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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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Abstract

The contractor analyzed the methods currently available to test the volatile organic compound (VOC) content of coatings. The contractor specifically examined the limitations and sources of error in United States Environmental Protection Agency (US EPA) Method 24 (an indirect method) and compared them to those for ASTM Method D6886 (a direct method). The contractor determined the expected uncertainties from published precision values for most coating types identified in the 2001 ARB Architectural Coatings Survey. The contractor installed and tested a new gas chromatography/flame ionization detection/mass spectral (GC/FID/MS) analysis system with static headspace analyzer to be used in methods development and VOC analysis of coatings.

The contractor collected samples of 67 coatings, including 11 two-component (2K) coatings, representing the categories listed in the 2001 ARB Architectural Coatings Survey. These samples were analyzed using Method 24 and direct analysis methods developed for this project based on ASTM D6886. The feasibility of using static headspace analysis was investigated. Specifically, new methods were developed for analysis of 2K coatings (both waterborne and solventborne), analysis of exempt solvents and hazardous air pollutants (HAPs), analysis of VOCs extracted from coatings, and of 2K coatings containing >90% solids. An extensive revision and expansion of ASTM D6886 was also undertaken. Specific VOC method analysis guidelines were developed for each class of coatings.

Selected coatings were chosen for inclusion in a mini-round robin validation study of the methods developed.

Results of all VOC determinations and the validation study were analyzed and the new methods were found to be superior to available methods in nearly all cases.

A unified architectural VOC testing manual for use by California air districts was developed.

Executive Summary

Background

Specific regulatory volatile organic compound (VOC) limits have been set for architectural coatings to insure emissions from these materials will decrease and air quality will improve. As regulations have lowered limits of allowed VOCs, a significant problem with enforceability of these regulations has developed since reliable methods for the analysis of these VOCs are not available. Currently, the United States Environmental Protection Agency's (US EPA) Method 24 is used to test the VOC content of coatings. It is widely accepted that Method 24 is not reliable for the analysis of low VOC water-borne coatings. Method 24 is not suitable for determining the VOC content of solventborne coatings containing exempt compounds or hazardous air pollutants (HAPs). Method 24 cannot be used to determine the VOCs in two-component (2K) waterborne coatings. In all cases the reason for the unreliability and unsuitability of Method 24 results from its being an *indirect* method of measuring VOCs in these types of coatings.

Methods

An extensive survey was made of VOC analysis methods currently in use by regulatory agencies and manufacturers. Direct methods of analysis for all types of architectural coatings were developed. These methods were primarily based on ASTM Method D6886, a direct method for determination of the VOC content of low-VOC content waterborne coatings. Research on new methods expanded on techniques used in the development of ASTM D6886. These methods not only determine the total fraction VOC but determine the fractional amount of each individual VOC in the coating. A sample of the coating dispersed in a solvent containing an internal standard is injected into a gas chromatograph. The gas chromatograph separates the components on the basis of their boiling points, providing a quantitative measure of each VOC. The possible use of static headspace analysis for determination of VOCs was investigated. In this technique, a sample of coating is placed in a sealed vial and a sample of the volatiles in the space above the coating sample is analyzed by gas chromatography (GC).

Methods to estimate the precision in VOC determinations were developed.

In conjunction with ARB staff, a list of coatings to be analyzed was chosen from the 2001 CARB Architectural Coatings Survey. Samples of sixty-seven coatings were obtained from manufacturers, along with formulation data and VOC data, when available. These coatings included eleven two-component (2K) coatings and eight coatings containing exempt solvents.

Twelve coatings were selected for a mini-round robin validation study of the methods developed. Coatings were selected because they provided the greatest challenges for VOC determination. Coatings selected included five 2K coatings (including both waterborne and solventborne), three coatings containing exempt compounds, and four

coatings containing unusual VOCs. Samples were sent to both regulatory and industrial laboratories.

Results

The following new methods were developed as a result of this project:

- Standard Test Method for Direct Analysis of the Volatile Organic Compounds (VOCs) in Waterborne Air-Dry Coatings by Gas Chromatography (Waterborne Method). This method is a revision of ASTM Method D 6886, Test Method for Speciation of the Volatile Organic Compounds (VOCs) in Low VOC Content Waterborne Air-Dry Coatings by Gas Chromatography.
- Standard Test Method for Direct Analysis of the VOC and HAP Content of Multi-Component Coatings by Gas Chromatography (2K Method)
- Standard Test Method for the Direct Analysis of the Common Hazardous Air Pollutants (HAPs) in Solventborne Air-Dry Coatings by Gas Chromatography (HAP Method)
- Standard Test Method for Determination of the VOC Content Remaining in Paint Films After Total Volatile Content Determination by ASTM Method D 2369 (Film Extraction Method)
- Standard Test Method for Solids Determination of 2K Coatings Containing More than 90% Solids (High Solids Method)

Specific VOC method analysis guidelines were developed for each class of coatings. These methods were used successfully to determine the VOC content of all 67 coatings samples. These results were compared with those obtained using EPA Method 24 when possible. Statistical analysis of the results show the new methods to be significantly more accurate the those obtained by Method 24 for nearly all classes of coatings. Although labs participating in the validation generally did not use the specific new methods supplied to them for analysis of the coatings, the results validated the superiority of the new methods in all cases.

Conclusions

New direct methods of VOC analysis using gas chromatography have been developed for all classes of architectural coatings. These new methods will allow the VOC content of all types of architectural coatings to be determined accurately. This remedies the current situation where existing methods are not capable of determining VOC levels of coatings formulated to meet lower VOC limit regulations.

INTRODUCTION

A. Statement of Significance

Specific regulatory volatile organic compound (VOC) limits have been set for architectural coatings to insure emissions from these materials will decrease and air quality will improve. As regulations have lowered limits of allowed VOCs, a significant problem with enforceability of these regulations has developed since reliable methods for the analysis of these VOCs are not available.

Currently, the United States Environmental Protection Agency's (US EPA) Method 24 is used to test the VOC content of coatings. It is widely accepted that Method 24 is not reliable for the analysis of low VOC water-borne coatings. Method 24 is also not suitable for determining the VOC content of solvent-borne coatings containing high levels of exempt compounds. In both cases the reason for the unreliability of Method 24 results from its being an *indirect* method of measuring VOCs in these types of coatings.

A California Air Resources Board (CARB) Method Survey states this clearly: "… the success in reducing the VOC content has created problems with Method 24 itself, due to the indirect way in which it calculates VOC content from other measurements".

Several other methods have been developed to deal with the problems of Method 24. However, none of these methods is applicable to all types of architectural coatings and none can deal with the specific problems mentioned above.

In addition, Method 24 cannot determine the level of hazardous air pollutants (HAPs) in coatings.

What is needed is a *direct* method (or methods) for determining the VOC content in architectural coatings. The goal of this project is the development of such methods. These methods should be suitable for direct determination of VOCs for all waterborne architectural coatings, even those with very low VOC levels. The methods should also be suitable for direct determination of HAPs and exempt compounds in solvent-borne coatings. The methods must be of suitable precision so that they can be used with confidence to determine whether or not a given coating meets the appropriate regulatory VOC level.

The development of a comprehensive set of direct test methods for VOC analysis will insure that the manufacture of architectural coatings sold in California meet regulatory guidelines and will provide CARB, other regulatory agencies, manufacturers, and testing laboratories with unified and common methods. This will eliminate the current situation where each agency has its own set of methods, many of which are non-validated versions of those referenced in EPA Method 24 itself.

B. Background and Objectives

Emissions from architectural coatings contribute a significant portion of the daily volatile organic compound (VOC) emissions in California. To ensure emission reductions occur from architectural coatings, specific VOC limits are set and enforced. Currently, the United States Environmental Protection Agency's (US EPA) Method 24 is used to test the VOC content of coatings. However, as VOC contents of water-borne coatings decrease (approaching 50 grams/liter) in order to meet more stringent VOC limits, Method 24 becomes less reliable. Alternative or improved test methods are urgently needed, since the VOC limits in some district rules are already in the 50 to 100 gram/liter range for some coating categories. This creates an enforceability challenge, with potential emissions increases due to an inadequate sensitivity of Method 24.

It is widely accepted that Method 24 is not reliable for the analysis of low VOC waterborne coatings. In a study reported by D. J. Mania, et al., (*Journal of Coatings Technology*, Vol. 73, August 2001) titled, Sources of Error in VOC Determination via EPA Method 24, the authors concluded

> The range of error (*using Method 24*) increased exponentially below about 250 g/L, reaching 1000% below 50 g/L

and

> The major sources of VOC error in all cases were in the water and nonvolatile determinations.

The US EPA recognizes that Method 24 lacks precision when a coating is high in water content. Section 9.2 and 12.6 of US EPA's Method 24 state:

- 9.2, Confidence Limits for Waterborne Coatings. Because of the inherent increased imprecision in the determination of the VOC content of waterborne coatings as the weight percent of water increases, measured parameters for waterborne coatings are replaced with appropriate confidence limits (Section 12.6). These confidence limits are based on measured parameters and inter-laboratory precision statements.
- 12.6, Confidence Limit Calculations for Waterborne Coatings. To calculate the lower confidence limit, subtract the appropriate inter-laboratory precision value from the measured mean value for that parameter. To calculate the upper confidence limit, add the appropriate inter-laboratory precision value to the measured mean value for that parameter.

The precision values referred to in Method 24 are the *Repeatability* and *Reproducibility* precision values that are determined by an inter-laboratory study (ILS, also called a round robin) and are required by ASTM in each of its standard methods. *Repeatability* (**r**), also called within-laboratory variability, is defined as the value within which the absolute difference between two individual test results obtained with the same method on identical test items in the same laboratory by the same operator using the same equipment within short time intervals, may be expected to occur with a probability of approximately 95%.

Reproducibility (**R**), also called reproducibility limit or between laboratory variability, is defined as the value within which the absolute difference between two test results obtained with the same method on identical test items in different laboratories with different operators using different equipment, may be expected to occur with a probability of approximately 95%. Selected values for **r** and **R** are given in Table1.

Table 1 - Precision Values Used in EPA Method 24

	ASTM Method	Repeatability r	Reproducibility R
Density	D1475-03	0.6%	1.8%
Volatile Content	D2369-04	1.5%	4.7%
Water by Karl-Fischer (KF) titration	D4017-02	3.5%	5.5%
Water by KF/methanol extraction	D4017-02	2.28%	7.46%
Water by KF/with homogenization	D4017-02	2.2%	4.2%
Water by GC	D3892-06	2.8%	5.0%

The precision values presented in Table 1 are considered to be relatively good and the individual test methods could probably not be improved to lower the values substantially. Thus, if the weight fraction of total volatile content and the weight fraction of water are relatively large and if their difference is very small (i.e., low VOC fraction), the overall precision in the VOC, measured as upper and lower 95% confidence limits, will be poor.

Lower and upper confidence limits for the VOC content of virtually any coating may be calculated if the individual method repeatability and reproducibility values have been established in an ILS. Alternatively, the **R** and **r** values may be used in a least-squares propagation of error analysis to estimate the overall uncertainty in a VOC measurement.

Several compounds have been listed as or are being evaluated as possible exempt solvents when used in coatings sold in California. Reproducibility and repeatability values have been determined for many of these exempt solvents and are reported in relevant ASTM methods. These values are listed below in Table 2.

Table 2 - Precision Values for Exempt Compounds

exempt solvent	ASTM method	Repeatability r	Reproducibility R
acetone	D6133-02	0.05	0.245
parachlorobenzotrifluoride	D6133-02	0.027	0.124
methyl acetate	D6133-02	0.046	0.293
t-butyl acetate	D6133-02	0.038	0.156
acetone	D6438-99	0.0118	0.0194
parachlorobenzotrifluoride	D6438-99	0.0097	0.0147
methyl acetate	D6438-99	0.0046	0.007
dichlormethane	D4457-02	0.03	0.179
1,1,1-trichloroethane	D4457-02	0.03	0.081

EPA Method 24 and of the various VOC methods based on EPA Method 24 currently being used by regulatory agencies rely on obtaining an **INDIRECT** VOC fraction value by subtracting the water fraction from the total volatile fraction. Cal Poly, San Luis Obispo developed a gas chromatographic method, published by ASTM in 2003 as D6886-03, Standard Test Method for Speciation of the Volatile Organic Compounds (VOCs) in Low VOC Content Waterborne Air-Dry Coatings by Gas Chromatography, which measures the VOC fraction directly. (**Note 1)**

> **Note 1**: "Speciation" in the title could just as easily read " Direct Analysis". This name change proposal was submitted to ASTM (Max Wills, subcommittee chair of ASTM D01.21.52) at the January, 2005 ASTM D01 meeting in Fort Lauderdale, Florida.

The method has an **R** value of 16.2% and **r** value of 7.5% for the weight fraction of VOC, f_{VOC}, which is significantly larger than any of the individual reproducibility or repeatability values of the ASTM methods used in performing a Method 24 measurement. However, since D6886 is a **DIRECT** method for measuring the VOC fraction, the overall precision in regulatory VOC measurement is significantly better. Values of selected **r** and **R** values used in calculating VOC content based on ASTM D6886 are given in Table 3.

Table 3 - Precision Values Used in VOC Determination Based on ASTM D6886

	ASTM Method	Repeatability r	Reproducibility R
Density	D1475-03	0.6%	1.8%
Volatile Content	D2369-04	1.5%	4.7%
VOC fraction	D6886-03	7.5%	16.2%

When the VOC content of a waterborne coating is measured directly, the water fraction can be calculated by subtracting the VOC fraction from the total volatile fraction, thus eliminating the need for a water determination.

Two different values of VOC are often reported. The first is the material VOC. This is simply the grams of VOC per liter of coating. The material VOC is not typically used in regulations. One case where coating VOC is used is for regulatory purposes is for low solids coatings, coatings with one pound or less of VOC per liter of material.

The value of VOC most commonly referred to in regulations is the coating VOC. The coating VOC is often referred to as the regulatory VOC. The coating VOC is the grams of VOC per liter of material less liters of water less liters of exempt compounds. The actually experimental data used to calculate these VOC values are listed below:

f_V = weight fraction of total volatile content (1 – weight fraction solids content)
f_{VOC} = weight fraction of VOC content
f_W = weight fraction of water content
D_P = density of paint in g/L
D_W = density of water in g/L
f_{ex} = weight fraction exempt solvent (must include term for each exempt solvent)
D_{ex} = density of exempt solvent in g/L

The equations used in calculating the various VOC values are given below in Table 4. We have applied these equations in all of our calculations for VOC.

As mentioned earlier, we can estimate the uncertainty in a VOC measurement by several means. One simple method would be to assume most of the total error results from the error in a particular quantity, say f_W for an indirect method (based on EPA Method 24) or f_{VOC} for a direct method based on ASTM D6886. We could then calculate VOC values using both maximum and minimum possible values of the quantity based on published precision values and use this as a measure of the range of possible VOC values.

Another approach would be to apply the method of propagation of errors. For a quantity F which is a function of x, y, and z, where the uncertainties in x, y, and z, given by σ_x, σ_y and σ_z, are known, the uncertainty in F, σ_F, can be calculated as shown below.

$$\sigma_F = \left[\left(\frac{\partial F}{\partial x}\right)^2 \sigma_x^2 + \left(\frac{\partial F}{\partial y}\right)^2 \sigma_y^2 + \left(\frac{\partial F}{\partial z}\right)^2 \sigma_z^2 \right]^{0.5}$$

where $\left(\frac{\partial F}{\partial x}\right)$ is the partial derivative of F with respect to x when the other variables are held constant. We have applied both of these methods in estimating the errors in VOC measurements.

Table 4 - Equations used to Calculate VOC Values

Indirect method, no exempt compounds

$$VOC_{coating} = \frac{(f_V - f_W)D_P}{1 - [f_W(D_P / D_W)]}$$

$$VOC_{material} = (f_V - f_W)D_P$$

f_V = weight fraction of total volatile content (1 – weight fraction solids content)
f_{VOC} = weight fraction of VOC content
f_W = weight fraction of water content
D_P = density of paint in g/L
D_W = density of water in g/L
f_{ex} = weight fraction exempt solvent (must include term for each exempt solvent)
D_{ex} = density of exempt solvent in g/L

Direct method, no exempt compounds

$$VOC_{coating} = \frac{f_{VOC}(D_P)}{1 - [(f_V - f_{VOC})(D_P / D_W)]}$$

$$VOC_{material} = f_{VOC}(D_P)$$

Indirect method, with exempt compounds

$$VOC_{coating} = \frac{(f_V - f_W - \sum f_{ex})D_P}{1 - [f_W(D_P / D_W) + \sum f_{ex}(D_P / D_{ex})]}$$

$$VOC_{material} = (f_V - f_W - \sum f_{ex})D_P$$

Direct method, with exempt compounds

$$VOC_{coating} = \frac{f_{VOC}(D_P)}{1 - [(f_V - f_{VOC})(D_P / D_W) + \sum f_{ex}(D_P / D_{ex})]}$$

$$VOC_{material} = f_{VOC}(D_P)$$

C. Comparison of Existing Methods

- Methods used by California regulatory agencies

We have compared methods used by the principle regulatory agencies in California with those of the U.S. Environmental Protection Agency and applicable ASTM methods. A summary of the methods used by California regulatory agencies is shown in Table 5 below.

Table 5 -VOC Analysis Methods used by California Regulatory Agencies

agency	method(s)	analysis	type of VOC analysis (indirect or direct)	uncertainties
California Air Resources Board (CARB)	310	VOCs and exempts in consumer products	indirect analysis of total volatile content, direct analysis of exempts using GC/FID	3% for total volatiles, none given for exempts
South Coast Air Quality Management District (SCAQMD)	313, 303	VOCs and exempts	direct analysis of VOC by GC/MS, exempt by GC/TC	none given
Bay Area Air Quality Management District (BAAQMD)	21, 22, 41, 43	VOCs and exempts in coatings	indirect analysis ot total volatile content, exempts by GC/TC and GC/FID	none given

The *CARB Method 310* provides a comprehensive set of procedures for determination of VOCs in all types of consumer products. Total VOC is determined by indirect analysis, essentially similar to EPA Method 24. All of the procedures are based on ASTM methods. The method lists a 95% confidence interval of 3.0% for total VOC based on analysis of seven representative products ranging in VOC from 6.2% to 81.2%. Each sample was divided into six portions and analyzed separately. It is not stated whether the analyses were performed in the same laboratory or different laboratories. It is also not stated how many of the samples were coatings nor what types of coatings were analyzed. Based on results we obtained from CARB for this project, CARB also can determine amounts of some VOCs directly.

The *SCAQMD Method 313* for VOC analysis uses GC/MS and determines amounts of each volatile organic compound based on a multilevel calibration curve of counts vs. micrograms of compound injected. No internal standard is used in the samples and response factors are not used. Samples are either headspace samples taken from septum capped vials or open cans or directly injected samples of material. If measured amounts fall out of range of the calibration curve for a particular compound, samples must be concentrated or diluted. SCAQMD Method 303 for exempt compounds requires samples to be distilled. Samples of distillate are then combined with diluent containing perchloroethylene (internal standard) in isooctane. The method essentially uses relative response factors to determine amounts of each exempt. No uncertainties are reported for either Method 313 or Method 303. Recently the SCAQMD has begun using ASTM D 6886 for analysis of water-borne coatings.

The *BAAQMD Methods 21 and 22* are essentially indirect methods similar to EPA Method 24. Exempt compounds are determined using gas chromatography with internal standards and measured response factors. BAAQMD Method 41 allows determination of parachlorobenzotrifluoride directly using gas chromatography with internal standard. BAAQMD Method 43 allows determination of volatile methylsiloxanes directly using gas chromatography with n-octane as internal standard in carbon disulfide solutions with measured response factors. None of the methods report any uncertainties or other precision factors. Based on results we obtained from the BAAQMD for this project, they can also determine amounts of VOCs directly but direct analysis is not part of any of their published methods.

Our analysis of these methods has not provided any suitable methods for use in this project not already available from published ASTM methods. Most of the methods for water-borne coatings are still based on EPA Method 24 and are, therefore, subject to the same inherent inaccuracies as EPA Method 24. SCAQMD Method 313 seems more complex and likely less reliable than ASTM D 6886. The lack of precision data for nearly all of these methods does not allow direct comparison of these methods with ASTM methods.

Other methods investigated

EPA Method 24: This method was originally developed to measure the VOC content of solvent-borne coatings and gives excellent precision for single-component air-dry solvent-borne coatings. Method 24 is a direct method for solvent-borne coatings because it measures the VOC content as total volatiles by weight loss when a sample is heated in a forced-draft oven (ASTM Method D 2369). The method becomes an indirect method when coatings contain water or exempt compounds and loses its precision (dramatically for coatings with low VOC, high-water content or low VOC, high exempt compound content). Issues involved in applying Method 24 to the VOC analysis of solvent-borne multi-component coatings will be addressed later in this report.

ASTM Method D 6886: This method, "Speciation of the Volatile Organic Compounds (VOCs) in Low VOC Content Waterborne Air-Dry Coatings by Gas Chromatography", was developed at Cal Poly and was published as an ASTM standard method in 2003. The method gives a significant improvement in precision to that of Method 24. The method measures the VOC fraction in water-borne coatings directly. "Speciation" in the title could just as easily read " Direct Analysis". When this method was first conceived it was determined that very low VOC levels in water-borne coatings were very difficult or impossible to measure by Method 24. It was decided that 5% or less weight percent VOC in water-borne coatings would represent the most difficult to measure by Method 24 and were chosen for analysis by this new direct GC method. Weight percent VOC was chosen as a criterion rather than regulatory VOC because different coatings with the same weight percent VOC content can have widely varying regulatory VOC contents depending on the amount of water in the coating (for example, if two different coatings have the same weight percent VOC content and the same density but differ in water content, the coating with the higher water content will have a larger value of regulatory

VOC). Method 6886 was validated in an inter-laboratory study using 5 different water-borne latex paints including a flat, an eggshell, a semi-gloss, a gloss, and a primer. These five coatings correspond to ARB's 2001 survey classification of flat, non-flat – low gloss, non-flat – medium gloss, non-flat high gloss, and primer/sealer/undercoater. These five classes of coatings comprise 82% of the sales of the entire ARB list of 44 classes of water-borne coatings. We believe that ASTM Method D 6886, while validated with architectural coatings containing only 0 to 5% by weight VOC, should be applicable for measuring the VOC content in water-borne coatings containing more than 5% by weight VOC. *One of the major efforts of this project is the analysis of a wide range of other architectural coatings by a method or methods based on ASTM D6886.*

The "Battelle" Method: In the mid-1990's the US EPA contracted with the Battelle Corporation to develop a direct method for the VOC analysis of waterborne-coatings. The method developed by Battelle was titled "Measurement of Total VOC in Paints and Coatings Using an Automated Thermal Desorber and Flame Ionization Detector". In this method a sample of paint is heated at 110ºC for one hour and the volatiles are collected on a solid sorbent by purging with helium. The collected volatiles are then subsequently desorbed by heating to 325ºC and transferred to a capillary GC column with flame ionization detection (FID). The method has several drawbacks which include: large lab to lab variability, highly inaccurate, long analysis times (a single sample can require an entire day), the method depends on solvent identification data from MSDSs, instrument specified in the draft method is no longer made.

