

Quarterly Progress Report on  
Standard Agreement No. 04-329  
For the Period  
March 1, 2008 through May 30, 2008

***Development of an Improved VOC Analysis Method for Architectural  
Coatings***

Prepared for California Air Resources Board  
and the California Environmental Protection Agency

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### **Disclaimer-**

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## **Acknowledgements**

This report was submitted in partial fulfillment of ARB Standard Agreement Number 04-329, *Development of an Improved VOC Analysis Method for Architectural Coatings*, by the Cal Poly Foundation under sponsorship of the California Air Resources Board.

## **I. Work This Reporting Period**

This report summarizes work performed on the project from March 1, 2008 through May 30, 2008.

### **A. Task 2 and Task 3 Activities**

During this time period, work was continued on Task 2 activities including

- Analysis of “zero-VOC” coatings

During this time period, work was begun on Task 3 activities including

- Preparation of final form of methods developed
- Preparation of Draft Final Report

### **B. Analysis of “zero-VOC” coatings**

The goal of this project is to develop a method or methods suitable for analysis of all types of architectural coatings. One segment of the architectural coatings market receiving significant attention from coatings producers and consumers is “zero-VOC” coatings. These coatings provide an advantage for the consumer in that they have no detectable odor and produce virtually no volatile materials upon drying other than water. Although we are not aware of any regulatory definition of “zero-VOC” coatings, these are typically coatings containing very small amounts of VOCs, generally less than 5 g/L. Even coatings formulated with no added VOCs will contain small amounts of VOCs from resins, additives, colorants and other components. Although zero-VOC coatings in the form of 100% solids industrial maintenance coatings have been available for many years, it is only recently that zero-VOC waterborne interior and exterior flats and non-flats have appeared in the marketplace. Since the methods developed for this project grew out of methods initially developed to enable reliable VOC values to be measured for low VOC waterborne coatings (less than 5% VOC), we felt it desirable to test these methods on waterborne coatings containing extremely low VOC levels.

We have analyzed 15 samples of waterborne flats and non-flats. Eleven of these were “zero-VOC” and three had more substantial quantities of VOCs. Samples were analyzed using the modified ASTM 6886 method we developed for this project (detailed method presented later in this report). A known mass of paint was added to a weighed vial containing a small quantity of ceramic beads. Solvent (either acetone or THF) and a known amount of internal standard (ethylene glycol diethyl ether – EGDE) were also added. The sample was shaken vigorously and a one microliter sample was injected into the gas chromatograph.

Since most of these samples contained extremely low levels of VOCs, we needed to insure the peaks we analyzed were from VOCs in the coating and not impurities in the solvents. By using both acetone and THF as solvents, we could overlay the chromatograms and only count peaks appearing in both chromatograms as VOCs. In most cases the amounts of VOC were

so small we were unable to make an unambiguous identification of each VOC. Several of the samples did contain ethylene glycol or propylene glycol or both as the major VOC component. Results obtained for these 15 coatings are given in Table 1.

**Table 1 Results for 15 waterborne flats and non-flats including “zero-VOC” coatings**

	sample 1		sample 2		sample 3		sample 4		sample 5	
solvent	acetone	THF	acetone	THF	acetone	THF	acetone	THF	acetone	THF
density g/L	1410	1410	1384	1384	1295	1295	1248	1248	1256	1256
solids fraction	0.6074	0.6074	0.5949	0.5949	0.5222	0.5222	0.4272	0.4272	0.5415	0.5415
VOC fraction	0.0003	0.0004	0.0001	0.0001	0.0009	0.0006	0.0003	0.0007	0.0004	0.0006
water fraction	0.3923	0.3922	0.4050	0.4050	0.4769	0.4771	0.5725	0.5721	0.4581	0.4579
water, liters	0.5531	0.5529	0.5606	0.5607	0.6174	0.6178	0.7144	0.7139	0.5753	0.5750
material VOC	0.4	0.5	0.2	0.2	1.1	0.8	0.3	0.9	0.5	0.8
coating VOC	0.9	1.2	0.4	0.4	3.0	2.1	1.1	3.1	1.3	1.9
major VOCs										
	sample 6		sample 7		sample 8		sample 9		sample 10	
solvent	acetone	THF	acetone	THF	acetone	THF	acetone	THF	acetone	THF
density g/L	1089	1089	1109	1109	1381	1381	1179	1179	1279	1279
solids fraction	0.4180	0.4180	0.4325	0.4325	0.5936	0.5936	0.4526	0.4526	0.5398	0.5398
VOC fraction	0.0002	0.0006	0.0008	0.0011	0.0005	0.0010	0.0005	0.0011	0.0038	0.0026
water fraction	0.5818	0.5814	0.5667	0.5664	0.4059	0.4054	0.5469	0.5463	0.4564	0.4576
water, liters	0.6336	0.6331	0.6285	0.6282	0.5608	0.5600	0.6451	0.6444	0.5836	0.5851
material VOC	0.2	0.7	0.9	1.2	0.7	1.4	0.6	1.3	4.8	3.3
coating VOC	0.6	1.8	2.3	3.1	1.5	3.1	1.7	3.7	11.5	7.9
major VOCs							propylene glycol		ethylene glycol	propylene glycol
	sample 11		sample 12		sample 13		sample 14		sample 15	
solvent	acetone	THF	acetone	THF	acetone	THF	acetone	THF	acetone	THF
density g/L	1207	1207	1247	1247	1207	1207	1253	1253	1332	1332
solids fraction	0.4715	0.4715	0.4576	0.4576	0.4189	0.4189	0.4675	0.4675	0.5156	0.5156
VOC fraction	0.0170	0.0181	0.0034	0.0027	0.0254	0.0258	0.0009	0.0006	0.0012	0.0007
water fraction	0.5115	0.5105	0.5389	0.5396	0.5556	0.5552	0.5316	0.5319	0.4832	0.4837
water, liters	0.6175	0.6162	0.6720	0.6729	0.6709	0.6704	0.6663	0.6666	0.6434	0.6440
material VOC	20.5	21.8	4.3	3.4	30.7	31.2	1.2	0.8	1.6	1.0
coating VOC	53.7	56.9	13.1	10.4	93.3	94.6	3.5	2.4	4.5	2.7
major VOCs	ethylene glycol		ethylene glycol		ethylene glycol				ethylene glycol	
	propylene glycol		propylene glycol							

The VOC content (as weight percent of total coating) of several of these coatings is in the 0.01% range. These are the lowest VOC levels we have seen in any coatings. These results show it is possible to formulate architectural coatings with extremely low levels of VOCs. These results also show it is possible to determine near-zero levels of VOCs using our direct method.

#### D. Draft Direct Analysis Method

VOC method development has been the major thrust of this project. Over the course of the project we have experimented with several modifications of existing methods. We have relied on ASTM method D6886 perhaps more than any other in this work. This method was developed in our laboratory and provided a reliable method for analysis of waterborne air-dry coatings containing less than 5% VOC by weight. We have expanded the utility of this method to include waterborne coatings containing greater than 5% VOC and solvent-borne

coatings. We have also shown, through work on this project, that this method is suitable for analysis of exempt solvents in coatings.

We have revised ASTM method D6886 incorporating these changes and will present this revision to ASTM for consideration this year. Our revision of ASTM D6886 follows.

# DRAFT DIRECT VOC ANALYSIS METHOD

## Standard Test Method for Speciation of the Volatile Organic Compounds (VOCs) in Air-Dry Coatings by Gas Chromatography<sup>1</sup>

This standard is issued under the fixed designation D 6886; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon ( $\epsilon$ ) indicates an editorial change since the last revision or reapproval.

### 1. Scope

- 1.1 This test method is for the determination of the weight percent of individual volatile organic compounds in air-dry coatings. The method is intended primarily for analysis of waterborne coatings in which the material VOC content is below 5 weight percent. The method has been used successfully with higher VOC content waterborne coatings and with solvent-borne coatings.
- 1.2 This method may also be used to measure the exempt volatile organic compound content (acetone, methyl acetate, *t*-butyl acetate and *p*-chlorobenzotrifluoride) of waterborne and solvent-borne coatings. The methodology is virtually identical to that used in Test Method D 6133 and similar to that used in Test Method D 6438.
- 1.3 Volatile compounds that are present at the 0.05 weight percent level or greater can be determined.
- 1.4 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

### 2. Referenced Documents

#### 2.1 ASTM Standards:

- D 1475 Test Method for Density of Liquid Coatings, Inks, and Related Products<sup>2</sup>
- D 2369 Test Method for Volatile Content of Coatings<sup>2</sup>
- D 3792 Test Method for Water Content of Coatings by Direct Injection Into a Gas Chromatograph<sup>2</sup>
- D 3925 Practice for Sampling Liquid Paints and Related Pigmented Coatings<sup>2</sup>
- D 3960 Practice for Determining Volatile Organic Compound (VOC) Content of Paints and Related Coatings<sup>2</sup>
- D 4017 Test Method for Water in Paints and Paint Materials by Karl Fischer Method<sup>2</sup>
- D 6133 Test Method for Acetone *p*-Chlorobenzotrifluoride Methyl Acetate or *t*-Butyl Acetate Content of Solventborne and Waterborne Paints, Coatings, Resins, and Raw Materials by Direct Injection into A Gas Chromatograph<sup>2</sup>
- D 6438 Test Method for Acetone, Methyl Acetate, and Parachlorobenzotrifluoride Content of Paints, and Coatings by Solid Phase Microextraction-Gas Chromatography<sup>2</sup>
- E 177 Practice for Use of the Terms Precision and Bias in ASTM Test Methods<sup>3</sup>

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<sup>1</sup>This test method is under the jurisdiction of ASTM Committee D01 on Paint and Related Coatings, Materials, and Applications and is the direct responsibility of Subcommittee D01.21 on Chemical Analysis of Paints and Paint Materials.

Current edition approved March 10, 2003. Published May 2003.

<sup>2</sup>Annual Book of ASTM Standards, Vol 06.01.

<sup>3</sup>Annual Book of ASTM Standards, Vol 14.02.

