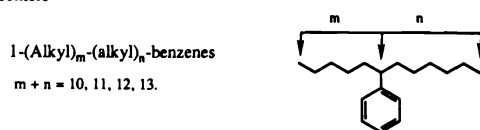
From the analytical results, the commercial LS cocktails are listed in Table 1 as their trade names in five categories, according to their solvent components. Because the LS cocktails in categories 1 and 2 contain a single solvent component or a mixture of two solvent components, their *I* values on DB-1 and DB-Wax columns are given. The LS cocktails in category 3 consist of complex mixtures of pseudocumene isomers and homologs, and are represented as  $C_8H_{10}$  through  $C_{10}H_{14}$  in Table 1. Figure 2 shows a chromatogram of Flo-Scint™ III of this category. Figure 3 shows possible structures of isomeric pseudocumenes and homologs. Due to space limitation, we will not give individual *I* values for the chromatographic peaks, but Table 1 lists the *I* values bracketing the cluster of chromatographic peaks.

One may also gain information on the origin of the scintillation solvent from gas chromatograms. The alkylbenzenes used as solvent components in commercial LS cocktails, listed in categories 4 and 5, appear to be from three different supply sources. The alkylbenzenes in cocktails Formula-989, Econo-Safe and Bio-Safe II contain less of the  $C_{19}H_{32}$  fraction than those in Opti-Fluor® and Flo-Scint™ V. In contrast, the alkylbenzenes in LS cocktails EcoLume™ and EcoLite™(+) have higher concentrations of the  $C_{19}H_{32}$  fraction than those in Opti-Fluor®. Figure 4 shows gas chro-

## 1. Pseudocumene isomers and homologs



## 2. Alkylbenzene isomers



## 3. Possible candidates for the unknown solvent component

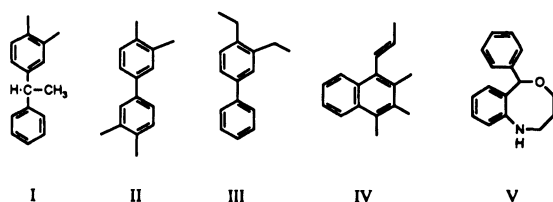


Fig. 3. Chemical structures of pseudocumene isomers and homologs, alkylbenzenes and compounds retrieved from GC/MS database search to match the mass spectrum of the unknown solvent component in EcoLite™(+)

matograms of LS cocktails from three manufacturers. In addition to alkylbenzenes, the EcoLume™ and EcoLite™(+) in category 6 contain, respectively, ~9.8% and 55% of an unknown aromatic solvent component. The unknown solvent component was later identified as 1,1-phenylxylylethane (PXE). The alkylbenzenes consist of more than 20 isomers and homologs; their structures are given in Figure 3, with the  $m$  value varying from 1 to  $(m+n)/2$  to the nearest integer and the value of  $(m+n)$  remaining constant and equal to 10, 11, 12 and 13. Peng, Hua and Maltby (1992) reported detailed information on the alkylbenzenes in LS cocktails.

### An Unknown Solvent Component Peak

The unknown solvent component in EcoLite™(+) and EcoLume™ is more polarizable than the alkylbenzene solvent components, and exhibits a larger  $I$  value on the DB-Wax column (see Table 2). The column difference ( $\Delta I$ ) of the unknown solvent component is about twice the value observed for alkylbenzenes. The large column difference ( $\Delta I$ ) suggests that the unknown solvent molecule may contain two phenyl rings as compared to alkylbenzenes, which contain only one phenyl ring. The mass fragmentation pattern of the unknown peak from GC/MS analysis is similar to the mass spectra of compounds II, III, IV and V retrieved from a database search. Figure 3 shows these structures. Since PXE was not among the compounds retrieved by the database search, we initially selected Compound III, 3,4-diethyl-1,1'-biphenyl, from the four retrieved structures as the mostly likely candidate for the unknown peak in EcoLite™ and EcoLume™. The selection was

TABLE 1. Classification of Commercial LS Cocktails, Based on Gas Chromatographic Data

