

Speciation of the Volatile Organic Compounds (VOCs) in Solventborne Aerosol Coatings by Solid Phase Microextraction-Gas Chromatography

Albert C. Censullo, Dane R. Jones, and Max T. Wills—California Polytechnic State University*

INTRODUCTION

The photochemical reactivity of a volatile organic compound (VOC) is a measure of its potential to enhance ozone formation in the air once emitted. In the presence of sunlight, VOCs in the air react with oxides of nitrogen (NO_x) to form ozone. Of the many different VOCs released into the atmosphere, each reacts at a different rate and through a different chemical reaction mechanism. The VOCs with high reactivity have a greater potential to form ozone, while other VOCs react slowly in the atmosphere, and are less likely to form ozone.

Prior to June 1, 2002, California's Aerosol Coatings Regulations, and virtually all other VOC regulations, limited total VOC content on a percent-by-weight basis, without consideration of the differences in VOC reactivity. In this type of control strategy all VOCs are treated similarly, or in some cases (exemptions), form very low amounts of ozone such that their contribution to ambient ozone concentrations is not considered. Therefore, a reactivity-based control strategy could be viewed as a "refinement" of mass-based control strategies, because each VOC is considered with its respective ozone formation potential. This type of control has the potential to lead to more efficient ozone reductions by targeting substitutions of highly reactive compounds with lower reactive compounds. For example, the ozone formed from one gram of m-xylene is over seven times more than that formed from one gram of hexane (Carter, 2000).¹ California's reactivity-based approach relies primarily on VOC substitution rather than VOC reduction. A reduction in the total VOC content may not always be necessary. Reactivity-based regulations went into effect in California for the general classes of aerosol coatings (clear coatings, flat paint products, fluorescent coatings, metallic coatings, nonflat paint products, and primers) on June 1, 2002. Reactivity-based regulations for specialty aerosol coatings went into effect on January 1, 2003.²

Research on VOC reactivities over the last several decades has led to the development of scales to serve as tools to compare one VOC's reactivity to another. One such scale is the MIR scale developed by Dr. William Carter at the

A method for the speciation of solventborne aerosol coatings is presented. Propellant from an aerosol coating is transferred to a gas collection bag and is then analyzed by GC-FID. The propellant-free liquid paint is then internally standardized with a mixture of C5 to C11 normal alkanes and analyzed on a 50-meter capillary column using solid phase microextraction (SPME) with GC-FID detection. This procedure makes it possible to assign linear retention indexes to virtually all of the individual volatile solvents in the coating with subsequent identification. After identification by SPME, the coating is dispersed in a high boiling solvent, internally standardized with a material not coeluting with the coating solvents, and is then analyzed by direct GC-FID. VOC regulations in California for aerosol coatings products require that the coatings have a reactivity (product weighted maximum incremental reactivity or PWMIR) which is below a designated value. Assignment of PWMIR values to aerosol coatings requires that the amount of each individual volatile component in a coating be known.

University of California at Riverside. This scale provides a numerical value to each VOC's potential to form ozone based on modeling analyses and other data derived from smog chamber studies. The higher the MIR value, the more ozone is likely to be formed by a compound. The California Air Resources Board (CARB) has proposed use of the MIR scale as the basis for setting reactivity limits.²

Presented at the 79th Annual Meeting of the Federation of Societies for Coatings Technology, November 5-7, 2001, in Atlanta, GA.

*Department of Chemistry, Polymers and Coatings, San Luis Obispo, CA 93407.

Table 1—Linear Retention Characteristics of Solventborne Aerosol Coatings Components as Determined on a 50 m x 0.25 mm PDMS Capillary Column^a