The EPC/ASC Method: The Emulsion Polymers Council and the Adhesive and Sealant Council supported the development of an improved "Battelle" method. The activity was coordinated by researchers of the Rohm and Haas Company. This new method was under development for presentation at the January 2005 meeting of ASTM D01.21. The method is a static, rather than dynamic, headspace method in which a 25mg sample of coating is placed in a 25mL headspace vial and is then heated for 10 minutes at 150ºC. A split of the headspace is then transferred to a GC column. The method has been tested with a wide variety of materials including a flat latex paint, a semigloss latex paint, an emulsion polymer, a caulk and several adhesives. The samples tested had actual VOC contents ranging from 0 to 6%. The method requires that a separate set of response factors be determined for each sample analyzed, requires the use of both a GC-mass spectrometer (GC-MS) and GC-FID and requires that these instruments be equipped with a headspace auto-sampler. We suspect that the instrument requirements and technical expertise required to perform this method may preclude its use by smaller paint manufacturers. An advantage of this new method, if it proves to be successful, is that it may provide a second direct method for VOC analysis of waterborne coatings. *A variation of this method was evaluated as part of this project and compared with the ASTM direct method D6886.*

EPA Method 311: In 2003 Cal Poly participated in an inter-laboratory study sponsored by the National Paint and Coatings Association (NPCA) to validate Method 311 for the analysis of HAPs in coatings. The HAPs which were determined included:

2-butoxyethanol,
Cumene
Ethyl Benzene
2-Hexyloxyethanol
Methyl Ethyl Ketone (MEK)
Methyl Isobutyl Ketone (MIBK)
Naphthalene
Toluene
Xylenes

2-butoxyethanol and methyl ethyl ketone have since been delisted as HAPs by EPA. The above indicated list of HAPs are those commonly found in solvent-borne coatings. The HAPs most commonly found in water-borne coatings are ethylene glycol and the monoethers of ethylene glycol. These are easily measured with ASTM D6886. Some water-borne coatings also contain the HAP methanol. *We have developed a modified D6886 procedure for HAPs as part of this project.*

ASTM D6133-02: Standard Test Method for Acetone, *p*-Chlorobenzotrifluoride, Methyl Acetate or *t*-Butyl Acetate Content of Solvent-borne and Waterborne Paints, Coatings, Resins, and Raw Materials by Direct Injection Into a Gas Chromatograph. The method is carried out by dissolving a known weight of internally standardized coating in tetrahydrofuran and injection of an aliquot of this solution onto a capillary column with GC-FID detection. *We have developed a direct method for analysis of exempt solvents as part of this project.*

ASTM D6438-99: Standard Test Method for Acetone, Methyl Acetate, and Parachlorobenzotrifluoride Content of Paints, and Coatings by Solid Phase Microextraction-Gas Chromatography. This method was developed at Cal Poly and was published as an ASTM method in 1999. The method uses a relatively new way of sampling a coating headspace using solid phase microextraction (SPME). In this sampling procedure a fused silica fiber, approximately 1 cm long and coated with a polymeric sorbent material (polyethylene glycol and polydimethylsiloxane are two examples of several such sorbents), is placed in contact with the room temperature headspace of a coating for two to four minutes. The volatiles are concentrated on the fiber and are then thermally desorbed onto a capillary column in the hot inlet of a GC-FID or GC-MS. Volatile emissions can be detected at the parts per million level. Typically, using GC-MS, an SPME run can be completed in less than 30 minutes. In our participation with the EPA Method 311 validation (described above), all of the coatings studied were initially screened by SPME to identify HAP's.

ASTM D4457-02: Standard Test Method for Determination of Dichloromethane and 1,1,1-Trichloroethane in Paints and Coatings by Direct Injection into a Gas Chromatograph. This standard was first published by ASTM in 1985 and, though re-approved every five years since then, has not changed substantially since its initial publications. The latest version of EPA Method 24 (February 2000) references the

version that was re-approved in 1991 and gives this as the only method for analyzing exempt compounds. As with water-borne coatings with a high water content, solvent-borne coatings with a high exempt compound content could give poor precision when using Method 24.

D. Coatings Chosen for Analysis

Based on results from the 2001 and 2005 CARB Architectural Coatings Surveys, a total of 67 coatings were chosen for analysis as part of this study. Of these, eleven are two-component (2K) coatings. Eight coatings contain exempt compounds. The coatings samples were chosen to represent the broadest possible range of architectural coatings products sold in California.

No coatings were chosen from the flats, nonflats and primer/sealer/undercoater categories since these coatings have been studied extensively by both indirect methods (based on EPA Method 24) and direct methods (based on ASTM D6886). In fact, ASTM D6886 was developed specifically to deal with problems encountered in determining VOCs of these coatings using EPA Method 24.

Manufacturers of the coatings supplied products directly to Cal Poly along with formulation and VOC data, when available. These coatings were catalogued and stored at Cal Poly. For those coatings included in validation studies of the methods developed here, the coating samples were split into four smaller samples. These samples were then used by the various laboratories involved in the validation studies for their analyses.

A complete list of the coatings included in this study is given in Table 6.

Table 6 - Coatings Analyzed

		WATERBORNE					SOLVENTBORNE		
sample #	Coating Category	Low VOC	High VOC	High Multi	Low Solids	High Multi	Low Solids	High Solids	High Exempt
1	Fire Resistive	X							
2	Recycled	X							
3	Industrial Maintenance					X-2K			
4	Bituminous Roof	X							
6	Driveway Sealer	X							
7	Metallic Pigmented	X							
8	Faux Finishing		X						
9	Stains - Clear/Semitransparent				X				
10	Stains - Opaque	X							
14	High Temperature								X
14-1	Industrial Maintenance							X-2K	
14-2	Industrial Maintenance							X-2K	
14-3	Industrial Maintenance							X-2K	
15-1	Industrial Maintenance							X-2K	
15-2	Industrial Maintenance							X-2K	
15-3	Industrial Maintenance							X-2K	
24	High Temperature								X
25	Swimming Pool					X-2K			
26	Swimming Pool			X-2K					
29	Varnishes-clear		X						
32-1	Lacquers	X							
32-2	Primer/stainblock	X							
34	Dry Fog	X							
35	Dry Fog	X							
37	Roof	X							
38	Waterproofing Concrete/Masonry Sealers	X							
39	Bituminous Roof	X							
40	Driveway Sealer	X							
41	Driveway Sealer	X							
43	Roof	X							
44	Magnesite Cement								X
44-2	Magnesite Cement								X
45	Varnishes - Clear			X-2K					
48	Wood Preservatives				X				
50	Mastic Texture	X							
51	Waterproofing Concrete/Masonry Sealers	X							

Table 6 - Coatings Analyzed (con't.)

		WATERBORNE				SOLVENTBORNE			
	Coating Category	Low VOC	High VOC	High Multi	Low Solids	High Multi	Low Solids	High Solids	High Exempt
52	Bond Breakers				X				
55	Rust Preventative		X						
56	Low Solids	X			X				
57-1	Lacquers						X		X
57-2	Lacquers						X		X
57-3	Lacquers						X		X
58	Concrete Stain				X				
60	Metallic Pigmented		X						
61	Varnishes - Clear		X						
62	Stains - Clear/Semitransparent								X
63	Floor		X						
64	Waterproofing Sealers				X				
65	Waterproofing Sealers	X			X				
73	Traffic Marking	X							
75	Bituminous Roof	X							
76-1	Faux Finishing		X		X				
76-3	Faux Finishing		X		X				
76-5	Faux Finishing		X		X				
77	Lacquer								X
79	Sanding Sealers				X				
80	Stains - Opaque	X			X				
81-1	Concrete Curing Compounds	X			X				
81-2	Concrete Curing Compounds	X			X				
82-1	Waterproofing Concrete/Masonry Sealers	X			X				
82-2	Waterproofing Concrete/Masonry Sealers	X			X				
83	Quick Dry Primer, Sealer, and Undercoater	X							
84	Shellacs - Clear						X		
85	Shellacs - Clear						X		
86	Wood Preservatives	X			X				
87	Varnish						X		

1. "Low VOC": <=3% VOCs by weight. "High VOC": >=10% VOCs by weight. "High Exempt": >=10% Exempt Compounds by weight.
2. "High Multi": Categories that have more than 10% multi-component products, by sales volume.
3. "Low Solids": 0-20% solids by volume. "High Solids": 80-100% solids by volume.
4. "Low Solids" and "High Solids" products only include single-component coatings.
The other classifications include both single-component and multi-component coatings.

E. Validation of Test Methods

An important part of this project is independent validation of the methods we have developed. We selected coatings in three categories to send to other laboratories: two-component coatings, unusual coatings (low solids, high VOC, unusual solvents) and coatings containing exempt solvents. Coatings selected for validation studies are listed in Table 7. Specific VOCs we identified in these coatings are also listed in the table. We sent samples to a total of five different laboratories, including both industrial laboratories and regulatory agencies. Some laboratories failed to analyze some or all of the samples we sent. In order to provide at least two additional sets of results for each of the samples, we conducted a second independent analysis of some of the samples in our laboratories using different instrumentation and different operators. The laboratories were provided with samples of the coatings split from our original samples along with whatever information we had on the coatings from the manufacturers. We also informed the laboratories of what VOCs might be present so they could determine response factors for these VOCs. We provided the laboratories with copies of the analysis procedures we developed. In most cases, the laboratories used their own analysis methods. The results of these validation tests will be discussed later in this report.

Table 7 - Samples Selected for Validation Studies

Sample #		Category		Type	solids (lb/gal)
3		Industrial Maintenance		2K, high solids	10.31
VOCs	furfuryl alcohol	ethylbenzene	m,p-xylene	o-xylene	Aromatic 100
15-2		Industrial Maintenance		2K, high solids	11.11
VOCs	benzyl alcohol				
15-3		Industrial Maintenance		2K, high solids	10.24
VOCs	1-butanol	toluene	ethylbenzene	m,p-xylene	o-xylene
	cumene	Aromatic 100	benzyl alcohol		
26		Swimming Pool		2K	5.77
VOCs	2-propoxyethanol	Aromatic 100			
45		Varnishes - Clear		2K	2.46
VOCs	propylene glycol monomethyl ether	benzyl alcohol			
86		Wood Preservatives		low solids, high water	0.33
VOCs	ethylene glycol	propylene glycol monopropyl ether	1-iodo-2-propynyl butyl carbamate		
76-1		Faux Finishing		very high VOC	1.36
VOCs	methyl ethyl ketone	propylene glycol			

Table 7 - Samples Selected for Validation Studies (con't.)

Sample #		Category	Product	Type	solids (lb/gal)
61		Varnishes - Clear		high VOC	2.49
VOCs	triethyl amine	propylene glycol	dipropylene glycol monomethyl ether	N-methyl pyrrolidinone	propylene glycol monobutyl ether
	Surfynol				
55		Rust Preventative		high VOC	4.47
VOCs	2-butanol	2-butoxyethanol	butyl carbitol		
60		Metallic		unusual solvents	4.99
VOCs	propylene glycol	diethylene glycol monomethyl ether	propylene glycol monobutyl ether	2-(2-ethylhexyl) ethanol	triethylene glycol
	dibutyl phthalate				
14		High Temperature		exempt solvent(s)	3.94
VOCs	toluene	metachloro benzotrifluoride	parachloro benzotrifluoride	ethylbenzene	m,p-xylene
	o-xylene	Aromatic 100	naphthalene		
44-2		Magnesite Cement		exempt solvent(s)	2.39
VOCs	acetone	ethylbenzene	m,p-xylene	o-xylene	Aromatic 100
	naphthalene				
57-3		Lacquers		exempt solvent(s)	1.83
VOCs	methanol	acetone	2-propanol	methyl acetate	MEK
	1-butanol	butyl acetate	ethylbenzene	m,p-xylene	2-heptanone
	o-xylene	2-butoxyethanol	4-methyl-3-heptanone		

MATERIALS AND METHODS

The VOC content of many of the architectural coatings sold in California can be determined successfully by current methods. Traditional one-component air-dry solventborne coatings containing no exempt solvents can be analyzed successfully using EPA Method 24. Waterborne air-dry coatings containing less than 5% VOC by weight can be analyzed successfully using ASTM D6886 in its original form.

We have developed the following additional methods as part of this project:

- Standard Test Method for Direct Analysis of the Volatile Organic Compounds (VOCs) in Waterborne Air-Dry Coatings by Gas Chromatography (Waterborne Method). This method is a revision of ASTM Method D6886, Test Method for Speciation of the Volatile Organic Compounds (VOCs) in Low VOC Content Waterborne Air-Dry Coatings by Gas Chromatography.
- Standard Test Method for Direct Analysis of the VOC and HAP Content of Multi-Component Coatings by Gas Chromatography (2K Method)
- Standard Test Method for the Direct Analysis of the Common Hazardous Air Pollutants (HAPs) in Solventborne Air-Dry Coatings by Gas Chromatography (HAP Method)
- Standard Test Method for Determination of the VOC Content Remaining in Paint Films After Total Volatile Content Determination by ASTM Method D2369 (Film Extraction Method)
- Standard Test Method for Solids Determination of 2K Coatings Containing More than 90% Solids (High Solids Method)

In this section each of these new methods will be summarized. The detailed methods are collected together as a manual for use in determination of the VOC content of architectural coatings sold in California (see *California Manual for Determination of the VOC Content of Architectural Coatings*, Appendix).

A. Standard Test Method for Direct Analysis of the Volatile Organic Compounds (VOCs) in Waterborne Air-Dry Coatings by Gas Chromatography

This method is a revision of ASTM Method D 6886, Test Method for Speciation of the Volatile Organic Compounds (VOCs) in Low VOC Content Waterborne Air-Dry Coatings by Gas Chromatography, and will be submitted to ASTM for balloting.

Initially, D6886 was designed for determination of the weight fraction VOC in waterborne air-dry coatings containing 5% VOC or less. We have significantly expanded the scope of D6886. While the method is still primarily designed to be used for air-dry waterborne coatings, we have shown it can be used successfully for solventborne coatings. In addition, this method may also be used to measure the exempt volatile organic compound content (acetone, methyl acetate, and p-chlorobenzotrifluoride) of

waterborne and solventborne coatings. The method is also suitable for determination of any of the other exempt solvents, although we have only seen acetone, methyl acetate and p-chlorobenzotrifluoride in these studies. We have also applied the method successfully to coatings containing silanes, siloxanes and silane-siloxane blends.

We have expanded the possible solvents used in the method to include THF, acetone and 2-propanol. We have recommended ethylene glycol diethyl ether (EGDE) as the internal standard of choice for use in the method (and the other methods developed for this project). EGDE is never found in coatings, is stable and soluble in all common solvents, and has a retention time well isolated from common VOCs.

We have also included a procedure to insure adequate mixing of the coating and the solvent through the use of small, inert ceramic beads.

Most of the analyses performed for this project were done using this method and results for a wide range of coatings are presented later in this report.

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

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

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 heated for 30 minutes at 110ºC. 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.

If the sample contains acetone, THF may be used as the solvent. Acetone and isopropyl alcohol have nearly the same retention time on a 5 % phenyl/95 % polydimethylsiloxane(PDMS) column (referred to here as a PMPS column) and if either is found, their identities should be confirmed using a Carbowax™ capillary column.

Using a PMPS column and the chromatographic conditions described in the procedure, certain compounds co-elute. These include, but are not limited to: PM acetate/ethylbenzene and 2-butoxyethanol(EB)/o-xylene. Separation may be obtained by changing the chromatographic heating rate.

This method has several advantages. The sample is allowed to cure under conditions simulating actual application. No solvent is added during this cure step which could

adversely affect the rate of the curing reaction. The volatiles are then analyzed directly by gas chromatography. Both the total fraction VOC and the fraction of any and all exempt solvents HAPs are determined. The method is suitable for use for both solventborne and waterborne coatings.

Results based on this method are given later in this report.

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

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. Volatile compounds that are present at the 0.01 weight percent level or greater can be determined.

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.

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.

Using a 5 % phenyl/95 % PDMS (PMPS) column and the chromatographic prescribed in the method, certain compounds co-elute. These include, and are not limited to: propylene glycol monomethyl ether acetate(PM acetate)/ethylbenzene and 2-butoxyethanol(EB)/o-xylene. If co-elution is suspected, separation may be obtained by changing the chromatographic heating rate.

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.

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.

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 capillary column described in the method.

D. Standard Test Method for Determination of the Semi-volatile Content Remaining in Paint Films After Total Volatile Content Determination by ASTM Method D 2369

A fundamental difference exists between EPA Method 24, and the direct method, ASTM D6886, when analyzing coatings where semi-volatile materials remain the coating film after heating for one hour at 110°C. In the Method 24 the semi-volatiles are not counted as VOCs since they make up part of the solids fraction in the ASTM D2369 determination. The direct analysis method determines all of the semi-volatiles in the coating. In order to obtain consistent VOC values for both methods, the amount of semi-volatile remaining in the paint film after heating for one hour at 110°C must be determined and this must be subtracted from the amount obtained by direct analysis of the coating to obtain results consistent with EPA Method 24.

In this method, immediately after the duplicate determination of the volatile content of a coating, the aluminum pans containing the coatings solids are cut up into several small pieces. These pieces are placed into a 120 mL Erlenmeyer flask and approximately 20 mL of acetone or methyl ethyl ketone and a Teflon-coated stir bar are added. The flask is stoppered and stirred for 12-24 hours. This process extracts VOCs remaining in the paint film into the acetone. After stirring, 5.0 mL of a THF or acetone solution containing approximately 0.5 mg/mL (known to 0.0001 mg) of internal standard (ethylene glycol diethyl ether, EGDE) is added. The contents are mixed and the solution is chromatographed according to Method D6886. The amounts of VOCs having boiling points greater than 250°C and retention times equal to and longer than Texanol® (2,2,4-trimetnyl-1,3-pentanediol monoisobutyrate) are determined.

Since the paint film may undergo oxidative degradation during the heating phase of the ASTM D2369 determination, chromatographic peaks may appear which were not present during the original (unheated sample) Method D6886 VOC determination. In calculating

the total VOC content of the coating in question, the VOC amounts determined in this extraction procedure should be subtracted from the original VOC amount.

E. Standard Test Method for Solids Determination of 2K Coatings Containing More than 90% Solids

US EPA has approved a proposed revision of Section 7 of ASTM D2369 for solids determination of 2K coatings containing more than 90% solids. In the past, there has been concern that the film thicknesses produced by D2369 for high solids material are inappropriate and do not represent actual application conditions. Concern also existed over the effect of added solvent on the rate of the cure reaction. The revision specifies new procedures to be followed for these coatings including no addition of solvent and a 24 hour induction time.

The specimen weight is to be representative of how the product is used (the lowest thickness which the manufacturer's literature recommends) where:
Weight (g) = Thickness (mm) x 3.14 x [Dish Diameter^2 (mm^2)/4] x Density (g/cc)/1000.
For example: the appropriate specimen weight for a coating with a density of 1 g/cc placed in a 50 mm diameter dish at a thickness of 0.5 mm calculates to 1.0 g.

We have used this method for coatings analyzed as part of this study.

F. Static Headspace Analysis

We have extensively evaluated the use of static headspace analysis for determining VOC content of coatings. Although this method initially looked attractive as an alternative to D6886, we encountered problems similar to those found by the Emulsion Polymers Council (EPC) when they were trying to develop their headspace method, primarily the difficulty in analyzing polar compounds. We have found certain conditions where headspace analysis can provide useful information but we do not feel this technique to be suitable for general VOC analysis at this time. An analysis of our results with the headspace method is provided in the discussion section on p. 33.

RESULTS

A. Recommended VOC Analysis Methods

Based on the experienced gained during this project in both using accepted VOC methods and developing new VOC analysis methods, we make the following recommendations for suitable methods based on coatings type (Table 8). We hope regulatory agencies will work with us in modifying these recommendations based on their past experience and future work with the new methods.

Table 8 – Recommended VOC Analysis Methods

Coatings Type	Recommended Methods
Air-dry waterborne coatings without exempt solvents, VOC content < 10%	Revised D6886 and Extraction Method
Air-dry waterborne coatings without exempt solvents, VOC content >10%	Revised D6886 or EPA Method 24
Air-dry solventborne coatings, without exempt solvents	EPA Method 24; Use Revised D6886 and HAP Method if HAP content is to be measured
Air-dry solventborne coatings, with exempt solvents	Revised D6886 to determine exempt solvents and speciated VOC content
Solventborne 2K coatings, solids content < 90%	EPA Method 24 for mass-based VOC content; new 2K method if HAP content or speciated content is desired
Solventborne 2K coatings, solids content >90%	EPA Method 24 with new High Solids volatile method
Waterborne 2K coatings	New 2K method
Coatings containing Silanes, Siloxanes and Silane-Siloxane Blends	ASTM D5095 for total volatile content and new D6886 for speciation
Coatings containing semi-volatile organic compounds and/or with boiling points greater than 250°C and D 6886 primary capillary column retention time greater than Texanol®	Revised D6886 and Extraction Method

B. VOC Results for Coatings Analyzed

We have analyzed all 67 coatings included in this study by the methods described above. We will present the results of our analyses by considering the coatings in three groups:

- Air-dry single component coatings with no exempt solvents
- Air-dry single component coatings with exempt solvents
- Two-component (2K) coatings

All three groups contain both waterborne and solventborne coatings. Whenever possible, samples were analyzed by both EPA Method 24 and one of the direct analysis methods based on gas chromatography we developed for this study. We have calculated both material and coatings VOC values for both methods, when possible. We have reported manufacturer-supplied VOC information, when available. We have also listed VOC values from the 2005 CARB Architectural Coatings Survey for most of the categories of coatings studied. The summary results for air-dry single component coatings without exempt solvents are given in Table 9.