### 3. Terminology

#### 3.1

3.1.1 *EGDE*—ethylene glycol diethyl ether

3.1.2 *DB*—2-(2-butoxyethoxy)ethanol; Butyl Carbitol™; diethylene glycol monobutyl ether

3.1.3 *EB*—2-butoxyethanol; Butyl Cellosolve™; ethylene glycol monobutyl ether

3.1.4 *EG*—ethylene glycol

3.1.5 *FID*—flame ionization detector

3.1.6 *F-VOC*—formulation data calculated volatile organic compound in g/(L-water)

3.1.7 *GC*—gas chromatograph

3.1.8 *PG*—propylene glycol

3.1.9 % *RSD*—percent relative standard deviation

3.1.10 *SPME*—solid phase microextraction

3.1.11 *Std Dev*—standard deviation

3.1.12 *TX*—2,2,4-trimethylpentane-1,3-diol, monoisobutyrate; Texanol™

3.1.13 *VOC*—volatile organic compound

3.1.14 *X-VOC*—experimental volatile organic compound in g/(L-water)

### 4. Summary of Test Method

4.1 A known weight of coating is dispersed in tetrahydrofuran (THF) or acetone, internally standardized, and analyzed by capillary gas chromatography to give a speciated composition of the volatile organic compounds and exempt organic compounds, if any, present in the coating. Summation of the individual volatile organic compound weight fractions gives the total VOC content of the coating measured in weight percent (Note 1).

NOTE 1—Using the provisions of Practice D 3960, the VOC content of coatings measured in g/L minus water, or other units, may be determined. Since the determination of weight percent VOC in the present method is by direct measurement, either the water fraction (Test Method D 3792 or Test Method D 4017) or the nonvolatile fraction (Test Method D 2369) may be determined indirectly in the application of Practice D 3960. The equations for calculating regulatory VOC content when no exempt volatile compounds are present are:

$$VOC = \frac{f_{VOC}(D_P)}{1 - [(1 - f_{NV} - f_{VOC})(D_P/D_W)]} \quad (1)$$

or

$$VOC = \frac{f_{VOC}(D_P)}{1 - [f_W(D_P/D_W)]} \quad (2)$$

where:

$D_P, f_{NV}, f_{VOC}$ , and  $f_W$  = coating density, nonvolatile fraction, VOC fraction, and water fraction, respectively.

4.2 Direct GC/FID, GC/MS and solid phase microextraction / gas chromatography (SPME/GC) of the coating may be used to facilitate identification of the volatile compounds present in a coating. Table X1.1 lists the GC retention times for the volatile compounds which may be found in low VOC content waterborne air-dry coatings and several possible internal standards, ordinarily not present in coatings, which may be used. (Note 2).

NOTE 2—The analyst should consult MSDS and product data sheets for possible information regarding solvents which may be present in a particular coating.

## 5. Significance and Use

5.1 In using Practice D 3960 to measure the regulatory VOC content of coatings, precision tends to be poor for low VOC content waterborne coatings because the VOC weight fraction is determined indirectly. The present method first identifies and then quantifies the weight fraction of individual VOCs directly in waterborne air-dry coatings. The total VOC weight fraction can be obtained by adding the individual weight fraction values (Note 3).

NOTE 3—The present method may also be used to speciate solvent-borne air-dry coatings. However, since these normally contain high, and often complex, solvent mixtures, precision tends to be better using EPA Method 24 where the VOC fraction is determined by an ASTM Method D2369 weight loss determination. An effort is currently underway in California to consider changing mass-based VOC regulations for architectural coatings to reactivity-based VOC regulations. In California, reactivity based regulations have already been implemented for aerosol coatings, that is, MIR-indexed regulations (California Air Resources Board). Reactivity based regulations would require knowing the weight fractions of each individual volatile compound present in a coating.

## 6. Apparatus

6.1 *Gas Chromatograph, FID Detection with Electronic Data Acquisition System*—Any capillary gas chromatograph equipped with a flame ionization detector and temperature programming capability may be used. Electronic flow control, which gives a constant carrier gas flow, is highly recommended.

6.2 *Standard FID Instrument Conditions* :

Detector	Flame ionization
Columns	Primary column: 30 m by 0.25 mm 5 % phenyl/95 % methyl siloxane (PMPS) (Note 4) , 1.0 μm film thickness. Confirmatory Columns: 30 m by 0.25 mm polydimethylsiloxane (PDMS), 0.25 μm film thickness; 30 m by 0.25 mm Carbowax™ (CW), 0.25 μm film thickness.
Carrier Gas	Helium
Flow Rate	1.0 mL per min, constant flow (24.9 cm/s at 40°)
Split Ratio	Variable
Temperatures, °C	
Inlet	260°
Detector	270°
Initial	40° for 4 min
Rate	10° per min to 250°, hold 5 min

NOTE 4—The column designated as PMPS is commercially available from several vendors by the following designations: DB-5, SPB-5, HP-5, AT-5, CP Sil 8CB, RTx-5, BP-5.

## 7. Reagents and Materials

- 7.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, all reagents shall conform to the available specifications of the Committee on Analytical Reagents of the American Chemical Society. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.
- 7.2 *Carrier Gas*, helium of 99.995 % or higher purity.
- 7.3 *Tetrahydrofuran (THF)*, HPLC grade.
- 7.4 Possible internal standards: *1-Propanol, p-fluorotoluene, cyclohexanol, p-chlorotoluene, ethylene glycol diethyl ether (EGDE), acetone-d-6 and p-cymene*, 99 + mole %.
- 7.5 *Fluorocarbon-faced septum vials* , 20 mL and 40 mL capacity.
- 7.6 Ceramic beads, 0.5-1.0 mm diameter.

## 8. Column Conditioning

8.1 The capillary columns should be conditioned according to the manufacturer's recommendation. The columns may then be used indefinitely without further conditioning.

## 9. Preparation of Standards

9.1 Prepare a stock mixture of ethylene glycol (EG), propylene glycol (PG), ethylene glycol monobutyl ether (EB), ethylene glycol diethyl ether (EGDE) [or other suitable internal standard], diethylene glycol monobutyl ether (DB), and Texanol (TX) by weighing one or two grams of each into an appropriate vial. The weight of each component should be approximately the same and determined to 0.1 mg. Mix the contents.

9.2 Transfer approximately 100  $\mu$ L of the stock mixture to a septum-capped vial containing 10 mL of THF and mix the contents (Note 5). This solution will contain each of the known analytes at a concentration of approximately 2 mg/mL.

NOTE 5—The solvents EG, PG, EB, DB and Texanol are widely used in the manufacture of waterborne air-dry coatings and may be expected as highly probable components of these coatings. The tetrahydrofuran solvent/dilute internal standard mixture must be analyzed by GC to determine if possible impurities interfere/coelute with the analytes being tested.

9.3 Chromatograph the solution in 9.2 by injecting 1  $\mu$ L into the PMPS column using the chromatographic conditions given in 6.2. Calculate the relative response factors for each of the analytes relative to the EGDE internal standard using the relationship:

$$RF = \frac{AA * MI}{AI * MA} \quad (3)$$

where:

<i>RF</i>	=	relative response factor,
<i>AA</i>	=	area of analyte,
<i>MI</i>	=	weight of internal standard (from 9.1),
<i>AI</i>	=	area of internal standard, and
<i>MA</i>	=	weight of analyte (from 9.1).

## 10. Paint Analysis

### A – Analysis of solvent-borne and waterborne coatings by GC/FID.

10.1 Using a 100 mL volumetric flask, make up a concentrated standard solution containing EGDE (or other suitable internal standard) in THF or acetone at a concentration of approximately 1 g per 100 mL and known to the nearest 0.1 mg.

- 10.2 Using standard quantitative dilution techniques, dilute the concentrated standard solution to give a working standard solution such that the internal standard concentration is near 1 mg per mL. Calculate the actual concentration.
- 10.3 Pipette 10 mL of working standard solution into a 20 or 40 mL vial containing 3-5g ceramic beads and close with a fluorocarbon-faced septum cap. Using a disposable 1 mL syringe, add approximately 0.6 to 0.8 g of the well-mixed paint through the septum cap and weigh to 0.1 mg (Note 6). Mix the contents vigorously by shaking for 1 min. Let the vial stand to permit pigments, if any, to settle. Alternatively, add the paint to the vial containing the ceramic beads and approximately 10-15mL of THF or acetone and weigh to 0.1mg. Using a dedicated syringe, add approximately 20 microliters of pure EGDE through the septum and weigh the amount added to 0.1mg. Shake the contents for 1 min.

NOTE 6—The paint should be drawn into the syringe without an attached syringe needle. Excess paint is wiped from the syringe and the needle is then attached for paint transfer. The mass of the paint may be determined by either the difference in the weight of the filled and empty syringe or by the difference in the weight of the vial before and after adding paint.

- 10.4 Chromatograph the solution in 10.3 by injecting 1  $\mu$ L into the PMPS capillary column using the standard conditions described in 6.3. Adjust the split ratio to give well-defined chromatographic peaks. Identify the volatile compounds present (Note 7) and calculate the weight fraction of each in the coating using the relationship:

$$\%X = \frac{(AA)(MI)(100)}{(AI)(RF)(MC)} \quad (4)$$

where:

<i>X</i>	=	one of several possible volatile compounds in the coating,
<i>RF</i>	=	relative response factor of compound X,
<i>AA</i>	=	peak area of compound X,
<i>MI</i>	=	weight of internal standard in 10 mL THF,
<i>AI</i>	=	peak area of internal standard, and
<i>MC</i>	=	weight of coating.

NOTE 7—If volatile compounds other than those in the standard (9.1) are present in the coating, the identity should be confirmed by retention time comparison with authentic material and the relative response factor should be determined as outlined in 9.1–9.3. Commercial Texanol may contain small amounts of 2,2,4-trimethylpentane-1,3-diol which elutes approximately 0.5 min before butyl carbitol. Acetone and isopropyl alcohol have nearly the same retention time on a 5 % phenyl/95 % PDMS column and if either is found, their identities should be confirmed on a different column. Isobutyl alcohol coelutes with the solvent (THF) and must be determined on a different column. SPME (11.2) is especially useful for confirming the presence of isobutyl alcohol since no THF is used in this procedure.

## B – Acetone analysis by GC/MS

- 10.5 Add approximately 0.5g of coating to a septum-capped vial containing 10-15mL of THF and 3-5g of ceramic beads. The paint should be added by means of a 1-mL disposable syringe by injecting it into the closed vial through the septum. Weigh the paint added to the nearest 0.1mg. Add acetone-d-6 to the closed vial with a dedicated syringe and weigh to the nearest 0.1mg. The amount of acetone-d-6 to be added should be approximately equal to the amount of acetone in the coating.
- 10.6 Chromatograph the solution in 10.5 by injecting 1  $\mu$ L into a GC/MS system using the chromatographic conditions described in 6.2. At the conclusion of the run extract the selected ions of mass 45 (isopropyl alcohol), 58 (acetone) and 64 (deuterated acetone). Calculate the concentration of isopropyl alcohol and acetone using the appropriate response factors. Response factors for isopropyl alcohol and acetone relative to acetone-d-6 may be determined by preparing a solution of known concentration of these analytes in THF and carrying out a GC/MS determination.