Retention Time	Linear Retention Index
Hydrocarbons	
5.32 Propane	300
5.64 Isobutane	353.7
5.91 Butane	400
6.04 2,2-Dimethylpropane	408.4
6.91 2-Methylbutane	464.9
7.45 Pentane	500
8.48 2,2-Dimethylbutane	526.0
9.58 Cyclopentane	553.7
9.62 2,3-Dimethylbutane	554.8
9.80 2-Methylpentane	559.4
10.50 3-Methylpentane	577.0
11.41 Hexane	600
12.86 2,2-Dimethylpentane	621.4
13.02 Methylcyclopentane	623.8
13.25 2,4-Dimethylpentane	627.1
13.60 2,2,3-Dimethylbutane	632.4
14.63 Benzene	647.5
14.93 3,3-Dimethylpentane	651.9
15.19 Cyclohexane	655.8
15.80 2-Methylhexane	664.8
15.93 2,3-Dimethylpentane	666.6
16.13 1,1-Dimethylcyclopentane	669.7
16.42 3-Methylhexane	673.9
16.89 Cis-1,3-Dimethylcyclopentane	680.8
17.09 Trans-1,3-Dimethylcyclopentane	683.8
17.15 3-Ethylpentane	684.7
17.28 Trans-1,2-dimethylcyclopentane	686.6
17.34 2,2,4-Trimethylpentane	687.5
18.19 Heptane	700
19.68 Methylcyclohexane/cis-1,2-dimethylcyclopentane	720.2
19.84 2,2-Dimethylhexane	722.5
19.89 1,1,3-Trimethylcyclopentane	723.1
20.54 Ethylcyclopentane/2,5-dimethylhexane/2,2,3-trimethylpentane	732.0
20.72 2,4-Dimethylhexane	734.4
21.16 1-Trans-2-cis-4-trimethylcyclopentane	740.4
21.25 3,3-Dimethylhexane	741.6
21.69 1-Trans-2-cis-3-trimethylcyclopentane	747.7
22.26 Toluene/2,3,3-trimethylpentane	755.4
22.68 1,1,2-Trimethylcyclopentane/2,3-dimethylhexane	761.1
22.78 2-Methyl-3-ethylpentane	762.4
23.10 2-Methylheptane	766.9
23.21 4-Methylheptane/3-methyl-3-ethylpentane	768.4
23.35 3,4-Dimethylhexane	770.2
23.65 3-Methylheptane	774.3
23.82 Cis-1,3-dimethylcyclohexane/1-cis-2-trans-4-trimethylcyclopentane	776.6
23.96 Trans-1,4-dimethylcyclohexane	778.5
24.38 1,1-Dimethylcyclohexane	784.2
24.60 Trans-1-methyl-3-ethylcyclopentane/2,2,5-trimethylhexane	787.1
24.75 Cis-1-methyl-3-ethylcyclopentane	789.2
24.85 Trans-1-methyl-2-ethylcyclopentane	790.5
25.01 1-Methyl-1-ethylcyclopentane/2,2,4-trimethylhexane	792.8
25.23 Trans-1,2-dimethylcyclohexane	795.7
25.54 Octane	800
25.64 1-Cis-2-cis-3-trimethylcyclopentane	801.4
25.73 Trans-1,3-dimethylcyclohexane/cis-1,4-Dimethylcyclohexane	802.8
26.22 Isopropylcyclopentane/2,4,4-trimethylhexane	810.1
26.93 Cis-1-ethyl-2-methylcyclopentane/2,3,5-trimethylhexane	820.6
27.21 2,2-Dimethylheptane	824.7
27.37 Cis-1,2-dimethylcyclohexane	827.2
27.65 Propylcyclopentane/1-cis-3-cis-5-trimethylcyclohexane	831.3

In order to determine the reactivity of a particular aerosol coating, the mass percent of each individual VOC in the coating must be known. When the products of the mass fraction of each VOC present in the coating times the reactivity of that VOC are summed, a product weighted MIR (PWMIR) value is obtained. For individual aerosol coating types, a reactivity limit determines how much of a specific solvent or solvent mixture may be used in the manufacture of that coating. All VOCs, including exempt solvents, are used in calculating PWMIR values. Solventborne aerosol coatings normally contain hydrocarbon mixtures such as VM&P naphtha for which speciated composition data is normally not available. The CARB has therefore included calculated MIR values for various hydrocarbon mixtures as a series of "Bin" numbers defined by boiling range and amount of aromatic hydrocarbon content.²

To carry out the laboratory determination of PWMIR values, a method is needed for the speciation of the individual VOCs present in a coating. Two ASTM methods for analyzing aerosol paints, ASTM Methods D 5200-92³ and D 5325-92⁴ were published in 1992. Both methods were designed for obtaining mass-based VOC information and were written for use prior to the introduction of exempt solvents in coatings. Since the majority of solventborne aerosol coatings currently being manufactured contain acetone, ASTM Method D 5200-92 is no longer applicable for VOC determination. The method described in this paper was developed for the complete speciation of solventborne aerosol coatings and is currently being examined by ASTM's D01 committee for adoption.

EXPERIMENTAL

Method Summary

Propellant is transferred from the aerosol container to a gas collection bag and the mass is determined by difference. The propellant is analyzed by gas chromatography (GC) to determine its composition. A mixture of normal alkanes, usually C5 to C11, is then added to a portion of the remaining liquid paint. This mixture

is sampled by solid phase microextraction (SPME) and analyzed by GC. Linear retention indexes are assigned to each of the volatile analytes present in the liquid paint and the analytes are identified. A known quantity of liquid paint is then dispersed in a high boiling solvent, internally standardized with a suitable standard, and then analyzed by direct injection onto a 50-meter polydimethylsiloxane coated capillary column. The amount of each component in the propellant and volatile component in the liquid paint are then combined to give a mass profile of the individual components in the aerosol coating.