We have also calculated precision values for these measurements based on two different methods. A propagation of errors calculation using reported R and r values for all quantities involved in each VOC measurement was used to estimate a precision value for the coating VOC for all one-component coatings, including coatings containing exempt compounds. We have also calculated an expected uncertainty range for the one-component coatings without exempt solvents. For VOC calculations based on EPA Method 24, the published R value for the water fraction determined by Karl-Fisher titration using a homogenizer was used to determine an upper and lower limit for the water fraction. These values were then used to estimate the range in VOC. For VOC calculations based on direct determination of the fraction VOC by gas chromatography, the published R value for the VOC fraction was used to determine an upper and lower limit for the VOC fraction. These values were then used to estimate the range in VOC. The results of the precision analysis for the air-dry single component coatings are given in Table 10. The precision data will be analyzed more fully in the discussion section.

Eight of the samples were found to contain exempt compounds. One sample (#62) was reported to contain exempt solvents but none were found during the analysis. The major exempt compound found was acetone which was present in seven of the samples in amounts ranging from 18% to 54%. Para-chlorobenzotrifluoride (Oxol 100®) was found in the remaining sample at a level of 47%. Small amounts of methyl acetate were found in three of the samples. The expected propagated error for these determinations was calculated using published R values for all quantities. Since two ASTM methods (ASTM D6133 and ASTM D6438) are available for determining exempts, we calculated errors using both values. Since we determined the amounts of exempt compounds by direct injection, the values based on D6133, a direct injection method, are probable the most reliable. The summary results for air-dry coatings containing exempt solvents are given in Table 11.

The eleven 2K coatings presented perhaps the greatest challenge. Considerable time and effort was spent developing the 2K method described earlier. The method was used to analyze the eight solventborne and three waterborne 2K coatings. We have not calculated precision values for the 2K samples, but we expect the precision should be comparable to that obtained for single component coatings without exempt compounds. Future work on the new 2K method and more extensive validation studies will allow precision values for this method to be determined. The summary results for the 2K coatings are given in Table 12.

A complete listing of all the VOCs found in the 67 coatings analyzed is given in Table 13.

Table 9 - Summary Results for Air-dry Single Component Coatings without Exempts

Sample Coating Category	#	VOC fraction		water fraction		Material VOC/(g/L)				Coating VOC(g/L)			
		GC direct	EPA24 indirect	GC indirect	EPA24 direct	GC	EPA 24	rept.	2005 CARB survey	GC	EPA 24	rept.	2005 CARB survey
Fire Resistive	1	0.0053	0.0026	0.5169	0.5194	6	3	9	8	12	6		18
Recycled	2	0.0157	0.0119	0.4772	0.4810	21	16		38	59	45	<100	92
Bituminous Roof	4	0.0003	0.0116	0.4740	0.4627	0	12	0	1	1	23	0	3
Driveway Sealer	6	0.0000	0.0284	0.4383	0.4099	0	39	0	2	0	89	0	8
Metallic Pigmented	7	0.0208	0.0364	0.6161	0.6006	23	40		2	70	117	40max	5
Faux Finishing	8	0.1019	0.1438	0.6840	0.6422	108	153		108	397	482	<350	344
Stain, Clear, Semitransp	9	0.0305	0.0395	0.7923	0.7834	31	40		45	161	199	<250	209
Stains - Opaque	10	0.0279	0.0351	0.5330	0.5258	32	40		30	81	100		82
Varnishes - Clear	29	0.0962	0.1018	0.5799	0.5743	101	106	106		255	266	266	266
Primer/stainblock	32.1	0.0027	0.0144	0.4930	0.4813	4	20	17	16	11	57	51	48
Primer/stainblock	32.2	0.0175	0.0364	0.4162	0.3973	22	47	29	28	48	95	61	59
Dry Fog	34	0.0244	0.0316	0.4596	0.4524	30	39		31	71	90		72
Dry Fog	35	0.0128	0.0328	0.4446	0.4246	17	44		26	43	103		66
Roof	37	0.0107	0.0166	0.3359	0.3300	14	23		34	27	41		62
Waterproofing Masonry Slr	38	0.0302	0.0480	0.3897	0.3719	40	63		33	81	122		70
Bituminous Roof	39	0.0013	0.0274	0.5251	0.4990	1	28		0	3	56	0	0
Driveway Sealer	40	0.0008	0.0058	0.4249	0.4198	1	8		0	3	19	<50	0
Driveway Sealer	41	0.0215	0.0265	0.4797	0.4747	27	33		1	65	79	<96	3
Roof	43	0.0137	-0.0056	0.5111	0.5304	17	-7		16	46	-20	<50	44
Wood Preservatives	48	0.0716	0.0508	0.7547	0.7755	72	51		327	303	236	<260	327
Mastic Texture	50	0.0199	0.0129	0.3375	0.3444	28	18	31	30	52	35	60	55
Waterproofing Masonry Slr	51	0.0291	0.0316	0.7515	0.7490	29	32	29	30	122	131	216	120
Bond Breakers	52	0.1061	0.1421	0.8069	0.7709	103	139	<120	87	485	558		300
Rust Preventative	55	0.1076	0.1110	0.4594	0.4560	133	137		140	308	315	318	340
Low Solids	56	0.0357	0.0884	0.9124	0.8596	35	87	<120	25	351	572	<600	25
Concrete Stain	58	0.0040	0.0240	0.8929	0.8729	4	24			44	216	<100	
Metallic Pigmented	60	0.1257	0.1165	0.3762	0.3854	151	140		127	275	260	<250	231
Varnishes - Clear	61	0.1096	0.1344	0.6038	0.5790	114	140		105	308	353	259	254
Stain, Clear, Semitransp	62	0.2815	0.2939	0.0000	0.0000	307	321		223	307	321	<250	248
Floor	63	0.0651	0.0896	0.5230	0.4984	74	102		33	182	234	<100	93
Waterproofing Sealers	64	0.0643	0.0546	0.7354	0.7452	66	56		41	271	240	<100	91
Waterproofing Sealers	65	0.0065	-0.0085	0.8957	0.9107	7	-9		3	68	-106	<100	21
Traffic Marking	73	0.0513	0.0494	0.1646	0.1665	84	81	50	48	116	112	75	72
Bituminous Roof	75	0.0241	0.0271	0.4610	0.4580	20	24		30	34	40	50	47
Faux Finishing	76.1	0.2962	0.2737	0.5522	0.5747	318	294		360	782	768	50	801
Faux Finishing	76.3	0.3153	0.2785	0.5502	0.5870	334	295		360	798	778		801
Faux Finishing	76.5	0.2689	0.2669	0.5825	0.5846	287	285		360	762	761		801
Sanding Sealers	79	0.0616	0.0495	0.7173	0.7294	63	50		81	234	197		297
Stains - Opaque	80	0.0089	-0.0048	0.9236	0.9372	9	-5		10	171	-125		207
Concrete Curing Cpd	81.1	0.0042	-0.0076	0.8064	0.8182	4	-8		31	21	-41	<100	80
Concrete Curing Cpd	81.2	0.0058	-0.0008	0.6456	0.6523	6	-1		31	15	-2	<100	80
Waterproofing Concrete/Masonry Sealers	82.1	0.0132	-0.0013	0.8740	0.8884	13	-1		15	116	-13	<200	70
Waterproofing Masonry Sealer	82.2	0.0487	0.0602	0.6537	0.6466	50	62		15	155	187	<200	70
Quick Dry Primer	83	0.0032	-0.0181	0.4840	0.5053	4	-23		5	11	-64	<5	5
Shellacs - Clear	84	0.7247	0.7236	0.0473	0.0484	632	631			659	659		
Shellacs - Clear	85	0.7259	0.7221	0.0518	0.0557	635	632		609	665	664	<730	658
Wood Preservatives	86	0.0185	0.0100	0.9424	0.9509	19	10		21	339	218	<350	236
Varnishes - Clear	87	0.7209	0.7294	0.0000	0.0000	601	601		614	614	608		614

Table 10 - Precision Data for Coating VOC of Air-dry Single Component Coatings without Exempt Solvents

							ASTM D6886				EPA Method 24			
								propagated error		VOC range		propagated error		VOC range
Sample code		fv	f_{water}, calc.	f_{water}, KF	fvoc	Dp (g/L)	VOC	GC	based on R values	VOCdirect R=16.2%	VOC	EPA 24	based on R values	KF water R=4.2%
1	Fire Resistive	0.5220	0.5169	0.5194	0.0053	1047	12	2	1	4	6	86	45	100
2	Recycled	0.4930	0.4772	0.4810	0.0157	1342	59	9	4	18	45	130	67	147
4	Bituminous Roof	0.4743	0.4740	0.4627	0.0003	1035	1	0	0	0	23	66	34	76
6	Driveway Sealer	0.4383	0.4383	0.4099	0.0000	1372	0	0	0	0	89	91	46	99
7	Metallic Pigmented	0.6370	0.6161	0.6006	0.0208	1096	70	11	5	21	117	134	67	144
8	Faux Finishing	0.7860	0.6840	0.6422	0.1019	1063	397	40	20	78	482	141	56	94
9	Stain, Clear, Semitransp	0.8229	0.7923	0.7834	0.0305	1018	161	22	11	44	199	261	127	272
10	Stains - Opaque	0.5609	0.5330	0.5258	0.0279	1139	81	12	6	24	100	105	53	113
29	Varnishes - Clear	0.6761	0.5799	0.5743	0.0962	1045	255	31	15	62	266	103	47	93
32.1	Primer/stainblock	0.4957	0.4930	0.4813	0.0027	1358	11	2	1	4	57	134	69	150
32.2	Primer/stainblock	0.4337	0.4162	0.3973	0.0175	1284	48	7	4	15	95	75	37	79
34	Dry Fog	0.4840	0.4596	0.4524	0.0244	1247	71	11	5	21	90	92	46	99
35	Dry Fog	0.4574	0.4446	0.4246	0.0128	1343	43	7	3	13	103	94	47	100
37	Roof	0.3466	0.3359	0.3300	0.0107	1355	27	4	2	8	41	58	30	65
38	Waterproof Masonry Seal	0.4199	0.3897	0.3719	0.0302	1309	81	12	6	24	122	68	33	70
39	Bituminous Roof	0.5264	0.5251	0.4990	0.0013	1011	3	0	0	1	56	73	37	81
40	Driveway Sealer	0.4256	0.4249	0.4198	0.0008	1368	3	0	0	1	19	97	51	112
41	Driveway Sealer	0.5012	0.4797	0.4747	0.0215	1236	65	10	5	20	79	101	51	110
43	Roof	0.5248	0.5111	0.5304	0.0137	1237	46	7	3	14	-20	139	74	165
48	Wood Preservative	0.8263	0.7547	0.7755	0.0716	1009	303	35	18	69	236	236	112	236
50	Mastic Texture	0.3573	0.3375	0.3444	0.0199	1394	52	8	4	16	35	67	34	75
51	Waterproof Masonry Slr	0.7806	0.7515	0.7490	0.0291	1010	122	18	9	35	131	213	106	231
52	Bond Breakers	0.9130	0.8069	0.7709	0.1061	975	485	43	23	81	558	188	73	114
55	Rust Preventative	0.5670	0.4594	0.4560	0.1076	1237	308	35	17	69	315	91	40	75
56	Low Solids	0.9480	0.9124	0.8596	0.0357	986	350	42	27	74	572	324	126	212
58	Concrete Stain	0.8969	0.8929	0.8729	0.0040	1016	44	7	4	14	216	509	247	579
60	Metallic Pigmented	0.5019	0.3762	0.3854	0.1257	1200	275	32	15	65	260	64	28	54
61	Varnishes - Clear	0.7134	0.6038	0.5790	0.1096	1042	308	35	17	69	353	105	45	83
62	Stain, Clear, Semitransp	0.2939	0.0000	0.0000	0.2815	1091	311	35	16	70	321	16	8	0
63	Floor	0.5880	0.5230	0.4984	0.0651	1135	182	24	11	48	234	91	42	84
64	Waterproofing Sealers	0.7998	0.7354	0.7452	0.0643	1028	271	33	16	64	240	215	102	213
65	Waterproofing Sealers	0.9022	0.8957	0.9107	0.0065	1009	68	11	6	21	-106	869	470	1362
73	Traffic Marking	0.2159	0.1646	0.1665	0.0513	1644	116	17	8	33	112	30	14	28
75	Bituminous Roof	0.4851	0.4610	0.4660	0.0241	877	34	6	3	11	40	28	40	57
76.1	Faux Finishing	0.8484	0.5522	0.5747	0.2962	1074	782	30	17	56	768	119	40	32
76.3	Faux Finishing	0.8655	0.5502	0.5870	0.3153	1058	798	28	17	53	778	121	40	31
76.5	Faux Finishing	0.8515	0.5825	0.5846	0.2689	1069	762	32	18	60	761	122	41	34
79	Sanding Sealers	0.7789	0.7173	0.7294	0.0616	1020	234	30	14	58	197	195	94	199
80	Stains - Opaque	0.9324	0.9236	0.9372	0.0089	1025	171	30	22	46	-125	1893	1027	46213
81.1	Concrete Curing Cpd	0.8106	0.8064	0.8182	0.0042	995	21	3	2	7	-41	323	172	396
81.2	Concrete Curing Cpd	0.6515	0.6456	0.6523	0.0058	975	15	2	1	5	-2	126	67	148
82.1	Waterproof Masonry Slr	0.8871	0.8740	0.8884	0.0132	1012	116	18	10	33	-13	649	343	881
82.2	Waterproof Masonry Slr	0.7068	0.6537	0.6466	0.0487	1033	157	22	10	43	187	137	66	138
83	Quick Dry Primer	0.4872	0.4840	0.5053	0.0032	1272	11	2	1	3	-64	133	72	162
84	Shellacs - Clear	0.7720	0.0473	0.0484	0.7247	872	659	37	17	74	659	35	11	1
85	Shellacs - Clear	0.7778	0.0518	0.0557	0.7259	875	665	36	17	73	664	36	12	1
86	Wood Preservative	0.9609	0.9424	0.9509	0.0185	1003	339	52	41	73	218	1323	645	5389
87	Varnish	0.7294	0.0000	0.0000	0.7209	833	608	39	25	73	601	31	14	0

Table 11 - Summary Results for Coatings Containing Exempt Compounds

Sample #	#14	#24	#44	#44-2	#57-1	#57-2	#57-3	#77
coating category	industrial maintenance	high temperature	magnesite cement	megnesite cement	lacquers	lacquers	lacquers	lacquers
acetone fraction, avg		0.1816	0.248	0.4694	0.3824	0.5366	0.3674	0.2845
PCBTF fraction, avg	0.47							
methyl acetate fraction, avg					0.0042	0.0016	0.0418	
direct VOC fraction by GC, avg	0.1795	0.2961	0.2736	0.2417	0.3773	0.2908	0.3695	0.3266
indirect VOC fraction by EPA 24	0.1279	0.2513	0.2589	0.2066	0.352	0.2512	0.347	0.3877
	VOC values in g/L							
Material VOC, GC, avg	211	335	290	213	343	257	332	307
Coating VOC, GC, avg	355	452	434	448	617	645	611	464
Material VOC, EPA 24	150	284	274	182	320	222	312	365
Coating VOC, EPA 24	253	384	410	383	576	557	573	551
Material VOC, reported			269	192	269	232	294	343
Coating VOC, reported	312	<420	416	419	550	550	550	547
propagated error based on GC/ASTM 6133 R	31	41	39	36	49	44	49	41
propagated error based on GC/ASTM 6438 R	28	37	35	28	39	32	39	35

Table 12 - Summary results for two-component coatings

				Coating VOC g/L			Material VOC g/L	
Sample #	coatings category	solids fraction	water fraction	EPA24	GC/ave	reported	GC/ave	reported
#3	industrial maintenance	0.8803		168	178	179.7		
#14-1	industrial maintenance	0.9697		41	46	7		
#14-2	industrial maintenance	0.8557		241	261	296		
#14-3	industrial maintenance	0.8826		209	216	170		
#15-1	industrial maintenance	0.9739		34	19	10		
#15-2	industrial maintenance	0.9612		54	87	12		
#15-3	industrial maintenance	0.8448		225	211	214		
#25	swimming pool	0.8147		291	305	325		
#26-WB	swimming pool	0.5682	0.3191		226	236	138	122
#45-WB	varnishes clear	0.2824	0.6363		247	244	83	82
#59-WB	floor	0.6447	0.3147		90	<100	54	

Table 13 - Volatile Organic Compounds Identified in 67 Coatings Samples

solvents identified		
(4-methylphenyl)phenylmethanone	butyl carbitol	nonane
1-butanol	cumene	o-xylene
1-propanol	dibutyl phthalate	parachlorobenzotrifluoride
2-(2-ethylhexyl)ethanol	diethylene glycol monomethyl ether	phthalic anhydride
2-butanol	diisopropyl naphthalene	polynuclear aromatic HCs
2-butoxyethanol	dipropylene glycol monobutyl ether	propylene glycol
2-ethoxyethanol	dipropylene glycol monomethyl ether	propylene glycol monobutyl ether
2-ethylhexanol	dipropylene glycol monopropyl ether	propylene glycol monomethyl ether acetate
2-ethylhexylbenzoate	ethanol	propylene glycol monophenyl ether
2-heptanone	ethylbenzene	propylene glycol monopropyl ether
2-methylphenoxy oxirane	furfuryl alcohol	propylene glycol mono-t-butyl ether
2-pentanone	glycerin	p-xylene
2-propanol	m,p-xylene	Stoddard solvent
2-propoxyethanol	metachlorobenzotrifluoride	styrene
4-methyl-3-heptanone	methanol	Surfynol¨
5-methyl-3-heptanone	methyl acetate	tetrachloroisopthalonitrile
acetaldehyde	methyl ethyl ketone	Texanol¨
acetone	methyl isobutyl ketone	toluene
Aromatic 100	methyl isopropyl ketone	triethyl amine
benzophenone	mineral spirits	triethylene glycol
benzyl alcohol	morpholine	
bis-2-ethylhexyl maleate	naphthalene	
butyl acetate	N-methylpyrrolidinone	

DISCUSSION

A. Air-dry Single Component Coatings with No Exempt Compounds

The VOC results for these coatings based on GC analysis all seem reasonable. As expected, results based on EPA Method 24 for low VOC waterborne coatings are unreliable. In some cases negative coating VOC values were obtained. Most of the measured coating VOC values are within the range of the values reported by the manufacturers. Samples 7, 8, 48, 61, 73, and 83 all had reported VOC values lower than the measured GC values.

These coatings often had volatile organic compounds present not found in simpler flat and non-flat architectural coatings. This emphasizes the importance of a method to identify the peaks in the gas chromatogram. This can be accomplished by developing a retention time library for the instrument and columns used. This must be done in any case to determine the relative response factors for each solvent.

We have determined the difference between the experimental coating VOC values determined by gas chromatography (D6886) and EPA Method 24 (VOC_{GC}-VOC_{EPA24}) and plotted this a function of VOC_{GC} in Figure 1. A few coatings with much larger differences were omitted to enable the more relevant trend to be identified.