Classification and product	Retention index			Solvent component
	DB-1	DB-Wax	$\Delta I$	
<i>1. Toluene-pseudocumene-based</i>				
Ready-Solv™ MP (Beckman)	862	1148	286	p-Xylene (C <sub>8</sub> H <sub>10</sub> )
	989	1300	311	Pseudocumene (C <sub>9</sub> H <sub>12</sub> )
Ready-Solv™ GP (Beckman)	760	1053	293	Toluene (C <sub>7</sub> H <sub>8</sub> )
Filter-Solv™ Solution (Beckman)	750	1050	300	Toluene (C <sub>7</sub> H <sub>8</sub> )
<i>2. Pseudocumene-based</i>				
Universol Cocktail (ICN Biomedicals)	991	1299	308	Pseudocumene (C <sub>9</sub> H <sub>12</sub> )
Insta-Gel® XF (Packard)	991	1316	325	Pseudocumene (C <sub>9</sub> H <sub>12</sub> )
Flo-Scint™ IV	991	1316	325	Pseudocumene (C <sub>9</sub> H <sub>12</sub> )
Uni/verse LSC Cocktail (J. T. Baker)	989	1299	310	Pseudocumene (C <sub>9</sub> H <sub>12</sub> )
<i>3. Pseudocumene-derivative-based</i>				
Flo-Scint™ II (Packard)	945–1049	1207–1373		Pseudocumene derivatives (C <sub>9</sub> H <sub>12</sub> –C <sub>10</sub> H <sub>14</sub> )
(Flo-Scint™ III (Packard)	946–1050	1208–1373		Pseudocumene derivatives (C <sub>9</sub> H <sub>12</sub> –C <sub>10</sub> H <sub>14</sub> )
Hydrofluor™ (National Diagnostics)	859–1047	1141–1369		Pseudocumene derivatives (C <sub>8</sub> H <sub>10</sub> –C <sub>10</sub> H <sub>14</sub> )
<i>4. Isomeric-alkylbenzene-based</i>				
Formula-989 (NEN/DuPont)	1532–1800	1741–1989		Isomeric alkylbenzenes (C <sub>16</sub> H <sub>26</sub> –C <sub>18</sub> H <sub>30</sub> )
Opti-Fluor® (Packard)	1526–1894	1720–2130		Isomeric alkylbenzenes (C <sub>16</sub> H <sub>26</sub> –C <sub>19</sub> H <sub>32</sub> )
Flo-Scint™ V (Packard)	1531–1865	1743–2163		Isomeric alkylbenzenes (C <sub>16</sub> H <sub>26</sub> –C <sub>19</sub> H <sub>32</sub> )
Econo-Safe™ (Research Products International Corp.)	1526–1821	1750–2064		Isomeric alkylbenzenes (C <sub>16</sub> H <sub>26</sub> –C <sub>19</sub> H <sub>32</sub> )
Bio-Safe II (Research Products International Corp.)	1526–1815	1754–2069		Isomeric alkylbenzenes (C <sub>16</sub> H <sub>26</sub> –C <sub>19</sub> H <sub>32</sub> )
<i>5. Alkylbenzenes and a biphenyl-derivative-based</i>				
Ecolume™ (ICN Biomedicals)	1526–1987	1766–2322		Isomeric alkylbenzenes (C <sub>16</sub> H <sub>26</sub> –C <sub>19</sub> H <sub>32</sub> ) and about 10% PXE (C <sub>16</sub> H <sub>18</sub> )
EcoLite™ (ICN Biomedicals)	1531–1865	1746–2326		Isomeric alkylbenzenes (C <sub>16</sub> H <sub>26</sub> –C <sub>19</sub> H <sub>32</sub> ) and about 55% PXE (C <sub>16</sub> H <sub>18</sub> )

based on matching the observed  $I$  values of the unknown peak to the predicted  $I$  values of any of the four retrieved compounds on DB-1 and DB-Wax columns, listed in Table 2. Peng *et al.* (1988, 1991) and Peng (1992) gave examples for predicting retention index from structures. Later, C. Dodson of Beckman Instruments, Inc. indicated that PXE has been used as a solvent component in LS cocktail. From the structure of PXE, the  $I$  values predicted for non-polar and polar columns closely match the  $I$  values of the unknown chromatographic peak much more so than the predicted  $I$  values of compound III. Co-chromatography with a known sample of PXE established that the unknown chromatographic peak is identical to PXE.

TABLE 2. Structure Assignment Based on Predicted Retention Indexes

Product structure	Retention index		Column difference $\Delta I$
	DB-1 (Observed)	DB-Wax (Predicted)	
Unknown solvent component in EcoLite™	1693	2334	641
Possible structures from GC/MS data	(Predicted)		
I (1,1-Phenylxylylethane)	1708	2350	642
II (3,3',4,4'-Tetramethyl-1,1-biphenyl)	1838	2480	642
III (3,4-Diethyl-1,1'-biphenyl)	1768	2340	572
IV (1,2,3-Trimethyl-4-propenyl-naphthalene)	1830	2520	690
V (3,4,5,6-Tetrahydro-1-phenyl-1H-2,5-benzoxazocine)	NA	NA	NA