Method Details

REMOVAL AND ANALYSIS OF PROPELLANT: Remove the cap and any paper label from the full aerosol paint can. Weigh the can and contents to the nearest 0.1 g. Cool the can to -20°C in an upright position and allow the contents to settle as much as possible (overnight or longer in a freezer is generally sufficient). Attach a can piercing device (commercially available) to the upper portion of the can approximately 0.5 in. below the can rim. Attach a transfer line from the can to a gas sampling bag. The transfer line may be constructed of copper or Teflon tubing. The line should contain a trap packed with glass wool, a pressure gauge, and needle valve. The trap may be constructed from any heavy-walled glass container having a volume of 100 to 250 mL and serves as an indicator that liquid paint is not being transferred to the gas sampling bag.

Attach the transfer line to the cold aerosol paint can taking special care not to mix the can contents and puncture the can. Open the needle valve and transfer the propellant to the gas sampling bag at such a rate that only propellant is transferred. In the course of the transfer, the can is allowed to warm slowly to room temperature. When the can has reached room temperature and when the gauge indicates that the pressure is close to atmospheric pressure, the can is sonicated at room temperature for 20 min to remove residual propellant. Reweigh the can after propellant removal to obtain the mass of propellant transferred to the collection bag. Standard aerosol paints containing

Table 1 (Continued)

Retention Time		Linear Retention Index
Hydrocarbons (continued)		
27.71	Ethylcyclohexane	832.2
28.09	1,1,3-Trimethylcyclohexane/2,5-dimethylheptane	837.8
28.25	1,1,4-Trimethylcyclohexane/3,5-dimethylheptane	840.2
28.96	Ethylbenzene	850.8
29.10	1-Trans-2-trans-4-trimethylcyclohexane	852.8
29.54	M-xylene	859.4
29.61	P-xylene	860.4
29.98	4-Methyloctane	865.9
30.04	2-Methyloctane	866.8
30.42	3-Ethylheptane	872.4
30.49	3-Methyloctane	873.5
30.63	1-Trans-2-cis-4-trimethylcyclohexane	875.6
30.74	1-Cis-2-cis-4-trimethylcyclohexane	877.1
31.05	O-xylene	881.8
31.83	Isobutylcyclopentane	893.3
32.28	Nonane	900
33.16	Isopropylbenzene	914.3
33.49	Isopropylcyclohexane/2,2-dimethyloctane	920.0
34.13	Propylcyclohexane	930.5
34.60	3,3-Dimethyloctane	938.4
34.97	Propylbenzene	944.4
35.44	3-Ethyltoluene	952.1
35.57	4-Ethyltoluene	954.2
35.75	2,3-Dimethyloctane	957.3
35.91	1,3,5-Trimethylbenzene	959.9
36.04	5-Methylnonane	962.1
36.14	4-Methylnonane	963.8
36.29	2-Methylnonane	966.2
36.51	2-Ethyltoluene	969.8
36.69	3-Methylnonane	972.8
37.41	1,2,4-Trimethylbenzene	984.7
38.23	Trans-1-methyl-2-propylcyclohexane	998.2
38.33	Decane	1000
39.03	1,2,3-Trimethylbenzene	1012.4
39.70	Indan	1024.5
40.19	Butylcyclohexane	1033.8
40.55	1,3-Diethylbenzene	1040.0
40.71	3-Propyltoluene	1042.9
40.92	1,4-Diethylbenzene	1046.8
41.08	1,3-Dimethyl-5-ethylbenzene	1049.6
41.54	5-Methyldecane	1058.3
41.58	2-Propyltoluene	1058.8
41.59	3-Ethylnonane	1059.3
41.77	4-Methyldecane	1062.4
41.96	2-Methyldecane	1065.9
42.12	1,4-Dimethyl-2-ethylbenzene	1068.8
42.24	1,3-Dimethyl-4-ethylbenzene	1070.8
42.32	3-Methyldecane	1072.4
42.57	1,2-Dimethyl-4-ethylbenzene	1076.8
42.91	1,3-Dimethyl-2-ethylbenzene	1081.8
43.66	1,2-Dimethyl-3-ethylbenzene	1096.5
43.83	Undecane	1100
44.32	1,2,4,5-Tetramethylbenzene	1109.4
44.50	1,2,3,5-Tetramethylbenzene	1113.0
46.16	1,2,3,4-Tetramethylbenzene	1145.3
46.60	Tetralin	1153.9
47.53	Naphthalene	1172.4
48.92	Dodecane	1200
Alcohols		
5.80	Methanol	372.7
6.63	Ethanol	443.8
7.50	2-Propanol	500
11.62	2-Butanol	602.2
13.24	2-Methyl-1-propanol	626.1
15.64	1-Butanol	661.5
16.45	1-Methoxy-2-propanol	673.4
25.72	2-Propoxyethanol	802.0
28.28	1-Propoxy-2-propanol	840.1
29.32	2-Propoxy-1-propanol	855.6
29.75	1-T-butoxy-2-propanol	862.0