Figure 1 - (VOC_{GC}-VOC_{EPA24}) vs. VOC_{GC}

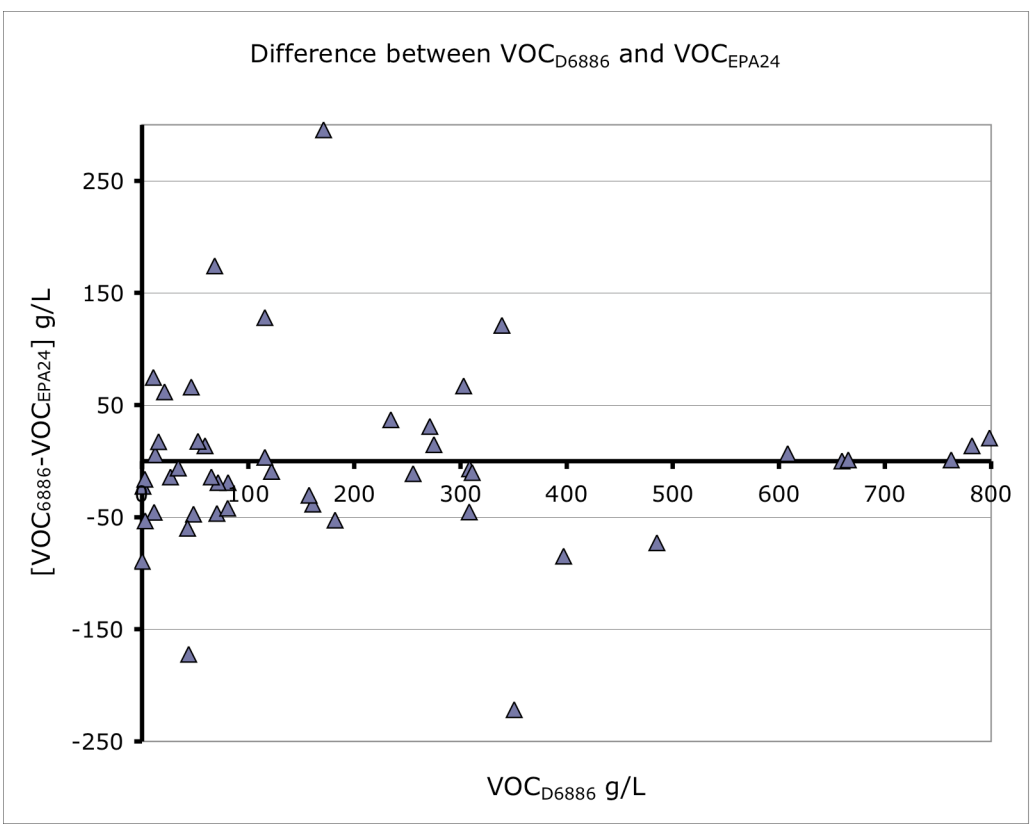
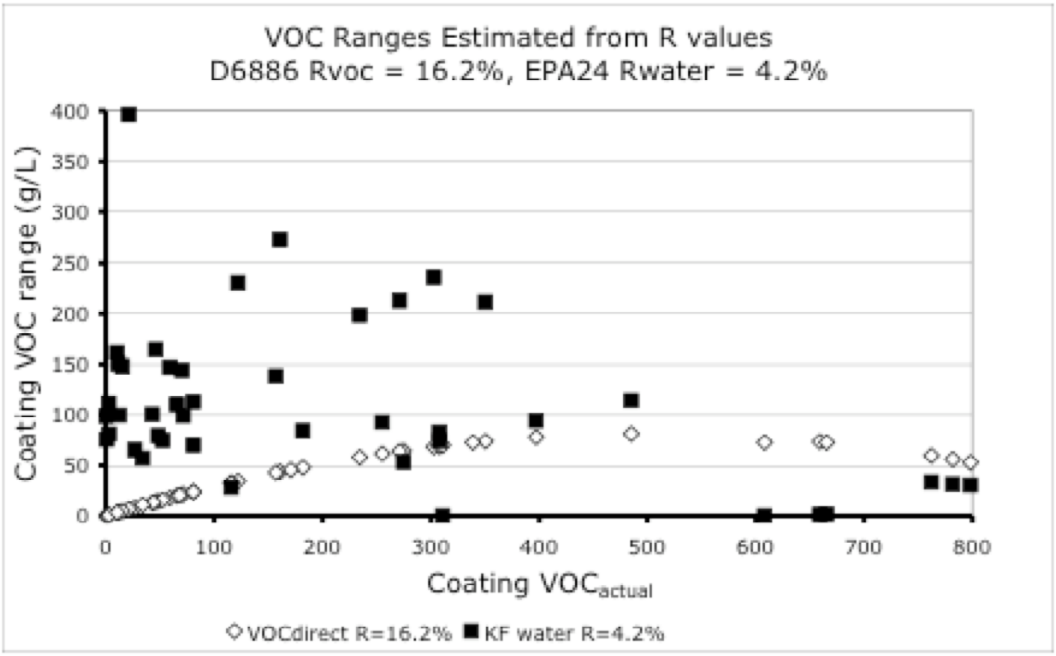


Figure 1 shows the difference between VOC_{6886} and VOC_{EPA24} is greatest at low VOC. This is exactly the same result we have seen for several years. For high VOC solventborne coatings, EPA Method 24 provides a direct measure of the total VOC fraction (as 1 – fraction solids) and provides excellent results. However, in waterborne systems at lower VOC levels, the uncertainties in the EPA 24 values can become huge because the small VOC fraction is measured indirectly.

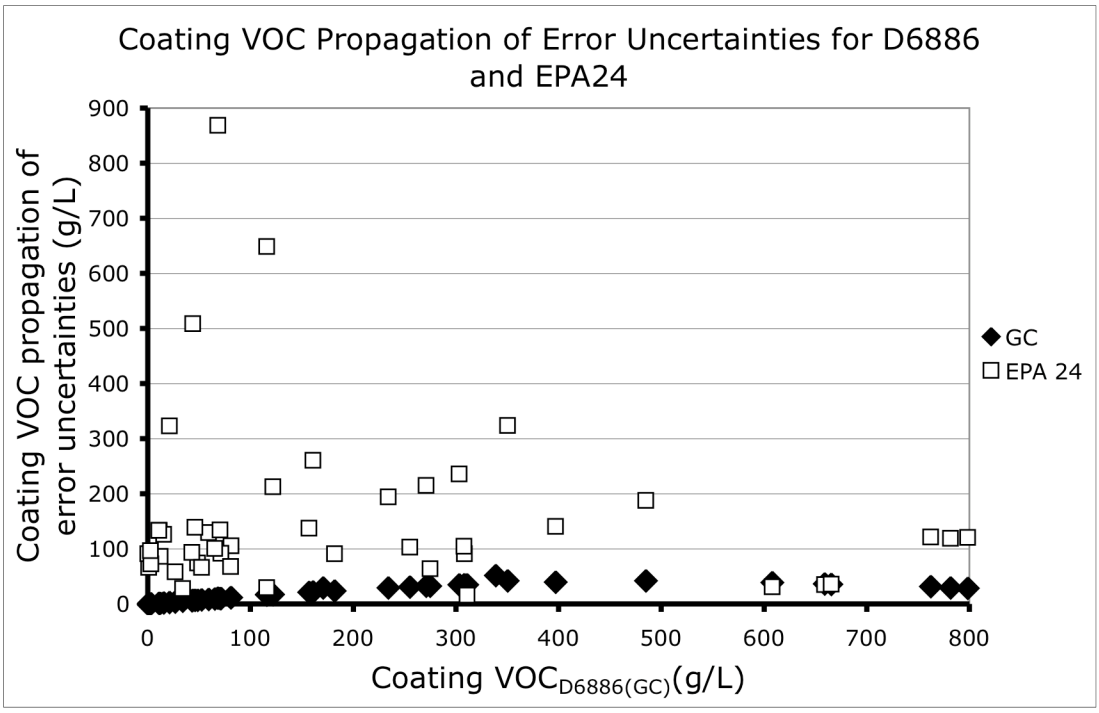
These differences in uncertainly are highlighted in Figure 2. Here, the "VOC range" values from Table 10 (the expected range of VOC values for coating VOC based on R values for fraction VOC for GC analysis and fraction water for EPA Method 24 analysis) are plotted as a function of coating VOC measured by GC. The range of "acceptable" uncertainty values for EPA 24 is huge, especially for lower VOC coatings. For example, if a coating has an actual VOC of 100 g/L and a range of 100 g/L, an acceptable experimental VOC would be any value between 50 g/Ltua and 150 g/L This again emphasizes the unsuitability of using EPA 24 for these coatings. The range is shown as being zero for a few coatings analyzed by EPA 24. This is an artifact because these coatings contained no water.

Figure 2 - Coating VOC Ranges Estimated from R_{VOC} (GC) and R_{water} (EPA 24)



A total error based on all published uncertainty values (R or r) used in a VOC calculation was calculated using the propagation of errors method discussed earlier (see Table 10). The propagation of error precision values for coating VOC determined by using published R values for all quantities used in the VOC calculation are plotted versus coating VOC measured by GC in Figure 3. Again, the lack of precision of EPA 24 for low VOC coatings is evident. Coatings with $VOC_{coatings}$ <100 often have errors of 100 g/L when measured using EPA 24. Errors are much smaller for the same coatings when VOCs are measured directly by GC.

Figure 3 - Uncertainties based on Propagation of Error Calculations for GC and EPA 24 VOC Analysis



B. Air-dry Single Component Coatings Containing Exempt Compounds

The results for these coatings given in Table 11 show relatively high levels in exempts in all of the coatings. All of the exempts were determined by GC analysis. Coating and material VOC values were calculated based on directly measured VOC fractions (GC data) and they were also calculated based on indirectly measured VOC fractions calculated by subtracting the measured fraction exempts from the calculated volatile fraction determined from the ASTM D2369 solids determination. The results for the two methods are generally within the calculated precision values. The results for Sample 14 containing 47% p-chlorobenzotrifluoride show the greatest discrepancy. The results are generally in agreement with manufacturer-supplied values with the exception of one lacquer, Sample 57-2, where the coating VOC measured directly was significantly greater than the reported VOC. These results show the VOC content of coatings containing

exempt compounds can be successfully determined using direct GC analysis. This method also provides a direct measure of all VOCs in a single experiment. Although reasonable values can also be obtained through a combination of a EPA Method 24 analysis and subsequent direct determination of exempt compounds, there is no real savings in time since the GC experiment has to be performed in any case.

C. Multicomponent Coatings without Exempt Compounds

The results in Table 12 show either EPA Method 24 or the direct GC method gives acceptable results for the VOC levels of solventborne 2K coatings. Both methods gave results in agreement with one another and with the manufacturer supplied values. However, no method currently exists for determination of VOCs in waterborne 2K systems. The new method developed for this project gave excellent results for these coatings and the values obtained were in good agreement with manufacturer supplied values. We feel this new 2K method will be very useful for analysis of VOCs in waterborne 2K systems.

More will be said about particular coatings and methods in the section on Validation Studies

D. Static Headspace Analysis

At approximately the same time that Cal Poly was working with CARB to carry out the present study on VOC method development, the Emulsion Polymers Council announced that some of its constituent laboratories were developing a static headspace method for measuring the VOC content of water-based coatings materials. In our proposal to ARB we wrote the following:

- The Emulsion Polymers Council and the Adhesive and Sealant Council are supporting the development of an improved "Battelle" method. The activity is being coordinated by researchers of the Rohm and Haas Company. This new method is currently under development and a draft ASTM method has been promised for presentation at the January 2005 meeting of ASTM D01.21. The method is a static, rather than dynamic, headspace method in which a 25mg sample of coating is placed in a 25mL headspace vial and is then heated for 10 minutes at 150^0C. A split of the headspace is then transferred to a GC column. The method has been tested with a wide variety of materials including a flat latex paint, a semigloss latex paint, an emulsion polymer, a caulk and several adhesives. The samples tested had actual VOC contents ranging from 0 to 6%. The method requires that a separate set of response factors be determined for each sample analyzed, requires the use of both a GC-MS and GC-FID and requires that these instruments be equipped with a headspace auto-sampler. We suspect that the instrument requirements and technical expertise required to perform this method may preclude its use by smaller paint manufacturers. An advantage of this new method, if it proves to be successful, is that it may provide a second direct method for VOC analysis of waterborne coatings. We believe that this method should be

evaluated as part of this proposal and compared with the ASTM direct method D6886. A second direct method would provide validation of D6886 and could serve as a primary direct method if Method D6886 proves not applicable to certain water-borne coatings categories.

A draft static headspace method was presented by EPC at the January, 2005 ASTM meeting in Fort Lauderdale, FL. The precision values for the method on various coating types was presented at that time and are given in Table 14. The method was not deemed acceptable because of the large reproducibility values. The cause of the high uncertainty was attributed primarily to the loss of polar VOCs during transfer from the headspace oven to the gas chromatograph. The EPC group attempted to make changes in the method to improve precision but has not yet succeeded. Static headspace method development by EPC is currently not active.

Table 14 - Intra- and Inter-Laboratory Precision Values for a Variety of Coatings Types Using Static Headspace Analysis

Sample Type	r, %	R, %
Styrene-Butadiene Emulsion Polymer	32%	110%
Vinyl Acrylic Copolymer Emulsion Adhesive	13%	54%
Acrylic Interior Semigloss Latex Paint	30%	112%
Acrylic Exterior Flat Latex Paint	20%	82%
Acrylic Caulk	25%	38%
Acrylic Copolymer Emulsion Adhesive	17%	52%
Water Based Contact Adhesive	22%	89%
Water Based Adhesive Mastic	36%	149%

Cal Poly has evaluated the static headspace method on waterborne architectural coatings to a very limited extent and observed similar difficulties in obtaining good precision for polar analytes such as ethylene glycol, propylene glycol, and other alcohols. We have used the method successfully in the analysis of coatings which do not contain highly polar analytes. Since Cal Poly was involved in a National Paint and Coatings Association (NPCA) sponsored EPA Method 311 round robin and since the completed round robin results were available, we evaluated the static headspace method with some of the same coatings that were used in the NPCA study. Our report to ASTM at the June, 2006 Toronto, Canada meeting is as follows:

Static Headspace Analysis

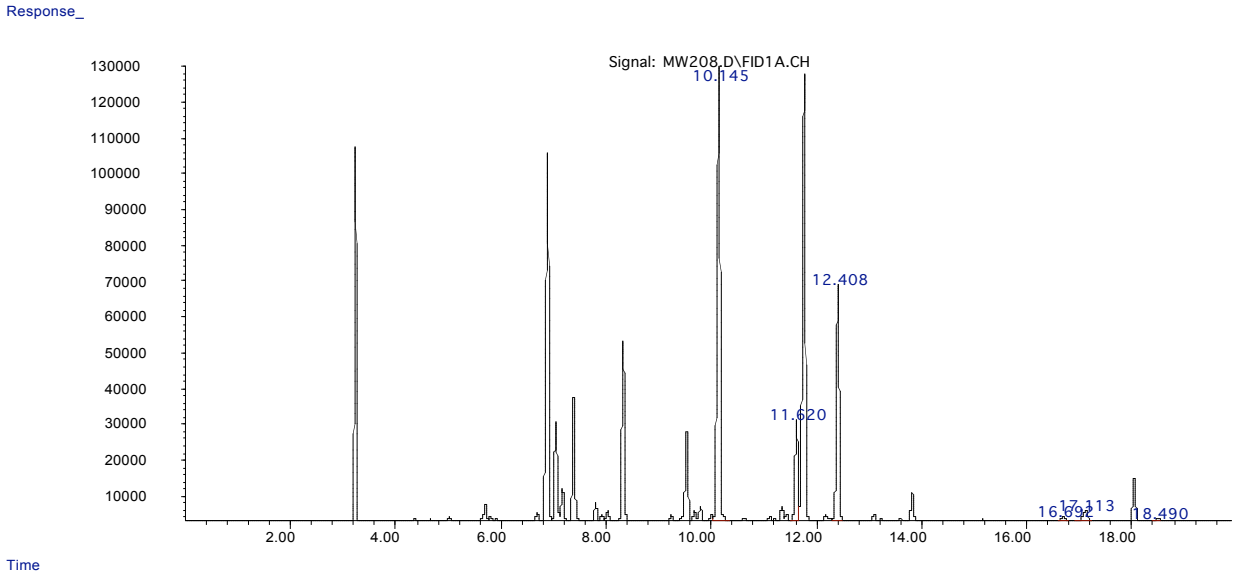
One of our goals is to develop methodology for analyzing coating HAP and exempt compound content of virtually any coating. The method of static headspace analysis described previously appears to work particularly well and may represent a replacement method for the current EPA Method 311. In the present study the coatings tested were the same solvent borne coatings analyzed in a NPCA Method 311 round robin conducted in 2003. The coatings analyzed

consisted of a nitrocellulose lacquer, a melamine-cure automotive primer, a melamine-cure automotive topcoat, and a UV-cure sealer. The study was conducted to evaluate the method since Method 311 round robin data was available to compare results with. The headspace method has also been employed to measure the VOC content of one powder coating and one two-component waterborne polyurethane architectural coating.

To prepare samples for static headspace analysis, a known amount of the neat liquid coating was placed in a 40mL vial containing ceramic beads. A known amount of internal standard was added and the contents were then mixed to obtain homogeneity. The internal standard used in this study was p-fluorotoluene though other internal standards would work equally well. The ceramic beads function as a mixing aid. After mixing, a small sample (typically 10 to 20 mg) was transferred to a 20mL headspace vial and closed with a crimp cap. The small sample was then equilibrated for 20 minutes in an Agilent G1888 Network Headspace Sampler and the analyzed by GC using flame ionization detection on an Agilent 6890 gas chromatograph. The HAP results for the four samples were as follows:

Figure 4 – Nitrocellulose Lacquer Chromatogram

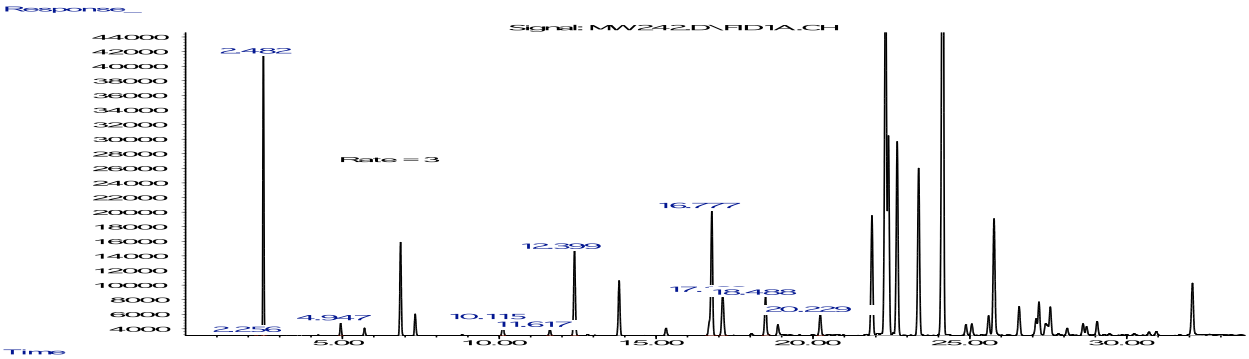
1. Nitrocellulose Lacquer



	Headspace, 150°C,rate 3°C/min	Method 311, Cal Poly	Method 311, All labs
Cpd	%	%	%
MIBK	14.52	14.09	14.57
Toluene	2.15	2.10	2.17
EtBz	0.10	0.10	0.09
m,p-Xy	0.37	0.34	
o-Xy	0.07	0.08	
Xylenes	0.44	0.42	0.35

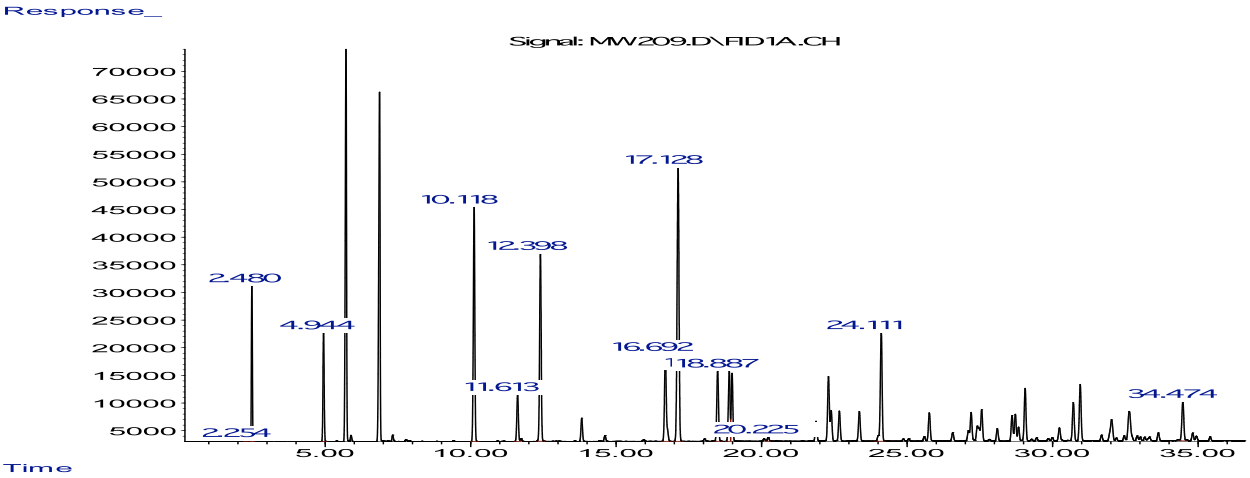
Figure 5 – Melamine-Cure Automotive Topcoat

2. Melamine-Cure Automotive Topcoat



	Headspace, 150°C,rate 3°C/min	Headspace, 150°C,rate 20°C/min	Method 311, Cal Poly	Method 311, All labs
Cpd	%	%	%	%
HCHO	0.023	0.027		
MeOH	4.52	5.29		
MEK	0.09	0.09	0.09	0.10
MIBK	0.13	0.13	0.11	0.25
Toluene	0.04	0.04	0.03	0.03
EtBz	NR	0.10	0.08	0.19
m,p-Xy	0.33	0.32	0.28	
o-Xy	0.28	NR	0.24	
xylenes	0.60			0.52
EB	0.15	NR	0.22	0.19
Cumene	0.17	0.17	0.14	0.12
1,2,4-TMB	5.20	5.16		

Figure 6 – Melamine-Cure Automotive Primer
3. Melamine-Cure Automotive Primer



	Headspace, 150°C,rate 3°C/min	Method 311, Cal Poly	Method 311, All labs
Cpd	%	%	%
HCHO	0.025		
MeOH	4.02		
MEK	1.65	1.50	1.76
MIBK	3.47	3.42	3.51
Toluene	0.49	0.46	0.48
EtBz	1.21	1.10	0.99
m,p-Xy	3.49	3.51	
o-Xy	0.81	0.84	
xylenes	4.30	4.35	4.46
EB	1.47	1.68	1.81
Cumene	0.05	0.05	0.06
Napth	0.45	0.56	0.53

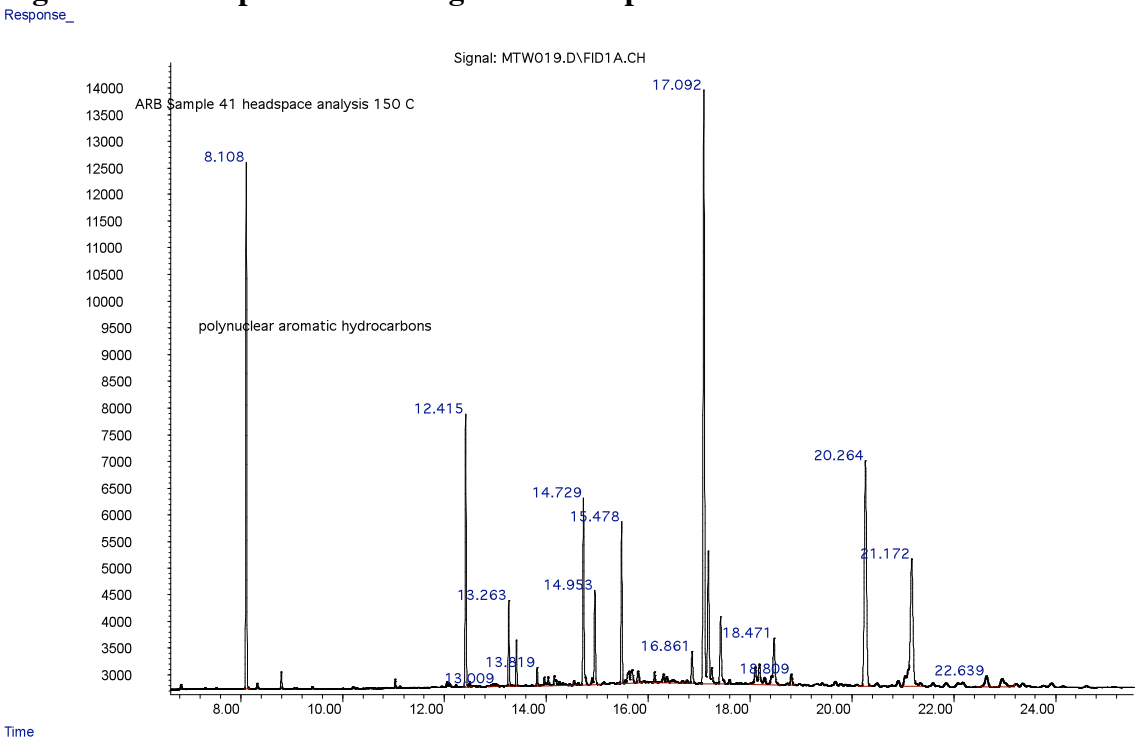
Conclusions: The static headspace method is relatively simple to run. Conditions for running the method are easily changed to give acceptable results. These method changes include chromatographic heating rates and column types. A particular advantage of static headspace is that the coating sample need not be dispersed in a solvent and also is not subjected to high inlet temperatures as is the case for the direct injection method that must be used in carrying out a Method 311 determination. The automotive coatings described above are an example of this. By the direct 311 method the sample is typically subjected to GC inlet temperatures exceeding 200^{0}C to give vaporization of the volatile components. Under these conditions the coating cures under extreme conditions and cure volatiles (methanol) is released in varying amounts. Using the static headspace conditions, the coating sample is subjected to the same cure conditions (temperature and time) that would normally be used in an actual application situation. The result is that the same volatiles are obtained in the test method which would be expected in the actual application process. While this conclusion

is based primarily on our work with automotive coatings, the same consideration are applicable to non-water containing architectural coating and would suffice for the analysis of virtually any solventborne architectural coating containing HAPs or exempt solvents.