## C – Residual Semi-Volatile VOCs in Paint Films

- 10.7. Carry out a duplicate ASTM Method D2369 total volatiles determination. After the 1 hour heating period, cool the aluminum dishes containing the paint solids, cut the aluminum dishes into small strips and place them into a 125mL Erlenmeyer flask. Add approximately 20mL of methyl ethyl ketone, 3-4g of ceramic beads and a stir bar. Stopper the flask and stir the mixture for 16 hours (overnight) to extract VOC's into the MEK. After extraction, add 5.0mL (pipette) of EGDE/THF solution (10.2), swirl the contents and chromatograph the solution as described in 10.3. Calculate the fraction of semi-volatile VOCS retained in the paint film.. Include only those VOCs which have retention times equal to or greater than that of Texanol.

## D – Overlapping Chromatographic Peaks

- 10.8 Isobutyl alcohol coelutes with the solvent THF. To determine isobutyl alcohol concentration in a coating, carry out the analysis on a different capillary column or use acetone instead of THF as the analysis solvent. Acetone and isopropyl alcohol coelute on a PMPS column. To determine if isopropyl alcohol is present in a coating, use a Carbowax<sup>TM</sup> capillary column or carry out the analysis by GC/MS/SIM as described in 10.5.
- 10.9 A number of VOCs in solvent-borne paints containing commercial xylene tend to overlap. These include PM Acetate/ethylbenzene and butoxyethanol/o-xylene. Resolution can generally be obtained by simply changing the chromatographic heating rate. See Appendix X2 for a detailed description on the effect of chromatographic heating rate on separation of selected VOCs.

## 12. Reporting Results

- 12.1 Prepare a table (as indicated below) which contains information on each of the VOC species found. Do not include any exempt volatile organic compounds in this table.

VOC Found	GC Retention Time	Weight % Found
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Total weight percent of all speciated VOCs =

12.2 List VOCs that are not identified as unknown (UK) and use the relative response factor for Texanol to calculate weight % for unknown VOCs. List any exempt compounds that may be present separately from those listed in the VOC table.

### 13. Alternate Identification Methods

13.1 The use of GC/MS for volatile compound identification is highly desirable. A convenient procedure is to sample the headspace of the coating using an SPME fiber. The fiber may be thermally desorbed onto any standard capillary column and the compounds identified mass spectrally. This technique is especially valuable for identifying oxygenates, aromatics and other non-hydrocarbon compounds.

### 14. Precision and Bias

14.1 An interlaboratory study of total weight percent VOC was conducted in accordance with Practice E 691 in seven laboratories with five materials, with each laboratory obtaining three test results for each material. Five commercial waterborne coatings, a flat, a satin, a semi-gloss and a gloss, ranging in weight percent VOC content from 0.25 to 4.50, were analyzed. Each of the laboratories analyzed the coatings three times according to protocols specified in Practice E 691.

14.2 Precision statistics were calculated for the total weight percent VOC found in each of the 5 coatings and are presented in Table 1. The terms repeatability limit and reproducibility limit are used as specified in Practice E 177.

14.3 *95 % Repeatability Limit (within laboratory)* —The within-laboratory coefficient of variation is 2.7 % relative. The 95 % confidence limit for the difference between two such averages is 7.5 % of the test result.

14.4 *95 % Reproducibility Limit (between laboratories)* —The between-laboratory coefficient of variation is 5.8 % relative. The 95 % confidence limit for the difference between two such averages is 16.2 % of the test result.

14.5 *Bias*—Bias has not been determined.

### 15. Keywords

15.1 exempt organic compounds; gas chromatography; HAPS (hazardous air pollutants); speciation; SPME (solid phase microextraction); waterborne coatings

**TABLE 1 Precision Statistics for Low VOC Content Waterborne Air-Dry Coatings Analyzed by Gas Chromatography**

Material	Total VOC in Weight Percent, Average	Repeatability Standard Deviation	Reproducibility Standard Deviation	Repeatability Limit	Reproducibility Limit
A	0.25	0.009	0.020	0.03	0.06
B	2.85	0.058	0.125	0.16	0.35
C	4.04	0.087	0.187	0.24	0.52
D	4.49	0.145	0.314	0.41	0.88

Material	Total VOC in Weight Percent, Average	Repeatability Standard Deviation	Reproducibility Standard Deviation	Repeatability Limit	Reproducibility Limit
E	4.50	0.100	0.215	0.28	0.60

**APPENDIX**  
**(Nonmandatory Information)**

**X1.**

X1.1 Precision statistics were calculated for each of the individual VOCs found in the 5 coatings analyzed in the interlaboratory study and are presented in Table X1.2. The experimental VOC content (X-VOC) is compared with the theoretical VOC (F-VOC) obtained from formulation data.

**TABLE X1.1 Retention Times (in Minutes) and FID Relative Response Factors (RRF) of Possible Volatile Organic Compounds and Exempt Compounds in Air-Dry Coatings**

Compound	RRF	PMPS	Retention Time, min	
			Carbowax™	PDMS
methanol	0.66	2.35	5.16	1.97
ethanol	1.00	2.75	5.85	2.08
acetone	1.02	3.12	3.93	2.21
2-propanol	1.02	3.13	5.71	2.19
t-butyl alcohol		3.42		
methyl acetate	0.60	3.59	4.1	2.31
1-propanol		3.82	7.91	2.44
vinyl acetate		4.40		
methyl ethyl ketone	1.25	4.74	5.24	2.7
2-butanol	1.18	4.78	7.63	2.72
ethyl acetate	0.83	5.05		
tetrahydrofuran (THF)		5.31	4.65	3.05
isobutyl alcohol	1.62	5.31	8.94	2.97
1-butanol	1.59	5.97	9.92	3.39
propylene glycol monomethyl ether	0.79	6.18	9.66	3.62
ethylene glycol	0.55	6.42	16.94	3.91
ethyl acrylate		6.48		
t-butyl acetate	1.22	6.65	5.31	4.18
methyl methacrylate		6.74		
2-ethoxyethanol	0.70	6.83		
methyl pivalate		7.00		
propylene glycol	0.73	7.18	16.48	4.8
AMP-95	0.84	7.46		
toluene	2.07	7.82	8.02	5.44
p-fluorotoluene		8.03		
ethylene glycol diethyl ether (EGDE)	1.00	8.12		
2-propoxyethanol	1.00	8.27	12.58	6.41
butyl acetate	1.16	8.33		
propylene glycol monopropyl ether	1.01	8.72	11.65	7.32
diacetone alcohol		8.73		
furfuryl alcohol	0.93	8.88		
ethylbenzene	2.04	8.92	10.87	7.75
parachlorobenzotrifluoride	1.02	8.93		
propylene glycol mono t-butyl ether	1.16	8.96	12.58	7.67
propylene glycol, methyl ether acetate	0.86	8.99		
p-xylene	2.17	9.19	9.72	7.6
m-xylene	2.17	9.19	9.87	7.81
butyl ether		9.20	9.99	7.81
2-heptanone	1.46	9.32		
cyclohexanol		9.32		
butyl acrylate		9.32		
butyl propionate		9.45		
o-Xylene	2.17	9.47		
2-butoxyethanol	1.11	9.51	10.78	8.28
hexylene glycol		9.62	14.05	8.6
diethylene glycol monomethyl ether	0.70	9.81	16.89	
propylene glycol monobutyl ether (PnB)	1.09	9.87	16.52	
diethylene glycol diethyl ether	0.68	9.88		
PnB (minor component)		10.05	13.15	9.41
diethylene glycol	0.53	10.10		

glycerin	0.17	10.12		
p-chlorotoluene		10.17	13.97	9.66
butyl methacrylate		10.20		
dipropylene glycol monomethyl ether (DPM)	0.80	10.46		
diethylene glycol monoethyl ether	0.69	10.49		
DPM (second of three peaks)		10.51	14.99	10.42
DPM (third of three peaks)		10.71	15.1	10.49
p-cymene	2.13	10.84	15.62	10.67
benzyl alcohol	1.65	10.89		
N-methylpyrrolidinone	0.72	10.96	12.18	10.94
ethylene glycol butyl ether acetate		11.25	17.73	
DP (diethylene glycol monopropyl ether)		11.34	14.8	11.85
dipropylene glycol monopropyl ether		11.79	17.78	
dipropylene glycol monopropyl ether	0.76	11.79		
DPnP (dipropylene glycol monopropyl ether)		11.82	16.32	
2,2,4-Trimethylpentane-1,3-diol		11.85	16.68	
trimethylpentanediol		11.85		
diethylene glycol monobutyl ether		12.12		
diethylene glycol monobutyl ether	0.93	12.12		
naphthalene	2.03	12.43		
2-(2-ethylhexyl)ethanol		12.51		
DPnB (dipropylene glycol monobutyl ether)	1.04	12.53	18.86	13.41
DPnB (second of two major peaks)		12.58	17.42	
propylene glycol monophenyl ether	1.14	12.67		
Texanol™	1.34	13.62		
Texanol™ (second of two peaks)		13.74		
triethylene glycol		14.42		
2,2,4-trimethylpentane-1,3-diol, diisobutyrate	1.17	15.15		
2-ethylhexyl benzoate	1.39	16.05		
dibutyl phthalate	1.16	18.50		
Mineral Spirits	2.23	9 to 11		
Aromatic100	2.10	9.2 to 10.6		

**TABLE X1.2 Precision Statistics for Individual VOCs Found in the Round Robin  
of Coatings A-E**

Paint		EG %	PG %	EB %	DB %	TX %	Total VOC, %	X-VOC <sup>A</sup>	F-VOC <sup>A</sup>
A	Average					0.25	0.25	10	11
	Std Dev					0.03	0.03	1.2	
	% RSD					11.93	11.93	11.8	
B	Average		1.53		0.14	1.19	2.85	92	92
	Std Dev		0.14		0.01	0.10	0.11	3.1	
	% RSD		9.18		9.13	8.13	3.76	3.4	
C	Average		2.49			1.55	4.04	145	147
	Std Dev		0.11			0.14	0.16	5.0	
	% RSD		4.61			8.76	4.00	3.4	
D	Average	2.31		1.04	0.09	1.05	4.49	113	121
	Std Dev	0.32		0.07	0.01	0.11	0.23	5.2	
	% RSD	13.65		6.73	8.51	10.17	5.09	4.6	
E	Average		2.40		0.64	1.45	4.50	142	138
	Std Dev		0.11		0.05	0.15	0.15	4.0	
	% RSD		4.66		8.23	9.99	3.29	2.8	

<sup>A</sup> Measured in grams per liter minus water.