Table 1 (Continued)

Retention Time		Linear Retention Index
Alcohols (continued)		
32.30	2-Butoxyethanol	900
34.52	1-Butoxy-2-propanol	936.7
35.39	2-Butoxy-1-propanol	951.0
Alcohols (Initial Temp = 40, Rate = 4)		
5.67	Methanol	378.2
6.37	Ethanol	443.2
7.07	2-Propanol	495.4
10.47	2-Butanol	600.6
11.87	2-Methyl-1-propanol	624.7
13.92	1-Butanol	660.1
14.68	1-Methoxy-2-propanol	673.2
22.38	2-Propoxyethanol	800.7
24.48	1-Propoxy-2-propanol	839.7
25.66	1-T-butoxy-2-propanol	861.6
27.65	2-Butoxyethanol	898.6
29.43	1-Butoxy-2-propanol	936.2
Ketones		
7.09	Acetone	475.3
10.71	Methyl ethyl ketone	581.6
14.64	3-Methyl-2-butanone	647.2
16.45	2-Pentanone	673.9
20.39	4-Methyl-2-pentanone	729.5
30.76	2-Heptanone	877.1
36.07	2,6-Dimethyl-4-heptanone	962.1
37.14	4,6-Dimethyl-2-heptanone	979.9
Esters		
8.29	Methyl acetate	517.2
12.24	Ethyl acetate	609.0
15.50	Isopropyl acetate	657.1
18.53	t-Butyl acetate	701.4
23.34	Isobutyl acetate	767.2
26.08	Butyl acetate	804.9
29.59	1-Methoxy-2-propanol acetate	857.3
32.84	Isobutyl isobutyrate	906.3
36.72	Ethyl-3-ethoxy propionate	970.7
Miscellaneous Compounds and Possible Internal Standards		
7.98	Dichloromethane	512.7
15.46	Fluorobenzene	659.4
21.98	Toluene d-8	751.6
23.39	4-Fluorotoluene	770.4
27.67	Chlorobenzene	831.2
30.97	Butyl ether	880.2
32.20	Anisole	898.4
35.00	4-Chlorotoluene	944.4
35.23	1-Chloroheptane	948.3

(a) The column used to obtain these retention indexes was a Supelco 50 m x 0.25 mm (0.5 µm film thickness) Petrocol DH capillary column. The column was obtained by cutting a 100 m Petrocol DH column in half.

340 g or less of paint require a 60 L gas collection bag. Aerosol paints containing more than 340 g require a 90 L collection bag.

Analyze the collected propellant by gas chromatography using the PDMS capillary column and the standard conditions given below by injecting a volume of 10 to 20 µL using a gas tight syringe. Determine the relative amounts of each component transferred to the gas sampling bag using the appropriate relative response factors. The response factors for propane, isobutane, and butane are assumed to be 1.0. In the case of aerosols containing

acetone, a considerable quantity of acetone evaporates with the hydrocarbon propellant. The response factor for acetone relative to the hydrocarbon propellant may be determined by adding known weights of propane, isobutane, and butane to an acetone solution in octane using a gas-tight 10 mL syringe. The acetone solution of octane should be sealed with a septum cap and propane, isobutane, and butane are bubbled into the solution through the septum cap. The amounts added are determined by weighing the vial before and after addition of the hydrocarbon propellants. Analyze the octane solution using the conditions described for liquid paint analysis.

Cool the can containing propellant-free liquid paint and mix well by shaking. The marble or steel ball in the can will begin to rattle when mixing is taking place. The puncture hole in the can may be closed using a hose clamp and a rubber or silicone septum. Transfer the mixed paint to an appropriate container and store cold. Since a small quantity of propellant remains in the liquid paint, care must be taken when opening any container holding the liquid paint by releasing pressure build-up prior to opening the container. Rinse the empty aerosol can with acetone to remove residual paint, dry the empty container, and reweigh to determine the quantity of liquid paint.

STANDARD ANALYSIS OF THE LIQUID PAINT: Weigh approximately 2 g of the liquid paint into a 40 mL fluorocarbon-faced septum vial. Add 0.5 to 1 mL of a mixture of normal hydrocarbons containing approximately equal amounts of pentane through dodecane. Mix the contents by swirling. Do not let the contents contact the inside face of the septum cap. Sample the headspace for 60 sec using a conditioned DVB/Carboxen/PDMS Stable Flex SPME fiber.⁵ Desorb the fiber for 10 sec onto a 50 m x 0.25 mm PDMS column and obtain the gas chromatogram using the standard chromatographic conditions described. Use a split ratio of approximately 150:1.