ARB Sample #41

Sample 41 is a low VOC waterborne driveway sealer. Upon analysis by direct injection the chromatogram showed several peaks at retention times longer than twelve minutes which we had not encountered in any other samples. We determined these peaks were all due to polynuclear aromatic hydrocarbons. Analyzing this sample accurately would require both a direct injection and an analysis of the extracted film to determine the amount of VOCs remaining in the dried film. We decided to try analyzing this sample by headspace analysis at 110ºC and 150ºC. The chromatogram for the 150ºC run is shown below in Figure 4. The peak at 8.1 minutes is due to internal standard.

Figure 7 - Headspace Chromatogram of Sample 41



Results for fraction volatiles obtained from direct analysis (first analyzing liquid then analyzing dried film and subtracting), and headspace analysis at 110ºC and 150ºC are shown below.

Method	fraction VOC
direct (liquid - film)	0.0215
Headspace 110C	0.0191
Headspace 150C	0.0383

The headspace results at 110ºC agree well with the more complex direct analysis. Using headspace analysis may provide a method to determine VOCs of coatings with significant amounts of high boiling volatiles without having to analyze both the liquid coating and the dried film.

Overall, we do not feel headspace analysis is suitable as a general VOC analysis method at this time. One of the motivations for our investigating headspace analysis initially was some encouraging results based on preliminary work done by the Emulsion Polymers Council (EPC). However, both we and the EPC have found difficulties in analyzing highly polar compounds, particularly glycols, by headspace. The EPC has not presented any new work on headspace analysis for over a year and has indicated to ASTM that they have no plans to continue their efforts to develop an ASTM headspace method for VOC determination. Clearly much more work is needed before headspace analysis can be used to analyze coatings containing significant amounts of polar analytes. In addition, the cost involved in headspace analysis probably places it beyond the capabilities of most coatings analysis laboratories.

E. Analysis of coatings containing semi-volatile components

In the course of analyzing 28 samples provided by South Coast's Rule 1113 VOC assessment it was found that some coatings contain semi-volatiles with boiling points higher than Texanol® which is itself considered a semi-volatile compound. These included dibutyl phthalate and benzyl butyl phthalate. In carrying out an ASTM Method D 6886 determination of the VOC content of a coating containing semi-volatile components, the semi-volatile component is measured in its entirety. The current US definition of VOC content is defined as the amount of VOC that evaporates from a sample during a specified heat/time cycle (Method D 2369). There exists, therefore, a disconnect between the amount of semi-volatile component which evaporates during a D 2369 determination and a D 6886 determination with the former giving lower numbers by an amount related to the nature of the semi-volatile component and the matrix that it is in. We have addressed this problem by analyzing the paint film after a D 2369 determination for residual semi-volatiles and subtracting this amount from the amount of the same component found during a D 6886 determination. This procedure adds an additional step to the D 6886 procedure and makes it more time consuming. The ISO community has gotten around this complication by defining VOC on boiling point and a GC boiling marker. For waterborne coatings this marker is diethyl adipate with a boiling point of 250ºC. Use of such a boiling point marker greatly simplifies the definition of VOC and would be very useful in simplifying the laboratory VOC determination by gas chromatography in the US. Additionally, a boiling point marker would allow us to integrate the static headspace method into the arsenal of new VOC methods with ease in that the equilibration temperature used in the static headspace method could be increased and give nearly complete evaporation of all the volatile and semi-volatile components in a coating. This concept is illustrated in Table 15 in which three paints are described containing the Texanol® and two other semi-volatile coalescents.

Table 15 - Comparison of Semi-volatile Evaporation Using D6886, Static Headspace at 110ºC and 150ºC, and D2369

Sample	coalescent	VOC fraction, direct injection, D6886	VOC fraction remaining in film after D2369	% VOC remaining in film after D2369	VOC fraction, static headspace, 110ºC	VOC fraction, static headspace, 150ºC
1	Texanol®	1.29	0.07	5.4	1.06	1.13
2	Semivol 1	1.07	0.60	56	0.38	1.14
3	Semivol 2	0.76	0.62	82	0.15	0.84

The data above show anywhere from 5-82% of the semi-volatile material remains in the film after heating at 110ºC for one hour. Our previous studies have shown this is highly variable depending on the coating matrix (resin, pigments, additive, etc.) and the semi-volatile. The results in the above table show use of headspace analysis with suitably high equilibration temperature allows determination of essentially all the semi-volatile contained in a paint. However, in the absence of a VOC definition defined by boiling point marker, we were unable to determine a static headspace equilibration temperature providing VOC fractions equal to those determined by EPA 24. This problem and the problems associated with highly polar VOCs (especially glycols) remaining in the headspace transfer line, caused us to postpone any attempt to include headspace analysis as part of the new architectural coatings methods.

F. Validation (Round Robin) Studies for Water-Borne Air-Dry Coatings

An important part of this project is independent validation of the methods we have developed. We selected coatings in three categories to send to other laboratories: five two-component coatings (both solventborne and waterborne), four unusual air-dry waterborne coatings (low solids, high VOC, unusual solvents) and three coatings containing exempt solvents. Coatings selected for validation studies are listed in Table 7. Specific VOCs we identified in these coatings are also listed in the table.

Four industrial laboratories, one government laboratory and three regulatory laboratories initially agreed to participate in this study. Two of the industrial laboratories and the governmental lab later declined to participate. We initially sent samples to two industrial laboratories and three regulatory laboratories (BAAQMD, CARB and SCAQMD). One industrial laboratory was unable to participate at all and the other was able to analyze half of the samples sent to them. Consequently, we only had two sets of results for some of the coatings. We analyzed these coatings at Cal Poly using a different instrument and operators, thus constituting an additional laboratory.

The BAAQMD analyzed one of the air-dry waterborne coatings and three of the solventborne coatings containing exempt solvents. The CARB laboratory analyzed all

four waterborne air-dry coatings and three solventborne coatings containing exempt solvents. The industrial laboratory analyzed the five 2K coatings. The SCAQMD laboratory performed Method 24 analyses on the five 2K coatings. A discussion of all the samples analyzed during the validation study follows.

Four air-dry waterborne samples were chosen for inter-laboratory testing. All contained relatively high water and high VOC levels. The VOC types were varied but relatively common for the types of coatings tested. Sample #55 contains the common alcohols 2-butanol, 2-butoxyethanol (butyl cellosolve) and butyl carbitol. Sample #60 contains propylene glycol, diethylene glycol monomethyl ether, propylene glycol monobutyl ether, 2-(2-ethylhexyl)ethanol, and dibutyl phthalate. The major volatiles in sample #61 are triethyl amine, dipropylene glycol monomethyl ether, N-methylpyrrolidinone, and dipropylene glycol monobutyl ether. Sample #76-1 contains a very high amount (> 25%) of propylene glycol. None of the samples chosen for this portion of the study contained exempt solvents. The labs participating in this part of the study were Cal Poly (two independent labs), CARB and BAAQMD.

The validation study data for air-dry waterborne coatings are given in Tables 16-19 and a discussion of each sample follows the table.

Table 16 - Sample #55, Waterborne Air-dry Rust Preventative Coating

	Lab 1, Cal Poly 6890				Lab 2, BAAQMD			Lab 3, CARB		
	Run 1	Run 2	Run 3	Average	Run 1	Run 2	Average	Run 1	Run 2	Average
2-butanol	0.0337	0.0342	0.0333	0.0337			0.0270			Not reptd
2-butoxyethanol	0.0582	0.0578	0.0588	0.0583			0.0592			0.0596
butyl carbitol	0.0138	0.0142	0.0147	0.0142			0.0135			0.0096
Total VOC fraction	0.1057	0.1063	0.1067	0.1062			0.0997			
Density, g/L				1237	1247	1252	1250			1252
solids fraction				0.4330	0.4258	0.4263	0.4261			0.4392
water fract, calcd				0.4608			0.4743			
L water, calcd				0.5701			0.5926			
water fract, direct				0.4560	0.4734	0.4679	0.4707	0.4458	0.4210	0.4334
L water, direct				0.5641	0.5905	0.5858	0.5881	0.5581	0.5271	0.5426
Mat VOC, GC	131	131	132	131			125			
Ctg VOC, GC	304	306	307	306			306			
Mat VOC, EPA 24				137	126	132	129	144	175	160
Ctg VOC, EPA 24				315	307	320	313	326	370	349
Mat VOC, reptd										
Ctg VOC, reptd	318									

Between-laboratory standard deviation, material VOC, GC = 4.8 g/L
Between-laboratory standard deviation, coating VOC, GC = 0.1 g/L
Between-laboratory standard deviation, material VOC, EPA 24 = 15.7 g/L
Between-laboratory standard deviation, coating VOC, EPA 24 = 19.9 g/L

Coating #55: The CARB laboratory, using their Method 310, did not identify one of the components of the coating, 2-butanol, present at a concentration of about 3%. Their gas chromatographic analysis therefore cannot be used for calculating the total VOC fraction. It would appear that their Method 310 only identifies specific volatiles and ignores those that are not on their analyte list. The CARB laboratory carried out water analysis by both a GC method (ASTM D 3792-99) and the Karl Fisher method (ASTM D 4017-96a). CARB averages the water results and calculates both a material and coatings VOC based on this average. For this coating there is a 2.5% difference in the water fraction and gives material VOC values of 144 and 175 g/L, respectively, and coatings VOC values of 326 and 370 g/L, respectively. For coatings that have lower VOC values, a similar range would occur. The BAAQMD results were virtually identical to the results obtained by Cal Poly using ASTM Method D 6886.

Table 17 - Sample #60, Waterborne Air-dry Metallic Pigmented Coating

	Lab 1, Cal Poly 6890			Lab 2, CARB			Lab 3, Cal Poly 5890		
	Run 1	Run 2	Average	Run 1	Run 2	Average	Run 1	Run 2	Average
2-butoxyethanol	Not reptd	Not reptd				0.0200			
propylene glycol	0.0441	0.0447	0.0444			0.0690	0.0374	0.0377	0.0376
diethylene glycol monomethyl ether	0.0278	0.0282	0.0280			Not reptd	0.0274	0.0237	0.0255
propylene glycol monobutyl ether	0.0164	0.0167	0.0166			Not reptd	0.0121	0.0146	0.0133
2-(2-ethylhexyl)ethanol	0.0142	0.0153	0.0148			Not reptd	0.0158	0.0152	0.0155
triethylene glycol	0.0037	0.0040	0.0038			Not reptd	0.0000	0.0000	0.0000
Total VOC fraction	0.1062	0.1089	0.1075				0.0926	0.0913	0.0920
dibutyl phthalate	0.0195	0.0168	0.0181			Not reptd	0.0236	0.0219	0.0227
Density, g/L			1200			1216			1195
solids fraction	0.4995	0.4972	0.4983			0.5076	0.4975	0.4974	0.4975
water fract, calcd	0.3943	0.3940	0.3941				0.4098	0.4114	0.4106
L water, calcd	0.4734	0.4729	0.4731				0.4920	0.4938	0.4929
water fract, direct			0.3854	0.4164	0.3771	0.3967			0.3854
L water, direct			0.4627	0.5063	0.4586	0.4824			0.4606
Mat VOC, GC	127	131	129				111	109	110
Ctg VOC, GC	242	248	245				218	215	217
Mat VOC, EPA 24	138	141	140	92	140	116	140	140	140
Ctg VOC, EPA 24	257	262	260	187	259	225	259	260	259
Mat VOC, reptd									
Ctg VOC, reptd	< 250								

Between-laboratory standard deviation, material VOC, GC = 13.6 g/L
Between-laboratory standard deviation, coating VOC, GC = 20.0 g/L
Between-laboratory standard deviation, material VOC, EPA 24 = 13.5 g/L
Between-laboratory standard deviation, coating VOC, EPA 24 = 20.0 g/L

Coating #60: Since results were obtained from only one other laboratory, Cal Poly carried out the analysis using two different gas chromatographs (Agilent Models 6890 and 5890, respectively) and different operators – this approach of establishing a separate in-house laboratory has been commonly used by ASTM members in carrying out other round robins. With this coating, the CARB laboratory identified a VOC which is not present in the coatings and failed to identify all of the VOCs present in the coating comprising approximately 12% of the total VOCs in the coating. In calculating the GC VOC total, the two Cal Poly laboratories did not count dibutyl phthalate as a VOC. Since dibutyl phthalate is a semi-volatile organic compound (boiling point = 340ºC), it probably contributes partially to the VOC emissions normally measured by ASTM Method D 2369 (total volatile content) and probably explains the higher VOC values obtained by EPA Method 24 in the analysis of this coating. If all of the butyl phthalate is counted as a

VOC, the material and coatings VOC values by GC would increase by approximately 20 and 35 g/L, respectively. Research conducted by us using static headspace analysis and extraction of paint films after the ASTM D 2369 total volatile determination indicate that dibutyl phthalate is volatile to the extent of about 50%.

Table 18 - Sample #61, Waterborne Air-Dry Clear Varnish

	Lab 1, Cal Poly 6890				Lab 2, CARB			Lab 3, Cal Poly 5890			
	Run 1	Run 2	Run 3	Average	Run 1	Run 2	Average	Run 1	Run 2	Run 3	Average
triethyl amine	0.0177	0.0130	0.0233	0.0180	Not reptd	Not reptd	Not reptd	0.0205	0.0240	0.0257	0.0234
propylene glycol	0.0075	0.0073	0.0075	0.0074	Not reptd	Not reptd	Not reptd	0.0071	0.0070	0.0065	0.0069
dipropylene glycol monomethyl ether	0.0461	0.0453	0.0454	0.0456	Not reptd	Not reptd	Not reptd	0.0437	0.0440	0.0412	0.0430
N-methylpyrrolidinone	0.0352	0.0323	0.0351	0.0342	Not reptd	Not reptd	Not reptd	0.0295	0.0315	0.0286	0.0299
dipropylene glycol monobutyl ether	0.0211	0.0194	0.0209	0.0204	Not reptd	Not reptd	Not reptd	0.0200	0.0216	0.0189	0.0202
Surfynol®	0.0044	0.0042	0.0048	0.0045	Not reptd	Not reptd	Not reptd	0.0052	0.0056	0.0046	0.0051
Total VOC fraction	0.1320	0.1215	0.1370	0.1301				0.1260	0.1337	0.1256	0.1284
Density, g/L				1042			1044				1042
solids fraction	0.2862	0.2862	0.2874	0.2866			0.3133	0.2867	0.2878	0.2878	0.2874
water fract, calcd	0.5818	0.5924	0.5756	0.5832				0.5873	0.5785	0.5866	0.5842
L water, calcd	0.6064	0.6174	0.5999	0.6079				0.6120	0.6028	0.6113	0.6087
water fract, direct				0.5790	0.6066	0.5564	0.5815				0.5790
L water, direct				0.6035	0.6333	0.5809	0.6071				0.6034
Mat VOC, GC	138	127	143	136				131	139	131	134
Ctg VOC, GC	349	331	357	346				338	351	337	342
Mat VOC, EPA 24	138	127	143	136	84	136	110	140	139	139	139
Ctg VOC, EPA 24	347	319	360	342	228	325	280	353	350	350	351
Mat VOC, reptd											
Ctg VOC, reptd	259										

Between-laboratory standard deviation, material VOC, GC = 1.3 g/L
Between-laboratory standard deviation, coating VOC, GC = 2.8 g/L
Between-laboratory standard deviation, material VOC, EPA 24 = 16.0 g/L
Between-laboratory standard deviation, coating VOC, EPA 24 = 38.9 g/L

Coating #61: The results obtained by both Cal Poly laboratories are in good agreement with each other. The CARB laboratory was unable to quantitate any of the VOCs present in this coating. Again, the CARB laboratory obtained a difference of about 5% in their two water determinations by different methods. This difference in water determinations gives values of 84 and 136 g/L for material VOC and 228 and 325 g/L for coating VOC. The Cal Poly Method D 6886 results are in good agreement with the manufacturer's reported value of coating VOC.

Table 19 - Sample #76-1, Waterborne Air-dry Faux Finish

	Lab 1, Cal Poly 6890					Lab 2, CARB			Lab 3, Cal Poly 5890		
analyte	Run 1	Run 2	Run 3	Run 4	Average	Run 1	Run 2	Average	Run 1	Run 2	Average
UK	0.0056	0.0084	0.0055	0.0080	0.0069			Not reptd			
MEK	0.0114	0.0063	0.0044	0.0060	0.0070			Not reptd	0.0161	0.0097	0.0129
UK	0.0005	0.0009	0.0006	0.0008	0.0007			Not reptd			
UK	0.0012	0.0018	0.0013	0.0015	0.0014			Not reptd			
propylene glycol	0.3028	0.2520	0.2593	0.2890	0.2758			0.2696	0.2699	0.2856	0.2778
UK	0.0045	0.0049	0.0035	0.0045	0.0043			Not reptd			
Total VOC fraction	0.3261	0.2742	0.2745	0.3098	0.2962			0.2696	0.2923	0.2856	0.2890
Density, g/L					1074			1093			1084
solids fraction	0.1517	0.1515			0.1516			0.1560	0.1511	0.1510	0.1511
water fract, calcd	0.5222	0.5743	0.5739	0.5386	0.5522	0.5487	0.5088	0.5744	0.5566	0.5633	0.5600
L water, calcd	0.5609	0.6169	0.6164	0.5786	0.5932	0.5997	0.5561	0.6278	0.5979	0.6051	0.6015
water fract, direct					0.5747			0.5287			0.5747
L water, direct					0.6173			0.5779			0.6227
Mat VOC, GC	350	295	295	333	318			295	317	310	313
Ctg VOC, GC	798	769	769	790	782			792	788	784	786
Mat VOC, EPA 24					294	323	366	345			297
Ctg VOC, EPA 24					768	806	825	816			788
Mat VOC, reptd											
Ctg VOC, reptd	Not Reptd										

Between-laboratory standard deviation, material VOC, GC = 12.3 g/L
Between-laboratory standard deviation, coating VOC, GC = 4.9 g/L
Between-laboratory standard deviation, material VOC, EPA 24 = 28.3 g/L
Between-laboratory standard deviation, coating VOC, EPA 24 = 24.2 g/L

Coating #76-1: This coating contains approximately 55% water and 25-30% propylene glycol as the principal VOC. All three laboratories obtained approximately the same results for the VOC content. The results indicate that ASTM Method D 6886 and CARB Method 310 give similar results. Precision results based on the limited number of laboratories indicate that the direct GC method (ASTM Method D 6886) is somewhat better than the indirect method (EPA Method 24).

G. Validation (Round Robin) Studies for Coatings Containing Exempt Solvents

Three architectural coatings samples were tested by three laboratories. These included Cal Poly, the Bay Area Air Quality Management District and the California Air Resources Board. The three samples selected were #14, #44-2, and #57-3. Sample #14 contains a large quantity of parachlorobenzotrifluoride (PCBTF), sample #44-2 contains a large quantity of acetone, and sample #57-3 contains a large amount of acetone and small quantity of methyl acetate. No other exempt solvents were detected in any of the other samples received by Cal Poly.

The validation study data for air-dry waterborne coatings are given in Tables 20-22 and a discussion of each sample follows the table.