## **E. Draft HAPs Method**

As part of this project, we have expanded the scope of ASTM Method 6886 to include the analysis of hazardous air pollutants or HAPs. This method is suitable for analysis of HAPs in solvent-borne, air-dry coatings. In most cases, the HAPs can be determined as part of the normal direct VOC analysis.

The draft HAP analysis method follows.

# DRAFT HAP ANALYSIS METHOD

## Standard Test Method for the Determination of the Common Hazardous Air Pollutants (HAPs) in Solventborne Air-Dry Coatings by Gas Chromatography

### 1. Scope

- 1.1. This test method is for the determination of the weight percent of the hazardous air pollutants (HAPs) commonly found in solventborne air-dry coatings. These include methyl isobutyl ketone (MIBK), toluene, commercial xylene, cumene, and naphthalene.
- 1.2. Volatile compounds that are present at the 0.01 weight percent level or greater can be determined.
- 1.3. *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

### 2. Referenced Documents

#### 2.1. ASTM Standards:

- D 1475 Test Method for Density of Liquid Coatings, Inks, and Related Products<sup>5</sup>
- D 2369 Test Method for Volatile Content of Coatings<sup>2</sup>
- D 3792 Test Method for Water Content of Coatings by Direct Injection Into a Gas Chromatograph<sup>2</sup>
- D 3925 Practice for Sampling Liquid Paints and Related Pigmented Coatings<sup>2</sup>
- D 3960 Practice for Determining Volatile Organic Compound (VOC) Content of Paints and Related Coatings<sup>2</sup>
- D 4017 Test Method for Water in Paints and Paint Materials by Karl Fischer Method<sup>2</sup>
- D 6133 Test Method for Acetone *p*-Chlorobenzotrifluoride Methyl Acetate or *t*-Butyl Acetate Content of Solventborne and Waterborne Paints, Coatings, Resins, and Raw Materials by Direct Injection into A Gas Chromatograph<sup>2</sup>
- D 6438 Test Method for Acetone, Methyl Acetate, and Parachlorobenzotrifluoride Content of Paints, and Coatings by Solid Phase Microextraction-Gas Chromatography<sup>2</sup>
- E 177 Practice for Use of the Terms Precision and Bias in ASTM Test Methods<sup>6</sup>
- E 691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method<sup>3</sup>

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<sup>5</sup>Annual Book of ASTM Standards, Vol 06.01.

<sup>6</sup>Annual Book of ASTM Standards, Vol 14.02.

### 3. Terminology

3.1. To be added

### 4. Summary of Test Method

4.1. A known weight of coating is dispersed in tetrahydrofuran (THF) or acetone, internally standardized, and analyzed by capillary gas chromatography to give a speciated composition of the volatile organic compounds in the coating. The HAPs present in the coating are identified and measured relative to the internal standard.

4.2. GC/FID or GC/MS using solid phase microextraction (SPME) of the coating may be used to facilitate identification of the volatile compounds present in a coating (Note 1).

NOTE 1—The analyst should consult MSDS and product data sheets for possible information regarding solvents which may be present in a particular coating. SPME/GC may be used to ascertain that decomposition volatiles are not measured.

### 5. Significance and Use

5.1. To be added

### 6. Apparatus

6.1. *SPME Sampling Apparatus and Fibers*,<sup>7</sup> manual SPME holders fitted with a 70  $\mu\text{m}$  Carbowax<sup>TM</sup>/Divinylbenzene (CW/DVB) StableFlex fiber assembly.

6.2. *Gas Chromatograph, FID Detection with Electronic Data Acquisition System*—Any capillary gas chromatograph equipped with a flame ionization detector and temperature programming capability may be used. Electronic flow control, which gives a constant carrier gas flow, is highly recommended.

6.3. *Standard FID Instrument Conditions* :

Detector	Flame ionization
Column	Primary column: 30 m by 0.25 mm 5 % phenyl/95 % methyl siloxane (PMPS) (Note 2) , 1.0 $\mu\text{m}$ film thickness.
Carrier Gas	Helium
Flow Rate	1.0 mL per min, constant flow
Split Ratio	Variable
Temperatures, °C	
Inlet	260°
Detector	270°
Initial	50° for 4 min
Rate	20° per min to 250°, hold 5 min

<sup>7</sup>Available from the Supelco Company, Supelco Park, Bellefonte, PA 16823-0048.

NOTE 2 —The column designated as PMPS is commercially available from several vendors by the following designations: DB-5, SPB-5, HP-5, AT-5, CP Sil 8CB, RTx-5, BP-5.

## 7. Reagents and Materials

- 7.1. *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, all reagents shall conform to the available specifications of the Committee on Analytical Reagents of the American Chemical Society. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.
- 7.2. *Carrier Gas*, helium of 99.995 % or higher purity.
- 7.3. *Tetrahydrofuran (THF)*, HPLC grade.
- 7.4. *Acetone*, 99 + mole %.
- 7.5. *Ethylene glycol diethyl ether (EGDE)*, 99 + mole %.
- 7.6. *Methyl isobutyl ketone (MIBK)*, *toluene*, *ethylbenzene*, *m- or p-xylene*, *o-xylene*, *cumene*, *naphthalene*, 99 + mole %.
- 7.7. *Commercial xylene*, *commercial Aromatic 100* and *commercial Aromatic 150*.
- 7.8. *Fluorocarbon-faced septum vials*, 20 mL and 40 mL capacity.

## 8. Column and Fiber Conditioning

- 8.1. The capillary column should be conditioned according to the manufacturer's recommendation. The column may then be used indefinitely without further conditioning.
- 8.2. The SPME fiber should be conditioned and used according to the manufacturer's recommendation.
- 8.3. The SPME fiber should be inserted into a 260°C injection port for 30 s prior to each sampling event.

## 9. Preparation of Standards

- 9.1. Prepare a stock mixture of the compounds listed in 7.5 and 7.6 by weighing one or two grams of each into an appropriate vial. The weight of each component should be approximately the same and determined to 0.1 mg. Mix the contents.
- 9.2. Transfer approximately 150  $\mu$ L of the stock mixture to a septum-capped vial containing 10-12 mL of THF or acetone and mix the contents. This solution will contain each of the known analytes and the internal standard (EGDE) at a concentration of approximately 2 mg/mL.
- 9.3. Chromatograph the solution in 9.2 by injecting 1  $\mu$ L using the PMPS column and the chromatographic conditions given in 6.3. Calculate the relative response factors for each of the analytes relative to the EGDE internal standard using the relationship:

$$RF = \frac{AA * MI}{AI * MA}$$

where:

<i>RF</i>	=	relative response factor,
<i>AA</i>	=	area of analyte,
<i>MI</i>	=	weight of internal standard (from 9.1),
<i>AI</i>	=	area of internal standard, and
<i>MA</i>	=	weight of analyte (from 9.1).

- 9.4. Prepare a solution of the following in THF or acetone (approximate concentration in mg/mL): MIBK (2), toluene (2), EGDE (2), commercial xylene (3), and commercial Aromatic 100 (5).
- 9.5. Prepare a solution of the following in THF or acetone (approximate concentration in mg/mL): MIBK (2), toluene (2), EGDE (2), commercial xylene (3), and commercial Aromatic 150 (5).
- 9.6. Chromatograph each of the solutions in 9.4 and 9.5 by injecting 1 $\mu$ L of the solution. The chromatograms should be obtained at heating rates of 20, 10, 5, and 2.5 degrees, respectively. Sample chromatograms that were obtained at a heating rate of 20 degrees per minute are given in Figures 1 and 2 below.

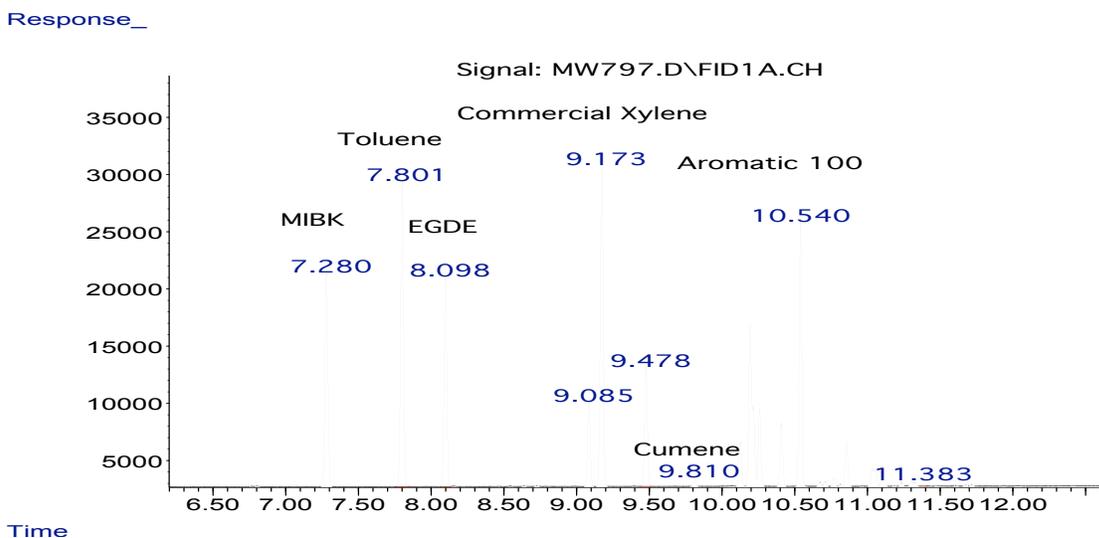


Figure 1. Chromatogram of standard HAP mixture containing MIBK, toluene, EGDE(internal standard), commercial xylene, and Aromatic 100. Heating rate = 20<sup>0</sup>C/minute.