Calculate the linear retention index⁶ of each component present in the sample using the relationship:

$$I_A = 100 * N + 100 \left(\frac{t_{R(A)} - t_{R(N)}}{t_{R(N+1)} - t_{R(N)}} \right)$$

where:

- I_A = linear retention index of component A eluting between $n-C_N$ and $n-C_{N+1}$
- N = number of carbons in a linear alkane
- $t_{R(A)}$ = retention time of component eluting between $n-C_N$ and $n-C_{N+1}$
- $t_{R(N)}$ = retention time of normal alkane eluting before component A

Using the retention index information obtained, identify the components present in the sample other than possible normal alkanes using the known retention indexes given in Table 1. Select a solvent (p-cymene, diethyl succinate, or diethyl adipate) which elutes after the long-

est retention time component found. Select a suitable internal standard from Table 1, which does not coelute with any of the components found.

Place 10 mL of the selected solvent into a 40 mL vial and close with a fluorocarbon-faced septum and cap. Using a disposable 1 mL syringe, add approximately 0.8 g of the well-mixed paint through the septum cap and weigh to 0.1 mg. Using a dedicated 100 µL syringe, add approximately 50 mg of the selected internal standard to the vial through the septum cap and weigh to the nearest 0.1 mg. Mix the contents vigorously by shaking and then let the vial stand to let pigments settle.

Chromatograph the solution by injecting 1 µL using the standard GC conditions described below. Adjust the split ratio to give well-defined chromatographic peaks. Integrate as many of the peaks as possible eluting ahead of the solvent peak. The sample may contain some of the normal alkanes as paint components.

Calculate analyte concentrations according to the following equations:

$$RF = \frac{AA * MI}{AI * MA} \quad \text{and} \quad \% \text{Analyte} = \frac{AA * MI * 100}{AI * RF * MC}$$

where:

RF = Relative response factor
AA = Area of analyte
MI = Mass of internal standard
AI = Area of internal standard

MA = Mass of analyte
MC = Mass of coating

The relative response factor for all hydrocarbon components, except benzene and toluene, is 1.00. Determine the response factor of benzene, toluene, and all other components relative to heptane and octane.

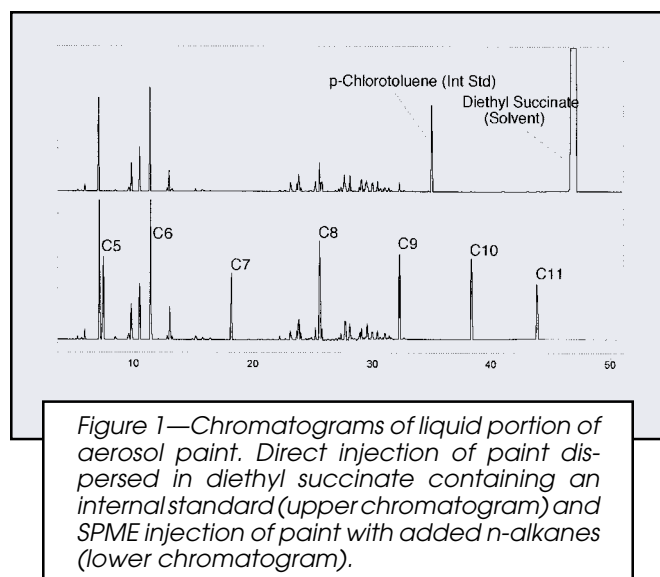
STANDARD FID INSTRUMENT CONDITIONS (POLYDIMETHYLSILOXANE COLUMN):

Detector: Flame ionization
Column: 50 m × 0.25 mm
Polydimethylsiloxane,
0.5 µm film thickness
Carrier Gas: Helium
Flow Rate: 1.0 mL per min (20 cm
per sec)
Split Ratio: Variable
Temperatures, °C
Inlet 260°
Detector 270°
Initial 35° for 10 min
Rate 3° per min to 200°,
hold 10 min

Table 2—Linear Retention Characteristics of Solventborne Aerosol Coatings Components as Determined on a 60 m x 0.25 mm Carbowax™ Capillary Column^a