Table 20 - Sample #14, Solventborne Air-dry High Temperature Coating with Exempt Solvents

	Lab 1, Cal Poly 6890			Lab 2, BAAQMD			Lab 3, CARB
	Run 1	Run 2	Average	Run 1	Run 2	Average	Average
toluene	0.0015	0.0015	0.0015			0.0017	0.0066
metachlorobenzotrifluoride	0.0013	0.0010	0.0012				
parachlorobenzotrifluoride	0.4458	0.4406	0.4432	0.4233	0.4062	0.4194	0.4398
ethylbenzene	0.0168	0.0169	0.0168			0.0171	0.0196
m,p-xylene	0.0786	0.0787	0.0786			0.0763	0.0749
o-xylene	0.0067	0.0067	0.0067			0.0081	0.0111
UK	0.0026	0.0020	0.0023			Not reptd	Not reptd
UK	0.0007	0.0007	0.0007			Not reptd	Not reptd
Aromatic 100	0.0667	0.0664	0.0665			0.0641	Not reptd
naphthalene	0.0053	0.0048	0.0050			0.0047	Not reptd
Total volatile fraction	0.6260	0.6193	0.6226			0.5914	0.5521
parachlorobenzotrifluoride, L	0.3865	0.3820	0.3842	0.3681	0.3548	0.3655	0.3813
Total VOC fraction	0.1802	0.1787	0.1795	0.1681	0.1852	0.1720	
Mass Balance, fract	1.0261	1.0218	1.0240			0.9871	0.9826
Density, g/L			1173.1	1176.5	1181.7	1179.1	1160
solids fraction	0.4001	0.4026	0.4013	0.3956	0.3958	0.3957	0.4305
Matl VOC, GC	211	210	211	198	219	208	
Coat VOC, GC	345	339	342	313	339	326	
Matl VOC, EPA 24	181	184	182	213	234	224	152
Coat VOC, EPA 24	295	298	296	337	363	350	246
Matl VOC, reptd							
Coat VOC, reptd	312						
PCBTF, reported	0.45						

Between-laboratory standard deviation, material VOC, GC = 1.6 g/L
Between-laboratory standard deviation, coating VOC, GC = 11.2 g/L
Between-laboratory standard deviation, material VOC, EPA 24 = 35.8 g/L
Between-laboratory standard deviation, coating VOC, EPA 24 = 52.0 g/L
Between-laboratory standard deviation, PCBTF fraction = 1.29%

Sample #14: The Cal Poly and BAAQMD labs obtained the same speciation results for all of the compounds present in this coating. CARB, using their Method 310 did not report the presence of a significant quantity of the solvent Aromatic 100 (approximately 6.5%). Accordingly, CARB's speciation results could not be used to calculate a VOC content by GC. Even though Aromatic 100 was not measured by the CARB laboratory, they obtained a mass balance of 98.26%.

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Table 21 - Sample #44-2, Solventborne Air-dry Magnesite Cement Coating with Exempt Solvents

	Lab 1, Cal Poly 6890			Lab 2, BAAQMD			Lab 3, CARB
	Run 1	Run 2	Average	Run 1	Run 2	Average	Average
acetone	0.4700	0.4688	0.4694	0.4111	0.4330	0.4221	0.4520
ethylbenzene	0.0138	0.0137	0.0138			0.0161	0.0179
m,p-xylene	0.0567	0.0564	0.0565			0.0607	0.0592
o-xylene	0.0217	0.0218	0.0217			0.0230	0.0259
UK	0.0124	0.0108	0.0116				
Aromatic 100	0.1378	0.1169	0.1274			0.1470	Not reptd
naphthalene	0.0115	0.0099	0.0107			0.0105	Not reptd
Total volatile fraction	0.7239	0.6983	0.7111			0.6783	
acetone. L	0.5246	0.5232	0.5239	0.4673	0.4944	0.4808	0.5126
Total VOC fraction	0.2539	0.2295	0.2417	0.2672	0.2453	0.2563	
Mass Balance, fract			1.0302			0.9863	
Density, g/L			883	899.1	903.1	901.1	897
solids fraction	0.3219	0.3262	0.3241	0.3074	0.3086	0.3080	0.3470
Matl VOC, GC	224	203	213	240	222	231	
Coat VOC, GC	472	425	448	451	438	445	
Matl VOC, EPA 24	184	181	182	253	233	243	180
Coat VOC, EPA 24	387	380	383	475	462	469	370
Matl VOC, reptd	192						
Coat VOC, reptd	419						
Acetone fraction, reptd	0.4844						

Between-laboratory standard deviation, material VOC, GC = 12.4 g/L
Between-laboratory standard deviation, coating VOC, GC = 2.5 g/L
Between-laboratory standard deviation, material VOC, EPA 24 = 35.7 g/L
Between-laboratory standard deviation, coating VOC, EPA 24 = 53.5 g/L
Between-laboratory standard deviation, acetone fraction = 2.18%

Sample #44-2: The Cal Poly and BAAQMD labs obtained the same speciation results for all of the compounds present in this coating. CARB, using their Method 310 did not report the presence of a significant quantity of the solvent Aromatic 100 (approximately 13%). Accordingly, CARB's speciation results could not be used to calculate a VOC content by GC. There is a substantial difference in the quantity of acetone measured by the three laboratories. The experimental values range from 41.1% to 47.0% and the manufacturer reports a value of 48.44%. Since acetone is a relatively low boiling solvent (BP = 56.3 °C), sample handling and sample preparation for analysis will require careful consideration.

Table 22 - Sample #57-3, Solventborne Air-dry Lacquer Coating with Exempt Solvents

	Lab 1, Cal Poly 6890				Lab 2, BAAQMD			Lab 3, CARB
	Run 1	Run 2	Run 3	Average	Run 1	Run 2	Average	Average
methanol	0.0143	0.0137	0.0156	0.0145			0.0150	0.0128
acetone	0.3681	0.3734	0.3794	0.3736			0.3742	0.3609
2-propanol	0.0345	0.0345	0.0345	0.0345			0.0327	0.0326
methyl acetate	0.0417	0.0420	0.0416	0.0418			0.0396	0.0376
MEK	0.0509	0.0510	0.0410	0.0476			0.0469	0.0490
1-butanol	0.0151	0.0151	0.0122	0.0141			0.0186	not reptd
butyl acetate	0.0333	0.0331	0.0321	0.0328			0.0301	not reptd
ethylbenzene	0.0168	0.0168	0.0165	0.0167			0.0160	0.0203
m,p-xylene	0.0681	0.0680	0.0673	0.0678			0.0782	0.0687
2-heptanone	0.0935	0.0933	0.0908	0.0925			0.0969	not reptd
o-xylene	0.0205	0.0203	0.0200	0.0203			0.0153	0.0236
2-butoxyethanol	0.0156	0.0154	0.0132	0.0147			0.0149	0.0216
4-methyl-3-heptanone	0.0084	0.0059	0.0000	0.0048			not reptd	not reptd
Total volatile fraction	0.7807	0.7825	0.7642	0.7758			0.7784	0.6271
acetone, L	0.4178	0.4238	0.4306	0.4240	0.4298	0.4312	0.4305	0.4148
methyl acetate, L	0.0399	0.0401	0.0397	0.0399	0.0383	0.0384	0.0383	0.0364
Total VOC fraction	0.3708	0.3671	0.3432	0.3604	0.3646	0.3646	0.3646	0.2286
Mass Balance, fract				1.0279			1.0177	0.8742
Density, g/L				897.7	908.5	911.4	910.0	909
solids fraction	0.2528	0.2514	0.2521	0.2521	0.2387	0.2399	0.2393	0.2471
Matl VOC, GC	333	330	308	324	331	332	332	
Coat VOC, GC	614	615	582	604	623	626	625	
Matl VOC, EPA 24	303	299	293	298	316	316	316	322
Coat VOC, EPA 24	558	558	554	557	593	595	594	587
Matl VOC, reptd	294							
Coat VOC, reptd	550							
Acetone, reptd	0.38							
Methyl acetate, reptd	0.04							

Between-laboratory standard deviation, material VOC, GC = 5.8 g/L
Between-laboratory standard deviation, coating VOC, GC = 14.9 g/L
Between-laboratory standard deviation, material VOC, EPA 24 = 12.2 g/L
Between-laboratory standard deviation, coating VOC, EPA 24 = 19.9 g/L
Between-laboratory standard deviation, acetone fraction = 95%

Sample #57-3: The Cal Poly and BAAQMD labs obtained the same speciation results for all of the compounds present in this coating. CARB, using their Method 310 did not report the presence of a significant quantity of 1-butanol (ca. 1.5%), 2-heptanone (ca. 9%), and butyl acetate (ca. 3.3%). Accordingly, CARB's speciation results could not be used to calculate a VOC content by GC.

H. Validation (Round Robin) Studies for Two-Component (2K) Architectural Coatings

The laboratories participating in the 2K validation study included two independent Cal Poly labs using different instruments and different operators, one industrial laboratory and one regulatory laboratory (SCAQMD). The coatings studied included three solvent-borne and two water-borne 2K coatings (#3, #15-2, #15-3, #26 and #45). The following considerations became apparent during this study and are discussed in detail below:

- The VOC content of 2K solvent-borne coatings may be measured by direct GC or indirectly by EPA Method 24
- The VOC content 2K coatings with solids content greater than 90% by weight must be determined by a modification of EPA Method 24
- The VOC content of water-borne 2K coatings may be determined by direct GC and cannot be measured accurately by EPA Method 24.

A. The VOC content of 2K solvent-borne coatings may be measured by direct GC or indirectly by EPA Method 24

A method was developed by us to measure the speciated VOC content of 2K coatings (Appendix). In this method the components of the paint system are mixed according the manufacturers recommended mix ratio and a sample of the mixture (ca. 100 mg) is placed in a headspace vial, is immediately sealed with a crimp cap and allowed to cure for a minimum of 24 hours. Any VOCs in the mixed sample are retained in the closed vial. After room-temperature cure, the sample is heated for 30 minutes at 110ºC, is allowed to cool, and is then extracted with acetone containing a known quantity of internal standard. Gas chromatography of the resulting solution gives the composition and amount of the VOCs present in the sample. At the same time that the uncured 2K mixture is placed in sealed vials, an ASTM D2369 total volatiles determination is carried out. The samples in the aluminum dishes are not diluted with solvent and are allowed to cure for 24 – 36 hours prior to heating at 110^0C for one hour. For solvent-borne 2K coatings that do not contain exempt VOCs, this procedure allows us to calculate the coatings VOC content by both EPA Method 24 and the new GC direct measurement method. The summary results of the round robin study of five 2K coatings are given in Table 23. Detailed results for the five samples are given in Tables 28-32.

Table 23 – Summary Results from Round-robin of 2K Coatings

	VOC g/L			
Sample #3, solventborne	Cal Poly 6890	Cal Poly 5890	Industrial	SCAQMD
Material VOC by GC	178	181	227	
Coating VOC by GC	178	181	227	
Material VOC by EPA 24	168	179	183	159
Coating VOC by EPA 24	168	179	183	162
Coating VOC rept. Manuf.	180			
Sample #15-2, solventborne				
Material VOC by GC	115	161	167	
Coating VOC by GC	115	161	167	
Material VOC by EPA 24	54	44	69	53
Coating VOC by EPA 24	54	44	69	54
Coating VOC rept. Manuf.	12			
Sample #15-3, solventborne				
Material VOC by GC	211	230	226	
Coating VOC by GC	211	230	226	
Material VOC by EPA 24	227	218	238	231
Coating VOC by EPA 24	227	218	238	233
Coating VOC rept. Manuf.	214			
Sample #26, waterborne				
Material VOC by GC	114	127	133	
Coating VOC by GC	193	211	222	
Material VOC by EPA 24				-51
Coating VOC by EPA 24				-134
Material VOC rept. Manuf.	122			
Coating VOC rept. Manuf.	236			
Sample #45, waterborne				
Material VOC by GC	85	89	102	
Coating VOC by GC	220	234	244	
Material VOC by EPA 24				91
Coating VOC by EPA 24				278
Material VOC rept. Manuf.	82	rept. 3rd party	68	
Coating VOC rept. Manuf.	244	rept. 3rd party	223	

A summary of the results for the three solvent-borne 2Kcoatings is given in Table 24.

Table 24 - Average Coating VOC, Solventborne 2K

Sample	Solids Fraction	Solids fract plus GC VOC fraction	Coating VOC, EPA 24	Std Dev, EPA 24	Coating VOC, GC	Std Dev, GC	Reptd Value
#3	0.87	1.013	173	10	195	27	180
#15-2,	0.96	1.066	55	10	147	28	12
#15-3,	0.84	0.996	229	8	222	10	214

Discussion of Table 23 and Table 24 results:
Sample 3. The results from one of the laboratories (industrial) are questionable. Their precision values on the ASTM D2369 total volatiles determination were well outside the accepted precision limits reported for the method and makes their EPA 24 results suspect. Their reported GC results were inconclusive in terms of identification of specific components. It would appear that directions supplied to them in the round robin were not strictly followed. When their results for sample #3 are removed from the study, the results for the remaining laboratories are in good agreement. Since this coating does not contain water or exempt solvents, the results obtained by EPA Method 24 are acceptable and the GC method is probably not required in order to obtain a mass-based VOC result. Since the major volatile components in this coating are hazardous air pollutants (HAPs), the GC method does provide a means for measuring these.
Sample 15-2. The major VOC in this coating is benzyl alcohol and the solids content is greater than 90%. Results for this coating are discussed below in section B.
Sample 15-3. The major volatile components in this coating are HAPs and both the GC method and EPA Method 24 give excellent results. If only a mass-based VOC number is required, EPA Method 24 is sufficient for carrying out the determination.

B. The VOC content 2K coatings with solids content greater than 90% by weight must be determined by a modification of EPA Method 24

Sample 15-2. We have previously reported (Quarterly Report, February 29, 2008) that the US EPA has ruled that coatings with a solids content greater than 90% may be analyzed for total volatile content using a modification of ASTM Method D2369. On October 2, 2007 the US EPA received a request from Mr. Frederick Gelfant (Stonhard/Epoplex Company) to approve two modifications to EPA Method 24 (Appendix A of 40 CFR Part 60) for modification of ASTM Method 2369 as it relates to high solids multi-component coatings. The EPA approved the request to carry out the total volatile determination omitting addition of a diluent solvent before curing the test sample and also agreed that the sample weight used should be representative of how the coating is applied. The net result of this change, in general, will be that larger sample

weights will be used to test the total volatile content. An effort is currently underway by the ASTM to conduct a round robin with selected high solids (>90% solids) coatings.

Three of the 2-K coatings in the present ARB study meet the definition of >90% solids (#14-1, 15-1, and 15-2). Two of these high solids coatings were reanalyzed using the provisions of the two EPA approvals. The results of this retesting are presented in Tables 25 and 26.

Table 25 - Results for Sample 14-1 Using Different Film Thicknesses

Sample 14-1. Recommended film thickness = 12-20 mils					
	volatile fraction				
	trial 1	trial 2	trial 3	average	coating VOC based on average
D2369, FT=12 mils	0.0220	0.0194	0.0199	0.0204	27
D2369, FT=6 mils	0.0258	0.0319	0.0314	0.0297	40
GC, 12 mils, extract 5 sec	0.0102	0.0078		0.0090	12
GC, 12 mils, extract 24 hour	0.0406	0.0414		0.0410	55
benzyl alcohol, uncured mixture	0.0426	0.0421		0.0424	57
Reported Coating VOC					7

Table 26 - Results for Sample 15-2 Using Different Film Thicknesses

Sample 15-2. Recommended film thickness = 6 - 12 mils					
	volatile fraction				
	trial 1	trial 2	trial 3	average	coating VOC based on average
D2369, FT=6.5 mils	0.0349	0.0350	0.0357	0.0352	49
D2369, FT= 11.4 mils	0.0242	0.0239	0.0205	0.0229	32
GC, 6.5 mils, extract 5 sec	0.0383	0.0459		0.0421	58
GC, 6.5 mils, extract 24 hour	0.0625	0.0484		0.0554	77
benzyl alcohol, uncured mixture	0.1158	0.1164		0.1161	161
Reported Coating VOC					12

Samples 14-1 and 15-2 contain benzyl alcohol as the major VOC component. The literature boiling point of benzyl alcohol is 205ºC and benzyl alcohol is apparently not released completely from coatings that cure by cross-linking. Based on manufacturer formulation VOC values, it would appear that benzyl alcohol is not counted as a VOC. Both coatings were analyzed for total benzyl alcohol content by gas chromatographic determination of the coating immediately after mixing the components, i.e., before onset of the cure reaction. Uncured coating 14-1 contained 4.24% benzyl alcohol and coating 15-2 contained 11.61% benzyl alcohol. If all of the benzyl alcohol in these coatings were to evaporate during a total volatile determination (ASTM Method 2369), the coating VOC values would have been 57 and 161 g/L , respectively. When the D2369 determination was carried out on 14-1, the VOC content when using the manufacturer's recommended minimum film thickness (12mils) was 27g/L. If a film thickness of half the

minimum recommended application thickness is used to measure total VOC content, the value increases to 40g/L. Similarly, for coating 15-2, the recommended minimum application film thickness (6mils) gives a VOC value of 49g/L and the recommended maximum application film thickness (12mils) gives a the lower VOC value of 32g/L. So clearly, benzyl alcohol evaporates only partially under the test conditions of ASTM 2369.

In the Cal Poly GC method the uncured coating mixture is placed into a closed headspace vial, is allowed to cure for 24 hours at room temperature, and is then heated for 1 hour at 110^0C (ASTM D2369). After cooling, a weighed amount of acetone containing an internal standard is injected into the sealed vial, the contents are mixed, and the resulting solution is then analyzed by GC. Apparently the mixing time in this procedure is critical in measuring only the evolved volatiles. When the mixing time is kept very short (5 seconds), the results obtained by GC match the D2369 results more closely while mixing for a long period of time (24 hours) gives higher GC results which match the total benzyl alcohol content more closely. At the outset of this project we postulated that the EPA Method 24 would probably give sufficient accuracy for solvent-borne coatings and that a GC method is not required as long as mass-based VOC regulations are in effect and this was found to be the case.

The EPA Method 24 results (ASTM D2369) of solvent-borne multi-component coatings with a solids content less than 90% and containing either none or small quantities of benzyl alcohol are nearly the same as those obtained by the Cal Poly GC method.

C. The VOC content of water-borne 2K coatings may be determined by direct GC

Samples 26 and 45 are waterborne 2K coatings. There is no EPA method for measuring the VOC content of 2K waterborne coatings. EPA Method 24 cannot be used reliably with waterborne multi-component coatings. These two coatings were analyzed by three labs (Cal Poly did two independent analyses) including an industrial lab and SCAQMD. SCAQMD only performed a Method 24 analysis. SCAQMD reports values of < 50 g/L for both the material and coating VOC for sample #26. Calculation of the actual values based on SCAQMD's reported solids fraction and water fraction (total of 104%) gives values of –51 and –134 g/L, respectively, for material and coatings VOC. .The GC method developed by us gives results that are in good agreement with manufacturer reported values and appears to give excellent precision as indicated by the three-laboratory round robin study. The summary results are presented below in Table 27.

Table 27 - Average Coating VOC, Waterborne 2K Coatings

Sample	Solids Fraction	Water Fraction, calcd	Material VOC, GC g/L	Coating VOC, GC g/L	Std Dev, Material VOC g/L	Std Dev, Coating VOC g/L	Rept, MaterialVOC g/L	Rept, Coating VOC g/L
#26	0.57	0.33	125	209	9	15	122	236
#45	0.28	0.58	92	233	9	12	82, 68	244, 223

Table 28 - Sample #3, Solventborne 2K Industrial Maintenance Coating

	Cal Poly 6890				Cal Poly 5890				Industry				SCAQMD
	Lab 1				Lab 2				Lab 3				Lab 4
VOC	Run 1	Run 2	Run 3	Average	Run 1	Run 2	Run 3	Average	Run 1	Run 2	Run 3	Average	
furfuryl alcohol	0.0203	0.0200	0.0206	0.0203	0.0167	0.0186	0.0177	0.0177					
ethylbenzene	0.0113	0.0109	0.0111	0.0111	0.0116	0.0116	0.0116	0.0116					
m,p-xylene	0.0505	0.0485	0.0497	0.0495	0.0453	0.0457	0.0455	0.0455					
o-xylene	0.0174	0.0167	0.0173	0.0171	0.0161	0.0164	0.0161	0.0162					
Aromatic 100	0.0280	0.0273	0.0316	0.0289	0.0332	0.0402	0.0410	0.0381					
Total VOC fraction	0.1274	0.1233	0.1303	0.1270	0.1229	0.1325	0.1319	0.1291	0.1633	0.1627	0.1589	0.1616	
Density, g/L				1402				1402				1402	1460
solids fraction	0.8777	0.8800	0.8832	0.8803	0.8714	0.8711	0.8747	0.8724	0.8960	0.8460	0.8670	0.8697	0.8800
KF water fraction													0.0110
KF water, L													0.0161
Mass balance				1.0073				1.0015				1.0313	
Material VOC by GC	179	173	183	178	172	186	185	181	229	228	223	227	
Coating VOC by GC	179	173	183	178	172	186	185	181	229	228	223	227	
Material VOC by EPA 24	171	168	164	168	180	181	176	179	146	216	186	183	159
Coating VOC by EPA 24	171	168	164	168	180	181	176	179	146	216	186	183	162
Coating VOC reported by manufacturer	179.7												

Table 29 - Sample #15.2, Solventborne 2K Industrial Maintenance Coating

	Cal Poly 6890				Cal Poly 5890				Industry				SCAQMD
	Lab 1				Lab 2				Lab 3				Lab 4
VOC	Run 1	Run 2	Run 3	Average	Run 1	Run 2	Run 3	Average	Run 1	Run 2	Run 3	Average	
benzyl alcohol	0.1164	0.0699	0.0629	0.0830	0.1033	0.1082	0.1367	0.1161	0.0943	0.1332	0.1332	0.1202	
Total VOC fraction	0.1164	0.0699	0.0629	0.0830	0.1033	0.1082	0.1367	0.1161	0.0943	0.1332	0.1332	0.1202	
benzyl alcohol in UNCURED SAMPLE	0.1158												
Density, g/L				1385				1385				1385	1400
solids fraction	0.9619	0.9612	0.9605	0.9612	0.9693	0.9682	0.9675	0.9683	0.9516	0.9461	0.9537	0.9505	0.9560
KF water fraction													0.0060
KF water, L													0.0084
Mass balance, fraction	1.0783	1.0311	1.0233	1.0442	1.0726	1.0764	1.1042	1.0844	1.0459	1.0793	1.0869	1.0707	
Material VOC by GC	161	97	87	115	143	150	189	161	131	184	184	167	
Coating VOC by GC	161	97	87	115	143	150	189	161	131	184	184	167	
Material VOC by EPA 24	53	54	55	54	43	44	45	44	67	75	64	69	53
Coating VOC by EPA 24	53	54	55	54	43	44	45	44	67	75	64	69	54
Coating VOC reported by manufacturer	12												