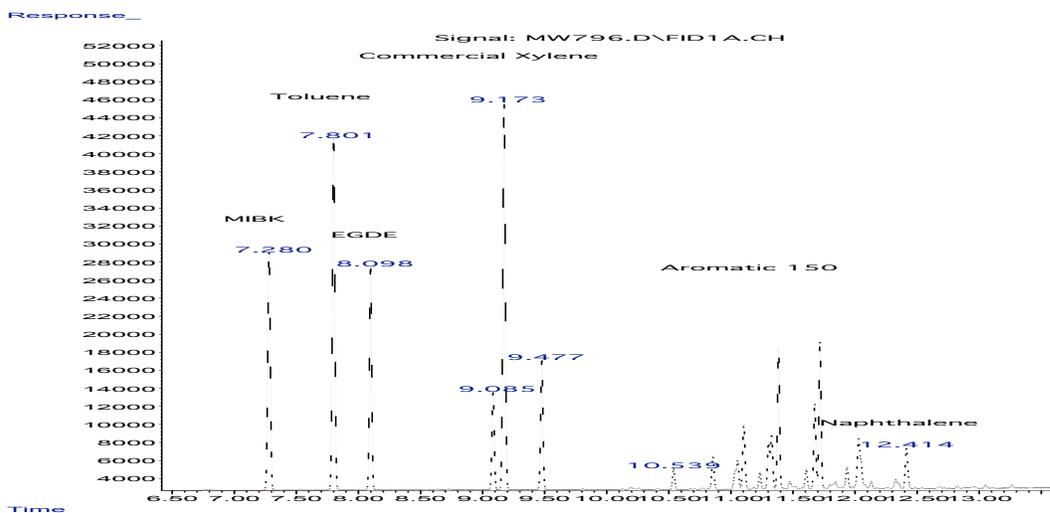


Figure 2. Chromatogram of standard HAP mixture containing MIBK, toluene, EGDE(internal standard), commercial xylene, and Aromatic 150. Heating rate = 20°C/minute.

## 10. Coating Analysis

- 10.1. Add approximately 15-20 mL of THF or acetone to a 40 mL vial containing 3-5g ceramic beads (Coo’s Mini Media “M”, 2.0mm) and close with a fluorocarbon-faced septum cap. Using a disposable 1 mL syringe, add approximately 0.5mL of the well-mixed coating through the septum cap and weigh to 0.1 mg (Note 3). Using a dedicated 100 or 200µL syringe, add approximately 50µL of EGDE internal standard and weigh to 0.1mg. Mix the contents vigorously by shaking for 1 minute. Let the vial stand to permit pigments, if any, to settle.

NOTE 3—The coating should be drawn into the syringe without an attached syringe needle. Excess coating is wiped from the syringe and the needle is then attached for transfer to the vial. The mass of the coating may be determined by either the difference in the weight of the filled and empty syringe or by the difference in the weight of the vial before and after adding paint.

- 10.2. Chromatograph the solution in 10.1 by injecting 1µL into the PMPS capillary column using the standard conditions described in 6.3. Adjust the split ratio to give well-defined chromatographic peaks. If necessary, the solution may be diluted with additional THF or acetone. Identify the HAP compounds present. The peak area of the internal standard (EGDE) should be approximately equal to the peak area of the HAP present in the highest concentration. This may be accomplished by adjusting the amount of sample used, the amount of internal standard used, or both. Calculate the weight fraction of each HAP in the coating using the relationship:

$$\%X = \frac{(AA)(MI)(100)}{(AI)(RF)(MC)}$$

where:

<i>X</i>	=	one of several possible HAPs in the coating,
<i>RF</i>	=	relative response factor of HAP X,
<i>AA</i>	=	peak area of HAP X,
<i>MI</i>	=	weight of internal standard
<i>AI</i>	=	peak area of internal standard, and
<i>MC</i>	=	weight of coating.

## 11. Chromatographic Resolution

11.1. Using a 5 % phenyl/95 % PDMS column and the chromatographic conditions of 6.3, certain compounds co-elute. These include, and are not limited to: PM acetate/ethylbenzene and 2-butoxyethanol(EB)/o-xylene. If co-elution is suspected, separation may be obtained by changing the chromatographic heating rate. See figures 3, 4, 5, and 6 for the effect of heating rate on commercial xylene containing PM acetate and 2-butoxyethanol.

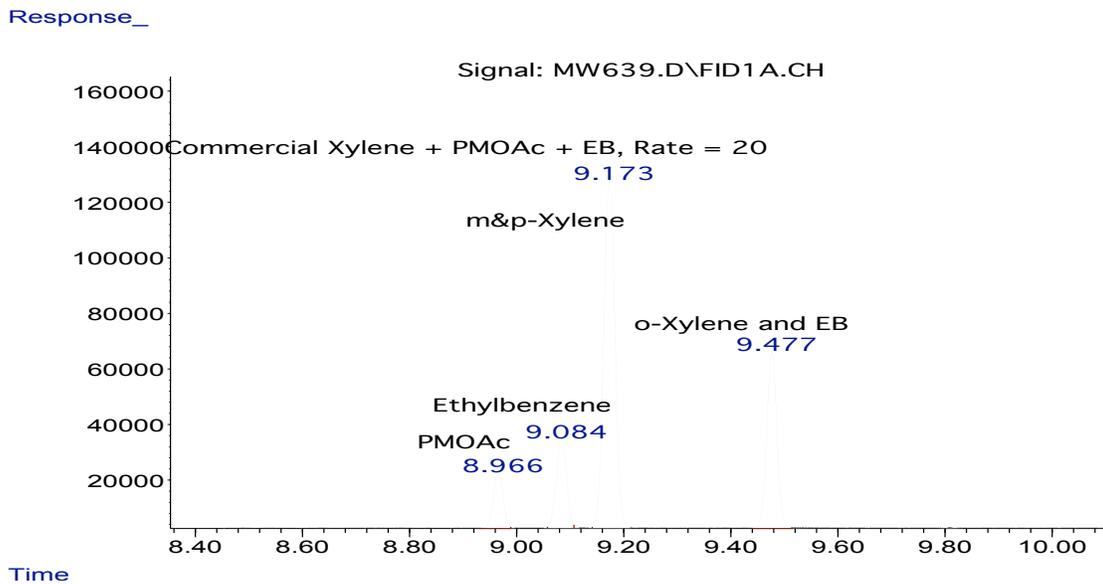


Figure 3. Commercial xylene with added PM acetate(PMOAc) and butoxyethanol (EB) at a chromatographic heating rate of 20°C/minute. EB and o-xylene co-elute. . Chromatography relatively fast.

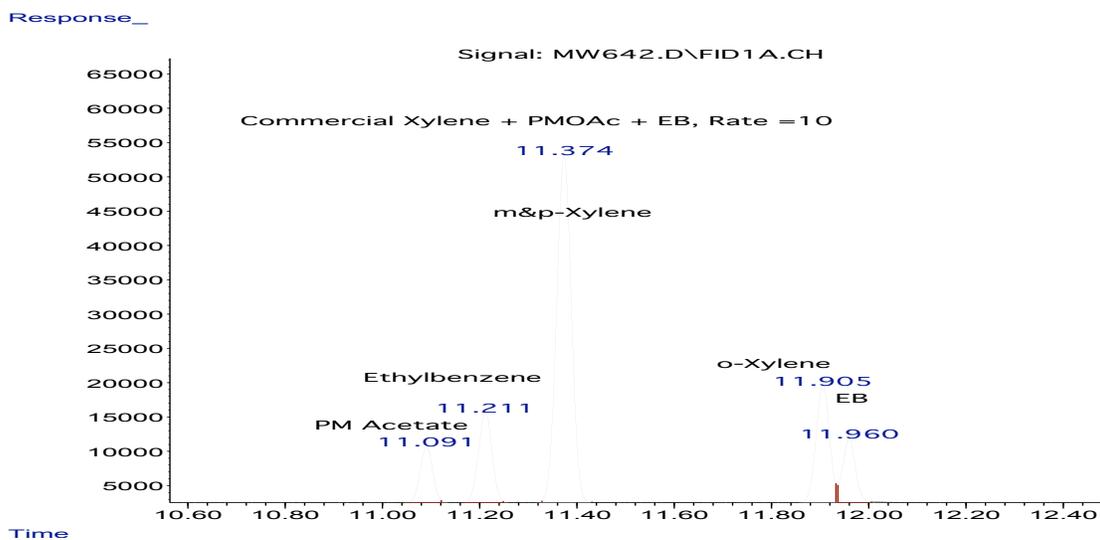


Figure 4. Commercial xylene with added PM acetate (PMOAc) and butoxyethanol (EB) at a chromatographic heating rate of 10°C/minute. EB and o-xylene separated.

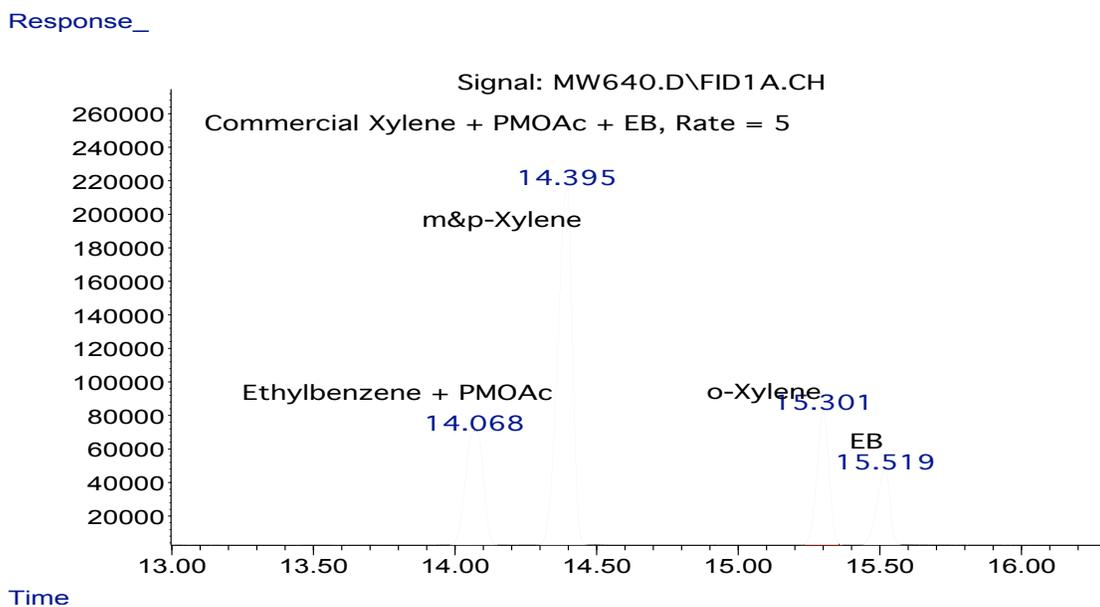


Figure 5 Commercial xylene with added PM acetate (PMOAc) and butoxyethanol (EB) at a chromatographic heating rate of 5°C/minute. EB and o-xylene separated. Ethylbenzene and PMOAc co-elute.