Compound Type	Approximate Retention Time	Compound	Linear Retention Index
Alkane	5.0	Pentane	500.0
Alkane	5.3	Hexane	600.0
Alkane	6.1	Heptane	700.0
Alkane	7.7	Octane	800.0
Ketone	8.3	Acetone	821.3
Ester	8.7	Methyl acetate	832.8
Alkane	10.9	Nonane	900.0
Ester	10.9	Ethyl acetate	900.0
Ester	11.3	Isopropyl acetate	909.4
Alcohol	11.3	Methanol	910.4
Ester	11.4	t-Butyl acetate	912.5
Ketone	11.4	2-Butanone	912.7
Misc	12.5	Dichloromethane	937.2
Alcohol	12.7	2-Propanol	941.4
Ketone	12.7	3-Methyl-2-butanone	943.2
Alcohol	13.0	Ethanol	948.8
Aromatic	13.2	Benzene	954.0
Ketone	14.9	2-pentanone	991.1
Alkane	15.4	Decane	1000.0
Ketone	16.2	4-Methyl-2-pentanone	1021.2
Ester	16.6	Isobutyl acetate	1027.0
Alcohol	17.1	2-butanol	1039.4
Aromatic	17.8	Toluene	1056.0
Ester	19.3	Butyl acetate	1086.8
Alkane	19.9	Undecane	1100.0
Alcohol	19.9	2-Methyl-1-propanol	1103.4
Ester	20.0	Isobutyl isobutyrate	1103.5
Aromatic	21.5	Ethylbenzene	1146.1
Alcohol	21.6	1-Methoxy-2-propanol	1146.9
Aromatic	21.9	p-Xylene	1154.2
Alcohol	22.1	1-butanol	1159.7
Aromatic	22.1	m-Xylene	1161.0
Aromatic	22.8	p-Chlorobenzotrifluoride	1178.4
Ketone	23.2	2,6-Dimethyl-4-heptanone	1189.5
Aromatic	23.3	Isopropylbenzene	1192.3
Alkane	23.7	Dodecane	1200.0
Ketone	23.6	2-Heptanone	1200.0
Aromatic	23.8	o-Xylene	1204.4
Alcohol	24.3	1-t-Butyl-2-propanol	1219.9
Aromatic	24.7	Propylbenzene	1231.4
Ester	25.0	1-Methoxy-2-propanol acetate	1238.3
Aromatic	25.1	4-Ethyltoluene	1245.7
Aromatic	25.2	3-Ethyltoluene	1248.1
Ketone	25.7	4,6-Dimethyl-2-heptanone	1262.4
Alcohol	25.7	1-Propoxy-2-propanol	1263.8
Aromatic	25.9	1,3,5-Trimethylbenzene	1268.3
Aromatic	26.5	2-Ethyltoluene	1286.7
Aromatic	26.8	p-Cymene	1293.3
Alkane	27.1	Tridecane	1300.0
Aromatic	27.2	1,2,4-Trimethylbenzene	1308.1
Alcohol	27.7	2-Propoxy-1-propanol	1323.2
Alcohol	27.7	2-Propoxyethanol	1325.9
Ester	28.6	Ethyl-3-ethoxypropionate	1351.0
Alcohol	28.9	1-Butoxy-2-propanol	1363.5
Aromatic	29.1	1,2,3-trimethylbenzene	1369.6
Alkane	30.1	Teradecane	1400.0
Alcohol	30.6	2-Butoxy-1-propanol	1422.2
Alcohol	30.8	2-Butoxyethanol	1429.7
Alkane	32.8	Pentadecane	1500.0
Alkane	35.3	Hexadecane	1600.0

(a) The column used to obtain these retention indexes was a J&W Scientific 60 m x 0.25 mm (0.5 µm film thickness) Carbowax™ capillary column.

**FID INSTRUMENT CONDITIONS (CARBOWAX™ COLUMN):**

Detector: Flame ionization
 Column: 60 m × 0.25 mm Carbowax™, 0.5 µm film thickness
 Carrier Gas: Helium
 Flow Rate: 1.0 mL per min
 Split Ratio: Variable
 Temperatures, °C
 Inlet 260°
 Detector 270°
 Initial 50° for 10 min
 Rate 5° per min to 250°, hold 10 min

PREPARATION OF STANDARDS: Add one part toluene to seven parts of a hydrocarbon mixture consisting of approximately equal quantities of the C5 to C11 normal alkanes. The mass of toluene, heptane, and octane should be determined to the nearest 0.1 mg. Inject 0.1 to 0.2 µL of this mixture into the gas chromatograph using the standard conditions given above. The retention time of toluene should be between 22 and 23 min. Adjust the helium carrier gas flow rate to give this retention time for toluene. Calculate the relative response factor of toluene using a value of 1 for heptane. Recalculate the relative response factor using a value of 1 for octane. The two values should

Table 3—Retention Indices of Aromatic Hydrocarbons on a PDMS and Carbowax™ Capillary Column

Compound	Retention Index, PDMS Column	Retention Index, Carbowax™ Column
Benzene	647.5	954.0
Toluene	755.4	1056.0
Ethylbenzene	850.8	1146.1
m-Xylene	859.4	1161.0
p-Xylene	860.4	1154.2
o-Xylene	881.8	1204.4
Isopropylbenzene	914.3	1192.3
Propylbenzene	944.4	1231.4
1,3,5-trimethylbenzene	959.9	1268.3
1,2,4-trimethylbenzene	984.7	1308.1
1,2,3-trimethylbenzene	1012.4	1369.6

be nearly the same. Adjust the split ratio to give well-defined chromatographic peaks.