Table 30 - Sample #15-3, Solventborne 2K Industrial Maintenance Coating

	Cal Poly 6890				Cal Poly 5890				Industry				SCAQMD
VOC	Lab 1				Lab 2				Lab 3				Lab 4
MEK	Run 1	Run 2	Run 3	Average	Run 1	Run 2	Run 3	Average	Run 1	Run 2	Run 3	Average	
1-butanol	0.0030	0.0031	0.0030	0.0030		0.0025		0.0025					
toluene	0.0035	0.0035	0.0035	0.0035	0.0042	0.0038	0.0042	0.0041					
ethylbenzene	0.0174	0.0179	0.0178	0.0177	0.0177	0.0189	0.0169	0.0178					
m,p-xylene	0.0140	0.0143	0.0143	0.0142	0.0158	0.0157	0.0148	0.0154					
o-xylene	0.0484	0.0499	0.0494	0.0492	0.0498	0.0493	0.0516	0.0502					
cumene	0.0128	0.0133	0.0132	0.0131	0.0137	0.0135	0.0142	0.0138					
Aromatic 100	0.0005	0.0005	0.0005	0.0005									
benzyl alcohol	0.0150	0.0160	0.0155	0.0155	0.0221	0.0228	0.0221	0.0223					
Total VOC fraction	0.0241	0.0260	0.0252	0.0251	0.0345	0.0275	0.0430	0.0350					
	0.1417	0.1479	0.1458	0.1451	0.1578	0.1516	0.1667	0.1587	0.1548	0.1599	0.1533	0.1560	
Density, g/L				1452				1452				1452	1420
solids fraction	0.8453	0.8459	0.8398	0.8437	0.8491	0.8503	0.8491	0.8495	0.8370	0.8410	0.8310	0.8363	0.8320
KF water fraction													0.0050
KF water, L													0.0071
Mass balance, fraction				0.9888				1.0082				0.9923	
Material VOC by GC	206	215	212	211	229	220	242	230	225	232	223	226	
Coating VOC by GC	206	215	212	211	229	220	242	230	225	232	223	226	
Material VOC by EPA 24	225	224	233	227	219	217	219	218	237	231	245	238	231
Coating VOC by EPA 24	225	224	233	227	219	217	219	218	237	231	245	238	233
Coating VOC reported by manufacturer	214												

Table 31 - Sample #26, Waterborne 2K Swimming Pool Coating

	Cal Poly 6890				Cal Poly 5890				Industry				SCAQMD
	Lab 1				Lab 2				Lab 3				Lab 4
VOC	Run 1	Run 2	Run 3	Average	Run 1	Run 2	Run 3	Average	Run 1	Run 2	Run 3	Average	
2-propoxyethanol	0.0829	0.0804	0.0809	0.0814	0.0906	0.0851	0.0786	0.0848	0.0997	0.0986	0.0976		
Aromatic 100	0.0130	0.0116	0.0132	0.0126	0.0162	0.0159	0.0267	0.0196	0.0105	0.0105	0.0105		
Total VOC fraction	0.0959	0.0920	0.0941	0.0940	0.1068	0.1010	0.1052	0.1044	0.1102	0.1091	0.1081	0.1091	
Density, g/L				1217				1217				1217	1280
solids fraction	0.5702	0.5715	0.5721	0.5713	0.5667	0.5686	0.5689	0.5681	0.5600	0.5580	0.5630	0.5603	0.5570
calcd water fraction	0.3339	0.3365	0.3338	0.3347	0.3265	0.3304	0.3259	0.3276	0.3298	0.3329	0.3289	0.3305	
calcd water, L	0.4063	0.4094	0.4061	0.4073	0.3972	0.4020	0.3964	0.3985	0.4012	0.4050	0.4002	0.4021	
KF water fraction													0.4830
KF water, L													0.6182
Material VOC by GC	117	112	115	114	130	123	128	127	134	133	132	133	
Coating VOC by GC	196	189	193	193	216	206	212	211	224	223	219	222	
Material VOC by EPA 24													-51
Coating VOC by EPA 24													-134
Material VOC reported by manufacturer	122												
Coating VOC reported by manufacturer	236												

Table 32 - Sample #45, Waterborne 2K Clear Varnish Coating

	Cal Poly 6890				Cal Poly 5890				Industry				SCAQMD
	Lab 1				Lab 2				Lab 3				Lab 4
VOC	Run 1	Run 2	Run 3	Average	Run 1	Run 2	Run 3	Average	Run 1	Run 2	Run 3	Average	
UK	0.0016	0.0016	0.0016	0.0016									
1-methoxy-2-propanol	0.0718	0.0718	0.0721	0.0719	0.0715	0.0722	0.0762	0.0733	0.0866	0.0853	0.0842	0.0854	
UK	0.0011	0.0011	0.0010	0.0011									
UK	0.0005	0.0005	0.0005	0.0005									
UK	0.0006	0.0007	0.0005	0.0006									
butyrolactone	0.0012	0.0012	0.0012	0.0012	0.0081	0.0074	0.0081	0.0078					
UK	0.0006	0.0006	0.0006	0.0006									
benzyl alcohol	0.0037	0.0037	0.0037	0.0037	0.0042	0.0040	0.0053	0.0045	0.0047	0.0046	0.0046	0.0046	
Total VOC fraction	0.0813	0.0812	0.0812	0.0813	0.0837	0.0835	0.0896	0.0856	0.0987	0.0973	0.0977	0.0979	
Density, g/L				1042				1042				1042	1050
solids fraction	0.2822	0.2825	0.2825	0.2824	0.2763	0.2771	0.2777	0.2770	0.2800	0.2810	0.2800	0.2803	0.2740
calcd water fraction	0.5903	0.5942	0.5872	0.5906	0.6008	0.5904	0.5904	0.5939	0.5567	0.5563	0.5611	0.5580	
calcd water, L	0.6151	0.6192	0.6119	0.6154	0.6260	0.6152	0.6152	0.6188	0.5801	0.5797	0.5847	0.5815	
KF water fraction													0.6390
KF water, L													0.6710
Material VOC by GC	85	85	85	85	87	87	93	89	103	101	102	102	
Coating VOC by GC	220	222	218	220	233	226	243	234	245	241	245	244	
Material VOC by EPA 24													91
Coating VOC by EPA 24													278
Material VOC reported by manufacturer	82	rept. 3rd party lab	68										
Coating VOC reported by manufacturer	244	rept. 3rd party lab	223										

SUMMARY AND CONCLUSIONS

We have developed a suite of VOC analysis methods suitable for use in analyzing any architectural coating sold in California. For high VOC solventborne coatings with no exempt compounds, EPA Method 24 provides an accurate and simple way to determine VOC. For virtually all other coatings types listed in the CARB survey of architectural coatings, another method must be used. We have investigated the application of methods similar to those we developed for ASTM D6886 to a wide variety of coatings. We have tested these methods on 67 different coatings, including air-dry single component coatings, coatings with exempt compounds, and 2K coatings. We have tested our methods against those used by regulatory agencies and industry and found our methods to be at least equal in quality and generally superior to other methods in use.

The new methods developed for this project are listed below:

- D 6886, Standard Test Method for Direct Analysis of the Volatile Organic Compounds (VOCs) in Waterborne Air-Dry Coatings by Gas Chromatography This method is a significant revision of ASTM Method D 6886, Test Method for Speciation of the Volatile Organic Compounds (VOCs) in Low VOC Content Waterborne Air-Dry Coatings by Gas Chromatography, and will be submitted to ASTM for balloting.
- Standard Test Method for the VOC and HAP Content of Multi-Component Coatings by Gas Chromatography
- HAP Method, Standard Test Method for the Determination of the Common Hazardous Air Pollutants (HAPs) in Solventborne Air-Dry Coatings by Gas Chromatography
- Extraction Method, Determination of the VOC Content Remaining in Paint Films After Total Volatile Content Determination by ASTM Method D 2369
- High Solids Volatiles Method, Solids Determination of 2K Coatings Containing More than 90% Solids

We have developed specific recommendations for VOC methods for each type of architectural coating as shown in Table 33 below (identical to Table 8).

Table 33 – Recommended Methods for VOC Analysis

Recommendation for Analysis of Specific Architectural Coatings Types

Coatings Type	**Recommended Methods**
Air-dry waterborne coatings without exempt solvents, VOC content < 10%	Revised D6886 and Extraction Method
Air-dry waterborne coatings without exempt solvents, VOC content >10%	Revised D6886 or EPA Method 24
Air-dry solventborne coatings, without exempt solvents	EPA Method 24; Use Revised D6886 and HAP Method if HAP content is to be measured
Air-dry solventborne coatings, with exempt solvents	Revised D6886 to determine exempt solvents and speciated VOC content
Solventborne 2K coatings, solids content < 90%	EPA Method 24 for mass-based VOC content; new 2K method if HAP content or speciated content is desired
Solventborne 2K coatings, solids content >90%	EPA Method 24 with new High Solids volatile method
Waterborne 2K coatings	New 2K method
Coatings containing Silanes, Siloxanes and Silane-Siloxane Blends	ASTM D5095 for total volatile content and new D6886 for speciation
Coatings containing semi-volatile organic compounds and/or with boiling points greater than 250°C and D 6886 primary capillary column retention time greater than Texanol®	Revised D6886 and Extraction Method

We have written a comprehensive VOC coatings analysis manual. It is our hope this manual will be used by regulatory agencies, manufacturers, private laboratories, and anyone interested in determination of VOC levels in architectural coatings sold in California. This is only a first step. It is expected these methods will undergo constant revision and upgrading, similar to what happens with ASTM methods. The goal of all is to have available methods to accurately determine the VOC levels of all classes of architectural coatings.

APPENDIX : California Manual for Determination of the VOC Content of Architectural Coatings

This manual is a compilation of new methods developed at California Polytechnic State University and a listing of required existing methods for use in the determination of the VOC content of all architectural coatings sold in California. These new methods are under development and have been presented to ASTM and will be submitted for comment and balloting before the end of the year. This manual is not intended to replace any of the existing district methods manuals but is intended to complement them. This manual will be revised on a regular basis to incorporate new methods and to update changes in existing methods.

The Existing ASTM Methods

- D1475 Test Method for Density of Liquid Coatings, Inks, and Related Products
- D2369 Test Method for Volatile Content of Coatings
- D3925 Practice for Sampling Liquid Paints and Related Pigmented Coatings
- D4017 Test Method for Water in Paints and Paint Materials by Karl Fischer Method
- D5095 Test Method for Determination of the Nonvolatile Content in Silanes, Siloxanes and Silane-Siloxane Blends Used in Masonry Water Repellent Treatments
- D6133 Test Method for Acetone -Chlorobenzotrifluoride, Methyl Acetate or -Butyl Acetate Content of Solvent-Reducible and Water-Reducible Paints, Coatings, Resins, and Raw Materials by Direct Injection into a Gas Chromatograph
- D6438 Test Method for Acetone, Methyl Acetate, and Parachlorobenzotrifluoride Content of Paints and Coatings by Solid Phase Microextraction-Gas Chromatography

The Existing Federal EPA Method

- EPA Federal Reference Method 24—Determination of Volatile Matter Content, Density, Volume Solids, and Weight Solids of Surface Coatings

The New Test Methods

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- D 6886, Standard Test Method for Direct Analysis of the Volatile Organic Compounds (VOCs) in Waterborne Air-Dry Coatings by Gas Chromatography This method is a revision of ASTM Method D 6886, Test Method for Speciation of the Volatile Organic Compounds (VOCs) in Low VOC Content Waterborne Air-Dry Coatings by Gas Chromatography, and will be submitted to ASTM for balloting.

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

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

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- Extraction Method, Determination of the VOC Content Remaining in Paint Films After Total Volatile Content Determination by ASTM Method D 2369

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- High Solids Volatiles Method, Solids Determination of 2K Coatings Containing More than 90% Solids

Recommendation for Analysis of Specific Architectural Coatings Types

Coatings Type	**Recommended Methods**
Air-dry waterborne coatings without exempt solvents, VOC content < 10%	Revised D6886 and Extraction Method
Air-dry waterborne coatings without exempt solvents, VOC content >10%	Revised D6886 or EPA Method 24
Air-dry solventborne coatings, without exempt solvents	EPA Method 24; Use Revised D6886 and HAP Method if HAP content is to be measured
Air-dry solventborne coatings, with exempt solvents	Revised D6886 to determine exempt solvents and speciated VOC content
Solventborne 2K coatings, solids content < 90%	EPA Method 24 for mass-based VOC content; new 2K method if HAP content or speciated content is desired
Solventborne 2K coatings, solids content >90%	EPA 24 with new High Solids volatile method
Waterborne 2K coatings	New 2K method
Coatings containing Silanes, Siloxanes and Silane-Siloxane Blends	ASTM D5095 for total volatile content and new D6886 for speciation
Coatings containing semi-volatile organic compounds and/or with boiling points greater than 250ºC and D 6886 primary capillary column retention time greater than Texanol®	Revised D6886 and Extraction Method

Standard Test Method for Direct Analysis of the Volatile Organic Compounds (VOCs) in Waterborne Air-Dry Coatings by Gas Chromatograpy[1]

(Note: This is a revised draft of ASTM Method D 6886 –03 and is under the jurisdiction of Subcommittee D01.21 and has not yet entered the ASTM balloting process. Accordingly, there could be substantial modifications to the method before it is adopted and published.)

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-chlorobezotrifluoride) 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[2]

D 2369 Test Method for Volatile Content of Coatings[2]

D 3792 Test Method for Water Content of Coatings by Direct Injection Into a Gas Chromatograph[2]

D 3925 Practice for Sampling Liquid Paints and Related Pigmented Coatings[2]

D 3960 Practice for Determining Volatile Organic Compound (VOC) Content of Paints and Related Coatings[2]

D 4017 Test Method for Water in Paints and Paint Materials by Karl Fischer Method[2]

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[2]

D 6438 Test Method for Acetone, Methyl Acetate, and Parachlorobenzotrifluoride Content of Paints, and Coatings by Solid Phase Microextraction-Gas Chromatography[2]

E 177 Practice for Use of the Terms Precision and Bias in ASTM Test Methods[3]

E 691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method[3]

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

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[1]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.

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[2]*Annual Book of ASTM Standards*, Vol 06.01.

[3]*Annual Book of ASTM Standards*, Vol 14.02.

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-trimethypentane-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:

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

or

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

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 presnt 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 µL 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/diltute 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 µL 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:

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

where:

RF	=	relative response factor,
AA	=	area of analyte,
MI	=	weight of internal standard (from 9.1),
AI	=	area of internal standard, and
MA	=	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 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. Altenatively, add the paint to the vial containg the ceramic beads and approximately 10-15mL of THF 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 µL 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:

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

where:

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

E –. Coating Containing Silanes, Siloxanes and Silane-Siloxane Blends

10.9 If the coating contains Silanes, Siloxanes and Silane-Siloxane Blends, approximately 50 mg of solid p-toluenesulfonic acid should be added to the solution in 10.3 and, after mixing, is allowed to remain at room temperature for 30 minutes prior to gas chromatography

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

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
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

		Retention Time, min		
Compound	RRF	PMPS	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 acetete	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 [A]	F-VOC [A]
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	

[A] Measured in grams per litre minus water.

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 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:

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

or

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

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 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 µm Carbowax™/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 µm film thickness.
	Confirmatory Column: 60 m by 0.25 mm Carbowax™ (CW) , 0.50 µm 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 percent of each in the coating using the relationship:

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

where:

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

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

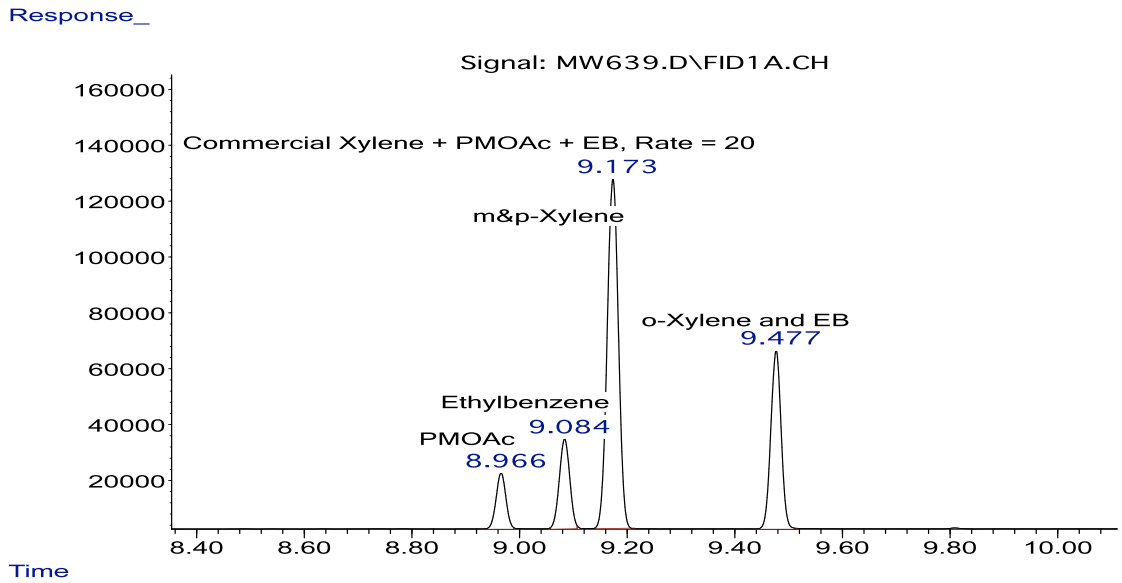

Figure 1. Chromatogram of Commercial Xylene Containing PM Acetate and Butoxyethanol. Heating Rate = 20°C per minute. EB and o-xylene co-elute at this heating rate.

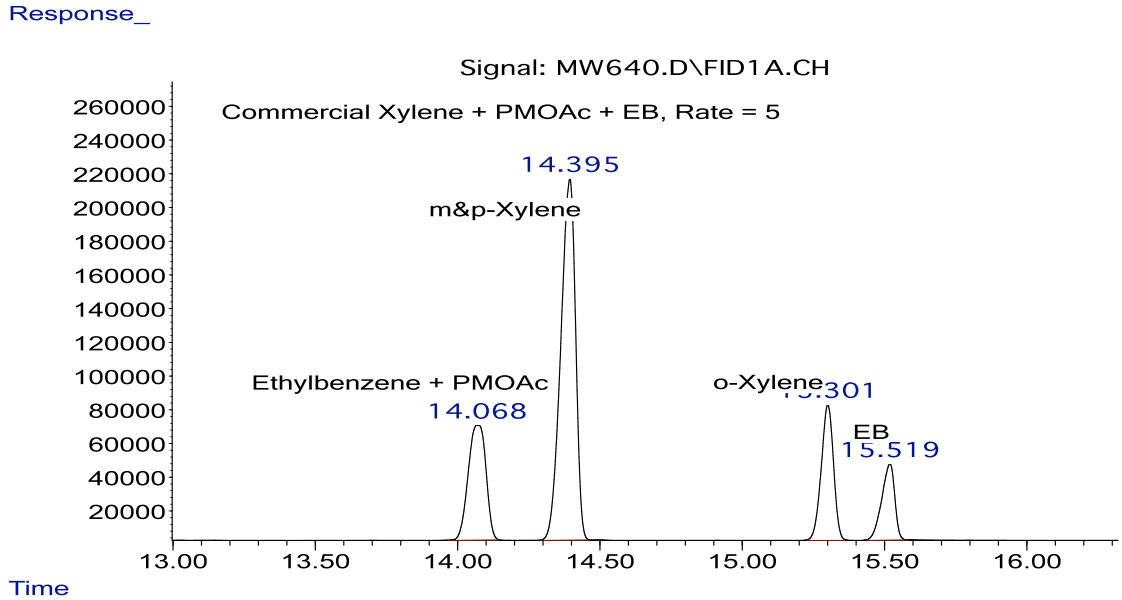

Figure 2. Chromatogram of Commercial Xylene Containing PM Acetate and Butoxyethanol. Heating Rate = 5°C per minute. EB and o-xylene are separated at this heating rate.

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-xylene and 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).

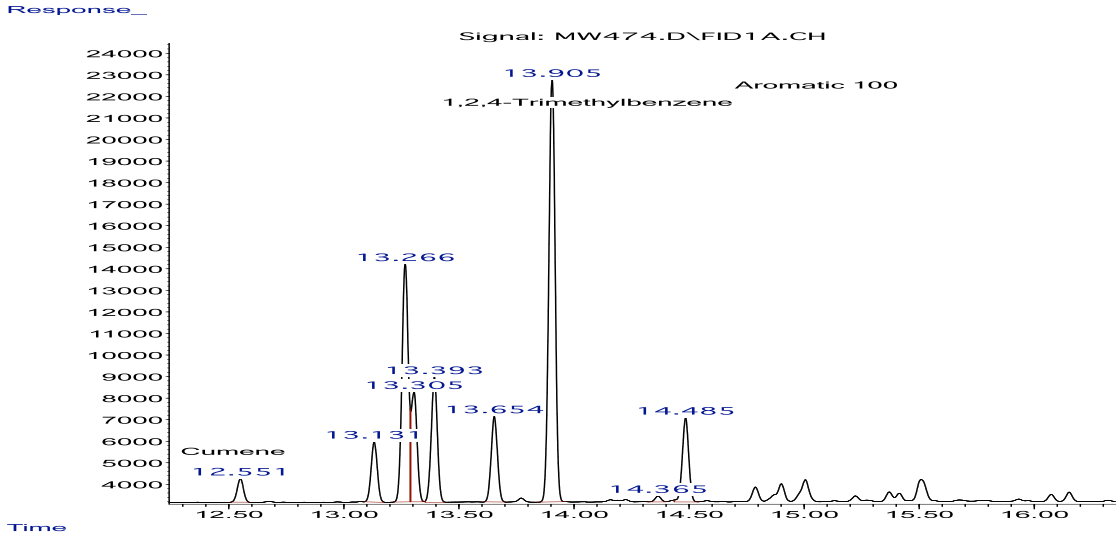

Figure 4. Commercial Aromatic 100 at a heating rate of 10°C per minute.