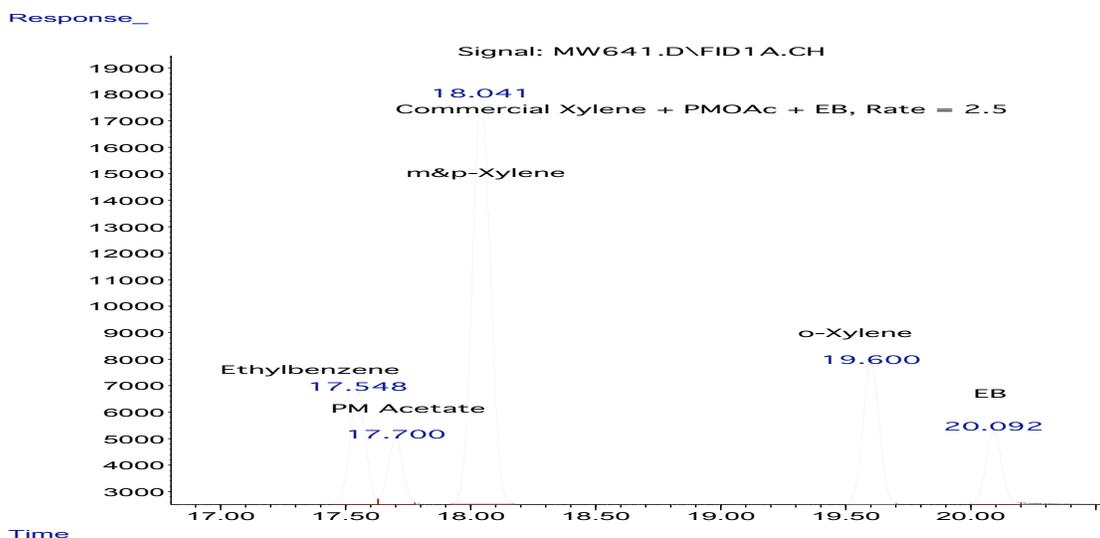


Figure 6. Commercial xylene with added PM acetate (PMOAc) and butoxyethanol (EB) at a chromatographic heating rate of  $2.5^{\circ}\text{C}/\text{minute}$ . All components separated. Chromatography is relatively slow.

- 11.2. Commercial xylene contains ethylbenzene, m-xylene, p-xylene and o-xylene. The meta and para isomers are not resolved on a PMPS capillary column. The three peaks for commercial xylene have a relatively constant area ratio consisting of 15-18% ethylbenzene, 62-65% m&p-xylene and 19-22% o-xylene. When this ratio is significantly different, co-elution with another substance is probably occurring and the chromatography should be carried out at a different heating rate to effect separation. Additionally, if the chromatographic peak symmetry appears distorted, this may indicate co-elution with another substance and a different chromatographic heating rate should be used to obtain separation.
- 11.3. Cumene is introduced into coating materials when the aromatic hydrocarbon mixture Aromatic 100 is added to a coating. This solvent mixture is the source of cumene in coatings. Cumene is normally not added to coatings as a pure material. The cumene content of Aromatic 100 is typically 1 to 2%. The average cumene content was found to be 1.4% in six samples of Aromatic 100 that were analyzed by GC. When measured as a percent of the 1,2,4-trimethylbenzene content (the major component in Aromatic 100) the value is 3 to 5%. Since cumene in a coating is a small component of a complex hydrocarbon mixture, its concentration in a coating will always be small, generally much less than 1%. Cumene is rarely, if ever, added to a coating as a pure solvent thus coatings containing cumene will exhibit the chromatographic peaks of Aromatic 100 (Figure 1).
- 11.4. Naphthalene is normally not added to coatings as a pure material. When naphthalene is present in a coating its source is almost always the solvent Aromatic 150, a complex mixture of predominantly C10 aromatic hydrocarbons. The naphthalene content of Aromatic 150 is typically 3 to 8%. The average naphthalene content was found to be 5.9% in five samples of Aromatic 150 that were analyzed by gas chromatography. If naphthalene is detected in a coating, the other components of the Aromatic 150 mixture should also be present (Figure

2). The major components of Aromatic 150 are 1,2-dimethyl-4-ethylbenzene (10-15%, ret time = 15.5min) and 1,2,4,5-tetramethylbenzene (10-15%, ret time = 16.2 min) at a heating rate of 10<sup>0</sup>C per minute on the PMPS capillary column described in 6.3.

## 12. Solid Phase Microextraction Procedure

- 12.1. Since a solution/dispersion of coating in THF or acetone is injected into a relatively hot GC injection port, peaks representing decomposition products may be observed and should not be considered as VOCs. Solid phase microextraction allows sampling of most VOCs at low temperature and may be used to determine if GC peaks observed in the direct GC analysis (Section 10) are actual VOCs or decomposition products. If desired, the SPME procedure may be used prior to direct analysis to determine which VOCs are present in the coating. If GC/MS is available, the SPME procedure is especially useful for identification of VOCs, HAPs and exempt compounds present in a coating sample.
- 12.2. Place approximately 2 to 3 g of liquid coating into a 40 mL fluorocarbon-faced septum vial. Close the vial with a fluorocarbon-faced septum cap and heat to 35 to 40°C in an oven or other suitable heat source (oil bath, water bath, heated metal block). Do not let the contents contact the inside face of the septum cap. Insert the SPME fiber through the septum cap and sample the headspace for 3 to 4 min using a conditioned CW/DVB SPME fiber. Desorb the fiber for 10 s onto the capillary column and obtain the gas chromatogram using the standard chromatographic conditions described in 6.3. Identify the volatile components present in the liquid paint using retention time values corresponding to those of authentic compounds. The peaks found by this SPME procedure should correspond to the peaks found by the direct procedure. If peaks found in the direct procedure are not found by the SPME procedure, decomposition may be taking place in the direct method.

## 13. Reporting Results

- 13.1. Prepare a table (as indicated below) which contains information on each of the HAPs found.

HAP Found	GC Retention Time (heating rate)	Weight % Found

## 14. Alternate Identification Methods

- 14.1. The use of GC/MS for volatile compound identification is highly desirable. A convenient procedure is to sample the headspace of the coating using an SPME fiber. The fiber may be thermally desorbed onto any standard

capillary column and the compounds identified mass spectrally. This technique is especially valuable for identifying oxygenates, aromatics and other non-hydrocarbon compounds.

## **15. Precision and Bias**

15.1. To be added

## **F. Draft 2-K Method**

The project was begun with the goal of developing VOC methods for all types of coatings represented in the CARB Architectural Coatings Surveys. One area of special interest was development of a direct method for determination of VOC and HAP content of solvent-borne and waterborne multi-component coatings that cure by chemical reaction. No direct method for analysis of these coatings was available. Development of this method required considerable experimentation and was one of the most challenging aspects of the project. The method we developed can also be used to determine the VOC and HAP content of coatings which cure by heating, including melamine coatings and powder coatings. Although these heat-cured coatings are not part of the CARB Architectural Coatings Survey, they represent a significant fraction of coatings used in California for which no suitable direct method of VOC analysis was available.

The draft 2-K VOC analysis method follows.

## DRAFT 2-K VOC ANALYSIS METHOD

### Standard Test Method for the VOC and HAP Content of Multi-Component Coatings by Gas Chromatography

#### 1. Scope

1.1 This test method is for the determination of the speciated VOC and HAP content of solvent-borne and waterborne multi-component coatings that cure by chemical reaction.

1.2 The method may also be used to determine the VOC and HAP content of multi-component coatings which cure by heating ( i.e., melamine-cure coatings and powder coating).

*This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and to determine the applicability of regulatory limitations prior to use.*

#### 2. Referenced Documents

##### 2.1 ASTM Standards:

D 1475 Test Method for Density of Liquid Coatings, Inks, and Related Products

D 2369 Test Method for Volatile Content of Coatings

D 3792 Test Method for Water Content of Coatings by Direct Injection Into a Gas Chromatograph

D 3925 Practice for Sampling Liquid Paints and Related Pigmented Coatings

D 3960 Practice for Determining Volatile Organic Compound (VOC) Content of Paints and Related Coatings

D 4017 Test Method for Water in Paints and Paint Materials by Karl Fischer Method

D 6133 Test Method for Acetone *p*-Chlorobenzotrifluoride Methyl Acetate or *t*-Butyl Acetate Content of Solventborne and Waterborne Paints, Coatings, Resins, and Raw Materials by Direct Injection into A Gas Chromatograph

D 6438 Test Method for Acetone, Methyl Acetate, and Parachlorobenzotrifluoride Content of Paints, and Coatings by Solid Phase Microextraction-Gas Chromatography

E 177 Practice for Use of the Terms Precision and Bias in ASTM Test Methods

E 691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method

#### 3. Terminology

3.1 To be added

#### 4. Summary of Test Method

4.1 The components are mixed, a sample of the mixture is weighed into a 20mL headspace vial, the vial is sealed with a crimp cap, and the mixture is allowed to cure for 24 to 36 hours at room temperature. After the initial room temperature cure the sample is

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heated for 30 minutes at 110°C. After cooling, a known quantity of acetone containing an internal standard is added to the sealed vial and the contents are mixed. The solution containing the VOCs and HAPs is then analyzed by gas chromatography (Note 1).

NOTE 1—Using the provisions of Practice D 3960, the VOC content of coatings measured in g/L minus water, or other units, may be determined. Since the determination of weight percent VOC in the present method is by direct measurement, either the water fraction (Test Method D 3792 or Test Method D 4017) or the nonvolatile fraction (Test Method D 2369) may be determined indirectly in the application of Practice D 3960. The equations for calculating regulatory VOC content when no exempt volatile compounds are present are:

$$VOC = \frac{f_{VOC}(D_P)}{1 - [(1 - f_{NV} - f_{VOC})(D_P/D_W)]} \quad (1)$$

or

$$VOC = \frac{f_{VOC}(D_P)}{1 - [f_W(D_P/D_W)]} \quad (2)$$

where:

$D_P, f_{NV}, f_{VOC}$  = coating density, nonvolatile fraction, VOC fraction, and water fraction, respectively.  
and  $f_W$

4.2 Direct GC/FID or GC/MS using solid phase microextraction (SPME) may be used to facilitate identification of the volatile compounds present in a coating (Note 2).

NOTE 2—The analyst should consult MSDS and product data sheets for possible information regarding solvents which may be present in a particular coating.

## 5. Significance and Use

5.1 In using Practice D 3960 to measure the regulatory VOC content of coatings, precision tends to be poor for waterborne coatings because the VOC weight fraction is determined indirectly. The present method first identifies and then quantifies the weight fraction of individual VOCs directly. The total VOC weight fraction can be obtained by adding the individual weight fraction values (Note 3).

NOTE 3—An effort is currently underway in California to consider changing mass-based VOC regulations for architectural coatings to reactivity-based VOC regulations. In California, reactivity based regulations have already been implemented for aerosol coatings, that is, MIR-indexed regulations (California Air Resources Board). Reactivity based regulations would require knowing the weight fraction of each individual volatile compound present in a coating.