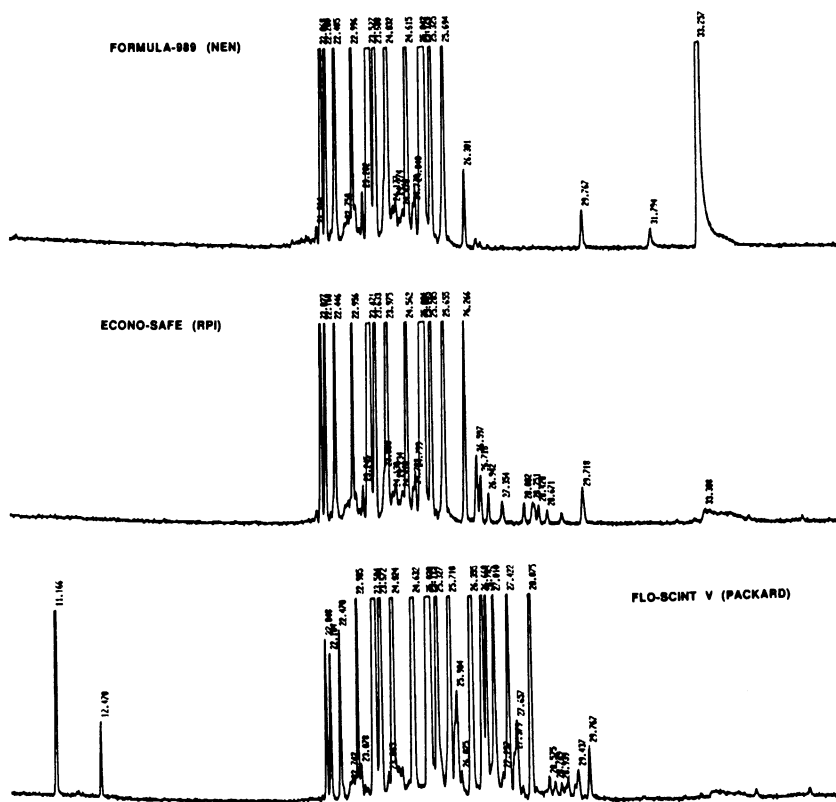


Fig. 4. Gas chromatograms (unigrams) of commercial LS cocktails Formula-989, Econo-Safe™ and Flo-Scint™V on a DB-1 column.

## CONCLUSION

This study shows that commercial LS cocktails can contain more than 20 solvent components when based on alkylbenzenes, and more than 15 solvent components when based on isomeric pseudocumenes. The alkylbenzenes have higher boiling points and are less flammable than aromatic solvents with lower boiling points. It is likely that these generically similar single phenyl ring isomers and homologs of aromatic hydrocarbons share a common metabolic fate in the final stages of biodegradation. Gas chromatograms of these LS cocktails show similar profiles on DB-1 and DB-Wax columns, except for the more polarizable component, indicating that the solvent components are isomeric and have comparable polarity and polarizability. These components would be difficult to separate by fractionation into pure products. No isomeric aromatic hydrocarbons are known to adversely affect the LSC efficiency; thus, it is unnecessary to fractionate further the petroleum distillate from which the LS solvent components are derived. The direct use of the unfractionated mixture may have accounted for the multiplicity of solvent components in "improved" LS cocktails.

Manufacturers often introduce a new formulation to enhance the counting efficiency of an LS cocktail. For example, alkylbenzene-based Flo-Scint™ V contains p-xylene and pseudocumene, and EcoLume™ and EcoLite™(+) contain PXE. Our analytical approach can readily analyze solvent components in LS cocktails by GC, and interpret the GC data using the structure-retention-index relation to generate enough structural information as a basis for understanding the function of LS cocktails and for safe handling and intelligent disposal of LS wastes.

## ACKNOWLEDGMENTS

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## REFERENCES

- McCormick, J. 1990 Evaluation of improved scintillation cocktails. *Transactions of the American Nuclear Society* 61: 10.
- Peng, C. T. 1992 A method for tentative identification of unknown gas chromatographic peaks by retention index. In Proceedings of the Second International Conference on Methods and Applications of Radioanalytical Chemistry. *Journal of Radioanalytical and Nuclear Chemistry* 160(2): 449-460.
- Peng, C. T., Ding, S. F., Hua, R. L. and Yang, Z. C. 1988 Prediction of retention indexes I. Structure-retention index relationship on apolar columns. *Journal of Chromatography* 436: 137-172.
- Peng, C. T., Hua, R. L. and Maltby, D. 1992 Prediction of retention indexes IV. Chain branching in alkylbenzene isomers with C<sub>10-13</sub> alkyl chains identified in a scintillator solvent. *Journal of Chromatography* 589: 231-239.
- Peng, C. T., Yang, Z. C. and Ding, S. F. 1991 Prediction of retention indexes II. Structure-retention index relationship on polar columns. *Journal of Chromatography* 586: 85-112.