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 10ºC per minute on the PMPS column described in 6.3.

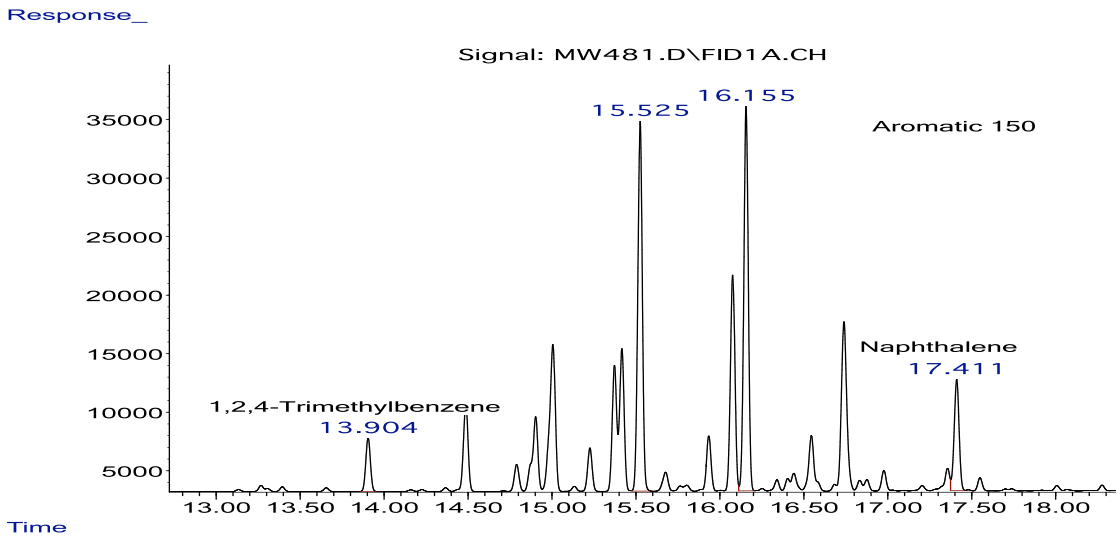

Figure 5. Commercial Aromatic 150 at a heating rate of 10ºC per minute.

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	*ethylene glycol, diethyl ether* (internal standard)	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, proyl 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

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

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[6]

D 2369 Test Method for Volatile Content of Coatings[2]

D 3792 Test Method for Water Content of Coatings by Direct Injection Into a Gas Chromatograph[2]

D 3925 Practice for Sampling Liquid Paints and Related Pigmented Coatings[2]

D 3960 Practice for Determining Volatile Organic Compound (VOC) Content of Paints and Related Coatings[2]

D 4017 Test Method for Water in Paints and Paint Materials by Karl Fischer Method[2]

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[2]

D 6438 Test Method for Acetone, Methyl Acetate, and Parachlorobenzotrifluoride Content of Paints, and Coatings by Solid Phase Microextraction-Gas Chromatography[2]

E 177 Practice for Use of the Terms Precision and Bias in ASTM Test Methods[7]

E 691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method[3]

3. Terminology

3.1. To be added

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[6] *Annual Book of ASTM Standards*, Vol 06.01.

[7] *Annual Book of ASTM Standards*, Vol 14.02.

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. *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
Column	Primary column: 30 m by 0.25 mm 5 % phenyl/95 % methyl siloxane (PMPS) (Note 2) , 1.0 μm 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 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. *Terahydrofuran (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 commerial Aromatic 150.*

7.8. *Fluorocarbon-faced septum vials*, 20 mL and 40 mL capacity.

8. Column 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.

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 µL 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 µL 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:

RF	=	relative response factor,
AA	=	area of analyte,
MI	=	weight of internal standard (from 9.1),
AI	=	area of internal standard, and
MA	=	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 1µL 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.

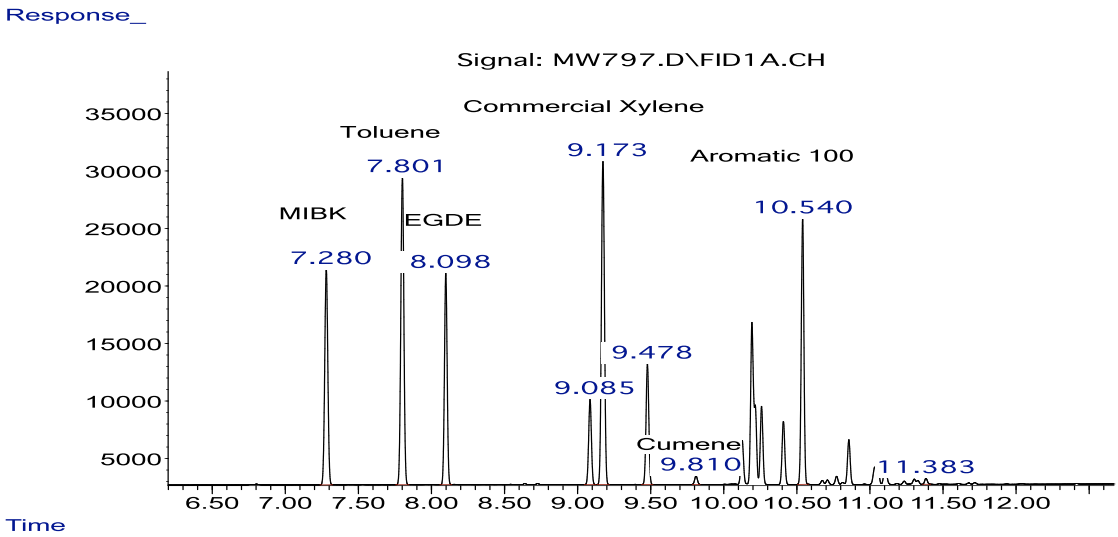

Figure 1. Chromatogram of standard HAP mixture containing MIBK, toluene, EGDE(internal standard), commercial xylene, and Aromatic 100. Heating rate = 20^0C/minute.

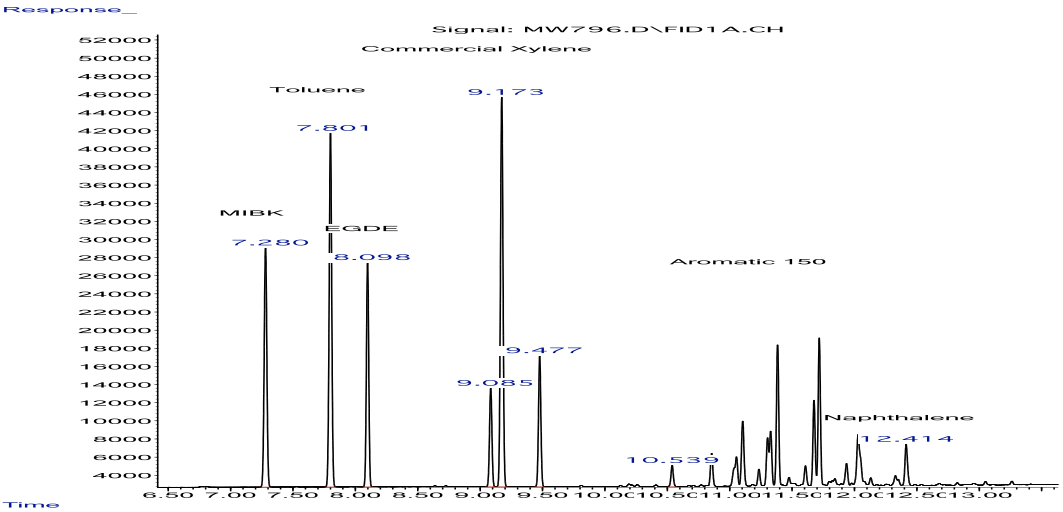

Figure 2. Chromatogram of standard HAP mixture containing MIBK, toluene, EGDE(internal standard), commercial xylene, and Aromatic 150. Heating rate = 20^0C/minute.

10. Coating Analysis

10.1. Add approximately 15-20 mL of THF or acetone to a 40 mL vial containing 3-5g ceramic beads (Coor'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:

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

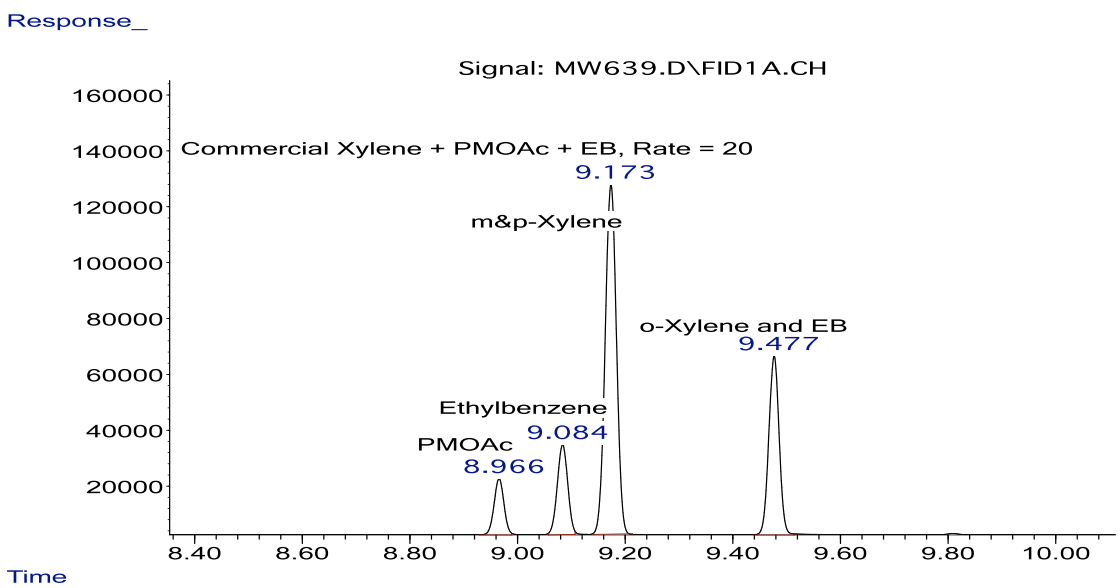

Figure 3. Commercial xylene with added PM acetate(PMOAc) and butoxyyethanol (EB) at a chromatographic heating rate of 20^0C/minute. EB and o-xylene co-elute. . Chromatography relatively fast.

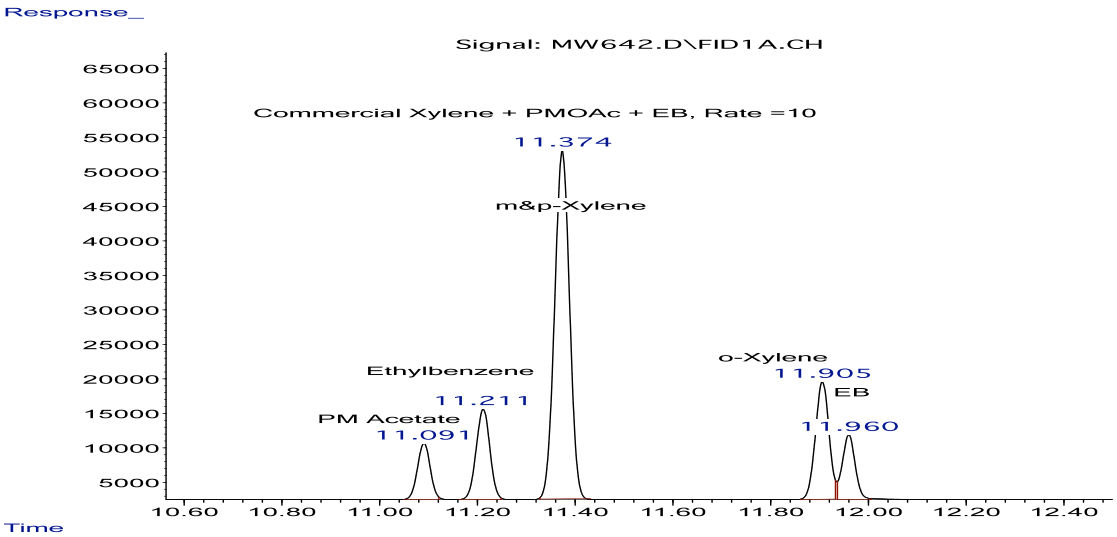

Figure 4. Commercial xylene with added PM acetate(PMOAc) and butoxyyethanol (EB) at a chromatographic heating rate of 10^0C/minute. EB and o-xylene separated.

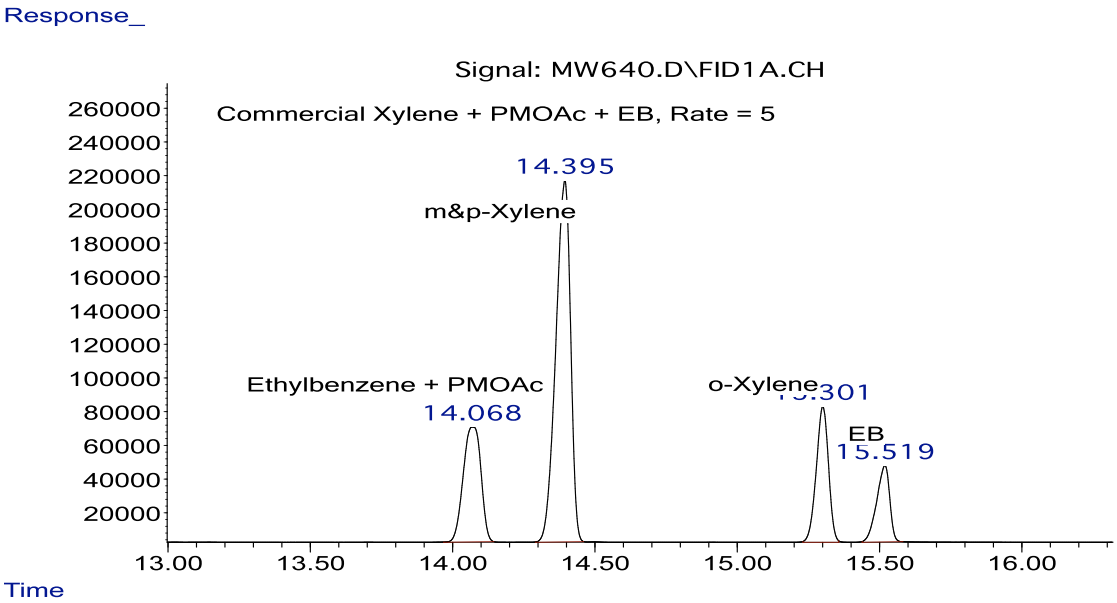

Figure 5 Commercial xylene with added PM acetate(PMOAc) and butoxyyethanol (EB) at a chromatographic heating rate of 5^0C/minute. EB and o-xylene separated. Ethylbenzene and PMOAc co-elute.

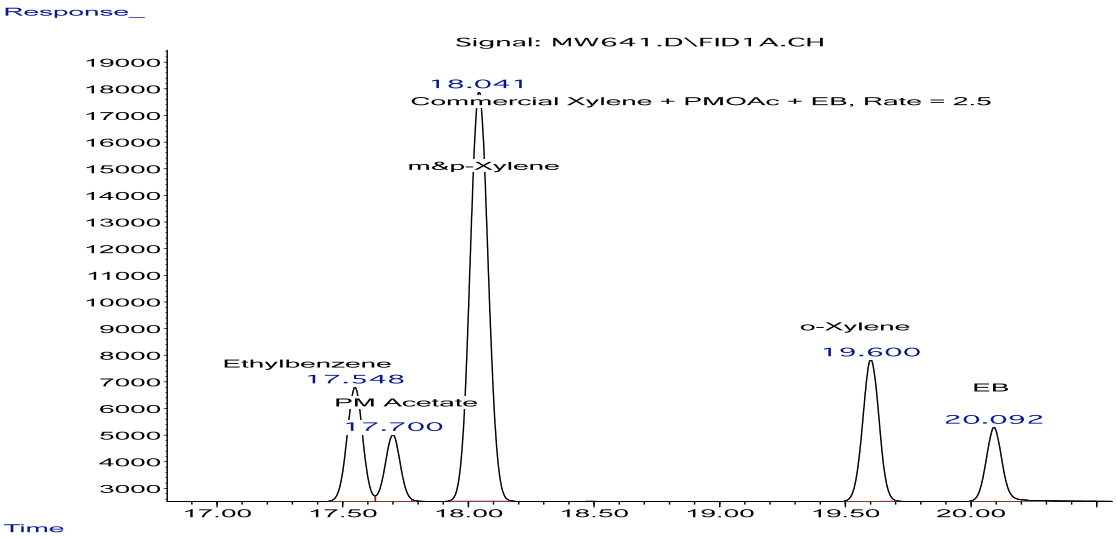

Figure 6. Commercial xylene with added PM acetate(PMOAc) and butoxyyethanol (EB) at a chromatographic heating rate of 2.5^0C/minute. All components separated. Chromatography is relatively slow.

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 10^0C per minute on the PMPS capillary column described in 6.3.

12. Reporting Results

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

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

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. To be added

Extraction Method for the Determination of the VOCs Remaining in Paint Films After Total Volatile Content Determination by ASTM Method D 2369

Immediately after the duplicate determination of the volatile content of a coating, cut the aluminum pans containing the coatings solids into several small pieces. Place these into a 125mL Erlenmeyer flask and add approximately 20 mL of acetone or methyl ethyl ketone and a Teflon-coated stir bar. Stopper the flask and stir the contents for 12 – 24 hours. This process extracts VOCs remaining in the paint film into the acetone. Add 5.0 mL of a THF or acetone solution containing approximately 0.5 mg/mL (known to 0.0001 mg) of internal standard (ethylene glycol diethyl ether, EGDE). Mix the contents and chromatograph the solution according to Method D 6886. Determine the amounts of VOCs that have boiling points greater than 250^{0}C and retention times equal to and longer than Texanol™ Since the paint film may undergo oxidative degradation during the heating phase of the ASTM D 2369 determination, chromatographic peaks may appear which were not present during the original (unheated sample) Method D 6886 VOC determination. In calculating the total VOC content of the coating in question, the VOC amounts determined in this extraction procedure should be subtracted from the original VOC amount.

High Solids Volatiles Method

ASTM Method D 2369 is currently undergoing revision for the total volatile content determination of 2K coatings containing more than 90% solids. This proposed revision has been approved by the USEPA. The draft revision pertaining to the specific changes in the method are given below:

7. Procedure (Draft # 3 – Proposed Revision of Section 7 of D2369, Nov. 9/2006)

7.1 Take a representative sample of the liquid coating (each component) in accordance with Practice D 3925. Mix thoroughly by hand before taking specimens.

7.2 For multi-component coatings, weigh each component in the proper proportion into a container that can be capped. Mix the components together thoroughly by hand before extracting specimens. Tightly close the container to prevent loss of volatile materials.

7.3 Weigh the preconditioned aluminum foil dish (see section 5.2) and record the weight to the nearest 0.1 mg (W_1). Use disposable (no talc) rubber or polyethylene gloves, tweezers or forceps to handle the dish.

7.4 To facilitate dispersing or spreading the specimen, a metal paper clip may be placed (partially unfolded) in the aluminum dish and weighed with the dish. If a paper clip is used, it must remain with the dish throughout the remainder of the procedure.

7.5 Add to the aluminum foil dish the appropriate type and amount of solvent according to Table 1.

7.6 Draw the coating specimen into the syringe. Remove the syringe from the specimen and then pull the plunger tip up 6 mm (1/4in.) in order to pull the specimen away from the neck of the syringe. Wipe the outer surface of the syringe to remove excess material and cap the syringe. Place the filled syringe on the scale and tare the scale. Use disposable (no talc) rubber or polyethylene gloves to handle the syringe.

7.7 Remove the cap and dispense from the syringe into the dish the target specimen weight as specified in Table 1. If solvent is used in the dish add the specimen dropwise to the solvent-containing dish. The paper clip may be used to help disperse the coating specimen in the solvent. If the material forms a lump that cannot be dispersed, discard the specimen and prepare a new one. If no solvent is used (See Table 1, Method E), spread out the specimen in the dish with the paper clip to cover the bottom of the dish completely with as uniform thickness as possible.

7.8 After dispensing the specimen, do not wipe the tip of the syringe. Remove the specimen from the neck of the syringe by pulling up the plunger. Cap and place the syringe on the balance (that was tared with the syringe before the specimen was dispensed) and record the weight to the nearest 0.1 mg as the Specimen Weight (S_A).

7.9 Repeat steps 7.3 to 7.8 to prepare a duplicate specimen for each sample.

7.10 For multi-component coatings, after the specimens are prepared, allow them to sit at ambient conditions for a prescribed induction time according to Table 1 before placing the dishes in the oven.

7.11 Heat the aluminum foil dishes containing the specimens in the forced draft oven (Section 5.3) for 60 minutes at 110 ± 5°C.

7.12 Remove each dish from the oven, place immediately in a desiccator, cool to ambient temperature, weigh to the nearest 0.1 mg and record this weight (W_2) for each specimen.

Table 1

Coating Type	Method A -1K Waterborne	Method B -1K Solventborne	Method C -2K Waterborne	Method D -2K Solventborne	Method E - 2K >90% Solids
Solvent type and amount	3+/-1 ml water (Section 6.2)	3 +/-1 ml solvent (Section 6.3)	3+/- 1 ml water (Section 6.2)	3 +/-1 ml solvent (Section 6.3)	none
Specimen Weight	0.3 +/- 0.1g if expected result is =<40%volatile (>= 60% non-volatile) 0.5 +/- 0.1 g if expected result is >40%volatile (< 60% non-volatile)				See Note 1
Induction Time	N/A	N/A	1 hr	1 hr	24 hr

Note 1 - Specimen weight to be representative of how the product is used (the lowest thickness which the manufacturer's literature recommends) where:
Weight (g) = Thickness (mm) x 3.14 x [Dish Diameter^2 (mm^2)/4] x Density (g/cc)/1000.
For example: the appropriate specimen weight for a coating with a density of 1 g/cc placed in a 50 mm diameter dish at a thickness of 0.5 mm calculates to 1.0 g.