Prepare a mixture of heptane, octane, and the alcohols listed in Table 1 by weighing each component to the nearest 0.1 mg. This may be accomplished by weighing approximately one or two grams into a 40 mL fluorocarbon-faced septum vial. The less volatile components should be added to the vial first. The more volatile components may be added by syringe through the septum containing a narrow bore needle as pressure relief. Chromatograph the mixture using the standard GC conditions described. Determine the response factor for each component relative to heptane and octane. Repeat this process for the ketones, esters, miscellaneous compounds, and possible internal standards listed in Table 1.

RESULTS AND DISCUSSION

The method described here is intended for potential use as a new ASTM method for the analysis of solventborne aerosol paints and is currently under consideration for adoption by ASTM's D01 committee on paints, related coatings, and aromatics. The method is a modification of procedures developed and used by us to speciate approximately 100 solventborne and waterborne aerosol paints obtained from manufacturers during the time period 1997 to 1999. This speciation study was carried out for the California Air Resources Board (CARB) as a part of their effort to change mass-based VOC regulations to reactivity-based VOC regulations of consumer products.⁷ The major modification consisted in changing from the use of a 100 meter capillary GC column to a 50 meter capillary GC column. This change was made primarily to reduce the time required for carrying out the analysis and resulted in a slight reduction in chromatographic resolution.

In the CARB study it was found that virtually all solventborne aerosol paints employ a propane/isobutane/butane mixture as propellant. In a few isolated instances methyl ether, normally used as the propellant for waterborne aerosol paints, is used as the propellant for solventborne aerosol paints. In addition, some solventborne aerosol paints contain added water. Many of the solventborne aerosols contain significant amounts of the exempt solvent acetone. Acetone was found at an average level of 28% in 56 out of 64 solventborne aerosols which were analyzed. By comparison, acetone was found at an average level of 15% in only three of 24 waterborne aerosols. Other common exempt solvents (p-chlorobenzotrifluoride and methyl acetate) were not found in any of the aerosol coatings studied by us.

Extensive speciation data is not available for most commercial hydrocarbon solvent mixtures. The California reactivity-based aerosol regulations allow manufacturers to use calculation derived "Bin" MIR values for hydrocarbon mixtures to calculate product-weighted MIR values. These Bin values are based on boiling point range and aromatic content of any hydrocarbon mixtures used in coating manufacture. For solvents such as VM&P naphtha, the Bin MIR values are 1.17, 1.62, and 1.82 for an aromatic content of <2%, 2–8%, and 8–22%, respectively. Knowing the exact aromatic content of a particular sol-

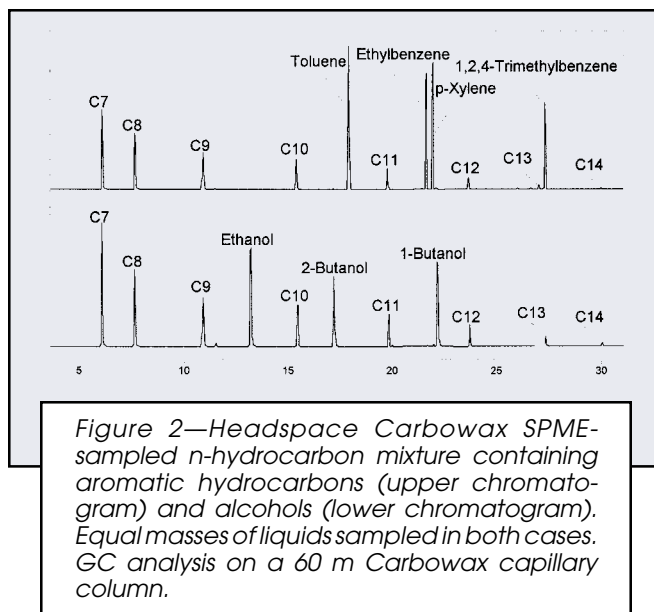
vent used could, therefore, make it possible to assign a lower PWMIR (reactivity) to a specific aerosol coating.