## 6. Apparatus

6.1 *SPME Sampling Apparatus and Fibers*, manual SPME holders fitted with a 70  $\mu\text{m}$  Carbowax<sup>TM</sup>/Divinylbenzene (CW/DVB) StableFlex fiber assembly.

6.2 *Gas Chromatograph, FID Detection with Electronic Data Acquisition System*—Any capillary gas chromatograph equipped with a flame ionization detector and temperature programming capability may be used. Electronic flow control, which gives a constant carrier gas flow, is highly recommended.

6.3 *Standard FID Instrument Conditions* :

Detector	Flame ionization
Columns	Primary column: 30 m by 0.25 mm 5 % phenyl/95 % methyl siloxane (PMPS) (Note 4) , 1.0 $\mu\text{m}$ film thickness. Confirmatory Column: 60 m by 0.25 mm Carbowax <sup>TM</sup> (CW) , 0.50 $\mu\text{m}$ film thickness
Carrier Gas	Helium
Flow Rate	1.0 mL per min, constant flow
Split Ratio	Variable
Temperatures, °C	
Inlet	260°
Detector	270°
Initial	50° for 4 min
Rate	20° per min to 250°, hold 5 min

NOTE 4—The column designated as PMPS is commercially available from several vendors by the following designations: DB-5, SPB-5, HP-5, AT-5, CP Sil 8CB, RTx-5, BP-5.

## 7. Reagents and Materials

7.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, all reagents shall conform to the available specifications of the Committee on Analytical Reagents of the American Chemical Society. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

7.2 *Carrier Gas*, helium of 99.995 % or higher purity.

7.3 *Acetone*, HPLC grade.

7.4 *Ethylene glycol diethyl ether (EGDE)*, 99 + mole %.

7.5 *Fluorocarbon-faced septum vials*, 20 mL and 40 mL; *headspace vials* (20mL), *crimp caps*, and *crimper*, Agilent Technologies part numbers: headspace vials - 5182-0837, crimp caps - 5183-4477 and crimper - 9301-0720, or equivalent.

## 8. Column and Fiber Conditioning

8.1 The capillary columns should be conditioned according to the manufacturer's recommendation. The columns may then be used indefinitely without further conditioning.

8.2 The SPME fiber should be conditioned and used according to the manufacturer's recommendation.

8.3 The SPME fiber should be inserted into a 260°C injection port for 30 s prior to each sampling event.

## 9. Coating Analysis

9.1 Determine the density of the individual components of the multi-component coating using ASTM Method D1475. Convert the manufacturer's recommended volume mix ratio to a weight mix ratio. Using a suitable container, prepare approximately 100 to 200g of the mixture and mix using a spatula or paint shaker. Immediately after mixing, transfer approximately 100 mg of the mixture to a 20 mL headspace vial and weigh to 0.1mg. Add a paper clip to the vial and seal with a crimp cap immediately after adding the coating mixture. Using an external magnet, spread the coating mixture evenly over the bottom surface of the vial. Prepare two more samples in the same way. At the same time that the headspace vials are being prepared, transfer approximately 0.5 g of the mixture to each of three aluminum foil dishes (58 mm in diameter by 18 mm high) containing a paperclip stirrer and weigh to 0.1 mg. Using the paper clip stirrer, spread the coating mixture as evenly as possible over the bottom surface of the aluminum foil pans. DO NOT ADD ANY SOLVENTS TO THE PANS. Let the vials and aluminum foil dishes containing the coating mixture stand at room temperature for a 24 to 36 hour cure. After the room temperature cure, place the sealed vials and aluminum foil pans in an oven at 110°C. The vials should remain in the oven for 30 minutes and the aluminum foil pans should remain in the oven for 60 minutes. Determine the total volatile content of the coating mixture by reweighing the cooled aluminum foil pans.

9.2 Prepare a stock solution of ethylene glycol diethyl ether (EGDE) in acetone at a concentration of approximately 10 mg/mL by weighing 1 gram of EGDE to the nearest 0.1 mg into a 100mL volumetric flask.

9.3 Dilute the stock solution quantitatively with acetone to obtain a working standard that has a concentration of approximately 1mg/mL. Convert the concentration of the working standard from mg/mL to mg/g by dividing by the density of acetone (0.79g/mL).

9.4 Using a dedicated glass syringe, add 3 to 4mL of the working standard from 9.3 to each of the cooled headspace vials from 9.1. Determine the weight of solution added to 0.1 mg. Mix the contents by briefly shaking the contents followed by sonication for 15 to 30 minutes. Remove the crimp cap and transfer the solution to a small screw-cap vial.

9.5 Chromatograph the solution in 9.4 by injecting 1µL into the PMPS capillary column using the standard conditions described in 6.3. Adjust the split ratio to give well-defined chromatographic peaks. Identify the volatile compounds present (Note 5) and calculate the weight fraction of each in the coating using the relationship:

$$\%X = \frac{(AA)(MI)(100)}{(AI)(RF)(MC)}$$

where:

<i>X</i>	=	one of several possible volatile compounds in the coating,
<i>RF</i>	=	relative response factor of compound X,
<i>AA</i>	=	peak area of compound X,
<i>MI</i>	=	weight of internal standard in 10 mL THF,
<i>AI</i>	=	peak area of internal standard, and
<i>MC</i>	=	weight of coating.

NOTE 5-Analytes may be identified using information available from product data sheets, MSDS, GC/MS, or FID retention time comparison with known compounds (see table 1).

## 10. Preparation of Standards

10.1 After identification of the VOCs present in the coating (from 9.5), prepare a mixture of the pure components and the internal standard (EGDE) by weighing approximately 1g (to 0.1mg) of each into an appropriate vial and mix the contents.

10.2 Dilute a portion of the mixture from 10.1 with acetone to give a solution with a concentration of each analyte of approximately 1 to 2 mg/mL.

10.3 Chromatograph the solution in 10.2 by injecting 1 µL into the PMPS column using the chromatographic conditions given in 6.3. Calculate the relative response factors for each of the analytes relative to the EGDE internal standard using the relationship:

$$RF = \frac{AA * MI}{AI * MA}$$

where:

<i>RF</i>	=	relative response factor,
<i>AA</i>	=	area of analyte,
<i>MI</i>	=	weight of internal standard,
<i>AI</i>	=	area of internal standard, and
<i>MA</i>	=	weight of analyte.

## 11. Chromatographic Resolution

11.1 Acetone and isopropyl alcohol have nearly the same retention time on a 5 % phenyl/95 % PDMS column and if either is found, their identities should be confirmed using a Carbowax™ capillary column.

11.2 Using a 5 % phenyl/95 % PDMS column and the chromatographic conditions of 6.3, certain compounds co-elute. These include, and are not limited to: PM acetate/ethylbenzene and 2-butoxyethanol(EB)/o-xylene. Separation may be obtained by changing the chromatographic heating rate. See figures 1 and 2 for the effect of heating rate on commercial xylene containing PM acetate and 2-butoxyethanol.

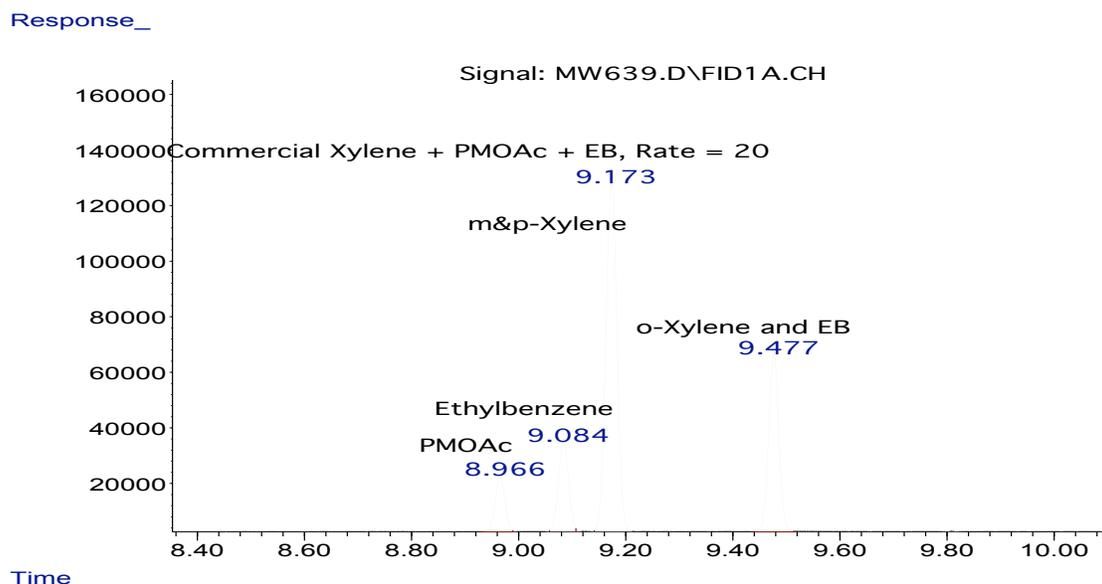


Figure 1. Chromatogram of Commercial Xylene Containing PM Acetate and Butoxyethanol. Heating Rate = 20°C per minute.

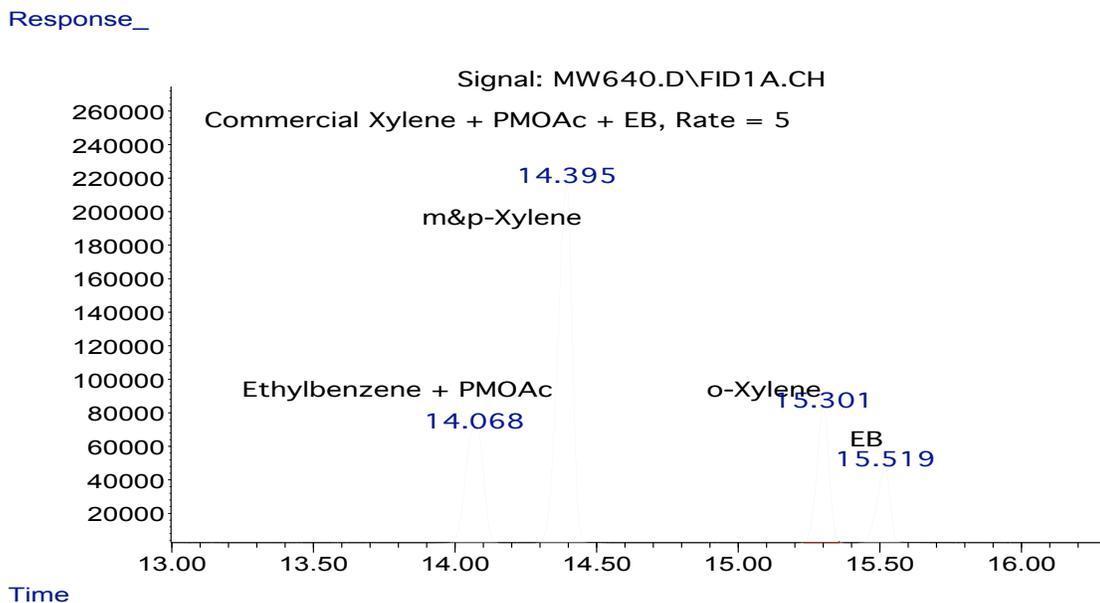


Figure 2. Chromatogram of Commercial Xylene Containing PM Acetate and Butoxyethanol. Heating Rate = 5<sup>0</sup>C per minute.

11.3 Commercial xylene contains ethylbenzene, m-xylene, p-xylene and o-xylene. The meta and para isomers are not resolved on a PMPS capillary column. The three peaks for commercial xylene have a relatively constant area ratio consisting of 15-18% ethylbenzene, 62-65% m&p-xylene and 19-22% o-xylene. When this ratio is significantly different, co-elution with another substance is probably occurring and the chromatography should be carried out at a different heating rate to effect separation. Additionally, if the chromatographic peak symmetry appears distorted, this may indicate co-elution with another substance and a different chromatographic heating rate should be used to obtain separation.

11.4 Cumene is introduced into coating materials when the aromatic hydrocarbon mixture Aromatic 100 is added to a coating. This solvent mixture is the source of cumene in coatings. Cumene is normally not added to coatings as a pure material. The cumene content of Aromatic 100 is typically 1 to 2%. The average cumene content was found to be 1.4% in six samples of Aromatic 100 that were analyzed by GC. When measured as a percent of the 1,2,4-trimethylbenzene content (the major component in Aromatic 100) the value is 3 to 5%. Since cumene in a coating is a small component of a complex hydrocarbon mixture, its concentration in a coating will always be small, generally much less than 1%. Cumene is rarely, if ever, added to a coating as a pure solvent thus coatings containing cumene will exhibit the chromatographic peaks of Aromatic 100 (Figure 4).

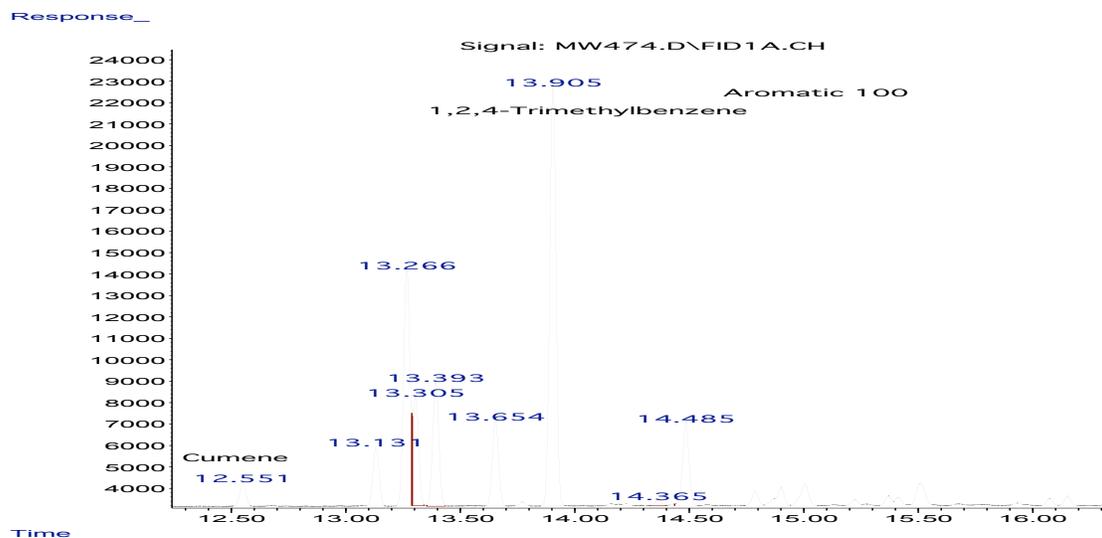


Figure 4. Commercial Aromatic 100 at a heating rate of 10°C per minute.

11.5 Naphthalene is normally not added to coatings as a pure material. When naphthalene is present in a coating its source is almost always the solvent Aromatic 150, a complex mixture of predominantly C10 aromatic hydrocarbons. The naphthalene content of Aromatic 150 is typically 3 to 8%. The average naphthalene content was found to be 5.9% in five samples of Aromatic 150 that were analyzed by gas chromatography. If naphthalene is detected in a coating, the other components of the Aromatic 150 mixture should also be present. The major components of Aromatic 150 are 1,2-dimethyl-4-ethylbenzene (10-15%, ret time = 15.5min) and 1,2,4,5-tetramethylbenzene (10-15%, ret time = 16.2 min) at a heating rate of 10°C per minute on the PMPS column described in 6.3.

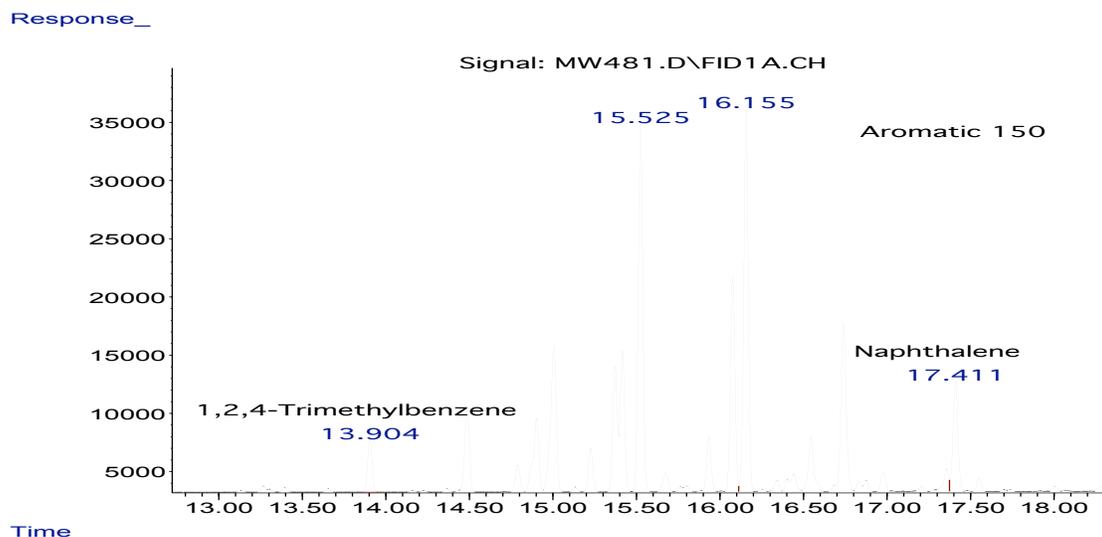


Figure 5. Commercial Aromatic 150 at a heating rate of 10°C per minute.

## 12. Reporting Results

12.1 Prepare a table (as indicated below) which contains information on each of the VOC species found.

VOC Found	GC Retention Time	Weight % Found

Total weight percent of all speciated VOCs =

12.2 List VOCs that are not identified as unknown (UK) and use the relative response factor of EGDE to calculate the weight % for unknown VOCs.

## 13. Alternate Identification Methods

13.1 The use of GC/MS for volatile compound identification is highly desirable. A convenient procedure is to sample the headspace of the cured coating in one of the headspace vials using an SPME fiber. The fiber may be thermally desorbed onto any standard capillary column and the compounds identified mass spectrally or by FID retention time comparison with known compounds (see table 1).

## 14. Precision and Bias

14.1 To be added

Table 1. FID retention times and response factors relative to EGDE using the chromatographic conditions described for the PMPS column in 6.3.

Ret time, minutes	Analyte	response factor relative to EGDE
2.35	methanol	0.66
2.76	ethanol	0.99
3.12	acetone	1.02
3.13	isopropyl alcohol	1.02
3.59	methyl acetate	0.60
4.74	methyl ethyl ketone	1.25
4.80	2-butanol	1.18
5.31	isobutyl alcohol	1.62
5.97	1-butanol	1.59
6.18	propylene glycol, methyl ether	0.79
6.44	ethylene glycol	0.55
6.68	t-butyl acetate	1.22
6.83	ethylene glycol, ethyl ether	0.70

7.17	propylene glycol	0.75
7.30	methyl isobutyl ketone	1.46
7.46	AMP95	0.83
7.82	toluene	2.08
8.12	<i>ethylene glycol, diethyl ether (internal standard)</i>	1.00
8.27	ethylene glycol, propyl ether	1.00
8.33	butyl acetate	1.16
8.73	propylene glycol, propyl ether	1.01
8.73	diacetone alcohol	
8.88	furfuryl alcohol	0.94
8.93	p-chlorobenzotrifluoride	1.02
8.97	propylene glycol, t-butyl ether	1.16
8.99	propylene glycol, methyl ether acetate	0.86
9.11	ethylbenzene	2.13
9.19	p-xylene	2.17
9.32	methyl amyl ketone	1.45
9.48	ethylene glycol, butyl ether	1.11
9.48	o-xylene	2.17
9.81	diethylene glycol, methyl ether	0.70
9.86	propylene glycol, butyl ether	1.09
9.88	diethylene glycol, diethyl ether	0.68
10.11	glycerin	0.17
10.10	diethylene glycol	0.53
10.45	dipropylene glycol, methyl ether	0.80
10.48	diethylene glycol, ethyl ether	0.70
10.84	p-cymene	2.13
10.89	benzyl alcohol	1.68
10.96	N-methylpyrrolidone	0.72
11.79	dipropylene glycol, propyl ether	0.75
12.13	diethylene glycol, butyl ether	0.92
12.43	naphthalene	2.03
12.53	dipropylene glycol, butyl ether	1.01
12.66	1-phenoxy-2-propanol	1.14
13.63	Texanol	1.34
18.49	dibutyl phthalate	1.16

## **G. Preparation of Draft Final Report**

We have begun the task of development of the Draft Final Report for this project. This entails not only preparation of methods developed in final form, as presented earlier in this report, but summarizing work presented in previous reports in an organized fashion.

## **II. Future Work**

We will be compiling and analyzing results from the shadowing studies as they become available.

We will also be completing the Draft Final Report.

## **III. Overall Progress of Project.**

Project is on budget. We have requested a one-year no-cost time extension for completion of the project since results from the validation study will not be available in time to complete the final report by the end of June, 2008.