An example of the SPME/GC chromatogram of a gloss solventborne aerosol derived liquid paint, spiked with the normal hydrocarbon C5–C11, is given in Figure 1 (lower chromatogram). It should be noted that all of the propellant (C3–C4) was not completely removed from the liquid paint. In fact, working with the liquid paint after propellant removal is somewhat problematic since closed containers holding the paint tend to build up pressure. Similarly, in paints containing acetone or low boiling hydrocarbons such as hexanes, these volatile solvents tend to be partially transferred to the gas collection bag during propellant removal. The upper chromatogram in Figure 1 shows the same paint analyzed directly as a dispersion in diethyl succinate and containing the internal standard p-chlorotoluene. Since GC analysis of liquid paint sometimes shows signals derived from paint solids decomposition in a hot injection port, the combination of SPME/GC followed by direct GC may be used to monitor any such decomposition process since SPME samples only the ambient temperature headspace of the liquid paint.

The analytical method described in this paper makes it possible to calculate precise amounts of individual solvents in aerosol coatings. The use of different capillary columns makes it possible to differentiate oxygenates and aromatic hydrocarbons from aliphatic hydrocarbons. Specifically, when a solvent mixture is analyzed on a PDMS phase and is subsequently analyzed on a Carbowax phase, retention indexes are substantially increased making it possible to distinguish aliphatic hydrocarbons from aromatic hydrocarbons, Table 3. In addition, when a Carbowax-coated SPME fiber is used in conjunction with a Carbowax capillary column, aromatics and oxygenates are adsorbed more strongly on the SPME fiber and are retained for a longer time on the column, Figure 2. Toluene, for example, which has a boiling point of 110.6°C elutes more than 10 min after n-octane which has a boiling point of 126°C and has a peak area which is approximately twice as large when the headspace of a liquid mixture containing equal masses of these two solvents is sampled by SPME.

There are numerous hydrocarbon standards available commercially⁵ to aid in the establishment of chromatographic retention data. The ASTM D02 committee on petroleum products and lubricants has established a method for the analysis of refinery petroleum streams including an alkylate, a naphtha, and a reformat standard. The refinery reference materials used in the ASTM Method D 5134 interlaboratory study validation have been archived and are commercially available with detailed chromatograms and data booklets. In addition, a 37-component isoparaffins mix, a 30-component naphthenes mix, and a 37-component aromatic hydrocarbons mix which are well characterized are also commercially available. The hydrocarbon mixtures used in the manufacture of aerosol coatings contain many of these materials and the reference materials are extremely valuable in building chromatographic retention data.

Despite the many advances in capillary gas chromatography instrumentation and the remarkable resolution



available, it has proven difficult to standardize a test method for a detailed analysis of the often complex mixture of volatile organic compounds present in solvent-based paints. Because of the proliferation of numerous, similar columns and the endless choices of phase thickness, column internal diameter, column length, etc., as well as instrument operating parameters, many laboratories use similar *but not identical* methods for the capillary GC analysis of solvents in paint. Even minute differences in column polarity or column oven temperature, for example, can change resolution or elution order of components and make their identification an individual interpretive process rather than the desirable, objective application of standard retention data. To avoid this, stringent column specifications and temperature and flow conditions have been adopted in this test method to ensure consistent elution order and resolution and reproducible retention times measured as linear retention indexes. Strict adherence to the specified conditions is essential to the successful application of this test method.

References

- (1) Carter, W.P.L., "Development of Ozone Reactivity Scales for Volatile Organic Compounds," *J. Air and Waste Management Assoc.*, 44:881-899 (1994); Carter, W.P.L., "The SAPRC-99 Chemical Mechanism and Updated VOC Reactivity Scales, Draft Version," Revised April, 11, 2000. Prepared for the California Air Resources Board Contracts Nos. 92-329 and 95-308. Appendix D, pp. D-1 to D-33 (2000). <http://www.cert.ucr.edu/~carter/reactdat.htm>.
- (2) <http://www.arb.ca.gov/regact/conspro/aerocoat/finreg.pdf>.
- (3) ASTM Method D 5200-92, "Determination of Weight Percent Volatile Content of Solvent-Borne Paints in Aerosol Cans," *Annual Book of ASTM Standards*, Vol 06.01.
- (4) ASTM Method D 5325-92, "Determination of Weight Percent Volatile Content of Water-Borne Aerosol Paints," *Annual Book of ASTM Standards*, Vol 06.01.
- (5) Available from the Supelco Company, Supelco Park, Bellefonte, PA 16823-0048.
- (6) Khorash, Gray, and Selucky, *J. Chromatog.*, 481, 1-16 (1989); Hayes and Pitzer, *J. Chromatog.*, 253, 179-198 (1982).
- (7) Censullo, A.C., Jones, D.R., and Wills, M.T., Final Report to California Air Resources Board, "Improvement of Species Profiles for Aerosol Coatings," June 1, 2000.